

グアニジンの立体特性を利用した
水溶性芳香族分子構築

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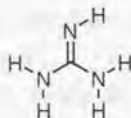
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第1章 序

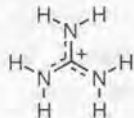
第1節 グアニジンとその化学的性質

グアニジンは3つのC-N結合からなる構造 (Figure 1-1) をもち、有機化合物の中でも強塩基性をもつ官能基として知られている¹⁾。その共役酸であるグアニジニウムイオン ($\text{C}(\text{NH}_2)_3$, Figure 1-1) のpKaは13.6であり、これはマロン酸エステルの活性メチレン (13) や水 (H_2O , 15.7) に匹敵する。

Figure 1-1



Guanidine

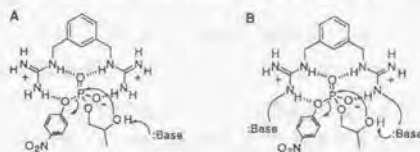
Guanidinium Ion
(π -delocalization)

このようなグアニジンの強塩基性を説明する考え方としてグアニジニウムイオンの π 型共役と呼ばれる共鳴安定化が1972年にGundにより提唱された²⁾。この考え方では、グアニジニウムイオンにおいて炭素カチオンを中心に3つの窒素原子の孤立電子対、計6 π 電子が π 字型に非局在化し、そのため、芳香族化合物に劣らぬ安定性をもつ性質に名付けられたものである。その後、分子軌道計算の進歩とともに様々なグループにより π 型共役の寄与の程度について計算がなされた³⁾。これに対してWibergの1990年の報告によれば、グアニジンがその比較化合物としてのPropane-2-imineと比べても、プロトン化による安定化がほとんど変わらないこと、そしてグアニジニウムイオンの回転障壁が小さいことなどから、 π 型共役による安定化はほとんどなく、グアニジニウムイオンの安定性は主に溶媒との強い水素結合によるものと考えられている⁴⁾。また、1993年にはFrenkingらが、計算によりグアニジンおよびグアニジニウムイオンの最安定構造は完全なplanarからはややはずれており、グアニジンの強塩基性はやはりグアニジニウムイオンの強い水素結合能に由来していると述べている⁵⁾。とはいえ、 π 型化合物の安定可能の根源についてはまだわからないことも多く、今後の研究に期待がもたれる分野である。

このように水素結合能をもつグアニジノ基は、そのドナーともアクセプターともなり、分子認識や分子集合体形成においても重要な役割を演じている^{6,7)}。例えば、Hamiltonらは、フォスフォジエステラーゼ酵素としてDNAやRNAの加水分解

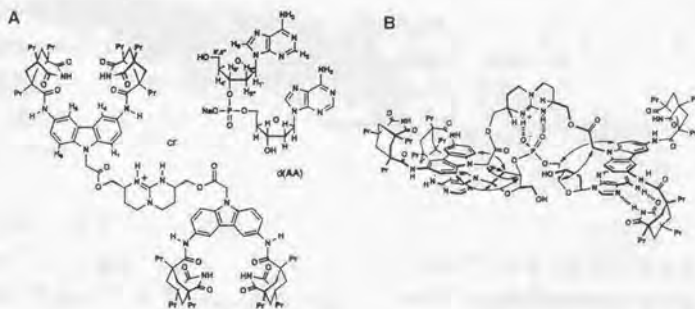
反応を加速させる Staphylococcal nuclease (SN) が Arg35 と Arg87 に活性部位があることにヒントを得て、Figure1-2に示すような人工レセプターを合成した⁶⁰⁾。この合

Figure 1-2 Acceleration of a Phosphate Diester Transesterification by bis(guanidinium) receptors and an added base (A) and by a bis-(guanidinium) receptor with an appended basic group (B).



成レセプターとフォスフォジエステルは、4つの水素結合を形成し、フォスフォジエステル基のリン原子上への求核攻撃を容易にし、その結果、フォスフォジエステルの開裂を加速していることが明らかとなった。また、Rebekらは、Figure1-3に示すような2'-deoxyadenylyl(3'→5')-2'-deoxyadenosine(d(AA))に対する人工レセプターを合成し、d(AA)と高い親和性を持つことをNMRにより明らかとした^{6a)}。この場合もやはり、bicyclicなグアニジニウムイオンが、フォスフォジエステルと水素結合を形成するための鍵構造となっている。

Figure 1-3 A Synthetic Receptor for d(AA) (A) and proposed structure for the complex (B). Arrows illustrate intermolecular NOE.



第2節 グアニジノ基の構造

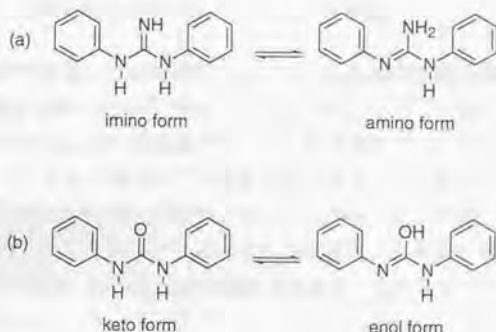
前節のように水素結合能を有する様々なグアニジンおよびグアニジニウムイオンの構造は、その結合様式や電子的性質を知るためにも重要であり、これまで多くの報告がなされてきた¹⁾。

最もシンプルな無置換のグアニジニウムイオン $C^+(NH_2)_3$ は、X線結晶解析⁸⁾、IR、Raman スペクトル⁹⁾や計算¹⁰⁾等により、その構造は平面であることが示唆されて

いる。更にメチルグアニジニウムイオン¹⁰⁾やクレアチン¹¹⁾等の置換グアニジニウムイオンも結晶中でグアニジノ基が平面性を保持していることが報告されている。

また、モノ置換あるいは置換グアニジンにはアミド基やウレア基等と異なり、イミノ型、アミノ型と名付けられる2つの互変異性体が存在する。例えば、*N,N'*-Diphenylguanidineの場合をFigure 1-4aに示した。もちろんアミド基、ウレア基にもこのような互変異性（例えば、*N,N'*-Diphenylureaの場合をFigure 1-4bに示す）が存在するが、一般には結合エネルギー的にケト型が圧倒的に有利であり、グアニジンの場合のような互変異性は問題にならない。グアニジン類の場合、¹⁵N-NMR、IR等のスペクトル解析により、*L*-arginine¹²⁾のようなmonoalkylguanidineではイミノ型、一方、monoaryl-guanidine¹³⁾やニトロ基・シアノ基等の電子吸引基を置換基にもつグアニジン¹⁴⁾ではアミノ型をとる傾向がみられた。結晶構造に関しては報告例が少ないこと及び多くのグアニジン化合物が結晶中で水素結合のネットワーク構造を形成してしまうため、法則性を見いだすには至らない。

Figure 1-4 Tautomerization of *N,N'*-diphenylguanidine and *N,N'*-diphenylurea.



第3節 グアニジンの医薬化学

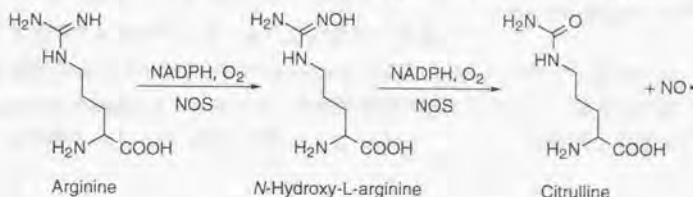
グアニジノ基は、これまで述べてきた化学的特性のほかにも、生体にもなじみの深い官能基でもあり、Arginineの側鎖としてペプチド等の機能発現に必要な構造要素としてもみいだされるほか、多くの医薬品の重要な部分構造としてみいだすことができる¹⁵⁾。

Arginineは、その構造内にグアニジノ基をもつ必須アミノ酸であり、尿素回路に関わるほか、免疫増強やホルモン分泌促進、近年では特に様々な生理活性をもつなど、重要な役割を果たしている¹⁶⁾。また最近注目されている一酸化窒素 (NO) の生成にもArginineが関与している¹⁷⁾。

一酸化窒素 (NO) は、一説によると、血管拡張を促進したり、血小板粘着と凝

集を抑制する働きをもつ血管内皮細胞由来弛緩因子 (EDRF) の本体であると考えられているが、生体内においては *L*-arginine のグアニジノ基の窒素から NO 合成酵素 (NOS) によって産生される。Fukutoらにより、*L*-arginine から Citrulline および NO への変換反応は中間体として *N*-Hydroxy-*L*-arginine を経る 2 段階反応であることが提唱されている (Figure 1-5) ^{17b)}。

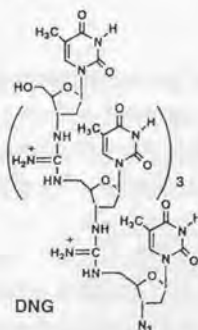
Figure 1-5 Pathway for the Conversion of Arginine to Citrulline and Nitric Oxide.



また、多くの蛋白 (受容体や酵素) の活性部位においても Arginine が重要な役割を果たしていることも種々報告されている¹⁸⁾。例えば、Arginine のグアニジノ基と、Phenylalanine、Tyrosine、Tryptophan 等の芳香族アミノ酸の芳香環とが、パラレルなスタッキング構造をとることにより特有の三次元構造を生み出し、それがしばしば機能発現に重要な役割を担っているとの報告もある。このグアニジノ基と芳香環の相互作用は水素結合ともイオンキレーションとも全く異なった性質のものと考えられている。また、基質側として Arginine が関与する例としてはトリプシンやトロンビン等が知られている。

一方、グアニジノ基の特性をいかした例として、核酸と相互作用するアンチセンスにグアニジノ基を利用した報告もある¹⁹⁾。DNA や RNA のリンキンググループであるフォスフォジエステル基はマイナス電荷をもつため、DNA や RNA が二重鎖や三重鎖を形成する際に電子的な反発がいくらか存在すると考えられる。また、アンチセンスを目的とした分子構築をする場合にはフォスフォジエステル基では各種ヌクレアーゼに弱いという欠点もでてくる。そこで、Bruce らは、リンキンググループをプラス電荷を有するグアニジニウムイオンに置き換えた DNG (Figure 1-6) を合成し、DNA、RNA との融解温度を測定した結果、DNG が溶

Figure 1-6 Guanidinium-Linked Nucleosides.

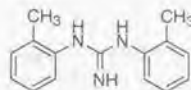


液中でDNA、RNAと二重鎖、三重鎖を形成することを明らかにした。この化合物は、有力なアンチセンス分子として今後の塩基選択性の克服へと期待がもたれる。

医薬化学におけるグアニジン類の最近の例として

Figure 1-7

は、 σ レセプターやN-Methyl-D-aspartate (NMDA) レセプターのリガンドとして芳香族グアニジンが注目されている。 σ レセプターは、1976年にMartinらによってオピオイドレセプターのサブタイプの一つとして提唱されたが²⁰⁾、その生化学的な作用機構は



N,N'-di-o-tolylguanidine (DTG)

未だ解明されていない。N,N'-di-o-tolylguanidine (DTG、Figure 1-7) は、Haloperidol-Sensitive σ レセプターの選択的なリガンドとして注目されており、特に、放射性ラベルした [³H] DTG は、 σ レセプターの存在の確認に重要な役割を果たしている²¹⁾。

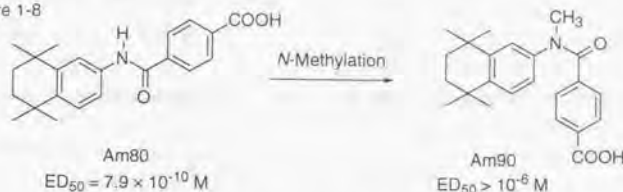
一方、 σ レセプターと密接な関係があるといわれているNMDAレセプターは、興奮性アミノ酸レセプターのサブタイプの一つで、中枢神経系の可塑性形成過程や脳虚血、脳外傷に伴う遅発性神経細胞壊死の発現に高い関連性をもつことが知られている。NMDAレセプターのリガンドのなかには、 σ レセプターと親和性を持つものも少なくない。ところが、NMDAレセプターに選択的なリガンドを探索していたReddyらは²²⁾、N,N'-diarylguanidineのN,N'位（すなわちarylと直接結合した窒素原子）に更にアルキル基を導入した3置換あるいは4置換グアニジン誘導体は、NMDAレセプターへの親和性は保持するが、 σ レセプターへの親和性は大幅に低下することをみいだした。彼らは、この理由として、N,N'位のアルキル化により、もとのdiarylguanidineと比べ、立体的なコンフォメーションの変化が起こっている可能性を挙げている。

第4節 芳香族アミドの立体化学

当薬化学研究室では、これまで立体化学的もしくは医薬化学的興味から種々の芳香族アミド・ウレア誘導体の合成と構造解析を行い、「N-メチル化に伴うシス型優先性」という興味深い立体特性を見いだしてきた。これらの知見は本論で述べる芳香族グアニジン類の立体特性と重要な関わり合いを持っているので、本節において説明する。

影近は合成レチノイドの構造と活性に関する研究²³⁾において、アミド結合をもつ活性化化合物がアミド基のN-メチル化により、その活性を著しく低下させるという結果を得た (Figure 1-8) ²⁴⁾。この事実から、N-メチル化による立体の大きな変

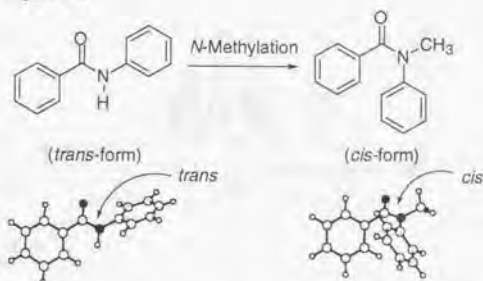
Figure 1-8



化が予測され、X線結晶解析、NMR等の各種スペクトルの吟味により、活性な二級アミド体 (Am80) が結晶中、溶液中ともにトランス型アミドで存在するのに対し、不活性な三級アミド体 (Am90) はシス型アミドで存在するという現象を見いだした²⁵⁾。

この考察をふまえて、東屋は芳香族アミドの立体特性の一般化と展開を行ってきた。すなわち、最も基本的な芳香族アミドであるBenzanilideが結晶中でそのアミド結合がトランス型で存在しているのに対して²⁶⁾、*N*-Methylbenzanilideは2

Figure 1-9



つのベンゼン環が向かい合ったシス型アミド構造で存在していることを明らかにした (Figure 1-9)²⁷⁾。また、Benzanilideと*N*-Methylbenzanilideの¹H-NMRスペクトルは大きく異なり、*N*-Methylbenzanilideの芳香環プロトンのケミカルシフトはBenzanilideに比べて高磁場シフトしている (Figure 1-10)。この高磁場シフトの程度はメチル基の電子的効果だけでは説明できず、溶液中でも*N*-Methylbenzanilideがシス型を優先していることを示している。そこで、*N*-Methylbenzanilideの¹H-NMRスペクトルの温度変化 (Dynamic NMR) を詳細に解析したところ、CD₂Cl₂中、室温では1種類のシグナルを与えるが、温度を下げるにつれ、シス/トランス異性化の過程が観測され、193Kではシス対トランスが98.3:1.7の比率で存在していることが明らかとなった (Figure 1-11)。この時、*N*-メチル基のケミカルシフト差 $\Delta\nu$ (56 Hz) と融合温度 (coalescence point, $233 \pm 5 \text{ K}$) とから、この温度におけるシス体からトランス体への異性化の活性化エネルギーは $13.2 \pm 0.2 \text{ kcal/mol}$ と求められている。この*N*-Methylbenzanilideのシス型優先性を応用してユニークな三次元構

造をもつアミド化合物が合成、解析されたが (Figure 1-12)²⁸⁻³⁰⁾、その幾つかについては本論中において解説した。

Figure 1-10 ^1H -NMR Spectra of Benzanilide and *N*-Methylanilide in CDCl_3 at 293 K

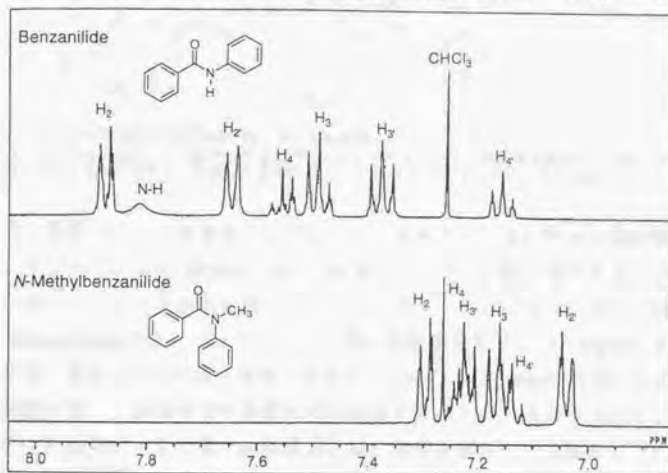
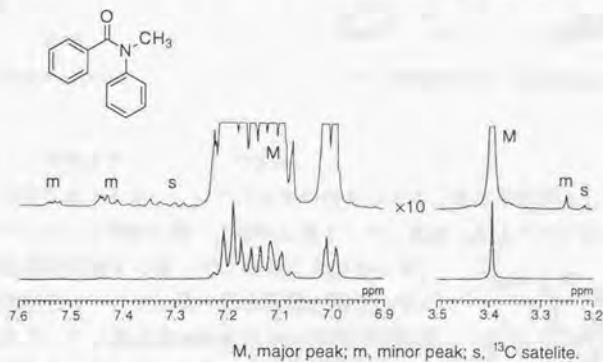
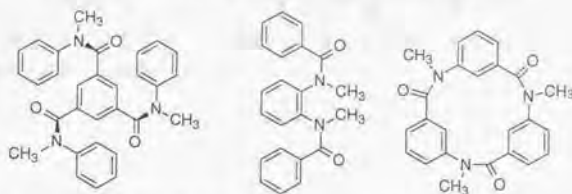


Figure 1-11 ^1H -NMR Spectra of *N*-Methylanilide in CDCl_3 at 193 K



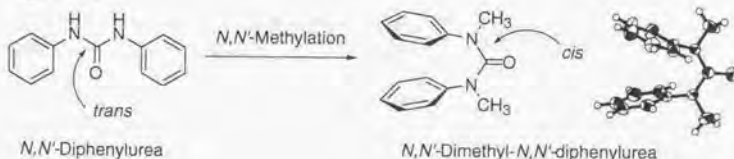
M, major peak; m, minor peak; s, ^{13}C satellite.

Figure 1-12 Unique Crystal Structure of Aromatic *cis*-Amides

- (左) 3つのN-Ph基が中央のPh基に対し同じ側に位置するトリアミド。
 (中) キラルな結晶として自然分晶するジアミド。そのキラリティーは低温下溶液中でも保たれる。
 (右) キラルなキャビティを形成する環状アミド。N-メチル体は1ステップで合成できる。

また、伊藤により、芳香族ウレアについてもN-メチル化に伴う立体転換が示された。すなわち、N,N'-Diphenylureaは結晶中、トランス型で存在することが知られているが³¹⁾、N-メチル基を導入することによりシス型となり、N,N'-Dimethyl-N,N'-diphenylureaでは、(シス、シス)型の結晶構造を示した (Figure 1-13)³²⁾。ウレア基の場合はアミド基の場合と異なり、cross conjugationのため、C-N結合の回転障壁が低く、溶液中での各異性体を識別することができなかったが、ケミカルシフトの比較により、各々結晶構造と同じ構造を溶液中でも優先していると考えられる。

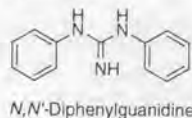
Figure 1-13



第5節 芳香族グアニジンへの展開

以上の芳香族アミド・ウレアの立体特性をふまえ、更なる展開として、私は芳香族グアニジンに興味を持ち、研究に着手した。前述したようにグアニジノ基は多くの生理活性物質に見いだされるにも関わらず、その立体化学については統一的研究がなされていない。グアニジノ基は構造的にはウレア基の酸素原子を窒素原子に置き換えただけの官能基であり、これまで当研究室で明らかにしてきた現象を土台にす

Figure 1-14



れば、芳香族グアニジンに対しても、より深い考察ができると考えた。そこで、*N,N'*-Diphenylguanidine (Figure 1-14) を基本骨格とし、種々の *N*-メチル化体、オリゴマーを合成することにより、芳香族グアニジノ基の立体特性を明らかとし、水溶性機能性分子へと展開した。

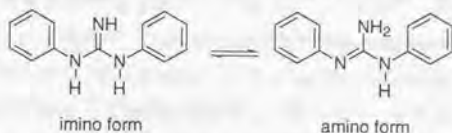


第 2 章 芳香族グアニジンの立体化学

第 1 節 序

前章「序」でも述べたように芳香族グアニジンは立体化学的にも医薬化学的にも興味深い分子であるのに、その結晶構造の報告は数少ない¹³⁾。本章では *N,N'*-diphenylguanidine とその *N*-メチル化体の構造解析の結果とアミド・ウレア類との立体特性の比較について述べる。

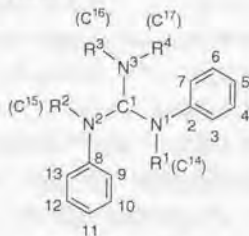
芳香族グアニジン類の立体は互変異性体の存在により複雑である。そこで便宜上、以下のように定義した。まず、互変異性体については、 $C=N$ 二重結合上にフェニル基をもたないものをイミノ型、もつものをアミノ型と名付けた。*N,N'*-diphenylguanidine の場合を Figure 2-1 に示したが、*N*-メチル化体の場合もメチル基の位置に関わらず、Figure 2-1 に従って名付けた。

Figure 2-1 Tautomerization of *N,N'*-Diphenylguanidine (1, E, E-form)

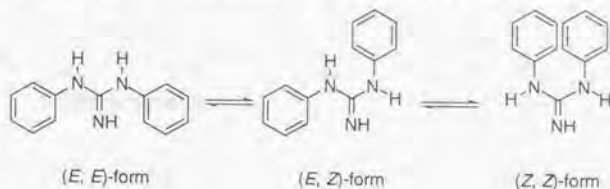
また、各原子には説明をわかりやすくするために、Figure 2-2 のように番号付けをした。すなわち、いずれの互変異性体でもフェニル基を有する 2 つの $C-N$ 結合のうち、短いほうの窒素原子を $N(1)$ 、長いほうを $N(2)$ 、フェニル基をもたない窒素原子を $N(3)$ として順番に番号付けした。炭素原子の番号付けも図示したとおり、この順番になった。よって、 $C(1)-N(1)$ 結合は常に $C(1)-N(2)$ 結合結合よりも 2 重結合性が強いことになる。

E/Z コンフォメーションに関しては、メチル置換基の有無や二重結合性の位置に関係なく、フェニル基同士の位置関係により定義した。例えば、イミノ型 *N,N'*-diphenylguanidine の 3 つのコンフォメーションは Figure 2-3 のように表現される。

Figure 2-2



- 1 ($R^2 = R^3 = R^4 = H$)
- 2 ($R^2 = CH_3, R^3 = R^4 = H$)
- 3 ($R^2 = R^4 = H, R^3 = CH_3$)
- 4a ($R^1 = R^2 = CH_3, R^3 = H$)
- 4b (HBr salt of 4a)
- 5 ($R^2 = R^3 = R^4 = CH_3$)
- 6 ($R^1 = R^2 = R^3 = R^4 = CH_3$)

Figure 2-3 Possible Conformations of the *N,N'*-Diphenylguanidine (imino form)

第2節 芳香族グアニジン類の合成

芳香族グアニジンの立体化学を調べるために、まず、Figure2-2に示す化合物1-5およびすべての窒素原子が置換されたグアニジニウムイオン6を合成することにした。グアニジノ基の構築はシアノ基とアミノ基の縮合もしくはウレア、チオウレアからの変換等の方法が一般的である³⁴⁾。また、Boc-基で保護されたチオウレアを用いる合成法等も有用な方法として知られているが³⁵⁾、多置換グアニジンの合成法には使えない。例えば、*N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4a) の合成は、Figure2-4に示したように*N*-Methyl-*N*-phenylcyanamideと*N*-Methylaniline hydrochlorideとをニートで150°Cで加熱して行った²³⁾。これはグアニジノ基の3つの窒素が反応性がほぼ等しく、グアニジノ基を構築した後に望みの位置にメチル基を導入することが困難なためである。しかもこの反応は出発原料の*N*-メチル化体の反応性がおちることから、以上のような過激な反応条件となり、56%の収率で4aを得ることができた。一方、3や5の合成では、*N,N'*-diphenylthioureaを酸化鉛で活性化した後、アミンと反応させる方法をとった (Figure2-5a)³⁶⁾。この方法は簡便なのでグアニジン合成に広く一般的に採用したいところだが、立体環境に大きく影響され、例えば、*N,N'*-Dimethyl-*N,N'*-diphenylthioureaから4aへの変換はできなかった (Figure2-5b)。合成した1-6はすべてNMR、元素分析、X線結晶解析によりその構造を決定した。詳しい合成法、物性については実験の部に記した。

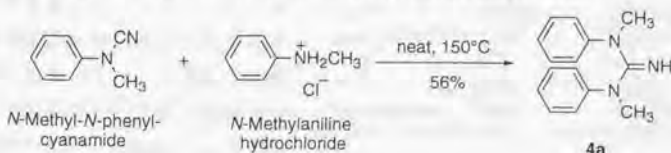
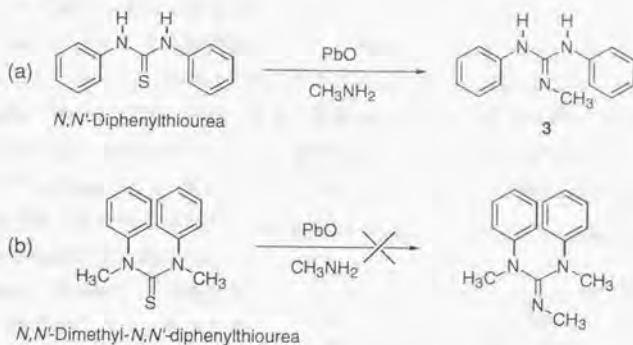
Figure 2-4 Synthesis of *N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4a)

Figure 2-5

第3節 *N,N'*-Diphenylguanidineの結晶構造

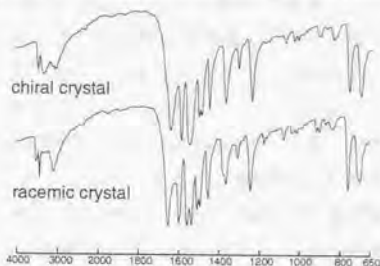
置換基をもたない*N,N'*-Diphenylguanidine (1) のX線結晶解析は、1980年にZakharovらによって行われている³⁷⁾。これに対し、筆者らがこの結晶解析を行ったところ、Zakharovらとは異なる1の結晶データを得た。しかも筆者が得た結晶はキラルな空間群をもつという興味深いものであった。そこで溶媒の条件を種々検討し再結晶を試みたところ、同じエタノールから再結晶しても2種類の異なった結晶が得られることがわかった。温度、濃度等の条件を様々に変えてみたが、結局、2種類の結晶をそれぞれ得るための再結晶条件は特定できなかったが、一方の結晶のタネを用いることで1つのフラスコ内に望みの結晶だけを析出させることができた。2種類の結晶は、その外形と空間群で区別することができる (Table 2-1)。すなわ

Table 2-1 Crystal Data of *N,N'*-Diphenylguanidines

| Compound | 1 (chiral) | 1 (racemic) |
|---|---|--|
| Formula | C ₁₃ H ₁₃ N ₃ | C ₁₃ H ₁₃ N ₃ |
| Mr | 211.27 | 211.27 |
| Recryst solvent | EtOH | EtOH |
| Crystal system | orthorhombic | monoclinic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>P</i> 2 ₁ /c |
| <i>a</i> , Å | 12.653(5) | 8.906(2) |
| <i>b</i> , Å | 20.54(2) | 12.342(1) |
| <i>c</i> , Å | 8.944(5) | 21.335(2) |
| α , ° | — | — |
| β , ° | — | 96.66(1) |
| γ , ° | — | — |
| <i>V</i> , Å ³ | 2324(2) | 2329.1(6) |
| <i>D</i> _{calc} , g·cm ⁻³ | 1.207 | 1.205 |
| <i>Z</i> | 8 | 8 |
| <i>R</i> | 0.085 | 0.048 |
| Crystal shape | Plate | Prisms |

ち、空間群 $P2_12_12_1$ に属するキラル結晶はプレート状の外形をしており、一方、空間群 $P2_1/c$ に属するラセミ結晶はプリズム状の結晶として得られ、このプリズム状ラセミ結晶は、その格子定数等のパラメータから Zakharov らのデータと一致していることがわかった。Table 2-1 からわかるようにキラル結晶もラセミ結晶もその格子定数が極めて似ているが、粉末 X 線解析により全く異なる結晶系であることが確認できた (Appendix)。また、両結晶は、IR スペクトルからも区別することができた (Figure 2-6)。例えば、キラル結晶の 1535cm^{-1} 、 1360cm^{-1} の吸収は、ラセミ結晶ではそれぞれ 2 つのピーク (1540cm^{-1} と 1520cm^{-1} 、 1365cm^{-1} と 1350cm^{-1}) に分裂している。IR スペクトルにおける差はもちろん再現性をもっているが、更に結晶構造と対応づけるために、1 つの単結晶を 2 つに割り、一方を IR サンプルに、もう一方を X 線結晶解析のサンプルに用いることで確認した。

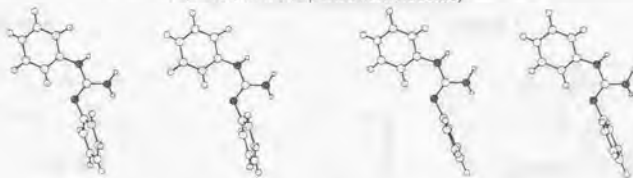
Figure 2-6 IR spectra of chiral and racemic crystals of 1



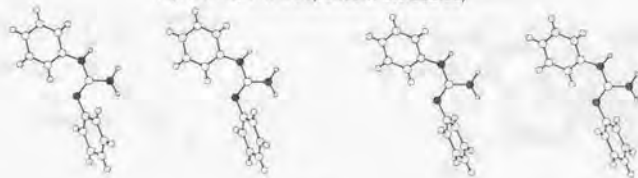
キラル結晶、ラセミ結晶はどちらも単位格子中に *N,N'*-diphenylguanidine (1) を 8 分子含んでおり、非対称単位には 2 分子存在していた (Figure 2-7)。いずれも

Figure 2-7 Stereoview Crystal Structures of 1

1 (chiral, two independent molecules)



1 (racemic, two independent molecules)



分子内のねじれによりキラルなコンフォメーションとなっているが、キラル結晶は一方のエナンチオマーのみ存在しているのに対し、ラセミ結晶では互いにエナンチオマーの関係にある分子が単位格子中に等量存在していることになる。*N,N'*-diphenylguanidine (1) の各結晶中における構造はどちらも類似していた (Figure 2-8)。このとき分子間水素結合は観測されず、どの分子も、芳香環を有する2つのC-N結合のうちの1つの長さ (C(1)-N(1), 1.28-1.30 Å) が、もう1つのC-N結合の長さ (C(1)-N(2), 1.37-1.39 Å) よりも短く、かつ、C=N二重結合長の標準値 (約1.28 Å) に近いことから、アミノ型で存在していることがわかる (Table 2-2)。グアニジノ基はその結合角およびねじれ角から、すべて平面性を保持していた。グアニジノ平面の3つの結合角とその反対側の結合長とは相関しており、例えば、N(2)-C(1)-N(3)結合角 (111-113°) は常に他の2つよりも小さい (Table 2-3)。

1のコンフォメーションは、キラル結晶でもラセミ結晶でも (*E,Z*) 型で、短いC(1)-N(1)結合が*E*型、長いC(1)-N(2)結合が*Z*型である (Figure 2-8)。2つの芳香環はどちらもグアニジノ平面に対して大きくねじれているが、特にN(1)上の芳香環はグアニジノ平面に対してほぼ直角である (65-87°)。一方、N(2)上の芳香環は、2面角が23-34°とやや浅くなっている。結果として、分子内の2つの芳香環同士の2面角も75-87°とかなり大きな値となっている。

Figure 2-8

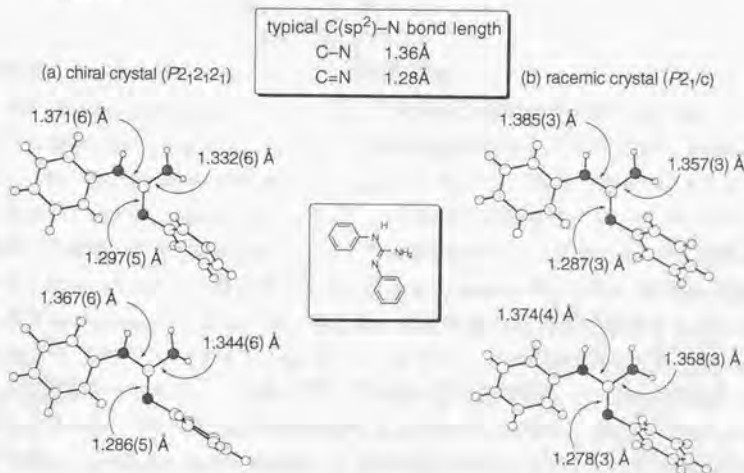


Table 2-2 Bond Lengths and Conformations of Guanidine Bonds

| Compound | N(1)-C(1) | | N(2)-C(1) | | N(3)-C(1) Length (Å) |
|--------------------------|------------|--------------|------------|--------------|-------------------------|
| | Length (Å) | Conformation | Length (Å) | Conformation | |
| 1 (chiral) ^a | 1.286(5) | E | 1.367(6) | Z | 1.344(6) |
| | 1.297(5) | E | 1.371(6) | Z | 1.332(6) |
| 1 (racemic) ^a | 1.287(3) | E | 1.385(3) | Z | 1.357(3) |
| | 1.278(3) | E | 1.374(4) | Z | 1.358(3) |

a) Two independent molecules exist in the asymmetric unit.

Table 2-3 Bond Angles (deg) in the Crystal Structures of 1

| Compound | 1 (chiral) ^a | 1 (racemic) ^a |
|----------------|-------------------------|--------------------------|
| Bond angles | | |
| N(1)-C(1)-N(2) | 122.5(4), 120.6(4) | 121.1(3), 122.4(3) |
| N(2)-C(1)-N(3) | 112.7(4), 113.4(4) | 111.3(3), 112.3(3) |
| N(3)-C(1)-N(1) | 124.9(4), 125.8(4) | 127.4(3), 125.3(3) |

a) Two independent molecules exist in the asymmetric unit.

第4節 N-メチル化芳香族グアニジンの結晶構造

N,N'-DiphenylguanidineをN-メチル化した可能な7種類の化合物(塩は除く)のうち4種類(2-5, Figure 2-2)についてX線結晶解析を行うことができた(Table 2-4)。特に*N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4a)は、室温においてはオイル状であるが、-20°Cで*n*-hexaneから再結晶し、-100°Cで平板イメージングプレートを装備した高速X線回折装置を用いることで結晶解析を行うことができた³⁸⁾。興味深いことに4a (Z=4)は、単位格子に水2分子と*n*-hexane 1分子を含んでいた。従って結晶のdisorderによるものか、結合長、結合角等の値の標準偏差が大きい(Table 2-5, 2-6)。この表からわかるようにグアニジンの場合は既して通常の(例えば芳香族アミドやウレアの解析データと比べて)標準偏差(1/1000-2/1000)よりも大きい、これらもdisorderの影響によるのかもしれない。また、グアニジニウム塩4a、6の場合も精密な結合長、結合角が得られていないが、これは共存する重原子(BrまたはI)アニオンによるものではないかと考えている。

Table 2-4 Crystal Data of Various Diphenylguanidines

| Compound | 2 | 3 | 4a | 4b | 5 | 6 |
|---|---|---|--|---------------------|--|---|
| Formula | $C_{14}H_{15}N_3$ | $C_{14}H_{15}N_3$ | $C_{15}H_{17}N_3 \cdot 1/2H_2O \cdot 1/4C_6H_{14}$ | $C_{15}H_{18}N_3Br$ | $C_{16}H_{19}N_3$ | $C_{17}H_{22}N_3 \cdot H_2O$ |
| M _r | 225.29 | 225.29 | 269.87 | 320.23 | 253.35 | 413.30 |
| Recryst solvent | CH_2Cl_2 | AcOEt/ <i>n</i> -C ₆ H ₁₄ | <i>n</i> -C ₆ H ₁₄ | CHCl ₃ | <i>n</i> -C ₆ H ₁₄ | CHCl ₃ /AcOEt |
| Crystal system | orthorhombic | monoclinic | triclinic | triclinic | monoclinic | orthorhombic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>C</i> 2 | <i>P</i> 1 | <i>P</i> 1 | <i>C</i> 2/c | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> , Å | 5.666(1) | 11.212(2) | 11.590(5) | 13.034(3) | 18.532(2) | 12.055(3) |
| <i>b</i> , Å | 10.126(3) | 12.757(2) | 16.44(2) | 13.216(4) | 7.736(2) | 14.776(3) |
| <i>c</i> , Å | 21.17(2) | 9.281(1) | 8.320(4) | 9.711(2) | 20.462(2) | 10.466(4) |
| α , ° | — | — | 97.21(7) | 91.85(2) | — | — |
| β , ° | — | 112.21(1) | 90.73(3) | 94.99(2) | 104.273(9) | — |
| γ , ° | — | — | 77.50(7) | 65.14(1) | — | — |
| <i>V</i> , Å ³ | 1214(3) | 1229.1(4) | 1535(2) | 1512.1(6) | 2842(1) | 1864.3(7) |
| <i>D</i> _{calc} , g·cm ⁻³ | 1.232 | 1.217 | 1.167 | 1.407 | 1.184 | 1.472 |
| <i>Z</i> | 4 | 4 | 4 ^a | 4 ^a | 8 | 4 |
| <i>R</i> | 0.075 | 0.062 | 0.097 | 0.079 | 0.069 | 0.065 |

a) Two independent molecules exist in the asymmetric unit.

Table 2-5 Bond Lengths and Conformations of Guanidines

| Compound | N(1)–C(1) | | N(2)–C(1) | | N(3)–C(1) |
|-----------------|------------|--------------|------------|--------------|------------|
| | Length (Å) | Conformation | Length (Å) | Conformation | Length (Å) |
| 2 | 1.284(6) | <i>E</i> | 1.394(6) | <i>Z</i> | 1.345(7) |
| 3 | 1.270(9) | <i>Z</i> | 1.380(9) | <i>Z</i> | 1.379(10) |
| 4a ^a | 1.40(1) | <i>Z</i> | 1.40(1) | <i>Z</i> | 1.27(1) |
| | 1.39(1) | <i>Z</i> | 1.40(1) | <i>Z</i> | 1.26(1) |
| 4b ^a | 1.35(2) | <i>Z</i> | 1.38(2) | <i>Z</i> | 1.33(2) |
| | 1.34(2) | <i>Z</i> | 1.35(1) | <i>Z</i> | 1.33(1) |
| 5 | 1.298(5) | <i>Z</i> | 1.409(5) | <i>E</i> | 1.345(5) |
| 6 ^b | 1.32(2) | <i>E</i> | 1.36(1) | <i>Z</i> | 1.32(1) |

a) Two independent molecules exist in the asymmetric unit.

b) The average values of (+)- and (–)-crystals are shown.

Table 2-6 Bond Angles (deg) in the Crystal Structures of Diphenylguanidines (1-6)

| Compound | 1 (chiral) ^a | 1 (racemic) ^a | 2 | 3 | 4a ^a | 4b ^a | 5 | 6 ^a |
|------------------------|-------------------------|--------------------------|-----------|-----------|----------------------|-----------------|----------|----------------|
| Bond angles | | | | | | | | |
| N(1)-C(1)-N(2) | 122.5(4), 120.6(4) | 121.1(3), 122.4(3) | 119.8(4) | 127.8(7) | 112(1), 113(1) | 116(1), 118(1) | 125.2(4) | 119.6(10) |
| N(2)-C(1)-N(3) | 112.7(4), 113.4(4) | 111.3(3), 112.3(3) | 115.1(4) | 111.4(7) | 124(1), 121(1) | 121(1), 120(1) | 115.5(4) | 117.6(10) |
| N(3)-C(1)-N(1) | 124.9(4), 125.8(4) | 127.4(3), 125.3(3) | 124.9(5) | 120.8(7) | 123(1), 125(1) | 122(1), 121(1) | 119.3(4) | 122.2(10) |
| C(1)-N(1)-C(2) | — | — | — | — | 123.0(10), 123.0(10) | 122(1), 122(1) | — | 122.5(9) |
| C(2)-N(1)-C(14) | — | — | — | — | 118(1), 117(1) | 118(1), 116(1) | — | 115.7(9) |
| C(14)-N(1)-C(1) | — | — | — | — | 117(1), 116(1) | 119(1), 120(1) | — | 121.8(9) |
| C(1)-N(2)-C(8) | — | — | 119.4(4) | — | 123.2(9), 121.9(9) | 122(1), 120(1) | 120.7(3) | 120.1(10) |
| C(8)-N(2)-C(15) | — | — | 118.1(4) | — | 118(1), 118.7(9) | 121(1), 117(1) | 120.6(4) | 117.6(10) |
| C(15)-N(2)-C(1) | — | — | 118.1(5) | — | 115(1), 118(1) | 115(1), 120(1) | 118.6(4) | 122.1(10) |
| C(1)-N(3)-C(16) | — | — | — | — | — | — | 118.6(4) | 121.8(10) |
| C(16)-N(3)-C(17) | — | — | — | — | — | — | 117.4(5) | 115.1(10) |
| C(17)-N(3)-C(1) | — | — | — | — | — | — | 122.9(5) | 122.6(10) |
| Torsion angles | | | | | | | | |
| C(2)-N(1)-C(1)-N(2) | 178.5(4), -172.7(4) | -171.9(3), 175.7(3) | -175.9(5) | 21(1) | -39(1), 31(1) | 149(1), -144(1) | -15.1(7) | 145.5(9) |
| C(2)-N(1)-C(1)-N(3) | -1.0(7), 12.5(7) | 12.9(5), -7.2(5) | 8.1(8) | -159.8(8) | 138(1), 149(1) | -50(1), -132(1) | 167.6(4) | -38(1) |
| C(8)-N(2)-C(1)-N(1) | -6.6(7), 26.7(8) | 28.0(5), -17.1(5) | 20.9(7) | 34(1) | -32(1), 39(1) | -48(1), 49(1) | 127.7(5) | -42(1) |
| C(8)-N(2)-C(1)-N(3) | 173.0(4), -157.9(5) | -156.1(3), 165.4(3) | -162.7(5) | -143.6(8) | -147(1), -140(1) | -30(1), 32(1) | -85.0(6) | 138.1(10) |
| C(3)-C(2)-N(1)-C(1) | -81.0(7), 69.68(6) | -124.1(3), -72.3(4) | -110.5(6) | -138.1(8) | 147(1), -136(1) | 147(1), -148(1) | -41.7(7) | -42(1) |
| C(9)-C(8)-N(2)-C(1) | 162.6(5), 178.3(4) | -177.7(3), 160.2(3) | 51.8(7) | 19(1) | -40(1), -147(1) | -32(1), 34(1) | -21.5(6) | -41(1) |
| Dihedral angles | | | | | | | | |
| Guanidine vs Ph | 86.7, 72.9 | 115.9, 73.6 | 75.9 | 59.8 | 62.0, 62.5 | 112.2, 72.9 | 49.2 | 69.6 |
| Ph vs Ph | 22.9, 23.7 | 28.8, 145.7 | 53.0 | 49.7 | 62.9, 62.1 | 111.0, 68.4 | 66.6 | 71.4 |
| | 105.0, 96.3 | 87.4, 75.5 | 115.4 | 59.3 | 37.0, 38.3 | 30.7, 31.1 | 79.6 | 107.8 |

a) Two independent molecules exist in the asymmetric unit. b) The average values of (+) and (-) crystals are shown.

N-Methyl-*N,N'*-diphenylguanidine (2) は、*N,N'*-Diphenylguanidine (1) と同様アミノ型をとっており、C(1)–N(1)の結合長が1.284Åと短い (Figure 2-9)。そのコンフォメーションも (*E,Z*) 型であり、メチル基により *N*(2)-フェニル基のダニジノ平面に対するねじれ角が大きく (63°) なっている以外

は1とよく類似している。ただし、窒素原子の周りの結合角をみると、N(2)原子の平面性がわずかではあるがずれていることがわかる。

N(2)の周りの3つの結合角の和は355.6°であり、N(2)は

それに結合する3つの炭素原子のつくる平面から約0.17Åの距離にある。この平面からのずれは以下に述べる

ような立体的に混んでいると思われる化合物5や6を含めて今回結晶解析した分子の中

でもこの窒素原子にしかみられない (Table 2-6)。

化合物2の結晶中における分子間相互作用を調べてみる

と、この一連の化合物の中では唯一例外的に水素結合のネットワークを形成していた (Figure 2-10)。また、2のN(2)のメチル基は、結晶中、隣接した分子のN(1)の芳香環の上にあり (図中、矢印の部分)、その距離 ($C_{Me}-Ph$ 間) は3.29Åと、CH/π相互作用が存在する可能性が示唆される³⁹⁾。これらの分子間相互作用の存在が分子構造に影響しているのかもしれない。

もう1つのモノメチル体である *N*-Methyl-*N',N''*-diphenylguanidine (3)

も、C(1)–N(1)の結合長が1.270Åとアミノ型であるが、1や2とは異なる (*Z,Z*) 型コンフォメーションを示

Figure 2-9 Crystal Structure of 2

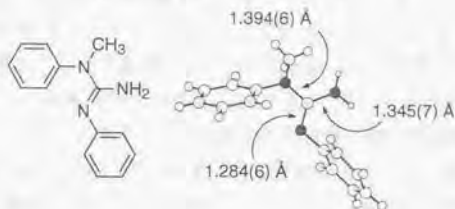


Figure 2-10 Hydrogen-bonding Network in the crystal of 2

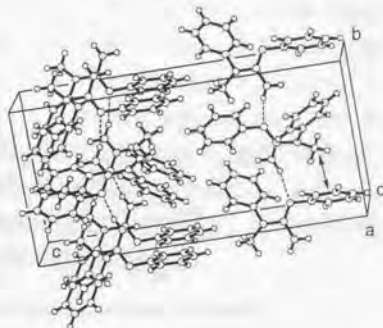


Figure 2-11 Stereoview Crystal Structures of 3



した (Figure 2-11)。これは *N*(3)-メチル基の存在により *N*(1)-フェニル基が混んでいる *Z* 側へ向いたと考えられる。

N,N'-Dimethyl-*N,N'*-diphenylguanidine (4a) も定義に従うと 3 と同様 (*Z,Z*) 型コンフォメーションであるが、この構造は明らかに 3 と異なっている (Figure 2-12)。まず、グアニジノ基の構造について 3 は 1 や 2 と同様アミノ型であったのに対し、4a は C(1)-N(3) の結合長が 1.26–1.27 Å と短く、イミノ型をとっている。更に両化合物の決定的な違いは、2 つの芳香環どうしの 2 面角である。3 では 2 つの芳香環どうしの 2 面角は 59° と大きく、異なる方向を向いているが、4a では 37–38° とかなり平行に近く、互いに向かいあっている。このことは、3 の 2 つの芳香環の中心間距離が 4.28 Å と大きいのにに対し、4a では $C_{ipso}-C_{ipso}$ で 2.89 Å、リングセンターどうして 3.85 Å となっていることからわかる。ゆえに 3 と 4a は、コンフォメーションの分類上では同じだが、その根源は全く異なったものである。4a における芳香環が層状に向かいあったイミノ型 (*Z,Z*) コンフォメーションは *N,N'*-Dimethyl-*N,N'*-diphenylurea の結晶構造とよく類似している (Figure 1-13)。いずれの構造においても 2 つの芳香環は平行から幾分ずれているが、これは π 電子同士の反発によるものと考えられる⁴⁰⁾。興味深いことに、この芳香環層状コンフォメーションは、4a の HBr 塩である 4b の結晶構造においてもみられた (Figure 2-12)。4b ではグアニジノ基の 3 つの C-N 結合の長さがほぼ等しく (Table 2-5)、部分二重結合性が同等に分布していることがわかり、Y 型共役の効果がうかがわれる。このようにグアニジニウムイオンが同じく層状構造をとることは興味深く、この結果は後述 (第 5 章) する水溶性芳香族多層分子の基本構造となる。

Figure 2-12 Stereoview Crystal Structures of 4a and 4b

4a (two independent molecules)



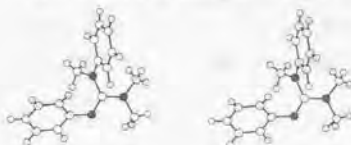
4b (two independent molecules)



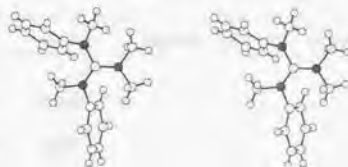
フリーの N,N' -ジフェニルグアニジン類では最多置換体である N,N,N' -Trimethyl- N',N'' -diphenylguanidine (5) のコンフォメーションは一見すると1や2と同じだが、短い $C(1)-N(1)$ 結合が Z 型、 $C(1)-N(2)$ 結合が E 型で、その点は逆といえる (Figure 2-13a)。5ではそのメチル基の立体障害から、二重結合性の弱い $C(1)-N(2)$ 結合 (1.409Å) のまわりのねじれ角が大きく (52–55°)、グアニジノ平面と2つの芳香環との2面角も大きい (49°と67°)。すなわち、この立体障害はグアニジノ基の平面性を崩すまでにはいたらないが、 N -置換基のグアニジノ平面からのねじれを増大させる。この現象は更にメチル化して得られる N,N,N',N'' -Tetramethyl- N',N'' -diphenylguanidinium ion (6) においては、一層顕著にみられる (Figure 2-13b)。6のコンフォメーションは (E,Z) 型であり、グアニジノ平面においては、芳香環を有する $C-N$ 結合はグアニジノ平面に対して34–42°ねじれ、同じく $C(1)-N(3)$ 結合もグアニジノ平面に対して26–31°ねじれている。この置換基が立体的に混み合うことによって生じるねじれ構造は、ユニークなプロペラ状構造を形成する要因となったわけであるが⁴¹⁾、これについては第4章で述べる。

Figure 2-13

(a) Stereoview Crystal Structures of 5



(b) Stereoview Crystal Structures of 6



第5節 芳香族グアニジン類の溶液中での立体化学

温度を変化させながらNMRを測定することにより、溶液中におけるその化合物の動的挙動を知ることができる⁴²⁾。アミド結合は共鳴効果により、その $C_{\text{co}}-N$ 結合が部分的な二重結合性をおびているため、 $C_{\text{co}}-N$ 結合の回転は、通常の単結合と比較してかなり束縛されている。一般にアミド結合の異性化の障壁は15–20kcal/mol程度であり、置換基の種類にもよるが、NMRのタイムスケールで異性化の観測が可能な場合が多い⁴³⁾。一方、ウレア結合は2つの窒素原子の孤立電子対がともにカルボニル基と共鳴する Cross-conjugation のため、アミド結合に比べ、 $C_{\text{co}}-N$ 結合の二重結合性は減少している⁴⁴⁾。そのため、 $C_{\text{co}}-N$ 結合の回転障壁は10kcal/molあるいはそれ以下であることも多く、NMRのタイムスケールでは異性

化の観測が困難である。

グアニジンでは、ウレアと同様のCross-conjugationに加え、窒素原子上の反転により回転障壁は一層低くなる⁴⁵⁾。実際、今回合成した芳香族グアニジン誘導体1、3、4は、 CD_2Cl_2 中で183Kまで温度を下げてでも単一の芳香環に対応するシグナルしか与えず、マイナーピークは観測されなかった。おそらくこれらの化合物は、2つの芳香環が等価となる対称なコンフォーマーで存在しているか、あるいはいくつかのコンフォーマー間の速い平衡にある可能性が考えられる。

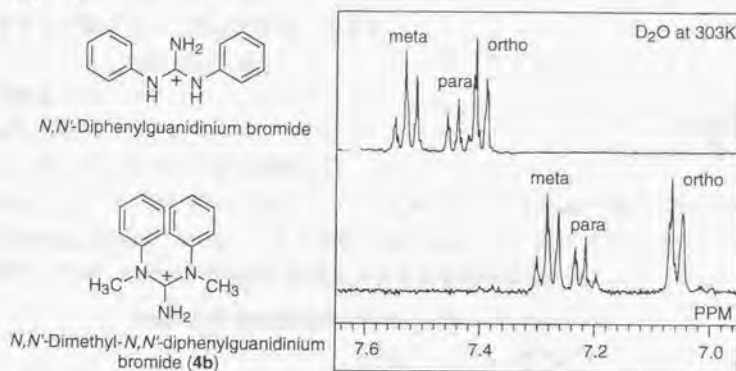
N,N'-Dimethyl-*N,N'*-diphenylguanidine (4a) の芳香環プロトンのケミカルシフトは*N,N'*-diphenylguanidine (1) や*N*-Methyl-*N',N''*-diphenylguanidine (3) よりも0.1-0.2ppm高磁場シフトしている (Table 2-7)。従って1では (Z,Z) 型の寄与はほとんどないが、4aでは結晶構造に対応する (Z,Z) 型コンフォメーションを優先していると考えられる。しかし、ケミカルシフト差を、トランス型、シス型構造をもつ芳香族アミド・ウレアと比べると小さい (Table 2-7)。

Table 2-7 Comparison of ^1H -NMR Chemical shifts (δ) of Aromatic Protons in Secondary and Tertiary Anilino Groups in CDCl_3 at 303 K.

| | ortho | meta | para | $\Delta\delta_{\text{ortho}}$ | $\Delta\delta_{\text{meta}}$ | $\Delta\delta_{\text{para}}$ |
|--|-------|------|------|-------------------------------|------------------------------|------------------------------|
| <i>N,N'</i> -Diphenylguanidine unsubstituted (1) | 7.12 | 7.31 | 7.06 | 0.19 | 0.14 | 0.10 |
| <i>N,N'</i> -dimethyl (4a) | 6.93 | 7.17 | 6.96 | | | |
| <i>N,N'</i> -Diphenylguanidinium salt unsubstituted | 7.31 | 7.46 | 7.37 | 0.51 | 0.30 | 0.25 |
| <i>N,N'</i> -dimethyl (4b) | 6.80 | 7.16 | 7.12 | | | |
| Benzanilide unsubstituted | 7.64 | 7.38 | 7.16 | 0.60 | 0.16 | 0.04 |
| <i>N</i> -methyl | 7.04 | 7.22 | 7.12 | | | |
| <i>N,N'</i> -Diphenylurea unsubstituted | 7.35 | 7.35 | 7.13 | 0.56 | 0.31 | 0.20 |
| <i>N,N'</i> -dimethyl | 6.79 | 7.04 | 6.93 | | | |

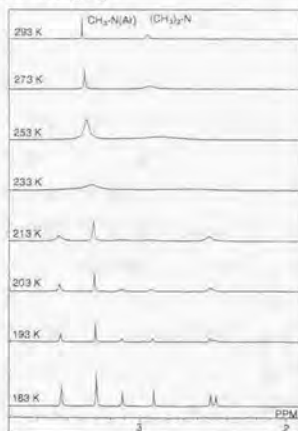
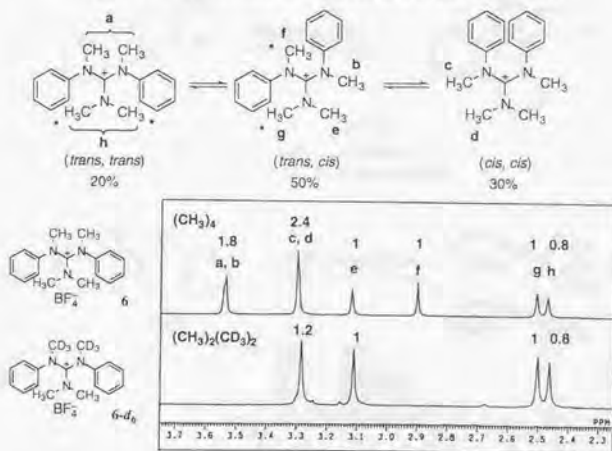
この違いの理由として *N,N'*-diphenylguanidine (1) の互変異性 (アミノ型) の寄与があると考えられる。実際、4a の HBr 塩 4b では、1 の塩と比較すると、更に顕著な高磁場シフトが観測され、具体的にはオルト位で 0.51 ppm、メタ位で 0.30 ppm、パラ位で 0.25 ppm だけ高磁場シフトしている。これらの値は、芳香族ウレアの場合とよく対応している。2 つのグアニジニウムイオンのケミカルシフトの差は同じく D_2O 中においてもみられた (Figure 2-14)。従って、*N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4a) およびそのグアニジニウムイオン 4b は、種々の有機溶媒中もしくは水溶液中で、2 つの芳香環が向かいあった (Z,Z) 構造を優先していることが示唆された³⁸⁾。

Figure 2-14



一方、*N,N,N',N''*-Tetramethyl-*N',N''*-diphenylguanidinium ion (6) はグアニジノ基のすべての窒素原子上にメチル基を持つグアニジニウムイオンであり、立体的に混み合っているため、回転障壁は大きくなると予想される。実際、6 について温度を変えながら NMR 測定を行ったところ、6 の *N*-メチル基は室温では単一のシグナルを与えるが、温度を下げていくにつれ融合点を経てピークは複雑になり、183K では 7 本のシングレットピークに分かれてくる (Figure 2-15)。6 の溶液中での可能な 3 種類のコンフォーマー (*E,E*)、(*E,Z*)、(*Z,Z*) では、それぞれ 2 本、4 本、2 本の非等価なメチル基が存在するため、これら 3 つのコンフォーマーの混ざりと考えてよい。このシグナルをアサインするために 6 の N(1) 位と N(2) 位のメチル基を d 置換した化合物 (6- d_6) を合成した (Figure 2-16)。化合物 6- d_6 の NMR チャートでは、N(3) 位のジメチルのピークしか観測されないことになる (Figure 2-16)。また、

3.0ppmよりも高磁場にあるピークは分子内の芳香環のアニソトロピー効果を受けたメチル基（星印を付けたメチル基）に対応すると考えられる。これらの情報と NMR チャートの積分値とを考察すると、7本に見えたピークはそれぞれ同じアルファベット記号をもつメチル基にアサインされ、その結果、6は CD_2Cl_2 中、183Kにおいては、(E,E)、(E,Z)、(Z,Z)のコンフォーマーがそれぞれ2:5:3の比の混ざりて存在すると決定できた。最安定のコンフォーマーは(E,Z)型であり、これは結晶中のコンフォーマーと同じである。また、4と同じ(ZZ)型コンフォーマーは、4つのメチル基の大きな立体障害にもかかわらず、30%の寄与がある。この結果は、メチル基をもたない N,N' -Diphenylguanidine (1) もしくはその塩においては(Z,Z)型コンフォメーションの寄与（存在）がわずかであることと比べると対照的である。

Figure 2-15 Temperature-dependent NMR of 6 in CD_2Cl_2 Figure 2-16 Conformational Behavior of 6 in CD_2Cl_2 at 183K

第3章 *N*-メチル化によるシス型優先性の一般化

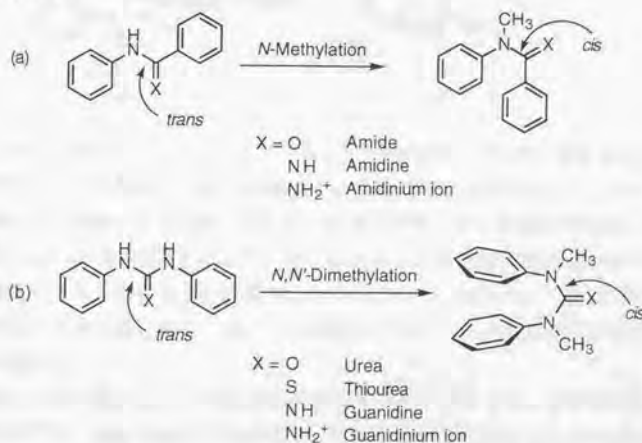
第1節 芳香族グアニジン類の立体特性

—芳香族アミド・ウレアとの比較—

これまで第1章で述べてきた芳香族アミド・ウレアでみられた立体特性に基づいて、第2章では芳香族グアニジン類の立体化学について論じてきた。この章では、これらの共通性についてまとめ、いくつか応用例も紹介したい。

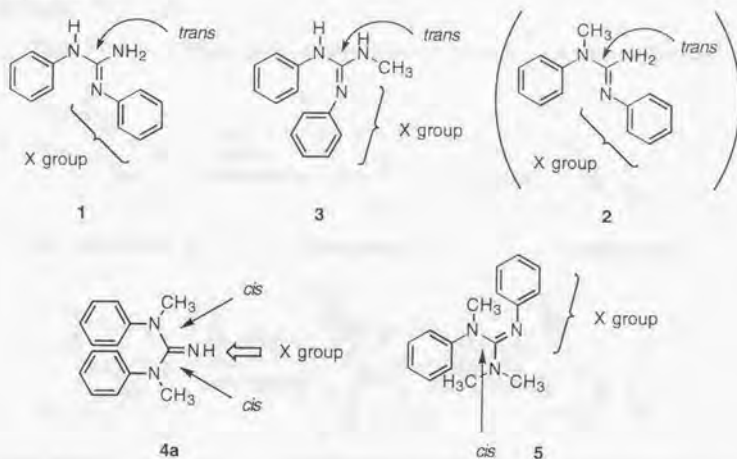
まず、*N*-メチル化によるコンフォメーション転換の一般式をFigure3-1に示す。第2章でグアニジンの立体を表現するのに用いていた*E/Z*表記との混同をさけるため、この章では一般的な立体（幾何異性）をあらわすものとしてトランス/シス表記を用いた。例えば、Figure3-1においてメチル基（または水素原子）がC=X二重結合に対して同じ側にあるのがシス型である。*N*-メチル化に伴うシス型への立体転換は、Xが酸素原子であるアミド・ウレアで一般的に成立する^{27,32)}。第2章で述べたグアニジン化合物はXが窒素原子に対応するわけだが、互変異性体が存在するため複雑になっているため、「*N*-メチル化に伴う立体転換」という式では統一的に表現できないが、「二級アニリドがトランス、*N*-メチル化アニリドがシス型を優先」という立体特性は共通している。

Figure 3-1



第2章の1-6の結晶のコンフォメーションを吟味してみると、1と3では、*N*(2)-フェニル基がC=N(Ph)二重結合 (X = NPh) に対してはトランス型であり、また4a (X = NH) と5 (X = NPh) では*N*-メチル基をもつフェニル基はシス型コンフォメーションをとっている (Figure 3-2)。唯一の例外としてこの法則を破っているのが2であり、*N*-メチル基はC(1)=N(1)二重結合に対してトランスに位置している。しかし、2は1-6の中で唯一水素結合 (およびCH/π相互作用) のネットワークが観測された化合物であるから、あるいは2のコンフォメーションがこのような分子間相互作用も少なからず影響されている可能性もある。

Figure 3-2

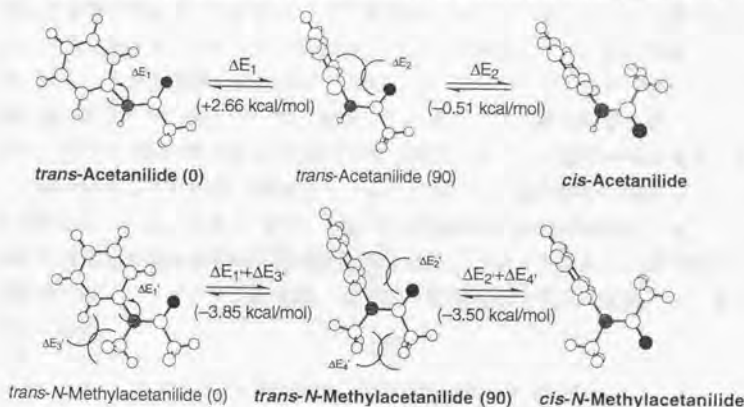


グアニジン類のもう1つのフェニル基は化合物4を除いてC=N二重結合上にあり、アミドやウレアの場合とは様子が異なる。結晶構造を比較すると、この二重結合上のフェニル基はより立体的にすいている方に配向している傾向がある。化合物3の*N*(1)-フェニル基が*Z*型となっていることから、メチル基と*N*(2)-フェニル基とでは立体的にメチル基の方がかさ高いといえるのかもしれない。これは球状のかさ高さをもつメチル基に対し、フェニル基は方向性をもったかさ高さを有しているためであろう。

この*N*-メチル化によるシス型優先性の根源は何であろうか。このシス/トランスのエネルギー差は非常に小さいため、計算化学的に解明することは困難であると予想される。斉藤・板井らの*ab initio*計算を用いた報告によれば、トランス型の

AcetanilideをN-メチル化すると、N-メチル基の立体障害やカルボニル基の非共有電子対とフェニル基の π 電子との電子的反発等によりトランス型コンフォメーションが不安定化し、その結果としてシス型が優先されるという説明がなされている (Figure 3-3)⁴⁶⁾。この説明が正しいかどうかはまだわからないが、このN-メチル化体のシス型優先性が**4b**のようなアミド・ウレア・グアニジンとは電子的性質の異なるグアニジニウムイオンにおいても観測されたことは興味深い。グアニジニウムイオンでは π 電子はY型共役により、広く分布しており、またカルボニル酸素のような非共有電子対はない。斉藤らの計算では2つの効果のうち前者の立体的効果が大きいと考えられており、グアニジニウムイオンの場合にもあてはまるのではないだろうか。

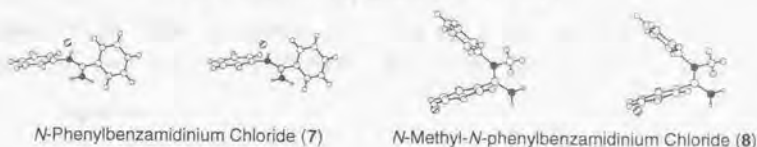
Figure 3-3 Energy Relationships of Conformers of Acetanilide and N-Methylacetanilide



第2節 芳香族アミジン類への応用

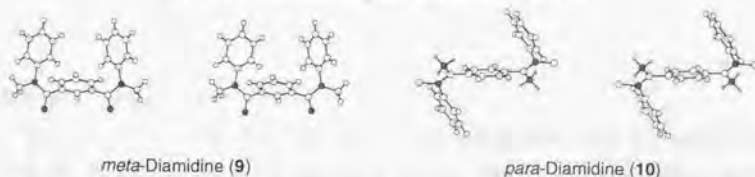
アミジノ基はアミド基の酸素原子を窒素原子に置き換えた官能基であり ($X = \text{NH}$, Figure 3-1a)、グアニジンと同様、塩基性を示すため塩にすることで、アミドの特性をもちながら水溶性をも兼ねそろえた分子の構築に利用できる。すなわち、グアニジン類がウレアに対応するのに対し、アミジン類はアミドに対応している。そこでまず、N-Phenylbenzamidinium hydrochloride (**7**) およびそのN-メチル化体であるN-Methyl-N-phenylbenzamidinium hydrochloride (**8**) を合成し、その結晶構造を解析した (Figure 3-4)。その結果、アミドの場合と極めてよく類似した立体特性をもつことがわかり、この場合もシス型優先性則に従っていた。

Figure 3-4 Stereoview Crystal Structures of 7 and 8



そこで、更に3つのベンゼン環を2つの*N*-メチルアミノ基でそれぞれメタ位、パラ位で連結した化合物(9および10)を合成し、そのX線結晶解析を行った(Figure3-5)。これらの化合物のアミド誘導体(9'および10')は東屋により既に合成・構造解析が行われている²⁸⁾。Figure3-5に示したようにアミドもアミジンもすべてシス型で存在するとともに、パラ置換体(10および10')では、末端の2つの*N*-フェニル基は中央のベンゼン環の面に対して反対側、アンチ型に位置しているのに対し、メタ置換体(9および9')では、2つの*N*-フェニル基が中央のベンゼン環の面に対して同じ側、シン型に配置しているという共通の特徴を有していた。メターアミド体9'の場合は¹H-NMRの詳細な解析により、低温では結晶構造と同じシン体を優先しているが、温度を上げるにつれアンチ型の割合が増加してくることが示されている。メターアミジン(9)でも同様の¹H-NMRの温度変化を示し、同様の立体変化がおこなっていることが示唆された。このメタ体のシン優先性および溶液中でのシン/アンチの変化は、芳香環-芳香環相互作用に起因していると考えている²⁸⁾。

Figure 3-5 Stereoview Crystal Structures of 9 and 10



また、*m*-(*N*-Methylamino)benzoic acidをピリジン中、Tetrachlorosilane (SiCl_4)で処理すると、環状アミド化合物(いずれも*N*-メチルアミド基はすべてシス型)を生成すること(Figure3-6a)も東屋により明らかにされたが³⁰⁾、同様に*m*-(*N*-Methylamino)benzonitrileを AlCl_3 と反応(160°C)させると、環状トリアミジン誘導

体11を低収率ながら得ることができた (Figure3-6b)。この化合物も*N*-メチルアミジノ基はすべてシス型のおわん状の結晶構造を示した (Figure3-7)。化合物11は後述 (第5章) するようにDNAとの相互作用が確認されており、現在、この化合物を含めて*N*-メチルアミジン類の構造と機能性分子への応用を進めている。

Figure 3-6

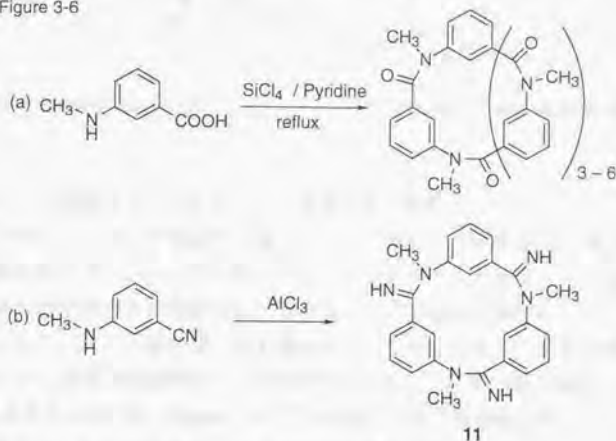
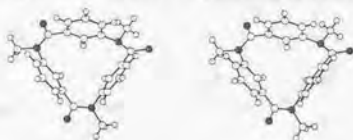


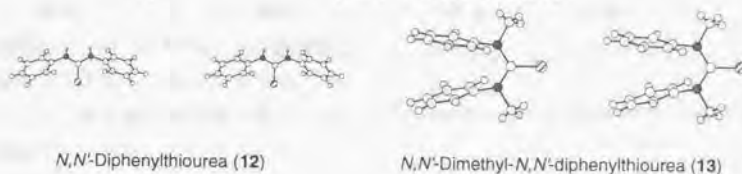
Figure 3-7 Stereoview Crystal Structure of 11



第3節 芳香族チオウレア

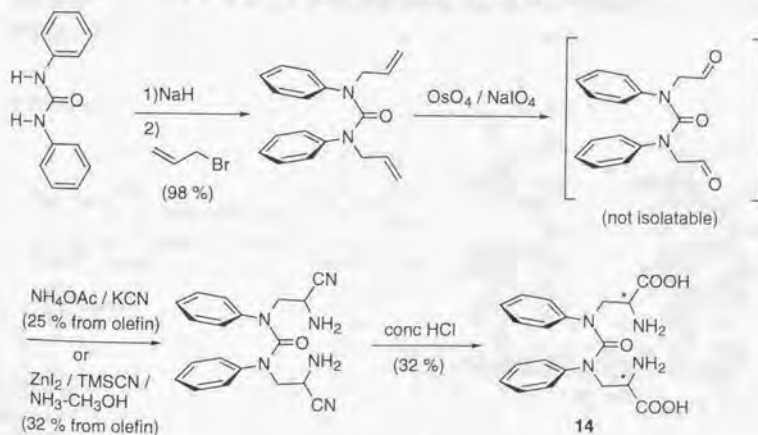
ウレア・グアニジンについてみられたシス型優先性がチオウレアでは成立するかを確かめるため、*N,N'*-Diphenylthiourea (12) と *N,N'*-Dimethyl-*N,N'*-diphenylthiourea (13) を合成し、X線結晶解析を行ったところ、予想したとおり、12はトランス型、13はシス型をとっていることがわかった (Figure3-8)。シス型のウレア、グアニジン誘導体と、2つの芳香環同士の2面角を比較したところ、チオウレア体が23°と、最も平行に近いことがわかった。これは硫黄原子が酸素原子や窒素原子に比べて大きいことによるのかもしれない。以上のことからFigure3-

1に示した一般式は、Xが酸素原子、窒素原子ばかりでなく、硫黄原子でも成立することがわかった。

Figure 3-8 Stereoview Crystal Structures of **12** and **13**

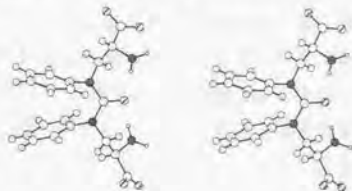
第4節 芳香族ウレアにおけるシス型優先性の拡張

N-メチル化によるシス型優先性則が、メチル基以外の置換基でも成立するかどうかを調べるために、*N*-メチル基のかわりにカルボキシル基やアミノ基を持つアルキル基で置き換えた芳香族ウレアを合成し、その構造を調べた。ここでは、その一例として、アミノ酸を持つ化合物**14**について紹介する。この化合物では光学活性なアミノ酸を出発原料とする合成法はうまくいかず、種々検討した結果、Strecker法を用いた方法 (Figure 3-9) でメソ体とラセミ体の混合物として合成することができた。このジアステレオマーを分離するために、アミノニトリル体をト

Figure 3-9 Synthesis of **14** using Strecker Method

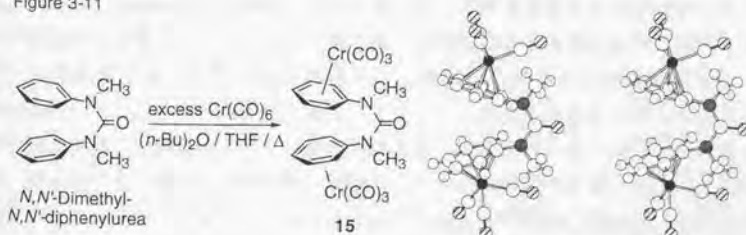
リフルオロアセチル化した後カラムで分離し、酸加水分解により目的物へと導いた。このうち、ラセミ体の結晶解析に成功し、その構造も *N,N'*-Dimethyl-*N,N'*-diphenylurea と同様のシス型構造を示すことを明らかとした (Figure 3-10)。他にも、酢酸、アミノアルキル基などを持つウレア誘導体もシス型構造を持つことも確認した。以上の結果はシス型優先性を生じさせるためには、必ずしも *N*-メチル基のような小さな基ばかりでなく、よりかさ高い基や極性基を

含んでいてもよいことを示している。従って、基本骨格としてアミノ基やグアニジノ基を有していなくても *N*-メチル基を修飾することによっても水溶性や機能性をもった層状芳香族分子の構築ができるといえよう。

Figure 3-10 Stereoview Crystal Structure of (*RR*/*SS*)-14

また、特殊な例として *N,N'*-Dimethyl-*N,N'*-diphenylurea の芳香環部のクロム錯体を合成したところ、低収率ながら得られたジクロミウム錯体 **15** も結晶中シス型構造を示した (Figure 3-11)。(この化合物も不安定でイメージングプレートを用いる迅速な X 線解析法でようやく結晶構造を明らかにすることができた。) 後述 (第 5 章) するように *N*-メチル化ウレアのシス型優先性を利用して芳香族多層構造を構築することができることと組み合わせると、何らかの機能性分子への発展が可能と考えている。

Figure 3-11

Stereoview Crystal Structure of **15**

第4章 プロペラ状グアニジウムイオンの分子不斉

第1節 分子不斉

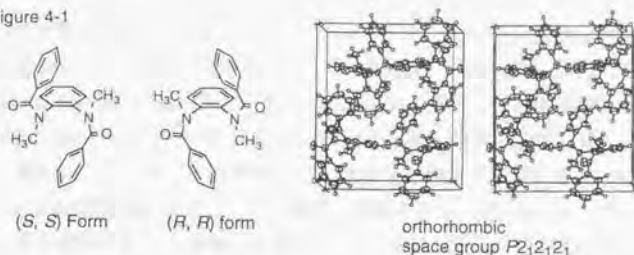
生理活性物質が結合する生体のレセプター空間がキラルであることは、そのレセプターを構成しているアミノ酸や糖が不斉炭素をもつ光学活性体であることを考えると、当然のことのように思われる。すなわち、キラルな生理活性物質の鏡像体はレセプターによって異なる物質として認識され、一般には同種の作用は発現しない。しかしながら、不斉炭素をもたない薬物分子が光学不活性であるかといえは必ずしもそうとは限らず、レセプターと相互作用する際にキラルなコンフォメーションをとっている場合もある。言い換えると、このような薬物分子では分子不斉が発生しており、不斉炭素をもたなくてもコンフォメーションにより生じた不斉の一方の鏡像体のみが作用を発現する。

当研究室では、アミド結合あるいはウレア結合を複数組み合わせた芳香族化合物の立体化学について研究を行ってきたが、その過程でいくつかの化合物が固定した不斉炭素を持たないにも関わらず、キラル分子として振るまうことを示してきた。特に最近、結晶化に伴う不斉の発生とその応用（例えばキラル結晶からの不斉合成）の報告が増えてきたが^{47,48)}、グアニジン類の分子不斉について述べる前に芳香族アミドにおける興味深い一例を次節で紹介する。

第2節 *o*-Bis(*N*-methyl-*N*-phenylamino)benzeneの分子不斉

当研究室の東屋は、芳香族アミドの結晶構造を調べている過程において、*o*-Bis(*N*-methyl-*N*-phenylamino)benzene ベンゼンが、それ自身固定した不斉中心をもたず室温下では種々のコンフォーマー間の速い平衡にあるにも関わらず、酢酸エチルから再結晶すると光学活性な結晶として自然分晶することを見いだした（Figure4-1）²⁹⁾。この時、再結晶の条件により、1つのフラスコより得られるすべての結晶が同一の鏡像体となり、絶対的な不斉の生成がおこる。この結晶構造では、2つのアミド基がシスであると同時に、互いに中央のベンゼン環の反対側に位置するアンチコンフォメーションをとっていた。この場合、Figure4-1に示すようにPh-N結合の回転により互いにエナンチオマーの関係となるが、結晶中においては単位格子内にある4分子がすべて一方の鏡像体として存在していることがわかった。

Figure 4-1



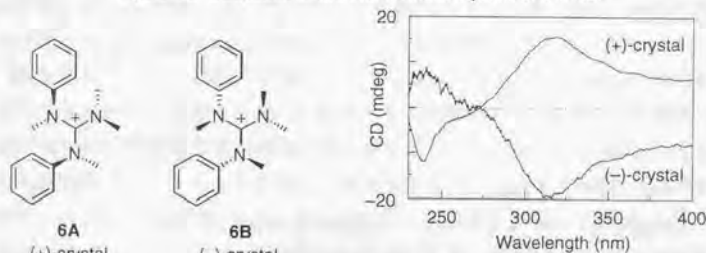
2種類の光学活性な結晶は、その結晶の外形からも区別可能であるが、対称なCDスペクトル(KBr中)によって識別される。上述したように、室温下では種々のコンフォーマー間の速い平衡にあるため、溶液中でのCDスペクトルは観測されないが、低温下(-100°C)で溶解させることにより、結晶の場合と対応したCDスペクトルを得ることができ、この結晶の光学活性が溶液中でも低温下で保持されることがわかった。また、この化合物とキラルな1,1'-bi-2-naphtholと再結晶すると一方のキラリティーをもったアミド化合物が1,1'-bi-2-naphtholと混晶してくることから、絶対構造の決定にも至っている。

第3節 N,N,N',N'' -Tetramethyl- N,N'' -diphenylguanidinium ion (6) の分子不斉

これまで扱ってきた7つの芳香族グアニジン類はもちろん固定した不斉をもたないが、3つがキラル結晶(1、2と6)を生じた(Table 2-4)。東屋らは約60の芳香族アミド、芳香族ウレアの結晶構造を調べたが、このうちわずか4種類の化合物しか光学活性な空間群をもつものがなかったことを考慮すると、グアニジン類のキラル結晶発生率は極めて高いといえるであろう。化合物1、2ではわずかな分子のねじれによるものであるが、 N,N,N',N'' -Tetramethyl- N,N'' -diphenylguanidinium ion (6) では窒素原子上の6つの置換基の存在により興味深い構造を示していたので詳細に解析した。

第2章で述べたように6はすべてのC(1)-N結合がグアニジノ平面に対して約40°ねじれており、そのねじれが一方向にそろったキラルなプロペラ状構造を形成していた(Figure 4-2)。6のキラルな結晶中には片方のエナンチオマーのみ含まれているのである。従ってこの場合もていねいに結晶化することにより、(ラセミ溶液から)一方のキラリティーをもつ結晶のみを得ることができ、タネを用いれば

望みのキラル結晶を生成させることができる。この互いにエナンチオマーの関係にあるキラル結晶はKBrを用いてタブレットにしたサンプルでCD測定することにより区別することができた(Figure 4-2)。そこで320nmのコットン効果の符号から(+)-crystal、(-)-crystalと名付けた。キラルな結晶中における分子の絶対構造を決める方法としてBijvoet法というのがある⁴⁹⁾。これはX線の異常散乱を利用する方法であるが、通常C、N、Oのような軽原子しか含まない低分子有機化合物ではエナンチオマーによる強度差が小さいために測定は困難である。幸い**6**ではカウンターアニオンにヨウ素原子という重原子を含んでいたためにBijvoet法を用いることができた。結局、**6**のキラル結晶について(+)-crystalが**6A**、(-)-crystalが**6B**と、その絶対構造を決定することができた(Table 4-1)。

Figure 4-2 CD spectra of two enantiomeric crystals of **6** in KBr

A mixture of 100 μ g of **6** and 100 mg of KBr was well ground and formed into a disk with a radius of 5mm.

Table 4-1 Determination of the Absolute Structure of **6**

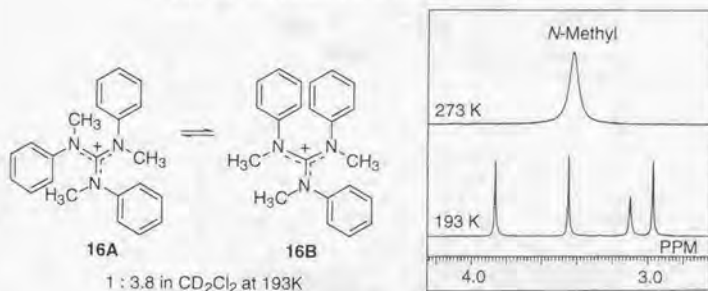
| Crystal | Assignment | Fridel pairs | R / Rw | Flack parameter |
|---------------|------------|----------------|---------------|-----------------|
| (+) - crystal | 6A | agree : 932 | 0.063 / 0.075 | 0.0044(11) |
| | | disagree : 262 | | |
| | 6B | agree : 262 | 0.088 / 0.104 | 0.9587(14) |
| | | disagree : 930 | | |
| (-) - crystal | 6A | agree : 336 | 0.089 / 0.100 | 1.2310(10) |
| | | disagree : 782 | | |
| | 6B | agree : 780 | 0.065 / 0.075 | -0.0108(78) |
| | | disagree : 339 | | |

第2章でも述べたように、溶液中での**6**の異性化は室温下では極めて速い。特に**6**のラセミ化は、3つのC(1)-N結合が回転する過程をへるにも関わらずとても速く、低温下で結晶を溶かすという手法を用いてもキラリティーを保持させることはできなかった。しかしながら、キララ試薬として1,1'-bi-2-naphtholを共存させてNMRを測定することにより、213K以下でキラリティーを識別することができた。

第4節 プロペラ状グアニジニウムイオン

前節で述べたように、立体的に混み合ったグアニジノ基は、Triphenylmethyl cationやTriphenylamine誘導体等と同様に、新しいタイプのキララなプロペラ分子を構築できることが分かった⁵⁰⁾。そこで**6**よりも更に対称性の高いプロペラ分子として、*NN'N''*-trimethyl-*NN'N''*-triphenylguanidinium iodide (**16**)をデザイン、合成した。**16**にはNMRによって区別しうる異性体としては、**16A**、**16B**の2種類のみが考えられる(Figure 4-3)。**16A**は、3つの芳香環がグアニジノ平面に対して同一方向に向いた、より対称性の高いコンフォマーであり、この**16A**の芳香環を1つまたは2つのC(1)-N結合を軸に回転させると**16B**が得られるが、これは**4**の結晶構造で見られた芳香環の層状構造を持ち合わせたコンフォマーである。 CD_2Cl_2 中、**16**は室温下では1本の*N*-メチルピークを与えるが、低温下では積分値が等しい3本のシングレット(2.16、3.44、3.85ppm)と一本のシングレット(3.10ppm)に分裂する(Figure 4-3)。このことから**16**は193Kにおいては、**16A**と**16B**は1:3.8の比率の平衡にあることが明らかになった。

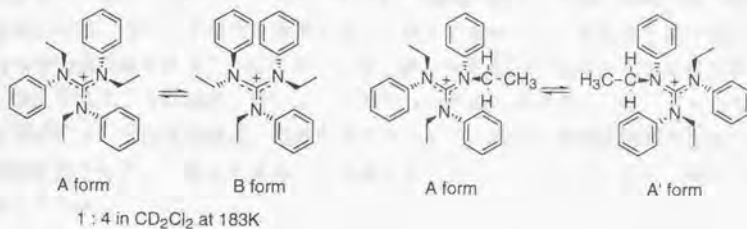
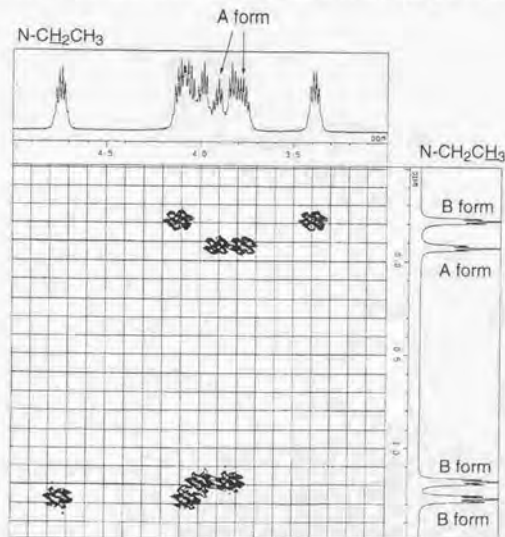
Figure 4-3 Temperature-dependent NMR of **16**



16の溶液中における分子不斉は、1,1'-bi-2-naphthol等のキラルな分子を共存させることによって識別できるが、より単純な方法として16のエチル誘導体である17によって観測を試みた。本来、NMRではエナンチオマーを区別することはできないが、17ではラセミ化がNMRのタイムスケールに対して遅くなると、エチル基

Figure 4-4 Conformational Behaviour of 17

Equilibrium between Conformational Isomers Equilibrium between Conformational Enantiomers

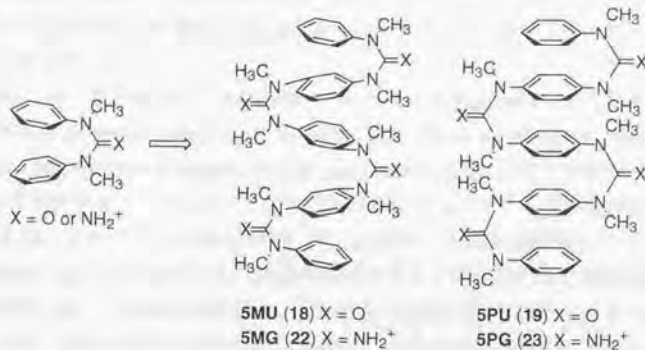
Figure 4-5 DQF-COSY NMR Spectra of 17 in CD_2Cl_2 at 183K

のメチレンの2つのジェミナルプロトンが非等価になって別々に観測できる (Figure 4-4)。16と同様、17にも17A、17Bの2種類の異性体が考えられるが、いずれのコンフォマーにもそのエナンチオマーが存在する。183KにおけるNMRのメチレンのシグナルは複雑であったが、2D-NMR (DQFCOSY, Figure 4-5) により17Aのメチレンピーク、17Bでの3種類のメチレンピークのすべてが2つに分裂し、計8つのピークが観測されることがわかり、低温下ではラセミ化が遅いことが示された。しかし、そのラセミ化速度は17Aと17B間の異性化速度に匹敵するくらいに速いため、ラセミ化速度を特定することはできなかった。残念なことに16も17もその結晶構造を得ることはできていないが、16は結晶のCDスペクトルからキラル結晶であることは確認している。このプロペラ状のグアニジニウムイオンの分子不斉については結晶構造、溶液中でのラセミ化、異性化速度定数の決定などの課題が残っており、種々の誘導体を合成することにより明らかにしていきたいと考えている。

第 5 章 水溶性芳香族多層状分子

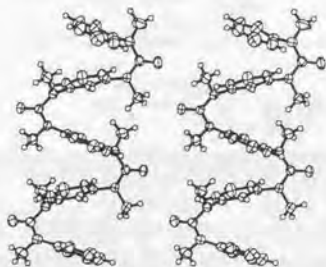
第 1 節 芳香族多層分子のデザイン

N,N'-Dimethyl-*N,N'*-diphenylguanidinium 塩 (4b) は、*N,N'*-Dimethyl-*N,N'*-diphenylurea 同様、シス型コンフォメーションを持ち、二つの芳香環が向かい合った層状構造をとっている。もし、これらのリンキンググループ (*N,N'*-ジメチルゲアニジノ基および *N,N'*-ジメチルウレア基) のシス型優先性が一般的であるならば、この特性を用いて芳香族多層分子を構築することができる (Figure 5-1)。

Figure 5-1 Design of Aromatic Layers Using *cis*-Preference of Urea and Guanidinium Group

芳香族多層ウレア化合物については、当研究室の伊藤によりメタ置換体 5MU (18) およびパラ置換体 5PU (19) が合成され、その多層構造が確認されている (Figure 5-2)^{51,52)}。このような多層構造は、電気伝導物質への応用なども期待される。そこで、更なる機能性分子への応用、特に生理活性物質へ応用していくためには水溶性であることが重要な鍵になると考え、*N,N*-ジメチルグアニ

Figure 5-2 Stereoview Crystal structure of 5MU (18)



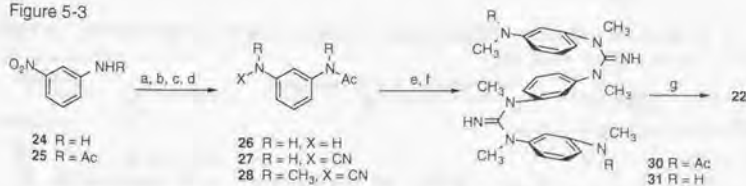
ジノ基で芳香環を3つ連結した化合物**3MG** (**20**、メタ体)、**3PG** (**21**、パラ体) および5つ連結した化合物**5MG** (**22**、メタ体)、**5PG** (**23**、パラ体) をデザイン・合成し、その構造と機能を検討した。

第2節 グアニジンオリゴマーの合成

グアニジノ基の3つの窒素原子の反応性はほとんど差がないため、特殊な保護基でも用いない限り、*N,N'*-ジメチルグアニジノ基を構築しようとする際に、*N*-メチル化をグアニジノ基を合成した後のステップで行うことはできない。このことがアミド・ウレアの場合とは異なり、合成スキームを組み立てる際の制約になり、中間体の難溶性等の問題ともあいまって、特に、**5MG** (**22**)、**5PG** (**23**) の合成を予想以上に困難にした。結局、*N,N'*-ジメチルグアニジノ基は、*N*-Methylaniline ユニットと *N*-methyl-*N*-phenylcyanamide ユニットのカップリングによって構築していくことになった。

5MG (**22**) の合成スキームを Figure 5-3 に示す。*m*-Nitroaniline から4ステップで得られる *N*-Acetyl-*N*-cyano-*N,N'*-dimethyl-*meta*-phenylenediamine (**28**) と *N,N'*-Dimethyl-*meta*-phenylenediamine dihydrogen chloride (**29**) とをクロロベンゼン中、160°C で加熱することによって、23% と低収率ながらジグアニジン体**30**を得ることができた。**30** のアセチル基をはずして、末端アミノ基を塩酸塩としてから、*N*-Methyl-*N*-phenylcyanamide と、**28** と **29** をカップリングさせたのと同様の条件で反応を試みたが、分解物のみを与え、目的とする**5MG** (**22**) は得られなかった。溶媒、温度、酸等の条件を種々検討した結果、 AlCl_3 存在下で反応させることで46% の収率で**5MG** (**22**) を得ることができた。

Figure 5-3

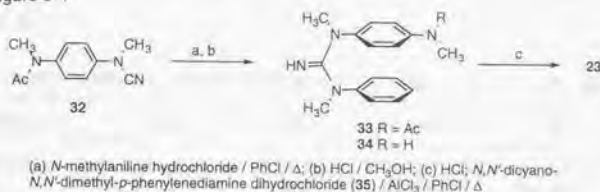


(a) Ac_2O ; (b) H_2 / 10% Pd-C / EtOH; (c) BrCN; (d) NaH / DMF, CH_3I ; (e) *N,N'*-dimethyl-*m*-phenylenediamine dihydrochloride (**29**) / PhCl / Δ ; (f) HCl / CH_3OH ; (g) HCl; *N*-methyl-*N*-phenylcyanamide / AlCl_3 / PhCl / Δ

一方、**5PG** (**23**) に関しても**5MG** (**22**) と同様のスキーム、すなわち、最終段階で連結する部分構造のベンゼン環の数で表記すると、[1+3+1]型スキームでの合成を試みたが、**30** に対応するパラ誘導体が非常に難溶性のため、カップリング反

応がうまく進行しなかった。そこでFigure 5-5に示した[2+1+2]型スキーム (Figure 5-4) に変更し、やはり最終段階で AlCl_3 を用いることにより5PG (23) を合成することができた。両化合物とも予想した通り、非常に高い親水性を示した。

Figure 5-4



第3節 グアニジンオリゴマーの溶液中での立体構造

5MG (22)、5PG (23) の ^1H -NMR測定をすると、芳香環プロトンのケミカルシフトがモノマーに相当する4bやシス型アミドと同じ高磁場シフトをしていることから、有機溶媒および水中で層状構造を優先していることが示唆された (Table 5-1)。層状構造の内側の芳香環プロトンは末端の芳香環プロトンよりも更に大きな高磁場シフトが観測された。これら N,N' -dimethylguanidineユニットが種々の溶媒中で層状構造を優先していることはNOEによっても支持された。しかし、 CD_2Cl_2 中、183Kまで温度を下げてNMR測定を行っても、複数のコンフォーマーへの分裂は観測されず、緩やかなブロードニングがみられるだけであった。また、様々なキラル試薬も用いたがキラルコンフォメーションの分離もできなかった。おそらく、メジャーである層状コンフォメーションといくつかのマイナーコンフォーマー

Table 5-1 ^1H NMR Chemical shifts of Aromatic Layered Guanidines (4b, 20 – 23) in D_2O at 303 K

| Compound | Chemical shifts (ppm) of aromatic protons ^a | | |
|----------|--|--|---------------------------------------|
| | Ph-1 | Ph-2 | Ph-3 |
| 4b | 7.06 (o), 7.28 (m), 7.22 (p) | — | — |
| 20 | 6.90 (o), 7.22 (m), 7.16 (p) | 6.32 (o,o), 6.88 (o, m), 7.15 (m, m) | — |
| 21 | 6.97 (o), 7.23 (m), 7.18 (p) | 6.81 | — |
| 22 | 6.83 (o), 7.17 (m), 7.15 (p) | 6.21 (o, o), 6.73&6.87 (o, m), 7.09 (m, m) | 6.19 (o, o), 6.77 (o, m), 7.09 (m, m) |
| 23 | 6.91 (o), 7.20 (m), 7.15 (p) | 6.71 & 6.76 | 6.71 |

a) Aromatic rings are numbered as Ph-1, Ph-2 or Ph-3 from the terminal. The positions of protons relative to guanidino group(s) are shown in parenthesis. Thus, (o, o) means protons ortho to two guanidino groups.

ションの速い平衡にあるのだろう。

第4節 グアニジンオリゴマーの結晶構造

合成したオリゴマー 4 種 (20-23) の結晶構造とデータを、Table 5-2、5-3およびFigure 5-5に示す。

Table 5-2 Crystal Data of Aromatic Di- and Tetraguanidinium Salts (20 - 23)

| Compound | 20 | 21 | 22 | 23 |
|---|----------------------|----------------------|-----------------------------|-----------------------------|
| Formula | $C_{24}H_{30}N_6I_2$ | $C_{26}H_{30}N_6I_2$ | $C_{42}H_{38}N_{12}Cl_4O_2$ | $C_{42}H_{62}N_{12}Cl_4O_4$ |
| M _r | 656.35 | 656.35 | 904.81 | 940.84 |
| Recryst solvent | MeOH/ether | MeOH/AcOEt | MeOH/AcOEt | MeOH |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/a$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| <i>a</i> , Å | 11.312(2) | 10.929(2) | 11.647(2) | 10.854(2) |
| <i>b</i> , Å | 15.420(2) | 11.173(2) | 25.027(3) | 20.205(2) |
| <i>c</i> , Å | 16.236(3) | 11.895(2) | 15.866(2) | 13.388(2) |
| α , ° | — | — | — | — |
| β , ° | 101.33(1) | 113.56(1) | 93.52(1) | 113.59(1) |
| γ , ° | — | — | — | — |
| <i>V</i> , Å ³ | 2776.9(8) | 1331.3(5) | 4616.1(9) | 2690.7(6) |
| <i>D</i> _{calc} , g·cm ⁻³ | 1.570 | 1.637 | 1.302 | 1.161 |
| <i>Z</i> | 4 | 2 | 4 | 2 |
| <i>R</i> | 0.057 | 0.041 | 0.066 | 0.069 |

Table 5-3 Dihedral Angles (deg) between Aromatic and Guanidino Planes^a in 20 - 23

| Compound | 20 | 21 | 22 | 23 |
|------------------|-------|-------|------|-------|
| Ph(1) vs Ph(2) | 34.0 | 152.0 | 31.7 | 28.9 |
| Ph(2) vs Ph(3) | 30.5 | 152.0 | 38.8 | 153.3 |
| Ph(3) vs Ph(4) | — | — | 30.4 | 153.3 |
| Ph(4) vs Ph(5) | — | — | 35.7 | 28.9 |
| Ph(1) vs Ph(3) | 4.8 | — | 17.3 | 155.5 |
| Ph(2) vs Ph(4) | — | — | 14.2 | — |
| Ph(3) vs Ph(5) | — | — | 12.8 | 155.5 |
| Gua(1) vs Gua(2) | 135.2 | — | 34.6 | 67.0 |
| Gua(2) vs Gua(3) | — | — | 37.4 | — |
| Gua(3) vs Gua(4) | — | — | 34.3 | 67.0 |
| Gua(1) vs Gua(3) | — | — | 8.6 | — |
| Gua(2) vs Gua(4) | — | — | 3.5 | — |

a) Aromatic rings and guanidino groups are numbered from the terminal.

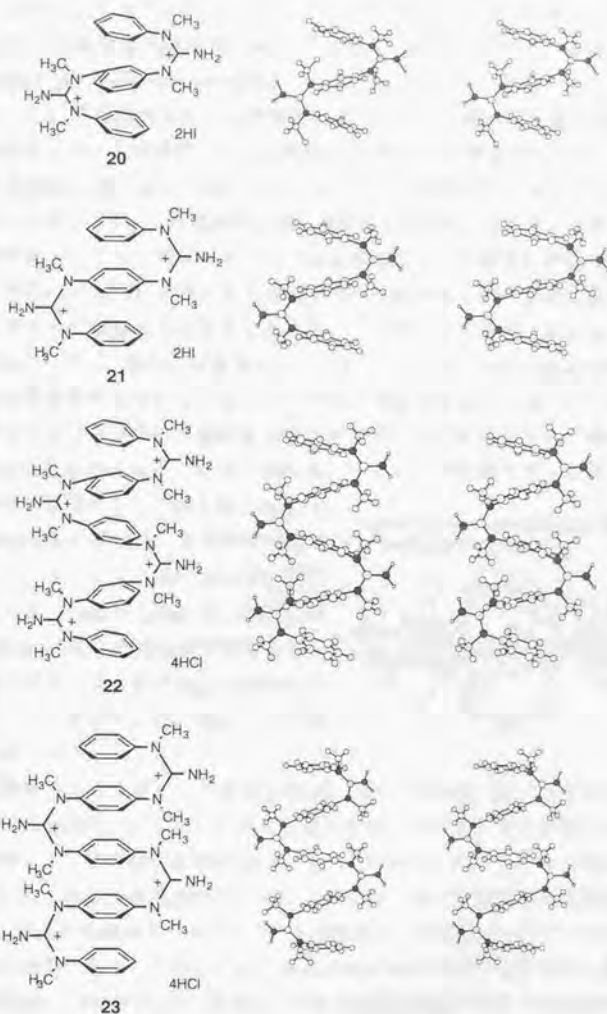


Figure 5-5 Stereoview Crystal Structures of Aromatic Layered Guanidines (20 – 23)
The counter anions and water molecules are omitted.

N,N'-Dimethyl-*N,N'*-diphenylguanidinium bromide (**4b**) の結晶構造から推測したように、いずれもすべてのグアニジノ基がシス型アンチコンフォメーションをとり、分子内で芳香族層状構造を形成していた。これらオリゴマーの部分構造 (*N,N'*-dimethyl-*N,N'*-diphenylguanidine ユニット) は、モノマー単位である **4b** とよく類似していた。芳香環同士または芳香環とグアニジノ平面の 2 面角 (Table 5-3) からわかるように芳香環同士のなす角は、いずれも 30° 程度であるが、**5PG** (**23**) のほうが **5MG** (**22**) よりも幾分平行に近い。芳香環同士が完全な平行から少しはずれているのは、 $\pi-\pi$ の反発的な相互作用によると考えられる。このことは、基本的モデルとしてベンゼンダイマーの安定構造について種々の計算が行われているが、それによると、ずれた平行構造や T 型構造のほうが、完全に重なった平行なサンドイッチ構造よりも安定であるという結果からも妥当であるといえよう³³⁾。いずれにしても、様々に自由度をもつはずのこの *N,N'*-dimethylguanidine ユニットが不安定要素を含んでいるにも関わらず芳香族層状構造をとるということは、これまでこのような分子内芳香族層状構造が固定された骨格を用いて構築されてきた点⁵⁴⁾を考えあわせると、非常に興味深い。また、芳香環どうしの 2 面角は、1 つおきの芳香環どうし (例えば、Ph(1) と Ph(3)、Ph(2)Ph(4) 等) が、より平行に近くなっている。グアニジノ基についても同じ傾向が見られ、Gua(1) と Gua(3)、あるいは Gua(2) と Gua(4) のなす角はほぼ平行である。この 2 組のグアニジノ基は Figure 5-6 からわかるように、層状ベンゼン環からみて同じ側に位置している。

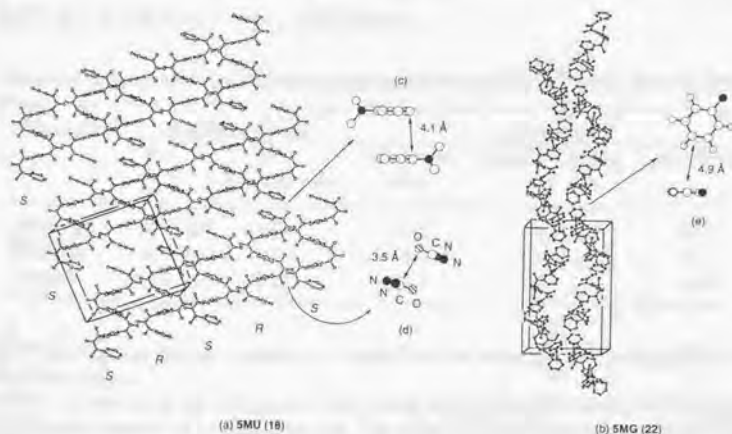
Figure 5-6. View of the crystal structure of **5MG** (**22**) from the top



さて、層状分子の中で、メタ置換体 **3MG** (**20**) と **5MG** (**22**) は分子の巻き方 (軸性不斉の方向性) により、らせん構造をなすのではないかと予測したが、実際、結晶中、すべての軸性不斉が all-*R* (もしくは all-*S*) のキラルならせん状分子となっていた。らせん状化合物としては、ヘリセンなどの固定された構造を持つもの⁵⁵⁾もしくは水素結合ネットワーク⁵⁶⁾や金属原子への配位 (ヘリケート)⁵⁷⁾を利用したものが主であり、このような自由度の高い分子が分子内でらせん構造をなすのは興味深い。同様のらせん構造は、ウレア誘導体 **5MU** (**18**) でもみられたが、これらの化合物の芳香環がメタ位でつながっているにも関わらず、らせん軸が 3₁もしくは 3₂ではなく 2₁をとっていた。これは、芳香環が完全に重なっておらず、ずれているためである (Figure 5-6)。いずれの化合物においても、単一の分子はキ

ラルらせん状構造であったが、単位格子に右巻きらせんをもつ分子と左巻きらせんをもつ分子を1:1で含むことによりラセミ結晶となっていることがわかった (Figure 5-7)²³。しかしながら、**5MU** (**18**) と **5MG** (**22**) のパッキング構造を比較すると大変おもしろい結果が得られた。**5MU** (**18**) では、分子間でもきれいに積み重なったパッキング構造を形成しており、隣り合う分子間での末端のベンゼン環同士はほぼ平行で、その距離は約4.1Åであった。各分子のキラリティーに注目すると、左巻き、右巻き、左巻き、右巻きと交互に配列していた。一方、**5MG** (**22**) ではジグザグ状の二本鎖を形成しており、各一本鎖は、単一のエナンチオマーで構成されていた。例えば、ある一本鎖が右巻きだけなら、その隣の一本鎖は左巻きだけといった具合である。この場合、一本の鎖中の隣り合う分子の末端のベンゼン環同士は、T型構造をとっており、その距離は約4.9Åとなっていた。このように**5MU** (**18**) と **5MG** (**22**) でパッキング様式に違いがみられるのは、リンキンググループの電子的性質やカウンターアニオンの有無に由来していると考えられている。

Figure 5-7 Packing Structures (stereoviews) of **5MU** (**18**, a), and **5MG** (**22**, b). The intramolecular relationships of terminal phenyl rings (parallel, c), urea bonds (d) of **5MU** (**18**), T-shaped terminal phenyl rings of **5MG** (**22**, e) are also shown.



第5節 グアニジンオリゴマーの新しい機能

-新規DNAマイナーグループ結合性分子-

前節までに述べてきた層状構造において、各芳香環の距離が2本鎖DNAの塩基対同士の距離と類似していることにヒントを得て考察したところ、層状分子の形状がDNAのマイナーグループによくフィットすることが予想された。すなわち、層状芳香環の両側に2つずつグアニジノ基が存在することになるが(例えばFigure5-6)、一方がDNAの中に入り核酸塩基と相互作用し、残りの一方がDNAの外側の環境(例えば水分子)と相互作用すると考えられる。この時、層状分子の大きさはマイナーグループの大きさによく適しており、大きなファンデルワールス相互作用が期待できる。

このような観点から、当教室の福富によって5MG (22)、5PG (23) とDNAとの相互作用の検討がなされた。その結果、限外濾過膜を用いた結合実験⁵⁸⁾により5MG (22)、5PG (23) はともに結合定数が 10^7 M⁻¹と大変高いDNA親和性を有しており、代表的なマイナーグループバインダーであるNetropsinよりも高い親和性を示した(Table5-4)。また、二本鎖DNAに熱を加えていくと、その構造がはぐされていく様子が観測でき、その転移の midpoint を融解温度 T_m と呼ぶが、この T_m 値はDNAと複合体をつくる化合物の添加により高くなることが知られている。Table5-4に示すように5MG (22)、5PG (23) は各種DNAの T_m 値を著しく高め、DNAと安定な複合体を形成していることがわかった。

Table 5-4 Binding Abilities of Aromatic Layered Guanidines 5MG (22) and 5PG (23) with DNAs.

| Compound | ultrafiltration assay ^a | | ΔT_m (deg) ^b | | |
|-----------|------------------------------------|------------------------|---------------------------------|-------------------|--------------------------|
| | K_a (M ⁻¹) | n (per base pair) | calf thymus DNA | poly(dT)-poly(dA) | poly(dA-dT) ₂ |
| 5MG (22) | 6.2×10^6 | 0.20 | 10.3 | 29.8 ^c | 25.1 |
| 5PG (23) | 1.2×10^7 | 0.19 | 9.9 | 25.8 ^c | 22.2 |
| netropsin | 1.0×10^5 | 0.52 | 23.0 | 53.4 | 45.4 |

a) Binding constant (K_a) and number of binding sites per base pair (n) were calculated from Scatchard analyses.

b) ΔT_m is defined as the difference of the melting temperature (T_m values) of DNAs in the presence and absence of the test compound. The molar ratio of the test compound to DNAs (per base pair) was 0.5. T_m values were measured at 260 nm, and those of calf thymus DNA, poly(dT)-poly(dA), and poly(dA-dT)₂ were 63.9, 45.4, and 39.0 °C, respectively.

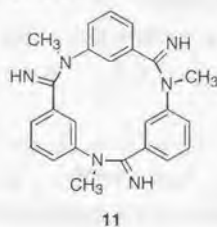
c) Biphasic T_m behavior was observed.

現在、福富によって更に詳細な結合様式の解析がなされているが、計算化学的もしくは各種スペクトルの結果は5MG (22)、SPG (23) が予想通りDNAのマイナーグループにぴったりはまりこんでいることが示唆されている。これまでマイナーグループバインダーとしては主にNetropsinのような平面的構造の化合物が多く知られているが^{59,60)}、5MG (22)、SPG (23) のように層状でしかもある程度厚みも持ち合わせた化合物は、新規なマイナーグループバインダーとして、今後の展開が期待できるであろう。

また、更に、第3章で述べた環状トリアミジン誘導体11 (Figure 5-8) も5MG (22)、SPG (23) ほど強くはないがDNAと結合 (約 $6 \times 10^4 \text{ M}^{-1}$ の結合定数) することもわかった。この化合物11は、5MG (22)、SPG (23) 等と異なり、おわん状のかさ高い構造をしており、メジャーグループへの結合の可能性も考えられ、現在解析中である。

ここでは、DNA結合性をとりあげたが、本章での最初にも述べたように電気伝導性などの物性も期待でき、水溶性多層グアニジン化合物は新たな機能性芳香族分子へと展開できると考えている。

Figure 5-8



結 論

アミド基・ウレア基でみられた*N*-メチル化に伴うシス型優先性がグアニジノ基やアミジノ基に対しても一般性をもつ立体的性質であることを示してきた。この立体特性は部分二重結合性が等しく分布しているグアニジニウムイオンにおいても成立し、水溶性分子構築への足がかりとなった。

また、グアニジノ基はそのねじれ構造から分子不斉を発生させる頻度が高く、この性質を詳細に解析することで、キラルなプロベラ状分子の構造を明らかにした。

更にシス型優先性による芳香環の層状構造とグアニジニウムイオンの水溶性を組み合わせることで、分子内多層構造をもつ水溶性分子**5MG**、**5PG**を構築することができた。特に芳香環をメタ位でつないだ**5MG**では、結晶中、左巻き、右巻きを等量含むきれいならせん状構造をとっていた。

また、これら層状構造が核酸塩基対の形状に類似していることにヒントを得て、DNAとの結合実験を行ったところ、強いDNA結合能があることが認められた。これに例示されるように以上述べてきた化合物は水溶性芳香族機能分子として今後様々な応用展開が期待できるであろう。

実験の部

General. Melting points were determined by using a Yanagimoto hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out in the Microanalytical Laboratory, Faculty of Pharmaceutical Sciences, University of Tokyo, and were within $\pm 0.3\%$ of the theoretical values. NMR spectra were recorded on a JEOL JNM-A500 (500 MHz) or a JEOL JNM-GX400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm relative to tetramethylsilane in CDCl_3 and $\text{DMSO}-d_6$, or sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O . IR spectra were taken with a Shimadzu IR-408 IR spectrometer and values are expressed in cm^{-1} . *N,N'*-Diphenylguanidine (**1**) was purchased from WAKO Co. and recrystallized from EtOH.

X-ray Crystallography. The X-ray crystal structure analyses were performed on crystals of compounds **1** – **12**. Diffraction data were obtained by a Rigaku AFC7S four-circle diffractometer and a Rigaku RAXISIIIC imaging plate diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54050 \text{ \AA}$) and $\text{MoK}\alpha$ ($\lambda = 0.71070 \text{ \AA}$) radiation, respectively. Generally, indexing was performed from 3 oscillation which were exposed for 4.0 minutes and a total of 15 oscillation images within the 2θ value of 50.0° were collected in the case of that using imaging plate area detector. The crystal data are given in Table 1 and 5. The crystal structures were solved by the direct method and the hydrogen atoms were located on a difference electron-density map.

***N*-Methyl-*N,N'*-diphenylguanidine (**2**).** A solution of cyanogen bromide (95%, 1.71 g, 15 mmol) in ether (10 ml) was added to a solution of aniline (2.02 g, 22 mmol) in ether (20 ml), and the mixture was stirred overnight. The reaction mixture was filtered, and the filtrate was washed twice with water, dried over Na_2SO_4 , and evaporated to give *N*-phenylcyanamide (1.15 g, 45 %). *N*-Phenylcyanamide: ^1H NMR (400 MHz, CDCl_3) δ 7.34 (t, 2 H, $J = 8.1 \text{ Hz}$), 7.09 (t, 1 H, $J = 7.5 \text{ Hz}$), 7.02 (d, 2 H, $J = 7.7 \text{ Hz}$), 6.70 (s, 1 H).

A mixture of *N*-phenylcyanamide (340 mg, 2.9 mmol) and *N*-methylaniline hydrochloride (432 mg, 3.0 mmol) was stirred at 150°C under an argon atmosphere. After 4 h, water was added to the reaction mixture, and the whole was washed with CH_2Cl_2 . The aqueous layer was basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography

(CH_2Cl_2 : MeOH: NH_4OH = 8:1:0.2) to give *N*-methyl-*N,N'*-diphenylguanidine (2, 390 mg, 60 %). *N*-Methyl-*N,N'*-diphenylguanidine (2): colorless prisms (CH_2Cl_2); mp 63°C; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (t, 2 H, J = 7.7 Hz), 7.24–7.35 (m, 5 H), 6.98 (m, 3 H), 3.70–4.30 (br s, 1 H), 3.41 (s, 3 H), 1.30–2.20 (br s, 1 H); Anal Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_3$: C, 74.64; H, 6.71; N, 18.65; Found: C, 74.43; H, 6.59; N, 18.48.

***N*-Methyl-*N',N''*-diphenylguanidine (3).** Lead monoxide³⁶⁾ (1002 mg, 4.5 mmol) was added to a solution of *N,N'*-diphenylthiourea (506 mg, 2.2 mmol) in 10 ml of MeOH at 60°C. The resulting black suspension was stirred for 15 min, and 3 ml of 40 % CH_3NH_2 in MeOH was added. The mixture was stirred for 4.5 h. The PbS precipitate was filtered off, and the solvent was evaporated to leave an oily residue which was purified by silica gel column chromatography (CH_2Cl_2 : MeOH: NH_4OH = 8:1:0.2) to give *N*-methyl-*N',N''*-diphenylguanidine (3, 403 mg, 81 %). *N*-Methyl-*N',N''*-diphenylguanidine (3): colorless prisms (AcOEt-*n*-hexane); mp 108°C; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, 4 H, J = 7.9 Hz), 7.05 (d, 6 H, J = 8.1 Hz), 3.80–4.40 (br, 2 H), 2.91 (s, 3 H); Anal Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_3$: C, 74.64; H, 6.71; N, 18.65; Found: C, 74.93; H, 6.98; N, 18.37.

***N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4).** NaH (60 %, 189 mg, 4.7 mmol) was washed twice with *n*-hexane, and suspended in 10 ml of dry DMF. A solution of *N*-phenylcyanamide (505 mg, 4.3 mol) in 5 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 10 min and then 2 ml of CH_3I was added to it. After 2 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , dried over Na_2SO_4 and evaporated to give *N*-methyl-*N*-phenylcyanamide (578 mg, quant). *N*-Methyl-*N*-phenylcyanamide: ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, 2 H, J = 8.1 Hz), 7.11 (m, 3 H), 3.35 (s, 3 H).

A mixture of *N*-methyl-*N*-phenylcyanamide (333 mg, 2.4 mmol) and *N*-methylaniline hydrochloride (340 g, 2.4 mmol) was stirred at 150°C under an argon atmosphere. After 6.5 h, water was added to the reaction mixture and the whole was washed with CH_2Cl_2 , basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated to give *N,N'*-dimethyl-*N,N'*-diphenylguanidine (4a, 339 mg, 56 %). *N,N'*-Dimethyl-*N,N'*-diphenylguanidine (4a): colorless oil (solidified below -10°C); ^1H NMR (400 MHz, CDCl_3) δ 7.17 (t, 4 H, J = 8.0 Hz), 6.97 (t, 2 H, J = 8.0 Hz), 6.93 (d, 4 H, J = 7.7 Hz), 5.70–6.50 (br s, 1 H), 3.15 (s, 6 H).

4a was converted to the hydrobromide salt (4b) in a conventional manner.

4b: colorless prisms (CHCl_3); mp 248°C ; ^1H NMR (400 MHz, CDCl_3) δ 9.01 (br s, 2 H), 7.10-7.18 (m, 6 H), 6.79 (d, 4 H, $J = 7.7$ Hz), 3.60 (s, 6 H); Anal Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{Br}$: C, 56.26; H, 5.67; N, 13.12; Found: C, 55.98; H, 5.59; N, 13.10.

N,N,N'-Trimethyl-*N',N''*-diphenylguanidine (5). NaH (60 %, 203 mg, 5.1 mmol) was washed twice with *n*-hexane, and suspended in 3 ml of dry DMF. A solution of *N*-methyl-*N',N''*-diphenylguanidine (3, 503 mg, 2.2 mmol) in 4 ml of dry DMF was added to this suspension at 0°C , the mixture was stirred for 10 min, and then 0.4 ml of CH_3I was added to it. After 2.5 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : $\text{NH}_4\text{OH} = 40 : 1$) to give *N,N,N'*-trimethyl-*N',N''*-diphenylguanidine (5, 261 mg, 46 %). *N,N,N'*-Trimethyl-*N',N''*-diphenylguanidine (5): colorless prisms (*n*-hexane); mp 77.5 - 78.5°C ; ^1H NMR (400 MHz, CDCl_3) δ 7.26 (t, 2 H, $J = 7.9$ Hz), 7.12 (t, 2 H, $J = 7.9$ Hz), 6.85-6.90 (m, 2 H), 6.78-6.83 (m, 4 H), 2.86 (br, 9 H); Anal Calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_3$: C, 75.85; H, 7.56; N, 16.59; Found: C, 75.74; H, 7.28; N, 16.45.

N,N,N',N''-Tetramethyl-*N',N''*-diphenylguanidinium iodide (6). NaH (60 %, 1.18 g, 29 mmol) was washed twice with *n*-hexane, and suspended in 10 ml of dry DMF. A solution of *N,N'*-diphenylguanidine (1, 1.87 g, 8.8 mmol) in 10 ml of dry DMF was added to this suspension at 0°C , the mixture was stirred for 30 min, and then 5 ml of CH_3I was added to it. After 24 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : $\text{MeOH} : \text{NH}_4\text{OH} = 8 : 1 : 0.2$) to give *N,N,N',N''*-tetramethyl-*N',N''*-diphenylguanidinium iodide (6, 2.68 g, 77 %). *N,N,N',N''*-Tetramethyl-*N',N''*-diphenylguanidinium iodide (6): colorless prisms (CHCl_3 -AcOEt); mp 189°C ; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (t, 4 H, $J = 7.9$ Hz), 7.27 (t, 2 H, $J = 7.5$ Hz), 7.20 (d, 4 H, $J = 7.7$ Hz), 3.52 (s, 6 H), 3.19 (s, 6 H); Anal Calcd. for $\text{C}_{17}\text{H}_{22}\text{N}_3\text{I}$: C, 49.40; H, 5.85; N, 10.17; Found: C, 49.23; H, 5.79; N, 9.87.

N-Phenylbenzamidinium Chloride (7). To a mixture of benzonitrile (2.27 g, 22 mmol)

and aniline (2.00 g, 22 mmol) was added aluminum chloride (3.00 g, 22 mmol) over 20 min, and the whole was heated at 185°C. After 1 h, the reaction mixture was poured into 0.15 N hydrochloric acid (160 ml). Activated carbon (2.0 g) was added to the aqueous solution. After filtration, the filtrate was poured into 4.6 N NaOH (120 ml), and the precipitates were collected by filtration, washed with water, and dried under vacuum to give *N*-phenylbenzamidinium (5.15 g, quant). *N*-Phenylbenzamidinium: colorless prisms (AcOEt-*n*-hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.86 (brs, 2 H), 7.43-7.51 (m, 3 H), 7.36 (t, 2 H, $J = 7.7$ Hz), 7.07 (t, 1 H, $J = 7.4$ Hz), 7.00 (d, 2 H, $J = 7.2$ Hz), 4.85 (br, 2 H); Anal Calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2$: C, 79.56; H, 6.16; N, 14.27; Found: C, 79.35; H, 6.14; N, 14.48.

A 1 N hydrochloric acid ether solution (7 ml) was added to a solution of *N*-phenylbenzamidinium (538 mg, 2.7 mmol) in CH_2Cl_2 (10 ml), and the mixture was stirred. The precipitates were collected by filtration to give *N*-phenylbenzamidinium chloride (7, 561 mg, 88 %). *N*-Phenylbenzamidinium Chloride (7): colorless prisms (MeOH-AcOEt); mp 243-244°C; Anal Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{Cl}$: C, 67.10; H, 5.63; N, 12.04; Found: C, 67.09; H, 5.55; N, 11.80.

***N*-Methyl-*N*-phenylbenzamidinium Chloride (8).** To a mixture of benzonitrile (5.15 g, 50 mmol) and *N*-methylaniline (5.35 g, 50 mmol) was added aluminum chloride (6.7 g, 50 mmol) over 20 min, and the whole was heated at 160°C.⁶¹⁾ After 20 min, the reaction mixture was poured into 0.12 N hydrochloric acid (200 ml). Activated carbon (2.0 g) was added to the aqueous solution. After filtration, the filtrate was poured into 5.5 N NaOH (100 ml), and extracted with AcOEt. The organic layer was dried over Na_2SO_4 , and evaporated to give *N*-methyl-*N*-phenylbenzamidinium (7.7 g, 74 %). *N*-Methyl-*N*-phenylbenzamidinium: ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, 2 H, $J = 7.7$ Hz), 7.12-7.20 (m, 5 H), 6.96-7.01 (m, 3 H), 3.51 (s, 3 H).

A 1 N hydrochloric acid ether solution (10 ml) was added to a solution of *N*-methyl-*N*-phenylbenzamidinium (1.09 g, 5.2 mmol) in ether (15 ml), and the mixture was stirred, then the precipitates were collected by filtration to give *N*-methyl-*N*-phenylbenzamidinium chloride (8, 1.15 g, 90 %). *N*-Methyl-*N*-phenylbenzamidinium Chloride (8): colorless prisms (MeOH-AcOEt).

***meta*-Diamidine (9).** A solution of isophthalonitrile (4.00 g, 31 mmol) and *N*-methylaniline (6.66 g, 62 mmol) in chlorobenzene (2 ml) was heated at 150°C and aluminum chloride

(8.50 g, 64 mmol) was slowly added to the mixture. After 20 min, the reaction mixture was poured into 0.2 N hydrochloric acid (200 ml). Activated carbon (2.0 g) was added to the aqueous solution. After filtration, the blue filtrate was poured into 5.5 N NaOH (100 ml), and the precipitates were collected by filtration, washed with water, and dried under vacuum to give *meta*-diamidine (9, 3.72 g, 35 %). *meta*-Diamidine (9): colorless prisms (AcOEt-*n*-hexane); mp 119.5-120.5°C; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (s, 1 H), 7.14 (t, 4 H, $J = 7.7$ Hz), 7.01-7.07 (m, 4 H), 6.96 (t, 1 H, $J = 7.7$ Hz), 6.81 (d, 4 H, $J = 7.7$ Hz), 3.45 (s, 6 H); Anal Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_4$: C, 77.16; H, 6.48; N, 16.36; Found: C, 76.91; H, 6.48; N, 16.20.

***para*-Diamidine (10).** A solution of terephthalonitrile (4.00 g, 31 mmol) and *N*-methylaniline (6.65 g, 62 mmol) in chlorobenzene (2 ml) was heated at 150°C and aluminum chloride (8.58 g, 64 mmol) was slowly added to the mixture. After 20 min, the reaction mixture was poured into 0.2 N hydrochloric acid (200 ml). Activated carbon (2.0 g) was added to the aqueous solution. After filtration, the blue filtrate was poured into 5.5 N NaOH (100 ml), and the precipitates were collected by filtration, washed with water, and dried under vacuum. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $\text{NH}_4\text{OH} = 8 : 1 : 0.2$) to give *para*-diamidine (10, 6.80 g, 64 %). *para*-Diamidine (10): colorless prisms (CH_2Cl_2); mp 210-211°C; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (t, 4 H, $J = 7.7$ Hz), 7.08 (s, 4 H), 7.00 (t, 2 H, $J = 7.2$ Hz), 6.85 (d, 4 H, $J = 8.0$ Hz), 3.45 (s, 6 H); Anal Calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_4$: C, 77.16; H, 6.48; N, 16.36; Found: C, 76.86; H, 6.31; N, 16.58.

***cyclic*-Triamidine (11).** To a solution of 3-(methylamino)benzonitrile (213 mg, 1.6 mmol) in 1 ml of chlorobenzene was added aluminum chloride (228 mg, 1.7 mmol), and the mixture was heated at 150°C. After 2 h, the reaction mixture was poured into 0.1 N hydrochloric acid (20 ml). Activated carbon (2.0 g) was added to the aqueous solution. After filtration, the filtrate was poured into 5.8 N NaOH (10 ml), and extracted with AcOEt, CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $\text{NH}_4\text{OH} = 8 : 1 : 0.2$) to give *cyclic*-triamidine (11). *cyclic*-Triamidine (11): colorless prisms (CH_2Cl_2 -AcOEt); mp 220°C (dec.); ^1H NMR (400 MHz, CDCl_3) δ 6.98 (t, 1 H, $J = 7.7$ Hz), 6.93-6.96 (m, 6 H), 6.85 (d, 3 H, $J = 7.1$ Hz), 3.33 (s, 9 H); FAB mass $[\text{M}+\text{H}]^+ = 397$.

N,N'-Bis(β -alanyl)-*N,N'*-diphenylurea (14). NaH (60 %, 2.3 g, 58 mmol) was washed twice with *n*-hexane, and suspended in 30 ml of dry THF. A solution of *N,N'*-diphenylurea (5.0 g, 24 mmol) in 20 ml of THF was added to this suspension, the mixture was stirred for 20 min and then 8 ml of allyl bromide was added to it. The whole was left overnight, then the solvent and excess allyl bromide were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with H_2O , dried over Na_2SO_4 and evaporated to give *N,N'*-diallyl-*N,N'*-diphenylurea (6.78 g, 98 %). *N,N'*-Diallyl-*N,N'*-diphenylurea: ^1H NMR (400 MHz, CDCl_3) δ 6.99 (t, 4 H, $J = 7.5$ Hz), 6.91 (t, 2 H, $J = 7.5$ Hz), 6.71 (d, 4 H, $J = 7.5$ Hz), 5.94 (m, 2 H), 5.04–5.09 (m, 4 H), 4.18 (d, 4 H, $J = 6.6$ Hz).

To a solution of *N,N'*-diallyl-*N,N'*-diphenylurea (5.99 g, 21 mmol) in 80 ml of ether and 80 ml of H_2O was added osmium tetroxide (557 mg, 2.2 mmol).⁶² After 15 min, sodium metaperiodate (18.01 g, 84 mmol) was added in small portions over 30 min, and the mixture was stirred for 1.5 h. The mixture was extracted with ether, and the extract was dried over Na_2SO_4 and evaporated to give *N,N'*-di(formylmethyl)-*N,N'*-diphenylurea. *N,N'*-Di(formylmethyl)-*N,N'*-diphenylurea: ^1H NMR (400 MHz, CDCl_3) δ 9.75 (s, 2 H), 7.02 (t, 4 H, $J = 7.3$ Hz), 6.94 (t, 2 H, $J = 7.3$ Hz), 6.91 (d, 4 H, $J = 7.0$ Hz), 4.37 (s, 4 H).

To a solution of *N,N'*-di(formylmethyl)-*N,N'*-diphenylurea and TMSCN (5.18 g, 52 mmol) in 20 ml of THF was added zinc iodide (319 mg, 1.0 mmol).⁶³ After stirring for 10 min, a saturated methanolic ammonia (90 ml) was added. The reaction mixture was stirred at 50°C for 6 h. After evaporation, the residue was purified by silica gel column chromatography (AcOEt : MeOH = 20 : 1) to give a mixture of diastereomeric *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylureas (2.28 g, 32 % from *N,N'*-diallyl-*N,N'*-diphenylurea).

Pyridine (2.9 ml) and trifluoroacetic anhydride (5.0 ml) were added to a solution of *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylureas (2.05 g, 5.9 mmol) in 60 ml of CH_2Cl_2 , and the mixture was stirred for 8 h. The reaction mixture was diluted with CH_2Cl_2 , washed successively with 2 N hydrochloric acid, H_2O , sat. NaHCO_3 , and H_2O . The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (AcOEt : *n*-Hexane = 1 : 3) to give a mixture of diastereomeric *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylureas (2.22 g, 70 %).

The two diastereomers were separated by silica gel column chromatography (CH_2Cl_2 : *n*-Hexane = 3 : 1). The diastereomer with high R_f could be assigned as racemic (*RR/SS*) by

crystal structure of **14** which was prepared from this isomer. Resultantly, the diastereomer with low Rf could be assigned meso (*RS*).

High Rf of *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylurea (racemic): ^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, 2 H, $J = 5.5$ Hz), 7.09 (brs, 6 H), 6.57 (brs, 4 H), 4.57-4.62 (ddd, 2 H, $J = 3.5, 5.5, 11$ Hz), 4.41-4.47 (dd, 2 H, $J = 11, 14$ Hz), 3.76-3.81 (dd, 2 H, $J = 3.5, 14$ Hz).

Low Rf isomer of *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylurea (meso): ^1H NMR (400 MHz, CDCl_3) δ 8.94 (d, 2 H, $J = 6.2$ Hz), 7.05-7.08 (m, 6 H), 6.64-6.65 (m, 4 H), 4.76-4.81 (ddd, 2 H, $J = 3.9, 6.2, 8.8$ Hz), 4.25-4.31 (dd, 2 H, $J = 8.8, 15$ Hz), 3.93-3.98 (dd, 2 H, $J = 3.9, 15$ Hz).

Hydrochloric acid (8 ml) was added to a solution of *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylurea (high Rf isomer, 763 mg, 1.4 mmol) in EtOH (80 ml), and the mixture was refluxed for 24 h. After removal of the solvent, the residue was basified with sat. NaHCO_3 , and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (AcOEt : MeOH = 10 : 1) to give *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (racemic, 319 mg, 65 %). *N,N'*-Bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (racemic): ^1H NMR (400 MHz, CDCl_3) δ 6.99-7.05 (m, 6 H), 6.80-6.83 (m, 4 H), 4.06 (t, 2 H, $J = 7.5$ Hz), 3.97-4.02 (dd, 2 H, $J = 7.3, 13$ Hz), 3.70-3.75 (dd, 2 H, $J = 7.3, 13$ Hz), 1.72 (brs, 4 H).

Hydrochloric acid (8 ml) was added to *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (racemic, 301 mg, 0.86 mmol), and the mixture was heated at 90°C. After 1.5 h, the reaction mixture was basified with sat. NaHCO_3 , and was purified by RP-silica gel chromatography (H_2O : MeOH = 1 : 1) to give *N,N'*-bis(β -alanyl)-*N,N'*-diphenylurea (**14**, racemic, 184 mg, 55 %). *N,N'*-Bis(β -alanyl)-*N,N'*-diphenylurea (**14**): colorless prisms (H_2O -MeOH); mp 226°C (dec.); ^1H NMR (400 MHz, D_2O , 30°C) δ 7.11-7.20 (m, 6 H), 6.95-7.00 (m, 4 H), 4.24-4.30 (dd, 2 H, $J = 8.4, 15$ Hz), 4.14-4.19 (dd, 2 H, $J = 2.9, 15$ Hz), 3.86-3.89 (dd, 2 H, $J = 2.9, 8.4$ Hz).

Similarly, low Rf isomer of *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylurea was converted to *N,N'*-bis(β -alanyl)-*N,N'*-diphenylurea (meso). Hydrochloric acid (6 ml) was added to a solution of *N,N'*-bis(2-cyano-2-trifluoroacetamino)-*N,N'*-diphenylurea (low Rf isomer, 546 mg, 1.0 mmol) in EtOH (60 ml), and the mixture was refluxed for 24 h. After removal of the solvent, the residue was basified with sat. NaHCO_3 , and extracted

with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (AcOEt : MeOH = 10 : 1) to give *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (meso, 266 mg, 76 %). *N,N'*-Bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (meso): ^1H NMR (400 MHz, CDCl_3) δ 6.97-7.05 (m, 6 H), 6.80-6.82 (m, 4 H), 3.99-4.07 (m, 4 H), 3.66-3.74 (m, 2 H), 1.72 (brs, 4 H).

Hydrochloric acid (6 ml) was added to *N,N'*-bis(2-amino-2-cyanoethyl)-*N,N'*-diphenylurea (meso, 247 mg, 0.71 mmol), and the mixture was heated at 100°C . After 1 h, the reaction mixture was basified with sat. NaHCO_3 , and was purified by RP-silica gel chromatography (H_2O : MeOH = 1 : 1) to give *N,N'*-bis(β -alanyl)-*N,N'*-diphenylurea (meso, 228 mg, 83 %). *N,N'*-Bis(β -alanyl)-*N,N'*-diphenylurea (meso): colorless prisms (H_2O -MeOH); mp 239°C (dec.); ^1H NMR (400 MHz, D_2O , 30°C) δ 7.09-7.18 (m, 6 H), 6.96 (d, 4 H, $J = 7.3$ Hz), 4.24 (m, 4 H), 3.90-3.93 (dd, 2 H, $J = 4.2, 6.0$ Hz).

***N,N'*-Dimethyl-*N,N'*-diphenylurea Bis[(tricarbonyl)chromium] Complex (15).** A mixture of *N,N'*-dimethyl-*N,N'*-diphenylurea (1.00 g, 4.2 mmol) and chromium hexacarbonyl (1.73 g, 7.9 mmol) in 30 ml of *n*-butylether and 5 ml of THF was heated at reflux under N_2 atmosphere for 36 h.⁽⁵⁴⁾ The solvent of the reaction mixture was removed under vacuum, the residue was diluted with benzene, and was filtered on celite. The filtrate was evaporated and was purified by silica gel column chromatography (AcOEt : *n*-hexane = 1 : 3) to give *N,N'*-dimethyl-*N,N'*-diphenylurea bis[(tricarbonyl)chromium] complex (**15**, 130mg, 6 %) besides monochromium complex. *N,N'*-Dimethyl-*N,N'*-diphenylurea Bis[(tricarbonyl)chromium] Complex (**15**): yellow prisms (AcOEt-ether); mp 162 - 167°C ; ^1H NMR (400 MHz, CD_3OD) δ 5.59 (d, 4 H, $J = 7.0$ Hz), 5.45 (t, 4 H, $J = 6.6$ Hz), 5.30 (t, 2 H, $J = 6.2$ Hz), 3.25 (s, 6 H); Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_7\text{Cr}_2$: C, 49.23; H, 3.15; N, 5.47; Found: C, 49.20; H, 2.96; N, 5.55.

***N,N',N''*-Trimethyl-*N,N',N''*-triphenylguanidinium iodide (16).** Lead monoxide was added to a solution of *N,N'*-diphenylthiourea (1.00 g, 4.4 mmol) in 14 ml of MeOH at 65°C . The resulting black suspension was stirred for 15 min, and a solution of aniline (0.46 g, 5.0 mmol) in 1 ml of MeOH was added. The mixture was stirred overnight. The PbS precipitate was filtered off and the solvent was evaporated to leave an oily residue, which was purified by silica gel column chromatography (CH_2Cl_2 : MeOH = 8 : 1) to give

N,N',N''-triphenylguanidine (1.12 g, 89 %). *N,N',N''*-Triphenylguanidine: colorless prisms (CH_2Cl_2 -*n*-hexane); mp 139-141°C; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, 6 H, $J = 7.9$ Hz), 7.19 (d, 6 H, $J = 7.7$ Hz), 7.05 (t, 3 H, $J = 7.3$ Hz); Anal Calcd. for $\text{C}_{18}\text{H}_{15}\text{N}_3$: C, 79.42; H, 5.96; N, 14.62; Found: C, 79.13; H, 5.97; N, 14.89.

NaH (60 %, 164 mg, 4.1 mmol) was washed twice with *n*-hexane, and suspended in 1 ml of dry DMF. A solution of *N,N',N''*-triphenylguanidine (500 mg, 1.7 mmol) in 3 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 10 min, and then 1 ml of CH_3I was added to it. After 3 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $\text{NH}_4\text{OH} = 10 : 1 : 0.4$) to give *N,N',N''*-trimethyl-*N,N',N''*-triphenylguanidinium iodide (7, 666 mg, 84 %). *N,N',N''*-Trimethyl-*N,N',N''*-triphenylguanidinium iodide (7): colorless prisms (CH_2Cl_2 -AcOEt); mp 209-210°C; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (t, 6 H, $J = 7.7$ Hz), 7.30 (d, 6 H, $J = 7.7$ Hz), 7.26 (t, 3 H, $J = 7.1$ Hz), 3.44 (s, 9 H); Anal Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_3\text{I}$: C, 57.78; H, 5.29; N, 9.19; Found: C, 57.83; H, 5.29; N, 8.92.

N,N',N''-Triethyl-*N,N',N''*-triphenylguanidinium iodide (17). NaH (60 %, 180 mg, 4.5 mmol) was washed twice with *n*-hexane, and suspended in 2 ml of dry DMF. A solution of *N,N',N''*-triphenylguanidine (500 mg, 1.7 mmol) in 4 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 30 min, and then 1 ml of $\text{C}_2\text{H}_5\text{I}$ was added to it. The whole was left overnight, then the solvent and excess $\text{C}_2\text{H}_5\text{I}$ were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $\text{NH}_4\text{OH} = 16 : 1 : 0.4$) to give *N,N'*-diethyl-*N,N',N''*-triphenylguanidine (410 mg, 69 %). Next, 1 ml of $\text{C}_2\text{H}_5\text{I}$ was added to a solution of *N,N'*-diethyl-*N,N',N''*-triphenylguanidine (203 mg, 0.59 mmol) in CH_2Cl_2 (5 ml) and the mixture was heated overnight at 70 °C. The solvent and excess $\text{C}_2\text{H}_5\text{I}$ were removed under vacuum and the crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $\text{NH}_4\text{OH} = 16 : 1 : 0.2$) to give *N,N',N''*-triethyl-*N,N',N''*-triphenylguanidinium iodide (8, 248 mg, 84 %). *N,N',N''*-triethyl-*N,N',N''*-triphenylguanidinium iodide (8): colorless needle (CHCl_3 -AcOEt); mp 232-232.5°C; Anal Calcd. for $\text{C}_{25}\text{H}_{30}\text{N}_3\text{I}$: C, 60.12; H, 6.05; N, 8.41; Found: C, 60.12; H, 6.16; N, 8.69.

meta-Substituted Diguanidine (20). Pyridine (25 ml) was added to a solution of *meta*-phenylenediamine (25.0 g, 0.23 mol) in acetic anhydride (100 ml) at 0°C, and the mixture was stirred at room temperature for 4 h, then poured into 2 N hydrochloric acid. The precipitates were collected by filtration, washed with water and dried under vacuum to give *N,N'*-diacetyl-*meta*-phenylenediamine (31.5 g, 71 %). *N,N'*-Diacetyl-*meta*-phenylenediamine: pale yellow prisms (MeOH-AcOEt); mp 151°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.92 (s, 2 H), 7.87 (s, 1 H), 7.25 (d, 2 H, *J* = 7.7 Hz), 7.16 (t, 1 H, *J* = 7.2 Hz), 2.02 (s, 6 H); Anal Calcd. for C₁₀H₁₂N₂O₂: C, 62.49; H, 6.29; N, 14.57; Found: C, 62.30; H, 6.35; N, 14.50.

NaH (60 %, 13.58 g, 0.34 mol) was washed twice with *n*-hexane, and suspended in 80 ml of dry DMF. A solution of *N,N'*-diacetyl-*meta*-phenylenediamine (28.19 g, 0.15 mol) in 80 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 30 min, and then 30 ml of CH₃I was added to it. After 2 h, the solvent and excess CH₃I were removed under vacuum. The residue was diluted with CH₂Cl₂. The organic layer was washed with 2 N hydrochloric acid and H₂O, and dried over Na₂SO₄. After removal of the solvent, the crude product was recrystallized from CH₂Cl₂-*n*-hexane to give *N,N'*-diacetyl-*N,N'*-dimethyl-*meta*-phenylenediamine (23.26 g, 72 %). *N,N'*-Diacetyl-*N,N'*-dimethyl-*meta*-phenylenediamine: colorless prisms (CH₂Cl₂-*n*-hexane); mp 153°C; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (t, 1 H, *J* = 7.7 Hz), 7.20 (d, 2 H, *J* = 7.2 Hz), 7.07 (s, 1 H), 3.29 (s, 6 H), 1.91 (s, 6 H); Anal Calcd. for C₁₂H₁₆N₂O₂: C, 65.43; H, 7.32; N, 12.72; Found: C, 65.53; H, 7.10; N, 12.44.

Hydrochloric acid (10 ml) was added to a solution of *N,N'*-diacetyl-*N,N'*-dimethyl-*meta*-phenylenediamine (10.25 g, 47 mmol) in EtOH (200 ml), and the mixture was refluxed for 27 h. After removal of the solvent, the residue was basified with 2N NaOH, and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and evaporated. The crude product was purified by silica gel column chromatography (CH₂Cl₂) to give *N,N'*-dimethyl-*meta*-phenylenediamine (**29**, 5.52 g, 87 %). *N,N'*-Dimethyl-*meta*-phenylenediamine (**29**): ¹H NMR (400 MHz, CDCl₃) δ 7.01 (t, 1 H, *J* = 8 Hz), 6.04 (dd, 2 H, *J* = 2, 8 Hz), 5.89 (t, 1 H, *J* = 2 Hz), 3.0-3.8 (brs, 2 H), 2.82 (s, 6 H).

A 1 N hydrochloric acid ether solution (80 ml) was added to a solution of *N,N'*-dimethyl-*meta*-phenylenediamine (**29**, 4.96 g, 36 mmol) in ether (40 ml), and the precipitates were collected by filtration to give *N,N'*-dimethyl-*meta*-phenylenediamine dihydrochloride

(7.23 g, 95 %). A mixture of *N,N'*-dimethyl-*meta*-phenylenediamine dihydrochloride (507 mg, 2.4 mmol) and *N*-methyl-*N*-phenylcyanamide (642 mg, 4.9 mmol) in chlorobenzene (1.5 ml) was heated at 150°C under an argon atmosphere. After 24 h, the reaction mixture was basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : NH_4OH = 8 : 1 : 0.2) to give **20a** (286 mg, 29 %). **20a**: ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, 4 H, J = 8.0 Hz), 6.99 (t, 1 H, J = 8.0 Hz), 6.96 (t, 2 H, J = 7.1 Hz), 6.88 (d, 4 H, J = 7.7 Hz), 6.57 (d, 2 H, J = 8.3 Hz), 6.38 (s, 1 H), 3.11 (s, 6 H), 3.01 (s, 6 H), 1.90 (brs, 2 H). **20b** (**20a**·2HI): pale brown prisms (MeOH-ether); mp 285–287°C; ^1H NMR (400 MHz, DMSO- d_6) δ 8.87 (s, 4 H), 7.17 (t, 4 H, J = 7.7 Hz), 7.08 (t, 2 H, J = 7.2 Hz), 7.03 (t, 1 H, J = 8.0 Hz), 6.92 (d, 4 H, J = 7.2 Hz), 6.80 (d, 2 H, J = 8.3 Hz), 6.45 (s, 1 H), 3.26 (s, 6 H), 3.11 (s, 6 H); Anal Calcd. for $\text{C}_{24}\text{H}_{30}\text{N}_6\text{I}_2$: C, 43.92; H, 4.61; N, 12.80; Found: C, 43.65; H, 4.65; N, 12.77.

para-Substituted Diguanidine (21). NaH (60 %, 210 mg, 5.3 mmol) was washed twice with *n*-hexane, and suspended in 2 ml of dry DMF. A solution of 1,4-phenylenebiscyanamide⁶⁵⁾ (326 mg, 2.1 mmol) in 5 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 10 min, and then 0.5 ml of CH_3I was added to it. After 5 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , and dried over Na_2SO_4 to give *N,N'*-dicyano-*N,N'*-dimethyl-*para*-phenylenediamine (412 mg, quant). *N,N'*-Dicyano-*N,N'*-dimethyl-*para*-phenylenediamine: ^1H NMR (400 MHz, CDCl_3) δ 7.11 (s, 4 H), 3.35 (s, 6 H).

A mixture of *N*-methylaniline hydrochloride (634 mg, 4.4 mmol) and *N,N'*-dicyano-*N,N'*-dimethyl-*para*-phenylenediamine (412 mg, 2.2 mmol) in chlorobenzene (3 ml) was heated at 140°C under an argon atmosphere. After 24 h, the reaction mixture was basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : NH_4OH 8 : 1 : 0.2) to give **21a** (357 mg, 40 %). **21a**: ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, 4 H, J = 8.0 Hz), 6.99 (t, 2 H, J = 7.4 Hz), 6.91 (d, 4 H, J = 7.7 Hz), 6.75 (s, 4 H), 3.15 (s, 6 H), 3.11 (s, 6 H). **21b** (**21a**·2HI): pale brown prisms (MeOH-AcOEt); mp >300°C; ^1H NMR (400 MHz, DMSO- d_6) δ 8.82 (s, 4 H), 7.21 (t, 4 H, J = 7.7 Hz), 7.13 (t, 2 H, J = 7.4 Hz), 7.01 (d, 4 H, J = 7.2 Hz), 6.88 (s, 4 H), 3.23 (s, 6 H), 3.22 (s, 6 H);

Anal Calcd. for $C_{24}H_{30}N_6I_2$: C, 43.92; H, 4.61; N, 12.80; Found: C, 44.00; H, 4.58; N, 12.68.

meta-Substituted Tetraguanidine (22). Pyridine (20 ml) was added to a solution of *meta*-nitroaniline (**24**, 42.58 g, 308 mmol) in acetic anhydride (300 ml) at 0°C, and the mixture was stirred at room temperature for 4 h, then poured into 2 N hydrochloric acid. The precipitates were collected by filtration, washed with water and dried under vacuum to give *meta*-nitroacetoanilide (**25**, 55.30 g, quant.). *meta*-Nitroacetoanilide (**25**): colorless prisms (AcOEt-*n*-hexane); mp 152°C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.43 (s, 1 H), 8.62 (s, 1 H), 7.88 (m, 2 H), 7.59 (t, 1 H, $J = 8.3$ Hz), 2.09 (s, 3 H); Anal Calcd. for $C_8H_6N_2O_3$: C, 53.33; H, 4.48; N, 15.55; Found: C, 53.35; H, 4.52; N, 15.44.

meta-Nitroacetoanilide (**25**, 10.15 g, 56 mmol) was hydrogenated with 10 % Pd-C in MeOH (200 ml). After 2 h, the reaction mixture was filtered and the filtrate was evaporated to give *N*-acetyl-*meta*-phenylenediamine (**26**, 8.88 g, quant.) as colorless prisms. *N*-Acetyl-*meta*-phenylenediamine (**26**): ^1H NMR (400 MHz, CDCl_3) δ 7.43 (brs, 1 H), 7.14 (s, 1 H), 7.06 (t, 1 H, $J = 8.0$ Hz), 6.67 (d, 1 H, $J = 8.3$ Hz), 6.43 (d, 1 H, $J = 8.3$ Hz), 3.10 (br, 2 H), 2.14 (s, 3 H).

Cyanogen bromide (95 %, 3.39 g, 30 mmol) and 1 N NaOH (45 ml) were added to a solution of *N*-acetyl-*meta*-phenylenediamine (**26**, 4.53 g, 30 mmol) in 90 % aqueous acetic acid (50 ml) at 0°C, and the mixture was stirred overnight. The colorless precipitates were collected by filtration and washed with water to give *N*-acetyl-*N'*-cyano-*meta*-phenylenediamine (**16**, 6.04 g, quant.). *N*-Acetyl-*N'*-cyano-*meta*-phenylenediamine (**27**): yellow prisms (MeOH); mp 146-147°C; ^1H NMR (400 MHz, DMSO- d_6) δ 10.15 (s, 1 H), 10.02 (s, 1 H), 7.45 (s, 1 H), 7.23 (t, 1 H, $J = 8.0$ Hz), 7.14 (d, 1 H, $J = 8.2$ Hz), 6.61 (d, 1 H, $J = 8.2$ Hz), 2.03 (s, 3 H); Anal Calcd. for $C_9H_7N_3O$: C, 61.70; H, 5.18; N, 23.99; Found: C, 61.55; H, 4.96; N, 24.13.

NaH (60 %, 9.72 g, 0.24 mol) was washed twice with *n*-hexane, and suspended in 50 ml of dry DMF. A solution of *N*-acetyl-*N'*-cyano-*meta*-phenylenediamine (**27**, 18.91 g, 0.11 mol) in 70 ml of dry DMF was added to this suspension at 0°C, the mixture was stirred for 30 min, and then 24 ml of CH_3I was added to it. After 1 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , and dried over Na_2SO_4 . After removal of the solvent, the crude product was recrystallized from AcOEt-*n*-hexane to give *N*-acetyl-*N'*-cyano-

N,N'-dimethyl-*meta*-phenylenediamine (**28**, 23.12 g, quant). *N*-Acetyl-*N'*-cyano-*N,N'*-dimethyl-*meta*-phenylenediamine (**28**): colorless prisms (AcOEt-*n*-hexane); mp 98°C; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (t, 1 H, *J* = 8.0 Hz), 7.07 (d, 1 H, *J* = 8.3 Hz), 6.95 (brd, 2 H), 3.37 (s, 3 H), 3.27 (s, 3 H), 1.90 (s, 3 H); Anal Calcd. for C₁₁H₁₃N₃O: C, 65.01; H, 6.45; N, 20.68; Found: C, 65.10; H, 6.52; N, 20.42.

A mixture of *N,N'*-dimethyl-*meta*-phenylenediamine dihydrochloride (**29**, 5.45 g, 26 mmol, see the section on synthesis of **20**) and *N*-acetyl-*N'*-cyano-*N,N'*-dimethyl-*meta*-phenylenediamine (**28**, 10.86 g, 53 mmol) in chlorobenzene (6 ml) was heated at 160°C under mechanical stirring in an argon atmosphere. After 2 h, the reaction mixture was basified with 2 N NaOH, and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, and evaporated. The crude product was purified by silica gel column chromatography (CH₂Cl₂: MeOH: NH₄OH = 8:1:0.2) to give **30** (3.2 g, 23 %). **30**: ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, 2 H, *J* = 8.1 Hz), 7.00 (t, 1 H, *J* = 8.0 Hz), 6.89 (d, 2 H, *J* = 8.3 Hz), 6.79 (d, 2 H, *J* = 6.6 Hz), 6.69 (s, 2 H), 6.55 (d, 2 H, *J* = 8.8 Hz), 6.50 (s, 1 H), 3.17 (s, 6 H), 3.15 (s, 6 H), 3.08 (s, 6 H), 1.76 (s, 6 H).

A solution of **30** (1.28 g, 2.4 mmol) in 2 N hydrochloric acid (30 ml) was refluxed at 120°C. After 22 h, the reaction mixture was neutralized with Na₂CO₃, and extracted with CH₂Cl₂. The extract was dried over Na₂SO₄, and evaporated. The crude product was purified by silica gel column chromatography (CH₂Cl₂: MeOH: NH₄OH = 8:1:0.2) to give **31** (751 mg, 69 %). **31**: ¹H NMR (400 MHz, CDCl₃) δ 7.14 (t, 1 H, *J* = 8.0 Hz), 7.04 (t, 2 H, *J* = 8.0 Hz), 6.76 (dd, 2 H, *J* = 2.2, 8.3 Hz), 6.61 (brt, 1 H), 6.35 (dd, 2 H, *J* = 1.4, 8.8 Hz), 6.31 (dd, 2 H, *J* = 1.7, 8.3 Hz), 6.23 (t, 2 H, *J* = 2.2 Hz), 3.24 (s, 6 H), 3.09 (s, 6 H), 2.73 (s, 6 H).

A 1 N hydrochloric acid ether solution (30 ml) was added to a solution of **31** (2.94 g, 6.4 mmol) in MeOH (10 ml), and the mixture was stirred for 30 min, then evaporated to give **31**-hydrochloride (3.96 g, quant). **31**-hydrochloride: ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.04 (brs, 4 H), 7.05 (t, 1 H, *J* = 8.3 Hz), 6.97 (t, 2 H, *J* = 8.0 Hz), 6.83 (dd, 2 H, *J* = 1.9, 8.0 Hz), 6.66 (brs, 1 H), 6.57 (br, 2 H), 6.25-6.46 (br, 4 H), 3.75 (br 4 H), 3.27 (s, 6 H), 3.19 (s, 6 H), 2.61 (s, 6 H).

Aluminum chloride (1.65 g, 12 mmol) was added to a solution of *N*-methyl-*N*-*meta*-phenylcyanamide (1.32 g, 10 mmol) in chlorobenzene (10 ml) and the mixture was heated at 160°C under mechanical stirring in an argon atmosphere. After 10 min, **31**-HCl (2.62 g, 4.3 mmol) was added and the mixture was refluxed for 22 h. Water was added, and the

whole was washed with CH_2Cl_2 , basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : NH_4OH = 8 : 1 : 0.2) to give **22a** (1.44 g, 46%). **22a**: ^1H NMR (400 MHz, CDCl_3) δ 7.15 (t, 4 H, J = 8.0 Hz), 6.95-7.01 (m, 5 H), 6.87 (d, 4 H, J = 7.7 Hz), 6.58 (d, 1 H, J = 8.8 Hz), 6.52-6.55 (m, 4 H), 6.42 (s, 1 H), 6.40 (s, 2 H), 3.16 (s, 6 H), 3.02 (s, 6 H), 3.00 (s, 6 H), 2.98 (s, 6 H). **22b** (**22a**·4HCl): colorless prisms (MeOH-AcOEt); mp 242-245°C; ^1H NMR (400 MHz, D_2O , 30°C) δ 7.14-7.19 (m, 6 H), 7.10 (t, 2, 3 H, J = 8.0 Hz), 6.87 (d, 2 H, J = 6.6 Hz), 6.83 (d, 4 H, J = 6.6 Hz), 6.77 (d, 2 H, J = 8.3 Hz), 6.72 (d, 2 H, J = 7.7 Hz), 6.21 (s, 2 H), 6.19 (s, 1 H), 3.32 (s, 6 H), 3.10 (s, 6 H), 3.09 (s, 6 H), 3.08 (s, 6 H); Anal. Calcd. for $\text{C}_{42}\text{H}_{34}\text{N}_{12}\text{Cl}_4 \cdot 3.5\text{H}_2\text{O}$: C, 54.14; H, 6.60; N, 18.04; Found: C, 54.00; H, 6.34; N, 17.69.

para-Substituted Tetraguanidine (23). Pyridine (15 ml) was added to a solution of *para*-nitroaniline (23.94 g, 173 mmol) in acetic anhydride (160 ml) at 0 °C, and the mixture was stirred at room temperature for 3 h, then poured into 2 N hydrochloric acid. The precipitates were collected by filtration, washed with water and dried under vacuum to give *para*-nitroacetanilide (30.28 g, 97%). *para*-Nitroacetanilide: colorless powder (AcOEt-*n*-hexane); mp 214.5-215.5°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.56 (s, 1 H), 8.21 (d, 2 H, J = 9.4 Hz), 7.82 (d, 2 H, J = 9.4 Hz), 2.11 (s, 3 H); Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$: C, 53.33; H, 4.48; N, 15.55; Found: C, 53.12; H, 4.35; N, 15.76.

para-Nitroacetanilide (8.87 g, 49 mmol) was hydrogenated over 10 % Pd-C in MeOH (200 ml). After 2 h, the reaction mixture was filtered and the filtrate was evaporated to give *N*-acetyl-*para*-phenylenediamine (6.96 g, 94%). *N*-Acetyl-*para*-phenylenediamine: pale brown prisms (MeOH-AcOEt); mp 166.5-167°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.47 (s, 1 H), 7.18 (d, 2 H, J = 8.6 Hz), 6.48 (d, 2 H, J = 8.3 Hz), 4.89 (brs, 2 H), 1.94 (s, 3 H); Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$: C, 63.98; H, 6.71; N, 18.65; Found: C, 63.85; H, 6.69; N, 18.35.

Cyanogen bromide (95 %, 3.04 g, 27 mmol) and 1 N NaOH (45 ml) were added to a solution of *N*-acetyl-*para*-phenylenediamine (4.12 g, 27 mmol) in 90 % aqueous acetic acid (50 ml) at 0 °C, and the mixture was stirred overnight. The colorless precipitates were collected by filtration and washed with water to give *N*-acetyl-*N'*-cyano-*para*-phenylenediamine (4.69 g, 97%). *N*-Acetyl-*N'*-cyano-*para*-phenylenediamine: colorless prisms (MeOH- CH_2Cl_2); mp 181-183°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.89 (s, 1 H),

7.54 (d, 2 H, $J = 8.8$ Hz), 6.88 (d, 2 H, $J = 8.8$ Hz), 2.00 (s, 3 H); Anal. Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99; Found: C, 61.44; H, 5.00; N, 24.21.

NaH (60 %, 3.29 g, 82 mmol) was washed twice with *n*-hexane, and suspended in 20 ml of dry DMF. A solution of *N*-acetyl-*N'*-cyano-*para*-phenylenediamine (6.58 g, 37 mmol) in 35 ml of dry DMF was added to this suspension at 0°C, and the mixture was stirred for 1 h. CH_3I (7 ml) was added to the reaction mixture. After 2 h, the solvent and excess CH_3I were removed under vacuum. The residue was diluted with CH_2Cl_2 , washed with 2 N hydrochloric acid and H_2O , and dried over Na_2SO_4 to give *N*-acetyl-*N'*-cyano-*N,N'*-dimethyl-*para*-phenylenediamine (**32**, 6.98 g, 91 %). *N*-Acetyl-*N'*-cyano-*N,N'*-dimethyl-*para*-phenylenediamine (**32**): pale yellow prisms (CH_2Cl_2 -*n*-hexane); mp 85-90 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 2 H, $J = 8.8$ Hz), 7.14 (d, 2 H, $J = 8.8$ Hz), 3.38 (s, 3 H), 3.24 (s, 3 H), 1.86 (s, 3 H); Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.45; N, 20.68; Found: C, 64.89; H, 6.35; N, 20.68.

A mixture of *N*-acetyl-*N'*-cyano-*N,N'*-dimethyl-*para*-phenylenediamine (**32**, 17.49 g, 86 mmol) and *N*-methylaniline hydrochloride (12.57 g, 88 mmol) in chlorobenzene (5 ml) was heated at 160°C under mechanical stirring in an argon atmosphere. After 4 h, the reaction mixture was basified with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $NH_4OH = 8 : 1 : 0.2$) to give **33** (6.15 g, 23 %). **33**: 1H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, 2 H, $J = 7.7$ Hz), 6.97 (t, 1 H, $J = 7.7$ Hz), 6.93 (d, 2 H, $J = 8.4$ Hz), 6.84-6.89 (m, 4 H), 3.25 (s, 3 H), 3.22 (s, 3 H), 2.18 (s, 3 H), 1.81 (s, 3 H).

A solution of **33** (4.22 g, 14 mmol) in 2 N hydrochloric acid (100 ml) was refluxed at 100°C. After 22 h, the reaction mixture was neutralized with Na_2CO_3 , and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : $NH_4OH = 8 : 1 : 0.2$) to give **34** (3.67 g, quant). **34**: 1H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, 2 H, $J = 7.7$ Hz), 7.08 (t, 1 H, $J = 7.5$ Hz), 6.94 (d, 2 H, $J = 7.3$ Hz), 6.72 (d, 2 H, $J = 8.8$ Hz), 6.42 (d, 2 H, $J = 8.8$ Hz), 3.75 (brs, 1 H), 3.33 (s, 3 H), 3.25 (s, 3 H), 2.79 (s, 3 H).

A 1 N hydrochloric acid ether solution (2 ml) was added to a solution of **34** (124 mg, 0.46 mmol) in MeOH (2 ml), then the mixture was stirred for 30 min, and evaporated to give **34**-dihydrochloride (166 g, quant). Aluminum chloride (1.76 g, 13 mmol) was added to a solution of *N,N'*-dicyano-*N,N'*-dimethyl-*para*-phenylenediamine (1.03 g, 5.5 mmol,

see the section on synthesis of **21**) in chlorobenzene (15 ml) and the mixture was heated at 160°C under mechanical stirring in an argon atmosphere. After 1 h, **34**·dihydrochloride (3.43 g, 10 mmol) was added, and the mixture was refluxed for 22 h. It was then neutralized with 2 N NaOH, and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 , and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : MeOH : NH_4OH = 8 : 1 : 0.2) to give **23a** (1.36 g, 37 %). **23a**: ^1H NMR (400 MHz, CDCl_3) δ 7.17 (t, 4 H, J = 7.9 Hz), 6.97 (t, 2 H, J = 7.3 Hz), 6.90 (d, 4 H, J = 7.3 Hz), 6.77 (m, 12 H), 3.13 (s, 6 H), 3.09 (s, 6 H), 3.04 (s, 12 H). **23b** (**23a**·4HCl): colorless prisms (MeOH-AcOEt); mp >300°C; ^1H NMR (400 MHz, D_2O , 30°C) δ 7.15-7.21 (m, 6 H), 6.91 (d, 4 H, J = 7.2 Hz), 6.76 (d, 4 H, J = 8.8 Hz), 6.71 (s, 4 H), 6.71 (d, 4 H, J = 8.8 Hz), 3.30 (s, 6 H), 3.27 (s, 12 H), 3.23 (s, 6 H).

参考文献

- 1 Yamamoto, Y.; Kojima, S. in "The Chemistry of Amidines and Imidates" vol. 2, Chap. 10, Patai, S.; Rappoport, Z. (eds.) John Wiley & Sons, New York, 1991.
- 2 Gund, P. *J. Chem. Educ.* **1972**, *49*, 100-103.
- 3 (a) Capitani, J. F.; Pedersen, L. *Chem. Phys. Lett.* **1978**, *54*, 547-550. (b) Sapse, A. M.; Massa, L. J. *J. Org. Chem.* **1980**, *45*, 719-721. (c) Mills, N. S.; Shapiro, J.; Hollingsworth, M. *J. Am. Chem. Soc.* **1981**, *103*, 1263-1264. (d) Ohwada, T.; Itai, A.; Ohta, T.; Shudo, K. *J. Am. Chem. Soc.* **1987**, *109*, 7036-7041. (e) Williams, M. L.; Gready, J. E. *J. Comput. Chem.* **1989**, *10*, 35-54.
- 4 Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 4177-4182.
- 5 Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362-2372.
- 6 (a) Galán, A.; de Mendoza, J.; Toiron, C.; Bruix, M.; Deslongchamps, G.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1991**, *113*, 9424-9425. (b) Deslongchamps, G.; Galán, A.; de Mendoza, J.; Rebek, J. Jr. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 61-63. (c) Kato, Y.; Conn, M. M.; Rebek, J. Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3279-3284. (d) Schiessl, P.; Schmidtchen, F. P. *J. Org. Chem.* **1994**, *59*, 509-511. (e) Peschke, W.; Schiessl, P.; Schmidtchen, F. P.; Bissinger, P.; Schier, A. *J. Org. Chem.* **1995**, *60*, 1039-1043. (f) Jubian, V.; Veronese, A.; Dixon, R. P.; Hamilton, A. D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1237-1239. (g) Molina, P.; Alajarin, M.; Sánchez-Andrada, P. *Tetrahedron Lett.* **1995**, *36*, 9405-9408. (h) Perreault, D. M.; Cabell, L. A.; Anslyn, E. V. *Bioorg. Med. Chem.* **1997**, *5*, 1209-1220.
- 7 (a) Sánchez-Quesada, J.; Seel, C.; Prados, P.; de Mendoza, J.; Dalcol, I.; Giral, E. *J. Am. Chem. Soc.* **1996**, *118*, 277-278. (b) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575-578.
- 8 (a) Haas, D. J.; Harris, D. R.; Mills, H. *Acta Crystallogr.* **1965**, *19*, 676-679. (b) Adams, J. M.; Small, R. W. H. *Acta Cryst.* **1974**, *B30*, 2191-2193. (c) Pajak, Z.; Grottel, M.; Koziol, A. E. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1529-1538. (d) Kozak, A.; Grottel, M.; Koziol, A. E.; Pajak, Z. *J. Phys. C* **1987**, *20*, 5433-5447.
- 9 Angell, C. L.; Sheppard, N.; Yamaguchi, A.; Shimanouchi, T.; Miyazawa, T.; Mizushima, S. *Trans. Faraday Soc.* **1957**, *53*, 589-600.
- 10 Cotton, F. A.; Day, V. W.; Hazen, Jr., E. E.; Larsen, S. *J. Am. Chem. Soc.* **1973**, *95*, 4834-4840.
- 11 Kato, Y.; Haimoto, Y.; Sakurai, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 233-234.
- 12 Kanamori, K.; Roberts, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 4698-4701.

- 13 Botto, R. E.; Schwartz, J. H.; Roberts, J. D. *Proc. Natl. Acad. Sci. USA* **1980**, *77*, 23-25.
- 14 (a) Bryden, J. H.; Burkardt, L. A.; Hughes, E. W.; Donohue, J. *Acta Crystallogr.* **1956**, *9*, 573. (b) Alléaume, M.; Gulko, A.; Herbstein, F. H.; Kapon, M.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 669. (c) Sullivan, G. R.; Roberts, J. D. *J. Org. Chem.* **1977**, *42*, 1095. (d) Moffat, J. B. *J. Mol. Struct.* **1981**, *86*, 119. (e) Boyar, A.; Marsh, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 1995-1998. (f) Rice, S.; Cheng, M. Y.; Cramer, R. E.; Mandel, M.; Mower, H. F.; Seff, K. Boyar, A.; Marsh, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 239-243.
- 15 (a) Greenhill, J. L.; Lue, P. in "Progress in Medicinal Chemistry" vol 30, Chapter 5, Ellis, G. P.; Luscombe, D. K. (eds.), Elsevier Science, 1993. (b) Greenhill, J. V.; Lue, P. *Prog. Med. Chem.* **1993**, *30*, 203-326.
- 16 医学のあゆみ **1994**, *170* (13), 1076-1077.
- 17 (a) White, K. A.; Marletta, M. A. *Biochemistry* **1992**, *31*, 6627-6631. (b) Ignarro, L. J. *Biochem. Soc. Trans.* **1992**, *20*, 465-469. (c) Fukuto J. M.; Stuehr D. J.; Feldman P. L.; Bova M. P.; Wong P., *J. Med. Chem.* **1993**, *36*, 2666-2670. (d) Beaumier, L.; Castillo, L.; Yu, Y. M.; Ajami, A. M.; Young, V. R. *Biomed. & Environment. Sci.* **1996**, *9*, 296-315.
- 18 (a) Mitchell, J. B. O.; Thornton, J. M.; Singh, J. *J. Mol. Biol.* **1992**, *226*, 251-262. (b) Flocco, M. M.; Mowbray, S. L. *J. Mol. Biol.* **1994**, *235*, 709-717.
- 19 (a) Dempcy, R. O.; Browne, K. A.; Bruice, T. *J. Am. Chem. Soc.* **1995**, *117*, 6140-6141. (b) Blaskó, A.; Dempcy, R. O.; Minyat, E. E.; Bruice, T. C. *J. Am. Chem. Soc.* **1996**, *118*, 7892-7899. (c) Luo, J.; Bruice, T. C. *J. Am. Chem. Soc.* **1997**, *119*, 6693-6701.
- 20 Martin, W. R. *J. Pharm. Exp. Ther.* **1976**, *197*, 517-532.
- 21 Scherz M. W.; Fialeix M.; Fischer J.B.; Reddy N. L.; Server A. C.; Sonders M. S.; Tester B. C.; Weber E.; Wong S. T.; Keana J. F. W. *J. Med. Chem.* **1990**, *33*, 2421-2429.
- 22 (a) Reddy, N. L.; Hu, L.-Y.; Cotter, R. E.; Fischer, J. B.; Wong, W. J.; McBurney, R. N.; Weber, E.; Holmes, D. L.; Wong, S. T.; Prasad, R.; Keana, J. F. K. *J. Med. Chem.* **1994**, *37*, 260-267. (b) Reddy, N. L.; Connaughton, S.; Daly, D.; Fischer, J. B. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 2259-2262.
- 23 Shudo, K.; Kagechika, H. Structural Evolution of Retinoids. *Adv. Drug Res.* **1993**, *24*, 81-119.
- 24 Kagechika, H.; Kawachi, E.; Hashimoto, Y.; Himi, T.; Shudo, K. *J. Med. Chem.* **1988**, *31*, 2182-2192.

- 25 (a) Kagechika, H.; Himi, T.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1989**, *32*, 2292-2296. (b) Toriumi, Y.; Kasuya, A.; Itai, A. *J. Org. Chem.* **1990**, *55*, 259.
- 26 Kashino, S.; Ito, K.; Haisa, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 365-369.
- 27 Itai, A.; Toriumi, Y.; Tomioka, N.; Kagechika, H.; Azumaya, I.; Shudo, K. *Tetrahedron Lett.* **1989**, *30*, 6177-6180.
- 28 Azumaya, I.; Kagechika, H.; Yamaguchi, K.; Shudo, K. *Tetrahedron* **1995**, *51*, 5277-5290.
- 29 Azumaya, I.; Yamaguchi, K.; Okamoto, I.; Kagechika, H.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 9083-9084.
- 30 Azumaya, I.; Kagechika, H.; Yamaguchi, K.; Shudo, K. *Tetrahedron Lett.* **1996**, *37*, 5003-5006.
- 31 Dannecker, W.; Kopf, J.; Rust, E. *Cryst. Struct. Comm.* **1979**, *8*, 429-432.
- 32 伊藤有史: マスター論文 (1992年)
- 33 (a) Carpy, P. A.; Leger, J.-M.; Wermuth, C.-G.; Leclerc, G. *Acta Cryst.* **1981**, *B37*, 885-889. (b) Brown, C. J.; Gash, D. J. *Acta Cryst.* **1984**, *C40*, 562-564. (c) Antolini, L.; Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *Aust. J. Chem.* **1991**, *44*, 1761-1769.
- 34 Levallet, C.; Lerpiniere, J.; Ko, S. Y. *Tetrahedron* **1997**, *53*, 5291-5304.
- 35 Ko, S. Y.; Lerpiniere, J.; Christofi, M. *SYNLETT* **1995**, 815-816.
- 36 Vidaluc, J.-L.; Calmel, F.; Bigg, D.; Carilla, E.; Stenger, A.; Chopin, P.; Briley, M. *J. Med. Chem.* **1994**, *37*, 689-695.
- 37 Zakhararov, L. N.; Adrianof, V. G.; Struchkov, Y. T. *Kristallografiya* **1980**, *25*, 65-71.
- 38 Tanatani, A.; Kagechika, H.; Azumaya, I.; Yamaguchi, K.; Shudo, K. *Chem. Pharm. Bull.* **1996**, *44*, 1135-1137.
- 39 Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665-8701.
- 40 (a) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603-3609. (b) Cozzi, F.; Cinquini, M.; Annuziata, R.; Dwyer, T.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 5729-5733. (c) Cozzi, F.; Cinquini, M.; Annuziata, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 5330-5331.
- 41 Santoro, A. V.; Mickevicius, G. *J. Org. Chem.* **1979**, *44*, 117-120.
- 42 Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers, Inc.: Florida, 1985.
- 43 (a) Gutowsky, H. S.; Holm, C. H.; *J. Chem. Phys.* **1956**, *25*, 1228-1234. (b) Jaeschke, A.; Muensch, H.; Schmid, H. C.; Friebohn, H.; Mannschreck, A. *J. Mol.*

- Spectrosc.* **1969**, *31*, 14-31.
- 44 Stewart, W. E.; Siddall, T. H. III *Chem. Rev.* **1970**, *70*, 517-551.
 - 45 Bally, T.; Diehl, P.; Haselbach, E.; Tracey, A. S. *Helv. Chem. Acta.* **1975**, *58*, 2398-2402.
 - 46 Saito, S.; Toriumi, Y.; Tomioka, N.; Itai, A. *J. Org. Chem.* **1995**, *60*, 4715-4720.
 - 47 化学増刊モレキュラー・キラリティー (原 昭二・古賀 憲司・首藤 絃一編) **1993**, 123.
 - 48 Recent selected papers on molecular chirality: (a) Toda, F.; Yagi, M.; Soda, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1413.; (b) Casarini, D.; Lunazzi, L.; Pasquali, F.; Gasparrini, F.; Villani, C. *J. Amer. Chem. Soc.* **1992**, *114*, 6521.; (c) Shieh, W.-C.; Carlson, J. A. *J. Org. Chem.* **1994**, *59*, 5463. (d) Gasparrini, F.; Lunazzi, L.; Misiti, D.; Villani, C. *Acc. Chem. Res.* **1995**, *28*, 163-170. (e) DeRossi, U.; Dähne, S.; Meskers, S. C. J.; Dekkers, P. J. M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 760-763. (f) Koshima, H.; Ding, K.; Chisaka, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1996**, *118*, 12059-12065. (g) Sakamoto, M. *Chem. Eur. J.* **1997**, *3*, 684-689. (h) Suh, I.-H.; Park, K. H.; Jensen, W. P.; Lewis, D. E. *J. Chem. Educ.* **1997**, *74*, 800-805.
 - 49 Bijvoet, J. M.; Peerdeman, A. F.; van Bommel, A. J. *Nature* **1951**, 271-271.
 - 50 (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1992**, *33*, 6669-6672. (b) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 3723-3726. (c) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1997**, *30*, 307-314.
 - 51 Yamaguchi, K.; Matsumura, G.; Kagechika, H.; Azumaya, I.; Ito, Y.; Itai, A.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 5474-5475.
 - 52 Tanatani, A.; Kagechika, H.; Azumaya, I.; Fukutomi, R.; Ito, Y.; Yamaguchi, K.; Shudo, K. *Tetrahedron Lett.* **1997**, *38*, 4425-4428.
 - 53 (a) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768-4774. (b) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534. (c) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Am. Chem. Soc.* **1994**, *116*, 3500-3506. (d) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217-11224.
 - 54 (a) Hopf, H.; Witulski, B.; Bubenitschek, P.; Jones, P. G. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1073-1074. (b) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848-3849. (c) Mataka, S.; Mitoma, Y.; Sawada, T.; Tashiro, M. *Tetrahedron Lett.* **1996**, *37*, 65-68. (d) Breidenbach, S.; Ohren, S.; Vögte, F. *Chem. Eur. J.* **1996**, *2*, 832-837.
 - 55 Martin, R. H. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649-660.
 - 56 Recent selected papers: (a) Geib, S. J.; Vicent, C.; Fan, E.; Hamilton, A. D. *Angew.*

- Chem. Int. Ed. Engl.* **1993**, 32, 119-121. (b) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 446-448. (c) Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1994**, 116, 4495-4496.
- 57 (a) Constable, E. C. *Tetrahedron* **1992**, 48, 10013-10059. (b) Lehn, J.-M. *Supramolecular Chemistry*, VCH, Weinheim, **1995**, Chapter 9. (c) Williams, A. *Chem. Eur. J.* **1997**, 3, 15-19.
- 58 Fukutomi, R.; Kagechika, H.; Hashimoto, Y.; Shudo, K. *Chem. Pharm. Bull.* **1996**, 44, 1983-1985.
- 59 (a) Turner, P. R.; Denny, W. A. *Mutation Res.* **1996**, 355, 141-169. (b) Neidle, S. *Biopoly.* **1997**, 44, 105-121.
- 60 最近、Distamycinが2分子並んでマイナーグループに結合するという報告や、Dervanらのヘアピン構造をもつマイナーグループバインダーの報告がある
(a) Pelton, J. G.; Wemmer, D. E. *Proc. Natl. Acad. Sci. USA* **1989**, 86, 5723-5727. (b) Pelton, J. G.; Wemmer, D. E. *J. Am. Chem. Soc.* **1990**, 112, 1393-1399. (c) Mrksich, M.; Wade, W. S.; Dwyer, T. J.; Geierstanger, B. H.; Wemmer, D. E.; Dervan, P. B. *Proc. Natl. Acad. Sci. USA* **1991**, 89, 7586-7590. (d) Wade, W. S.; Mrksich, W.; Dervan, P. B. *J. Am. Chem. Soc.* **1991**, 114, 8783-8794. (e) Chen, X.; Ramakrishnan, B.; Rao, S. T.; Sundaralingam, M. *Nature Str. Biol.* **1994**, 1, 169-175. (f) Parks, M. E.; Dervan, P. B. *Bioorg. Med. Chem.* **1996**, 4, 1045-1050.
- 61 Oxley, P.; Partridge, M. W.; Short, W. F. *J. Chem. Soc.* **1947**, 1110-1116.
- 62 Pappo, R.; Allen, D. S. Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, 21, 478-479.
- 63 Mai, K.; Patil, G. *Tetrahedron Lett.* **1984**, 25, 4583-4586.
- 64 Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, 64, 1288-1297.
- 65 Fauss, R.; Riebel, H. J. *Chem. Abstr.* 106; 49795j.

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Appendix

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X-ray Structure Reports

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Powder X-ray Crystallographical Data of 1

s89 – s90

N,N'-Diphenylguanidine (1, chiral crystal)

| | |
|---|---|
| A. Crystal Data | |
| Empirical Formula | C ₁₃ H ₁₃ N ₃ |
| Formula Weight | 211.27 |
| Crystal Color, Habit | clear, prism |
| Crystal Dimensions | 0.30 X 0.30 X 0.30 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| Indexing Images | 3 oscillations @ 5.0 minutes |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| Lattice Parameters | a = 12.653(5) Å b = 20.54(2) Å c = 8.944(5) Å V = 2324(2) Å ³ |
| Space Group | P2 ₁ 2 ₁ 2 ₁ (#19) |
| Z value | 8 |
| D _{calc} | 1.207 g/cm ³ |
| F ₀₀₀ | 896.00 |
| μ(MoKα) | 0.75 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | RAXIS-II |
| Radiation | MoKα (λ = 0.71070 Å) graphite monochromated |
| Detector Aperture | 200 mm x 200 mm |
| Data Images | 15 exposures @ 5.0 minutes |
| Oscillation Range | 7.0° |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| 2θ _{max} | 54.1° |
| No. of Reflections Measured | Total: 4670 Unique: 3231 (R _{int} = 0.069) |
| Corrections | Lorentz-polarization Secondary Extinction (coefficient: 3.72051e-05) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SAPI91) |
| Refinement | Full-matrix least-squares |
| Function Minimized | Σ w (F _o - F _c) ² |
| Least Squares Weights | w = 1/[σ ² (F _o) + P ² + P] |
| p-factor | 0.0100 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 1.5σ(I)) | 2694 |
| No. Variables | 290 |
| Reflection/Parameter Ratio | 9.29 |
| Residuals: R; Rw | 0.085 ; 0.091 |
| Goodness of Fit Indicator | 1.78 |
| Max Shift/Error in Final Cycle | 0.02 |
| Maximum peak in Final Diff. Map | 0.25 e/Å ³ |
| Minimum peak in Final Diff. Map | -0.25 e/Å ³ |

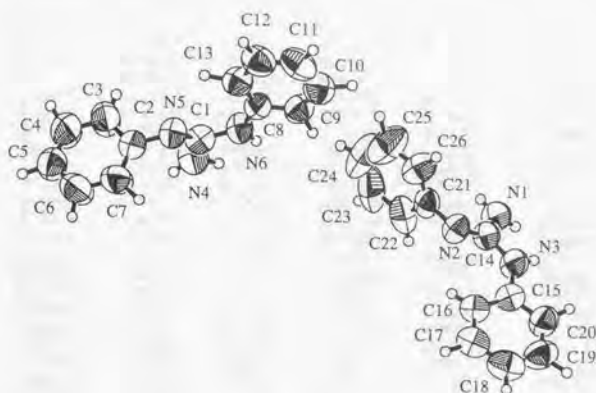


Table 1-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|-----------|------------|----------|
| N(1) | 0.7685(3) | 0.2667(2) | -0.0320(4) | 8.0(1) |
| N(2) | 0.7048(3) | 0.2798(2) | 0.2116(4) | 7.18(9) |
| N(3) | 0.6508(3) | 0.1944(2) | 0.0602(4) | 7.9(1) |
| N(4) | 0.7466(4) | 0.8330(2) | -0.0440(4) | 9.0(1) |
| N(5) | 0.7889(3) | 0.8228(2) | 0.2088(4) | 7.10(9) |
| N(6) | 0.8439(3) | 0.7471(2) | 0.0318(4) | 7.27(10) |
| C(1) | 0.7920(4) | 0.8026(2) | 0.0727(4) | 6.8(1) |
| C(2) | 0.7353(3) | 0.8818(2) | 0.2397(4) | 6.8(1) |
| C(3) | 0.7850(5) | 0.9399(3) | 0.239(1) | 12.5(2) |
| C(4) | 0.7331(7) | 0.9966(4) | 0.276(2) | 14.8(3) |
| C(5) | 0.6373(6) | 0.9970(3) | 0.3221(8) | 9.7(2) |
| C(6) | 0.5862(5) | 0.9408(4) | 0.3292(9) | 11.5(2) |
| C(7) | 0.6346(4) | 0.8827(3) | 0.2903(9) | 10.3(2) |
| C(8) | 0.9085(3) | 0.7062(2) | 0.1163(5) | 6.5(1) |
| C(9) | 0.9271(4) | 0.6440(2) | 0.0591(6) | 8.0(1) |
| C(10) | 0.9896(5) | 0.6012(3) | 0.1333(8) | 9.4(2) |
| C(11) | 1.0353(4) | 0.6188(4) | 0.2667(8) | 10.3(2) |
| C(12) | 1.0183(4) | 0.6791(4) | 0.3223(7) | 9.8(2) |
| C(13) | 0.9562(4) | 0.7233(3) | 0.2489(5) | 8.1(1) |
| C(14) | 0.7077(4) | 0.2504(2) | 0.0834(4) | 6.9(1) |
| C(15) | 0.5586(4) | 0.1720(2) | 0.1272(5) | 7.0(1) |
| C(16) | 0.5056(4) | 0.2065(2) | 0.2368(5) | 7.3(1) |
| C(17) | 0.4160(4) | 0.1812(3) | 0.2995(6) | 8.8(2) |
| C(18) | 0.3758(5) | 0.1229(4) | 0.2521(8) | 10.0(2) |
| C(19) | 0.4258(5) | 0.0901(3) | 0.1427(9) | 10.0(2) |
| C(20) | 0.5165(5) | 0.1135(3) | 0.0781(6) | 9.0(2) |
| C(21) | 0.7552(4) | 0.3412(2) | 0.2217(5) | 7.6(1) |
| C(22) | 0.7127(5) | 0.3948(3) | 0.1481(7) | 10.4(2) |
| C(23) | 0.7614(9) | 0.4552(4) | 0.178(1) | 14.4(3) |
| C(24) | 0.840(1) | 0.4630(6) | 0.273(1) | 15.1(4) |
| C(25) | 0.8794(8) | 0.4101(6) | 0.3403(8) | 13.6(3) |
| C(26) | 0.8379(5) | 0.3494(3) | 0.3154(6) | 9.7(2) |

Table 1-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| N(1) | 0.103(3) | 0.126(3) | 0.073(2) | -0.011(2) | 0.018(2) | -0.012(2) |
| N(2) | 0.112(3) | 0.096(3) | 0.066(2) | -0.014(2) | 0.007(2) | -0.004(2) |
| N(3) | 0.109(3) | 0.116(3) | 0.077(2) | -0.011(2) | 0.015(2) | -0.020(2) |
| N(4) | 0.147(4) | 0.119(3) | 0.076(2) | 0.027(2) | -0.011(2) | 0.004(2) |
| N(5) | 0.113(3) | 0.088(2) | 0.069(2) | 0.004(2) | -0.006(2) | -0.003(2) |
| N(6) | 0.113(3) | 0.096(3) | 0.067(2) | 0.013(2) | -0.006(2) | -0.004(2) |
| C(1) | 0.100(3) | 0.090(3) | 0.070(2) | -0.005(2) | -0.001(2) | 0.014(2) |
| C(2) | 0.099(3) | 0.087(3) | 0.071(2) | -0.001(2) | 0.001(2) | 0.004(2) |
| C(3) | 0.130(4) | 0.102(5) | 0.244(9) | -0.020(3) | 0.075(5) | -0.028(5) |
| C(4) | 0.142(6) | 0.104(5) | 0.32(1) | -0.027(4) | 0.058(7) | -0.038(6) |
| C(5) | 0.131(5) | 0.104(4) | 0.134(5) | -0.001(4) | 0.008(3) | -0.005(3) |
| C(6) | 0.107(4) | 0.141(6) | 0.188(6) | 0.018(4) | 0.024(4) | 0.002(5) |
| C(7) | 0.094(4) | 0.104(4) | 0.195(6) | -0.002(3) | 0.015(4) | 0.008(4) |
| C(8) | 0.083(3) | 0.087(3) | 0.077(2) | -0.009(2) | 0.009(2) | 0.002(2) |
| C(9) | 0.102(3) | 0.093(3) | 0.109(3) | -0.008(2) | -0.008(3) | 0.003(3) |
| C(10) | 0.119(4) | 0.105(4) | 0.131(5) | 0.005(3) | -0.001(4) | 0.014(3) |
| C(11) | 0.108(4) | 0.149(5) | 0.136(5) | 0.033(4) | -0.003(4) | 0.031(5) |
| C(12) | 0.103(4) | 0.162(6) | 0.106(4) | 0.021(4) | -0.016(3) | 0.001(4) |
| C(13) | 0.102(3) | 0.121(4) | 0.085(3) | 0.001(3) | -0.008(2) | -0.004(3) |
| C(14) | 0.095(3) | 0.100(3) | 0.067(2) | 0.000(2) | 0.009(2) | -0.005(2) |
| C(15) | 0.096(3) | 0.096(3) | 0.076(2) | -0.005(2) | -0.004(2) | 0.011(2) |
| C(16) | 0.094(3) | 0.107(3) | 0.078(3) | -0.004(2) | 0.002(2) | 0.011(3) |
| C(17) | 0.105(4) | 0.133(5) | 0.096(3) | 0.006(3) | 0.006(3) | 0.023(3) |
| C(18) | 0.104(4) | 0.137(5) | 0.140(5) | -0.005(4) | 0.009(4) | 0.048(5) |
| C(19) | 0.111(4) | 0.104(4) | 0.165(6) | -0.024(3) | -0.014(4) | 0.020(4) |
| C(20) | 0.121(4) | 0.095(4) | 0.127(4) | -0.009(3) | -0.003(3) | -0.004(3) |
| C(21) | 0.111(3) | 0.095(4) | 0.081(3) | -0.005(3) | 0.023(2) | -0.015(2) |
| C(22) | 0.162(5) | 0.102(5) | 0.130(4) | 0.024(4) | 0.038(4) | -0.003(4) |
| C(23) | 0.26(1) | 0.082(5) | 0.208(9) | 0.021(6) | 0.093(8) | -0.007(5) |
| C(24) | 0.27(1) | 0.155(9) | 0.147(8) | -0.111(9) | 0.077(8) | -0.059(7) |
| C(25) | 0.205(8) | 0.196(9) | 0.115(5) | -0.096(8) | 0.033(5) | -0.028(6) |
| C(26) | 0.133(4) | 0.150(5) | 0.085(3) | -0.040(4) | 0.005(3) | -0.006(3) |

Table 1-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|-----------|
| N(1) | C(14) | 1.332(6) | N(2) | C(14) | 1.297(5) |
| N(2) | C(21) | 1.416(6) | N(3) | C(14) | 1.371(6) |
| N(3) | C(15) | 1.390(6) | N(4) | C(1) | 1.344(6) |
| N(5) | C(1) | 1.286(5) | N(5) | C(2) | 1.416(6) |
| N(6) | C(1) | 1.367(6) | N(6) | C(8) | 1.395(6) |
| C(2) | C(3) | 1.349(7) | C(2) | C(7) | 1.353(7) |
| C(3) | C(4) | 1.38(1) | C(4) | C(5) | 1.282(10) |
| C(5) | C(6) | 1.325(9) | C(6) | C(7) | 1.387(9) |
| C(8) | C(9) | 1.395(6) | C(8) | C(13) | 1.375(6) |
| C(9) | C(10) | 1.356(7) | C(10) | C(11) | 1.373(9) |
| C(11) | C(12) | 1.351(9) | C(12) | C(13) | 1.368(8) |
| C(15) | C(16) | 1.384(7) | C(15) | C(20) | 1.386(7) |
| C(16) | C(17) | 1.368(7) | C(17) | C(18) | 1.367(9) |
| C(18) | C(19) | 1.347(9) | C(19) | C(20) | 1.372(9) |
| C(21) | C(22) | 1.390(8) | C(21) | C(26) | 1.349(8) |
| C(22) | C(23) | 1.41(1) | C(23) | C(24) | 1.31(2) |
| C(24) | C(25) | 1.34(2) | C(25) | C(26) | 1.37(1) |

Table 1-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|----------|
| C(14) | N(2) | C(21) | 117.2(4) | C(14) | N(3) | C(15) | 130.6(4) |
| C(1) | N(5) | C(2) | 118.4(3) | C(1) | N(6) | C(8) | 129.8(3) |
| N(4) | C(1) | N(5) | 124.9(4) | N(4) | C(1) | N(6) | 112.7(4) |
| N(5) | C(1) | N(6) | 122.5(4) | N(5) | C(2) | C(3) | 122.3(4) |
| N(5) | C(2) | C(7) | 122.0(4) | C(3) | C(2) | C(7) | 115.2(5) |
| C(2) | C(3) | C(4) | 121.8(6) | C(3) | C(4) | C(5) | 122.3(6) |
| C(4) | C(5) | C(6) | 118.1(6) | C(5) | C(6) | C(7) | 121.4(6) |
| C(2) | C(7) | C(6) | 120.9(5) | N(6) | C(8) | C(9) | 116.9(4) |
| N(6) | C(8) | C(13) | 124.8(4) | C(9) | C(8) | C(13) | 118.4(5) |
| C(8) | C(9) | C(10) | 120.9(5) | C(9) | C(10) | C(11) | 119.9(6) |
| C(10) | C(11) | C(12) | 119.5(6) | C(11) | C(12) | C(13) | 121.5(5) |
| C(8) | C(13) | C(12) | 119.7(5) | N(1) | C(14) | N(2) | 125.8(4) |
| N(1) | C(14) | N(3) | 113.4(4) | N(2) | C(14) | N(3) | 120.6(4) |
| N(3) | C(15) | C(16) | 123.1(4) | N(3) | C(15) | C(20) | 118.1(4) |
| C(16) | C(15) | C(20) | 118.8(5) | C(15) | C(16) | C(17) | 120.0(5) |
| C(16) | C(17) | C(18) | 120.8(5) | C(17) | C(18) | C(19) | 119.3(5) |
| C(18) | C(19) | C(20) | 121.7(6) | C(15) | C(20) | C(19) | 119.4(6) |
| N(2) | C(21) | C(22) | 120.1(5) | N(2) | C(21) | C(26) | 119.8(5) |
| C(22) | C(21) | C(26) | 119.7(5) | C(21) | C(22) | C(23) | 116.0(8) |
| C(22) | C(23) | C(24) | 124.0(10) | C(23) | C(24) | C(25) | 118.1(8) |
| C(24) | C(25) | C(26) | 121.6(9) | C(21) | C(26) | C(25) | 120.6(7) |

Table 1-5. Least Squares Planes

| Plane number 1 | | | Plane number 4 | | |
|--------------------------------------|----------|----------------|----------------------|----------|-----------|
| Atoms defining plane | | | Atoms defining plane | | |
| C(1) | Distance | -0.002(4) | N(1) | Distance | 0.007(4) |
| N(4) | | 0.001(5) | N(2) | | 0.007(4) |
| N(5) | | 0.001(4) | N(3) | | 0.006(4) |
| N(6) | | 0.001(4) | C(14) | | -0.026(5) |
| Plane number 2 | | | Plane number 5 | | |
| Atoms defining plane | | | Atoms defining plane | | |
| C(2) | Distance | -0.007(4) | C(15) | Distance | 0.011(4) |
| C(3) | | 0.036(10) | C(16) | | -0.014(5) |
| C(4) | | -0.01(1) | C(17) | | 0.005(5) |
| C(5) | | -0.005(7) | C(18) | | 0.006(6) |
| C(6) | | -0.002(8) | C(19) | | -0.005(6) |
| C(7) | | 0.016(7) | C(20) | | -0.009(6) |
| Plane number 3 | | | Plane number 6 | | |
| Atoms defining plane | | | Atoms defining plane | | |
| C(8) | Distance | -0.004(4) | C(21) | Distance | -0.002(4) |
| C(9) | | 0.003(5) | C(22) | | -0.001(6) |
| C(10) | | 0.004(6) | C(23) | | 0.015(8) |
| C(11) | | -0.006(6) | C(24) | | -0.015(9) |
| C(12) | | -0.002(6) | C(25) | | -0.003(8) |
| C(13) | | 0.008(5) | C(26) | | 0.006(5) |
| Summary | | | CHI ² | | |
| plane | | mean deviation | 1 | | 0.4 |
| 2 | | 0.0132 | 2 | | 22.2 |
| 3 | | 0.0045 | 3 | | 5.5 |
| 4 | | 0.0115 | 4 | | 40.0 |
| 5 | | 0.0083 | 5 | | 21.5 |
| 6 | | 0.0071 | 6 | | 7.2 |
| Dihedral angles between planes (deg) | | | | | |
| plane | 1 | 2 | 3 | 4 | 5 |
| 2 | 86.70 | | | | |
| 3 | 22.89 | 105.03 | | | |
| 4 | 73.59 | 50.57 | 76.37 | | |
| 5 | 84.17 | 28.14 | 94.16 | 23.68 | |
| 6 | 55.12 | 119.60 | 33.16 | 72.89 | 96.34 |

***N,N'*-Diphenylguanidine (1, racemic crystal)**

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{13}H_{13}N_3$ |
| Formula Weight | 211.27 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.30 X 0.30 X 0.48 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit Cell Determination (2θ range) | 20 ($28.2 - 31.4^\circ$) |
| Omega Scan Peak Width at Half-height | 0.37° |
| Lattice Parameters | $a = 8.906(2) \text{ \AA}$ $b = 12.342(1) \text{ \AA}$ $c = 21.335(2) \text{ \AA}$ $\beta = 96.66(1)^\circ$ $V = 2329.1(6) \text{ \AA}^3$ |
| Space Group | $P2_1/c$ (#14) |
| Z value | 8 |
| D_{calc} | 1.205 g/cm^3 |
| $F_{(00)}$ | 896.00 |
| $\mu(\text{CuK}\alpha)$ | 5.83 cm^{-1} |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC7S |
| Radiation | $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated |
| Attenuator | Ni foil (factor = 8.99) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 235 mm |
| Temperature | 23.0°C |
| Scan Type | $\omega-2\theta$ |
| Scan Rate | $16.0^\circ/\text{min}$ (in ω) (up to 3 scans) |
| Scan Width | $(1.68 + 0.30 \tan \theta)^\circ$ |
| $2\theta_{max}$ | 120.2° |
| No. of Reflections Measured | Total: 3913 Unique: 3650 (Rint = 0.021) |
| Corrections | Lorentz-polarization Secondary Extinction (coefficient: 2.69339×10^{-5}) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w(F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0010 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 2677 |
| No. Variables | 316 |
| Reflection/Parameter Ratio | 8.47 |
| Residuals: R ; R_w | 0.048 ; 0.039 |
| Goodness of Fit Indicator | 3.72 |
| Max Shift/Error in Final Cycle | 1.47 |
| Maximum peak in Final Diff. Map | $0.16 \text{ e}/\text{\AA}^3$ |
| Minimum peak in Final Diff. Map | $-0.13 \text{ e}/\text{\AA}^3$ |

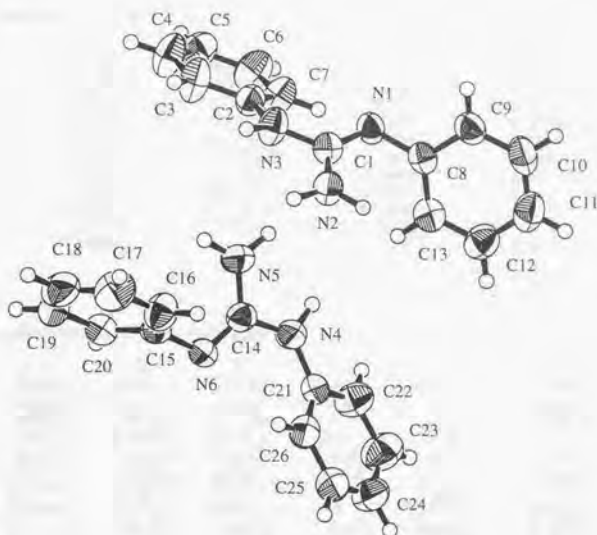


Table 2-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|-----------|----------|
| N(1) | 0.0264(3) | 0.1098(2) | 0.4107(1) | 4.22(6) |
| N(2) | 0.2684(3) | 0.0409(2) | 0.4487(1) | 4.66(7) |
| N(3) | 0.1434(3) | -0.0265(2) | 0.3586(1) | 5.02(7) |
| N(4) | 0.3108(3) | 0.5580(2) | 0.1260(1) | 4.84(7) |
| N(5) | 0.2254(3) | 0.3869(2) | 0.1058(1) | 5.67(8) |
| N(6) | 0.4824(3) | 0.4253(2) | 0.1040(1) | 4.41(7) |
| C(1) | 0.1418(3) | 0.0484(2) | 0.4069(1) | 4.17(8) |
| C(2) | 0.0654(3) | -0.0223(2) | 0.2969(1) | 4.26(8) |
| C(3) | 0.0822(4) | -0.1099(3) | 0.2583(2) | 6.5(1) |
| C(4) | 0.0113(5) | -0.1112(3) | 0.1972(2) | 7.1(1) |
| C(5) | -0.0745(4) | -0.0254(3) | 0.1738(2) | 6.1(1) |
| C(6) | -0.0900(4) | 0.0613(3) | 0.2119(2) | 6.3(1) |
| C(7) | -0.0209(4) | 0.0640(3) | 0.2731(2) | 5.27(9) |
| C(8) | 0.0424(3) | 0.1933(2) | 0.4565(1) | 3.94(7) |
| C(9) | -0.0583(3) | 0.1988(3) | 0.5012(1) | 4.77(8) |
| C(10) | -0.0479(4) | 0.2814(3) | 0.5451(2) | 5.8(1) |
| C(11) | 0.0617(4) | 0.3596(3) | 0.5451(2) | 6.1(1) |
| C(12) | 0.1613(4) | 0.3561(3) | 0.5000(2) | 5.64(10) |
| C(13) | 0.1521(4) | 0.2737(3) | 0.4563(1) | 4.75(8) |
| C(14) | 0.3478(3) | 0.4533(2) | 0.1121(1) | 4.15(8) |
| C(15) | 0.5082(3) | 0.3138(2) | 0.0943(1) | 4.20(8) |

Table 2-1. Atomic coordinates and Biso/Beq (Continued)

| atom | x | y | z | Beq |
|-------|-----------|-----------|-----------|---------|
| C(16) | 0.5100(4) | 0.2400(3) | 0.1427(2) | 5.7(1) |
| C(17) | 0.5379(5) | 0.1319(3) | 0.1338(2) | 7.0(1) |
| C(18) | 0.5690(4) | 0.0952(3) | 0.0761(2) | 6.7(1) |
| C(19) | 0.5720(4) | 0.1676(3) | 0.0274(2) | 6.0(1) |
| C(20) | 0.5423(3) | 0.2764(3) | 0.0363(2) | 4.85(9) |
| C(21) | 0.4070(3) | 0.6422(3) | 0.1483(1) | 4.46(8) |
| C(22) | 0.3525(4) | 0.7460(3) | 0.1402(2) | 6.0(1) |
| C(23) | 0.4364(5) | 0.8337(3) | 0.1633(2) | 7.5(1) |
| C(24) | 0.5790(5) | 0.8181(4) | 0.1942(2) | 7.2(1) |
| C(25) | 0.6347(4) | 0.7157(4) | 0.2029(2) | 7.0(1) |
| C(26) | 0.5489(4) | 0.6267(3) | 0.1805(2) | 5.8(1) |

Table 2-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| N(1) | 0.046(1) | 0.062(2) | 0.052(2) | 0.009(1) | 0.003(1) | -0.006(1) |
| N(2) | 0.056(2) | 0.065(2) | 0.053(2) | 0.014(1) | -0.007(1) | -0.006(1) |
| N(3) | 0.075(2) | 0.057(2) | 0.055(2) | 0.017(2) | -0.006(1) | -0.008(1) |
| N(4) | 0.045(2) | 0.059(2) | 0.079(2) | 0.001(1) | 0.004(1) | -0.012(1) |
| N(5) | 0.049(2) | 0.068(2) | 0.097(2) | -0.008(1) | 0.004(2) | -0.020(2) |
| N(6) | 0.048(2) | 0.050(2) | 0.072(2) | -0.002(1) | 0.015(1) | -0.006(1) |
| C(1) | 0.057(2) | 0.055(2) | 0.047(2) | 0.004(2) | 0.005(2) | 0.003(2) |
| C(2) | 0.058(2) | 0.053(2) | 0.050(2) | -0.001(2) | 0.005(2) | -0.006(2) |
| C(3) | 0.108(3) | 0.069(3) | 0.066(2) | 0.024(2) | -0.003(2) | -0.016(2) |
| C(4) | 0.118(4) | 0.083(3) | 0.067(3) | 0.006(3) | -0.003(2) | -0.027(2) |
| C(5) | 0.095(3) | 0.079(3) | 0.055(2) | -0.013(2) | -0.001(2) | -0.004(2) |
| C(6) | 0.105(3) | 0.069(3) | 0.061(2) | 0.004(2) | -0.014(2) | 0.001(2) |
| C(7) | 0.086(3) | 0.055(2) | 0.057(2) | 0.004(2) | -0.004(2) | -0.005(2) |
| C(8) | 0.045(2) | 0.058(2) | 0.046(2) | 0.013(2) | 0.000(1) | 0.004(2) |
| C(9) | 0.047(2) | 0.072(2) | 0.062(2) | 0.007(2) | 0.006(2) | -0.003(2) |
| C(10) | 0.063(2) | 0.094(3) | 0.064(2) | 0.021(2) | 0.012(2) | -0.013(2) |
| C(11) | 0.081(3) | 0.070(3) | 0.079(3) | 0.019(2) | -0.003(2) | -0.019(2) |
| C(12) | 0.077(3) | 0.056(2) | 0.080(3) | 0.002(2) | 0.001(2) | -0.002(2) |
| C(13) | 0.064(2) | 0.060(2) | 0.057(2) | 0.005(2) | 0.010(2) | 0.006(2) |
| C(14) | 0.053(2) | 0.057(2) | 0.047(2) | -0.006(2) | 0.003(2) | -0.003(2) |
| C(15) | 0.044(2) | 0.052(2) | 0.064(2) | -0.005(1) | 0.004(2) | -0.003(2) |
| C(16) | 0.093(3) | 0.064(2) | 0.061(2) | -0.003(2) | 0.012(2) | -0.001(2) |
| C(17) | 0.104(3) | 0.060(3) | 0.099(3) | 0.002(2) | 0.006(3) | 0.012(3) |
| C(18) | 0.074(3) | 0.054(3) | 0.126(4) | -0.001(2) | 0.004(3) | -0.013(3) |
| C(19) | 0.069(3) | 0.075(3) | 0.084(3) | -0.002(2) | 0.012(2) | -0.028(2) |
| C(20) | 0.054(2) | 0.064(2) | 0.067(2) | -0.001(2) | 0.010(2) | -0.004(2) |
| C(21) | 0.053(2) | 0.063(2) | 0.056(2) | -0.005(2) | 0.017(2) | -0.010(2) |
| C(22) | 0.081(3) | 0.060(2) | 0.084(3) | -0.009(2) | 0.001(2) | 0.003(2) |
| C(23) | 0.112(4) | 0.066(3) | 0.107(4) | -0.019(3) | 0.013(3) | 0.002(2) |
| C(24) | 0.097(3) | 0.086(3) | 0.094(3) | -0.035(3) | 0.027(3) | -0.024(3) |
| C(25) | 0.063(3) | 0.110(4) | 0.094(3) | -0.009(2) | 0.012(2) | -0.042(3) |
| C(26) | 0.058(2) | 0.078(3) | 0.085(3) | 0.002(2) | 0.006(2) | -0.027(2) |

Table 2-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.287(3) | N(1) | C(8) | 1.416(3) |
| N(2) | C(1) | 1.357(3) | N(3) | C(1) | 1.385(3) |
| N(3) | C(2) | 1.417(3) | N(4) | C(14) | 1.374(4) |
| N(4) | C(21) | 1.395(4) | N(5) | C(14) | 1.358(3) |
| N(6) | C(14) | 1.278(3) | N(6) | C(15) | 1.415(3) |
| C(2) | C(3) | 1.377(4) | C(2) | C(7) | 1.375(4) |
| C(3) | C(4) | 1.382(4) | C(4) | C(5) | 1.366(5) |
| C(5) | C(6) | 1.361(4) | C(6) | C(7) | 1.378(4) |
| C(8) | C(9) | 1.385(4) | C(8) | C(13) | 1.393(4) |
| C(9) | C(10) | 1.380(4) | C(10) | C(11) | 1.373(5) |
| C(11) | C(12) | 1.383(4) | C(12) | C(13) | 1.375(4) |
| C(15) | C(16) | 1.375(4) | C(15) | C(20) | 1.387(4) |
| C(16) | C(17) | 1.374(4) | C(17) | C(18) | 1.369(5) |
| C(18) | C(19) | 1.372(5) | C(19) | C(20) | 1.386(4) |
| C(21) | C(22) | 1.375(4) | C(21) | C(26) | 1.379(4) |
| C(22) | C(23) | 1.373(4) | C(23) | C(24) | 1.375(5) |
| C(24) | C(25) | 1.363(5) | C(25) | C(26) | 1.390(4) |

Table 2-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(1) | C(8) | 117.1(2) | C(1) | N(3) | C(2) | 128.3(3) |
| C(14) | N(4) | C(21) | 128.4(3) | C(14) | N(6) | C(15) | 117.0(3) |
| N(1) | C(1) | N(2) | 127.4(3) | N(1) | C(1) | N(3) | 121.1(3) |
| N(2) | C(1) | N(3) | 111.3(3) | N(3) | C(2) | C(3) | 116.8(3) |
| N(3) | C(2) | C(7) | 124.3(3) | C(3) | C(2) | C(7) | 118.9(3) |
| C(2) | C(3) | C(4) | 120.2(4) | C(3) | C(4) | C(5) | 120.7(4) |
| C(4) | C(5) | C(6) | 118.8(4) | C(5) | C(6) | C(7) | 121.4(4) |
| C(2) | C(7) | C(6) | 120.0(3) | N(1) | C(8) | C(9) | 119.3(3) |
| N(1) | C(8) | C(13) | 122.1(3) | C(9) | C(8) | C(13) | 118.5(3) |
| C(8) | C(9) | C(10) | 120.4(3) | C(9) | C(10) | C(11) | 120.7(3) |
| C(10) | C(11) | C(12) | 119.4(3) | C(11) | C(12) | C(13) | 120.1(4) |
| C(8) | C(13) | C(12) | 120.8(3) | N(4) | C(14) | N(5) | 112.3(3) |
| N(4) | C(14) | N(6) | 122.4(3) | N(5) | C(14) | N(6) | 125.3(3) |
| N(6) | C(15) | C(16) | 121.5(3) | N(6) | C(15) | C(20) | 120.6(3) |
| C(16) | C(15) | C(20) | 117.7(3) | C(15) | C(16) | C(17) | 121.7(4) |
| C(16) | C(17) | C(18) | 120.3(4) | C(17) | C(18) | C(19) | 119.2(4) |
| C(18) | C(19) | C(20) | 120.4(4) | C(15) | C(20) | C(19) | 120.6(3) |
| N(4) | C(21) | C(22) | 117.2(3) | N(4) | C(21) | C(26) | 123.9(3) |
| C(22) | C(21) | C(26) | 118.8(3) | C(21) | C(22) | C(23) | 121.3(4) |
| C(22) | C(23) | C(24) | 119.7(4) | C(23) | C(24) | C(25) | 119.7(4) |
| C(24) | C(25) | C(26) | 120.6(4) | C(21) | C(26) | C(25) | 119.7(4) |

Table 2-5. Least Squares Planes

| Plane number 1 | | Plane number 4 | |
|----------------------|--------------|----------------------|-------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(2) | -0.0030(29) | C(15) | -0.0111(28) |
| C(3) | 0.0052(39) | C(16) | 0.0138(35) |
| C(4) | -0.0028(41) | C(17) | -0.0022(39) |
| C(5) | -0.0005(36) | C(18) | -0.0078(36) |
| C(6) | 0.0005(37) | C(19) | 0.0036(33) |
| C(7) | 0.0016(33) | C(20) | 0.0058(30) |
| Plane number 2 | | Plane number 5 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(8) | 0.0052(26) | C(21) | 0.0043(29) |
| C(9) | -0.0052(30) | C(22) | 0.0025(36) |
| C(10) | -0.0013(33) | C(23) | -0.0104(40) |
| C(11) | 0.0076(34) | C(24) | 0.0065(38) |
| C(12) | -0.0049(32) | C(25) | 0.0036(38) |
| C(13) | -0.00228(29) | C(26) | -0.0083(34) |
| Plane number 3 | | Plane number 6 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(1) | 0.0228(29) | C(14) | 0.0133(28) |
| N(1) | -0.0070(24) | N(4) | -0.0044(25) |
| N(2) | -0.0070(25) | N(5) | -0.0048(27) |
| N(3) | -0.0070(26) | N(6) | -0.0046(24) |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0023 | 3.0 |
| | 2 | 0.0044 | 13.4 |
| | 3 | 0.0110 | 77.2 |
| | 4 | 0.0074 | 36.1 |
| | 5 | 0.0059 | 15.8 |
| | 6 | 0.0067 | 27.7 |

| Dihedral angles between planes (deg) | | | | |
|--------------------------------------|--------|--------|--------|-------|
| plane | 1 | 2 | 3 | 4 |
| 2 | 87.41 | | | |
| 3 | 28.78 | 115.89 | | |
| 4 | 37.54 | 52.95 | 63.93 | |
| 5 | 43.85 | 107.08 | 41.67 | 75.49 |
| 6 | 110.24 | 40.70 | 129.57 | 73.56 |

145.69

N-Methyl-*N,N'*-diphenylguanidine (2)

| | |
|--------------------------------------|--|
| A. Crystal Data | |
| Empirical Formula | C ₁₅ H ₁₅ N ₃ |
| Formula Weight | 225.29 |
| Crystal Color, Habit | clear, prism |
| Crystal Dimensions | 0.50 X 0.35 X 0.22 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| Indexing Images | 3 oscillations @ 5.0 minutes |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| Lattice Parameters | a = 5.666(1) Å b = 10.126(3) Å c = 21.17(2) Å V = 1214(3) Å ³ P2 ₁ 2 ₁ 2 ₁ (#19) |
| Space Group | 4 |
| Z value | 1.232 g/cm ³ |
| D _{calc} | 480.00 |
| F ₀₀₀ | 0.00 cm ⁻¹ |
| μ(MoKα) | |
| B. Intensity Measurements | |
| Diffractionmeter | RAXIS-II |
| Radiation | MoKα (λ = 0.71070 Å) |
| | graphite monochromated |
| | 200 mm x 200 mm |
| | 15 exposures @ 5.0 minutes |
| Detector Aperture | 7.0° |
| Data Images | 86.33 mm |
| Oscillation Range | 0.00° |
| Detector Position | 0.203 mm |
| Detector Swing Angle | 44.0° |
| Pixel Size | |
| 2θ _{max} | Total: 819 |
| No. of Reflections Measured | Lorentz-polarization |
| Corrections | |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR88) |
| Refinement | Full-matrix least-squares |
| Function Minimized | Σ w (F _o - F _c) ² |
| Least Squares Weights | w = 1/[σ ² (F _o) ² + P ² + P] |
| p-factor | 0.0100 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 4.5σ(I)) | 775 |
| No. Variables | 214 |
| Reflection/Parameter Ratio | 3.62 |
| Residuals: R; Rw | 0.075 ; 0.076 |
| Goodness of Fit Indicator | 3.58 |
| Max Shift/Error in Final Cycle | 2.22 |
| Maximum peak in Final Diff. Map | 0.33 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.34 e-/Å ³ |

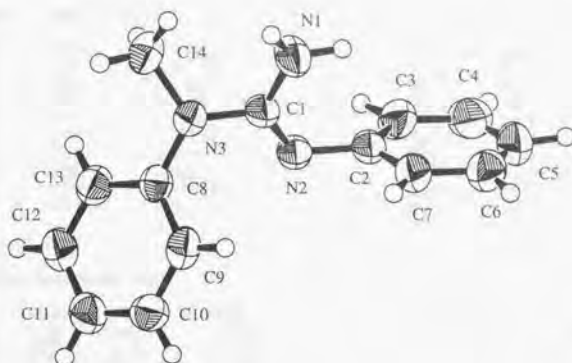


Table 3-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-------------|------------|-----------|--------|
| N(1) | -0.1252(9) | 0.1342(5) | 0.7345(2) | 4.8(1) |
| N(2) | -0.0336(7) | -0.0901(4) | 0.7301(2) | 3.7(1) |
| N(3) | 0.0289(8) | 0.0287(4) | 0.8221(2) | 3.9(1) |
| C(1) | -0.0409(10) | 0.0212(5) | 0.7591(2) | 3.6(1) |
| C(2) | -0.0909(9) | -0.0925(6) | 0.6649(2) | 3.9(1) |
| C(3) | -0.299(1) | -0.1528(7) | 0.6457(3) | 5.4(2) |
| C(4) | -0.347(1) | -0.1622(9) | 0.5821(3) | 6.6(2) |
| C(5) | -0.194(1) | -0.1137(7) | 0.5379(3) | 6.3(2) |
| C(6) | 0.008(1) | -0.0556(7) | 0.5567(3) | 5.6(2) |
| C(7) | 0.062(1) | -0.0450(6) | 0.6203(3) | 4.6(1) |
| C(8) | 0.1782(9) | -0.0712(5) | 0.8476(2) | 3.6(1) |
| C(9) | 0.386(1) | -0.1050(6) | 0.8171(3) | 4.4(1) |
| C(10) | 0.538(1) | -0.1976(6) | 0.8424(3) | 4.5(1) |
| C(11) | 0.480(1) | -0.2595(6) | 0.8985(3) | 5.0(2) |
| C(12) | 0.278(1) | -0.2244(7) | 0.9292(3) | 5.1(2) |
| C(13) | 0.125(1) | -0.1336(6) | 0.9037(2) | 4.3(1) |
| C(14) | -0.119(1) | 0.1038(7) | 0.8659(3) | 4.7(2) |

Table 3-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| N(1) | 0.086(4) | 0.043(3) | 0.054(3) | 0.008(3) | -0.015(3) | -0.001(2) |
| N(2) | 0.057(2) | 0.038(3) | 0.047(3) | 0.006(2) | -0.002(2) | -0.001(2) |
| N(3) | 0.055(2) | 0.050(3) | 0.042(2) | 0.007(2) | -0.001(2) | -0.004(2) |
| C(1) | 0.051(3) | 0.040(4) | 0.047(3) | 0.008(3) | -0.003(2) | -0.001(2) |
| C(2) | 0.059(3) | 0.042(4) | 0.045(3) | 0.010(3) | -0.004(3) | -0.002(2) |
| C(3) | 0.057(4) | 0.091(5) | 0.057(3) | 0.009(4) | -0.006(3) | -0.021(3) |
| C(4) | 0.071(5) | 0.100(6) | 0.080(5) | 0.022(4) | -0.021(5) | -0.032(4) |
| C(5) | 0.101(6) | 0.086(5) | 0.051(4) | 0.023(5) | -0.019(4) | -0.012(3) |
| C(6) | 0.090(5) | 0.067(4) | 0.056(3) | 0.015(4) | 0.008(4) | 0.006(3) |
| C(7) | 0.068(4) | 0.059(4) | 0.049(3) | 0.008(3) | -0.001(3) | 0.002(3) |
| C(8) | 0.051(3) | 0.043(3) | 0.041(3) | -0.005(3) | -0.002(3) | -0.004(2) |
| C(9) | 0.058(3) | 0.065(4) | 0.043(3) | -0.008(3) | 0.000(3) | -0.005(3) |
| C(10) | 0.055(4) | 0.058(4) | 0.058(4) | 0.005(3) | -0.006(3) | -0.010(3) |
| C(11) | 0.077(5) | 0.058(4) | 0.054(3) | 0.009(4) | -0.015(3) | -0.008(3) |
| C(12) | 0.076(4) | 0.069(4) | 0.047(3) | 0.006(4) | -0.004(3) | 0.007(3) |
| C(13) | 0.055(4) | 0.063(4) | 0.047(3) | -0.001(3) | 0.003(3) | -0.002(3) |
| C(14) | 0.072(4) | 0.062(4) | 0.046(3) | -0.001(4) | 0.004(3) | -0.009(3) |

Table 3-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|-----------|-------|-------|----------|
| N(1) | C(1) | 1.345(7) | N(2) | C(1) | 1.284(6) |
| N(2) | C(2) | 1.418(6) | N(3) | C(1) | 1.394(6) |
| N(3) | C(8) | 1.424(7) | N(3) | C(14) | 1.463(8) |
| C(2) | C(3) | 1.387(9) | C(2) | C(7) | 1.367(9) |
| C(3) | C(4) | 1.377(10) | C(4) | C(5) | 1.36(1) |
| C(5) | C(6) | 1.35(1) | C(6) | C(7) | 1.383(9) |
| C(8) | C(9) | 1.388(8) | C(8) | C(13) | 1.379(8) |
| C(9) | C(10) | 1.378(9) | C(10) | C(11) | 1.383(9) |
| C(11) | C(12) | 1.365(10) | C(12) | C(13) | 1.375(9) |

Table 3-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(2) | C(2) | 118.3(4) | C(1) | N(3) | C(8) | 119.4(4) |
| C(1) | N(3) | C(14) | 118.1(5) | C(8) | N(3) | C(14) | 118.1(4) |
| N(1) | C(1) | N(2) | 124.9(5) | N(1) | C(1) | N(3) | 115.1(4) |
| N(2) | C(1) | N(3) | 119.8(4) | N(2) | C(2) | C(3) | 119.2(5) |
| N(2) | C(2) | C(7) | 121.4(5) | C(3) | C(2) | C(7) | 119.2(6) |
| C(2) | C(3) | C(4) | 119.0(8) | C(3) | C(4) | C(5) | 121.4(8) |
| C(4) | C(5) | C(6) | 119.4(7) | C(5) | C(6) | C(7) | 120.5(8) |
| C(2) | C(7) | C(6) | 120.4(7) | N(3) | C(8) | C(9) | 120.3(5) |
| N(3) | C(8) | C(13) | 121.4(5) | C(9) | C(8) | C(13) | 118.3(6) |
| C(8) | C(9) | C(10) | 121.1(6) | C(9) | C(10) | C(11) | 119.7(7) |
| C(10) | C(11) | C(12) | 119.3(7) | C(11) | C(12) | C(13) | 121.1(6) |
| C(8) | C(13) | C(12) | 120.4(6) | | | | |

Table 3-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-----------|----------------------|-----------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(2) | -0.003(6) | C(8) | 0.001(5) |
| C(3) | 0.003(7) | C(9) | 0.001(6) |
| C(4) | 0.002(8) | C(10) | 0.005(6) |
| C(5) | -0.002(7) | C(11) | -0.011(6) |
| C(6) | 0.000(7) | C(12) | 0.017(7) |
| C(7) | 0.003(6) | C(13) | -0.008(6) |

| Plane number 3 | |
|----------------------|-----------|
| Atoms defining plane | Distance |
| C(1) | 0.021(6) |
| N(1) | -0.007(5) |
| N(2) | -0.002(4) |
| N(3) | -0.003(4) |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0021 | 0.8 |
| | 2 | 0.0073 | 12.0 |
| | 3 | 0.0085 | 17.6 |

| Dihedral angles between planes (deg) | | |
|--------------------------------------|--------|-------|
| plane | 1 | 2 |
| 2 | 115.41 | |
| 3 | 75.88 | 63.04 |

N-Methyl-*N'*,*N''*-diphenylguanidine (3)

| | |
|--|--|
| A. Crystal Data | |
| Empirical Formula | C ₁₄ H ₁₃ N ₃ |
| Formula Weight | 225.29 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.45 X 0.30 X 0.20 mm |
| Crystal System | monoclinic |
| Lattice Type | C-centered |
| No. of Reflections Used for Unit | 19 (48.9 - 54.2°) |
| Cell Determination (2 θ range) | 0.24° |
| Omega Scan Peak Width at Half-height | a = 11.212(2) Å |
| Lattice Parameters | b = 12.757(2) Å |
| | c = 9.281(1) Å |
| | β = 112.21(1)° |
| | V = 1229.1(4) Å ³ |
| Space Group | Cc (#9) |
| Z value | 4 |
| D _{calc} | 1.217 g/cm ³ |
| F ₀₀₀ | 480.00 |
| μ (CuK α) | 5.82 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuK α (λ = 1.54178 Å) |
| | graphite monochromated |
| | Ni foil (factors = 1.00, 3.57, 12.70, 45.11) |
| Attenuator | 6.0° |
| Take-off Angle | 9.0 mm horizontal |
| Detector Aperture | 13.0 mm vertical |
| | 258 mm |
| Crystal to Detector Distance | 23.0°C |
| Temperature | ω -2 θ |
| Scan Type | 16.0°/min (in ω) (up to 3 scans) |
| Scan Rate | (1.57 + 0.30 tan θ)° |
| Scan Width | 135.0° |
| 2 θ _{max} | Total: 1197 Unique: 1135 (Rint = 0.110) |
| No. of Reflections Measured | Lorentz-polarization |
| Corrections | Absorption |
| | (trans. factors: 0.7703 - 1.1204) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0020 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 3.00 σ (I)) | 1004 |
| No. Variables | 212 |
| Reflection/Parameter Ratio | 4.74 |
| Residuals: R; R _w | 0.062; 0.064 |
| Goodness of Fit Indicator | 6.69 |
| Max Shift/Error in Final Cycle | 5.14 |
| Maximum peak in Final Diff. Map | 0.30 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.24 e-/Å ³ |

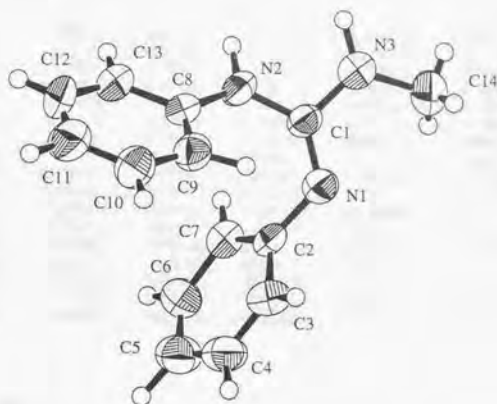


Table 4-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|-------------|--------|
| N(1) | 0.6496 | 0.0787(5) | 0.0378 | 4.1(1) |
| N(2) | 0.7015(8) | 0.0523(5) | -0.1857(9) | 4.6(2) |
| N(3) | 0.5635(9) | -0.0579(5) | -0.1323(10) | 4.7(2) |
| C(1) | 0.6399(9) | 0.0301(5) | -0.0856(9) | 3.7(2) |
| C(2) | 0.6918(9) | 0.1837(5) | 0.0648(10) | 3.8(2) |
| C(3) | 0.7756(10) | 0.2127(7) | 0.209(1) | 4.6(2) |
| C(4) | 0.8125(10) | 0.3143(7) | 0.246(1) | 5.3(2) |
| C(5) | 0.765(1) | 0.3928(8) | 0.134(1) | 5.8(2) |
| C(6) | 0.680(1) | 0.3640(7) | -0.008(1) | 5.5(2) |
| C(7) | 0.6436(10) | 0.2610(6) | -0.047(1) | 4.4(2) |
| C(8) | 0.8273(9) | 0.0924(5) | -0.1460(10) | 4.0(2) |
| C(9) | 0.9197(10) | 0.0872(6) | 0.003(1) | 4.6(2) |
| C(10) | 1.0445(10) | 0.1229(7) | 0.032(1) | 5.3(2) |
| C(11) | 1.074(1) | 0.1615(8) | -0.085(1) | 6.0(3) |
| C(12) | 0.986(1) | 0.1639(7) | -0.231(1) | 6.4(3) |
| C(13) | 0.861(1) | 0.1342(7) | -0.263(1) | 5.3(2) |
| C(14) | 0.471(1) | -0.0839(8) | -0.062(1) | 5.4(2) |

Table 4-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|----------|-----------|
| N(1) | 0.065(4) | 0.048(3) | 0.047(3) | -0.001(3) | 0.026(3) | -0.001(3) |
| N(2) | 0.063(4) | 0.073(4) | 0.049(4) | -0.013(3) | 0.034(3) | -0.014(3) |
| N(3) | 0.068(4) | 0.062(4) | 0.055(4) | -0.006(3) | 0.030(3) | -0.006(3) |
| C(1) | 0.062(4) | 0.045(4) | 0.039(4) | 0.003(3) | 0.023(3) | 0.000(3) |
| C(2) | 0.059(4) | 0.054(4) | 0.041(4) | 0.000(3) | 0.030(3) | -0.003(3) |
| C(3) | 0.057(5) | 0.064(5) | 0.050(5) | 0.009(4) | 0.017(4) | -0.009(4) |
| C(4) | 0.060(5) | 0.076(6) | 0.065(5) | -0.007(4) | 0.024(4) | -0.024(5) |
| C(5) | 0.073(6) | 0.071(7) | 0.083(6) | -0.006(5) | 0.035(5) | -0.022(5) |
| C(6) | 0.092(7) | 0.050(5) | 0.077(6) | -0.005(5) | 0.043(6) | -0.005(5) |
| C(7) | 0.062(5) | 0.061(5) | 0.050(5) | -0.001(4) | 0.027(4) | -0.001(4) |
| C(8) | 0.064(4) | 0.051(4) | 0.046(4) | -0.007(4) | 0.030(4) | -0.011(3) |
| C(9) | 0.069(5) | 0.051(5) | 0.066(5) | 0.005(4) | 0.037(4) | 0.000(4) |
| C(10) | 0.056(5) | 0.074(6) | 0.081(6) | 0.001(4) | 0.038(5) | -0.005(5) |
| C(11) | 0.076(6) | 0.088(7) | 0.081(7) | -0.010(5) | 0.047(6) | -0.017(5) |
| C(12) | 0.113(8) | 0.077(6) | 0.090(7) | -0.023(5) | 0.079(7) | -0.010(5) |
| C(13) | 0.087(6) | 0.074(6) | 0.054(5) | -0.018(5) | 0.041(5) | -0.013(4) |
| C(14) | 0.069(6) | 0.068(6) | 0.075(6) | -0.008(5) | 0.037(5) | 0.003(5) |

Table 4-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|-----------|-------|-------|----------|
| N(1) | C(1) | 1.270(9) | N(1) | C(2) | 1.411(9) |
| N(2) | C(1) | 1.380(9) | N(2) | C(8) | 1.412(9) |
| N(3) | C(1) | 1.379(10) | N(3) | C(14) | 1.46(1) |
| C(2) | C(3) | 1.37(1) | C(2) | C(7) | 1.38(1) |
| C(3) | C(4) | 1.36(1) | C(4) | C(5) | 1.39(1) |
| C(5) | C(6) | 1.35(1) | C(6) | C(7) | 1.38(1) |
| C(8) | C(9) | 1.38(1) | C(8) | C(13) | 1.39(1) |
| C(9) | C(10) | 1.40(1) | C(10) | C(11) | 1.34(1) |
| C(11) | C(12) | 1.34(2) | C(12) | C(13) | 1.36(1) |

Table 4-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|-----------|
| C(1) | N(1) | C(2) | 122.2(6) | C(1) | N(2) | C(8) | 127.1(7) |
| C(1) | N(3) | C(14) | 120.5(8) | N(1) | C(1) | N(2) | 127.8(7) |
| N(1) | C(1) | N(3) | 120.8(7) | N(2) | C(1) | N(3) | 111.4(7) |
| N(1) | C(2) | C(3) | 119.4(8) | N(1) | C(2) | C(7) | 122.2(7) |
| C(3) | C(2) | C(7) | 118.2(8) | C(2) | C(3) | C(4) | 122.1(10) |
| C(3) | C(4) | C(5) | 120.2(10) | C(4) | C(5) | C(6) | 117(1) |
| C(5) | C(6) | C(7) | 122(1) | C(2) | C(7) | C(6) | 119.2(9) |
| N(2) | C(8) | C(9) | 122.8(7) | N(2) | C(8) | C(13) | 118.6(8) |
| C(9) | C(8) | C(13) | 118.5(8) | C(8) | C(9) | C(10) | 119.7(8) |
| C(9) | C(10) | C(11) | 119(1) | C(10) | C(11) | C(12) | 120(1) |
| C(11) | C(12) | C(13) | 121.3(10) | C(8) | C(13) | C(12) | 119.7(10) |

Table 4-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|--------------|----------------------|----------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(8) | 0.0031(82) | C(2) | 0.0009(96) |
| C(9) | 0.0041(92) | C(3) | -0.0023(107) |
| C(10) | -0.0065(99) | C(4) | 0.0018(111) |
| C(11) | -0.0123(114) | C(5) | 0.0076(114) |
| C(12) | 0.0258(112) | C(6) | -0.0116(115) |
| C(13) | -0.0204(104) | C(7) | 0.0057(112) |
| Plane number 3 | | | |
| Atoms defining plane | Distance | | |
| N(1) | 0.0009(39) | | |
| N(2) | 0.0014(92) | | |
| N(3) | 0.0017(98) | | |
| C(1) | -0.0098(91) | | |
| Summary | | plane | mean deviation |
| | | 1 | 0.0120 |
| | | 2 | 0.0050 |
| | | 3 | 0.0034 |
| | | CHI ² | |
| | | 1 | 10.6 |
| | | 2 | 2.4 |
| | | 3 | 1.7 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|-------|
| 2 | 59.28 | |
| 3 | 49.74 | 59.84 |

N,N'-Dimethyl-*N,N'*-diphenylguanidine (4a)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{16.50}H_{21.50}N_3O_{0.50}$ |
| Formula Weight | 269.87 |
| Crystal Color, Habit | clear, prism |
| Crystal Dimensions | 0.30 X 0.30 X 0.30 mm |
| Crystal System | triclinic |
| Lattice Type | Primitive |
| Indexing Images | 3 oscillations @ 5.0 minutes |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| Lattice Parameters | a = 11.590(5) Å b = 16.44(2) Å c = 8.320(4) Å $\alpha = 97.21(7)^\circ$ $\beta = 90.73(3)^\circ$ $\gamma = 77.50(7)^\circ$ V = 1535(2) Å ³ |
| Space Group | P $\bar{1}$ (#2) |
| Z value | 4 |
| D _{calc} | 1.167 g/cm ³ |
| F ₀₀₀ | 582.00 |
| μ (MoK α) | 0.72 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | RAXIS-II |
| Radiation | MoK α ($\lambda = 0.71070$ Å) graphite monochromated 200 mm x 200 mm 15 exposures @ 5.0 minutes 7.0° |
| Detector Aperture | 86.33 mm |
| Data Images | 0.00° |
| Oscillation Range | 0.203 mm |
| Detector Position | 54.2° |
| Detector Swing Angle | Total: 4425 |
| Pixel Size | Lorentz-polarization |
| 2 θ_{max} | |
| No. of Reflections Measured | Direct Methods (SHELXS86) |
| Corrections | Full-matrix least-squares |
| C. Structure Solution and Refinement | |
| Structure Solution | $\Sigma w (F_o - F_c)^2$ |
| Refinement | $w = 1/(\sigma^2(F_o^2) + P^2 + P)$ |
| Function Minimized | 0.0100 |
| Least Squares Weights | All non-hydrogen atoms |
| p-factor | 2320 |
| Anomalous Dispersion | 517 |
| No. Observations ($I > 4.50\sigma(I)$) | 4.49 |
| No. Variables | 0.097 ; 0.127 |
| Reflection/Parameter Ratio | 3.87 |
| Residuals: R; Rw | 4.03 |
| Goodness of Fit Indicator | 0.43 e-/Å ³ |
| Max Shift/Error in Final Cycle | -0.45 e-/Å ³ |
| Maximum peak in Final Diff. Map | |
| Minimum peak in Final Diff. Map | |

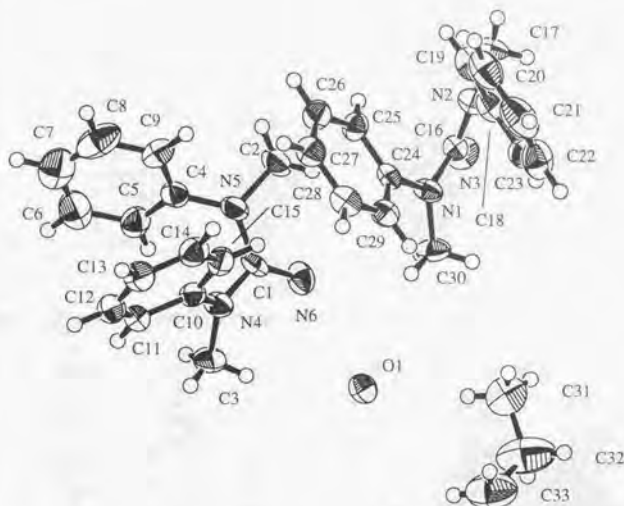


Table 5-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|-----------|-----------|--------|
| O(1) | 0.9398(6) | 0.4988(5) | 0.2470(9) | 3.5(2) |
| N(1) | 0.7797(8) | 0.6899(5) | 0.798(1) | 3.3(2) |
| N(2) | 0.7440(8) | 0.7167(6) | 1.076(1) | 3.2(2) |
| N(3) | 0.8665(9) | 0.5894(6) | 0.962(1) | 4.0(3) |
| N(4) | 1.1114(8) | 0.6852(5) | 0.302(1) | 3.4(2) |
| N(5) | 1.1520(8) | 0.7094(6) | 0.576(1) | 3.4(2) |
| N(6) | 1.0813(9) | 0.5888(6) | 0.474(1) | 4.0(3) |
| C(1) | 1.1135(10) | 0.6557(8) | 0.453(1) | 3.2(3) |
| C(2) | 1.126(1) | 0.6969(9) | 0.742(1) | 4.1(4) |
| C(3) | 1.147(1) | 0.6233(9) | 0.159(2) | 4.2(4) |
| C(4) | 1.235(1) | 0.7578(8) | 0.550(1) | 3.4(3) |
| C(5) | 1.332(1) | 0.7236(9) | 0.450(2) | 4.3(4) |
| C(6) | 1.411(1) | 0.775(1) | 0.417(2) | 6.0(5) |
| C(7) | 1.394(2) | 0.858(1) | 0.491(2) | 6.6(5) |
| C(8) | 1.295(2) | 0.889(1) | 0.593(2) | 6.5(5) |
| C(9) | 1.215(1) | 0.8401(8) | 0.624(2) | 4.1(3) |
| C(10) | 1.074(1) | 0.7702(7) | 0.282(1) | 3.0(3) |
| C(11) | 1.125(1) | 0.8041(8) | 0.159(1) | 3.4(3) |
| C(12) | 1.088(1) | 0.8874(8) | 0.139(2) | 3.9(3) |
| C(13) | 1.000(1) | 0.9386(9) | 0.237(2) | 4.1(4) |
| C(14) | 0.950(1) | 0.9065(8) | 0.360(2) | 4.0(3) |
| C(15) | 0.987(1) | 0.8215(8) | 0.382(1) | 3.5(3) |
| C(16) | 0.801(1) | 0.6606(8) | 0.949(1) | 3.3(3) |
| C(17) | 0.780(1) | 0.6987(9) | 1.242(1) | 3.8(3) |
| C(18) | 0.633(1) | 0.7726(8) | 1.060(1) | 3.5(3) |
| C(19) | 0.619(1) | 0.8557(8) | 1.134(2) | 4.1(3) |

Table 5-1. Atomic coordinates and Biso/Beq (Continued)

| atom | x | y | z | Beq |
|-------|------------|------------|----------|--------|
| C(20) | 0.510(1) | 0.9110(10) | 1.116(2) | 5.6(4) |
| C(21) | 0.420(2) | 0.884(1) | 1.021(2) | 6.3(5) |
| C(22) | 0.439(1) | 0.800(1) | 0.946(2) | 5.5(4) |
| C(23) | 0.547(1) | 0.7434(9) | 0.968(2) | 4.0(3) |
| C(24) | 0.7741(9) | 0.7748(7) | 0.777(1) | 2.9(3) |
| C(25) | 0.8427(10) | 0.8221(7) | 0.872(1) | 3.3(3) |
| C(26) | 0.835(1) | 0.9052(8) | 0.846(2) | 3.9(3) |
| C(27) | 0.764(1) | 0.9417(8) | 0.728(1) | 3.8(3) |
| C(28) | 0.695(1) | 0.8934(8) | 0.635(1) | 3.8(3) |
| C(29) | 0.698(1) | 0.8116(8) | 0.660(1) | 3.4(3) |
| C(30) | 0.778(1) | 0.6291(9) | 0.654(2) | 4.2(4) |
| C(31) | 0.618(2) | 0.503(1) | 0.348(3) | 7.2(6) |
| C(32) | 0.553(2) | 0.471(1) | 0.209(3) | 9.7(7) |
| C(33) | 0.533(2) | 0.517(1) | 0.071(2) | 8.1(6) |

Table 5-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|----------|------------|-----------|-----------|
| O(1) | 0.046(5) | 0.043(5) | 0.042(5) | -0.005(4) | -0.002(4) | 0.016(4) |
| N(1) | 0.065(7) | 0.032(5) | 0.027(5) | -0.007(5) | 0.000(4) | 0.005(4) |
| N(2) | 0.047(6) | 0.038(5) | 0.034(6) | 0.000(5) | -0.002(4) | 0.007(5) |
| N(3) | 0.054(7) | 0.029(6) | 0.064(7) | 0.000(5) | -0.009(5) | 0.010(5) |
| N(4) | 0.060(7) | 0.032(6) | 0.035(6) | -0.009(5) | 0.003(5) | 0.003(5) |
| N(5) | 0.056(7) | 0.047(6) | 0.027(5) | -0.013(5) | 0.001(4) | 0.007(5) |
| N(6) | 0.063(7) | 0.037(6) | 0.056(7) | -0.011(5) | 0.012(5) | 0.012(5) |
| C(1) | 0.040(7) | 0.054(8) | 0.023(7) | -0.003(6) | 0.008(5) | 0.003(6) |
| C(2) | 0.07(1) | 0.058(9) | 0.033(8) | -0.015(8) | 0.004(6) | 0.012(7) |
| C(3) | 0.07(1) | 0.045(8) | 0.042(8) | -0.012(7) | 0.010(7) | -0.014(6) |
| C(4) | 0.041(8) | 0.058(8) | 0.033(7) | -0.013(6) | -0.006(5) | 0.011(6) |
| C(5) | 0.048(9) | 0.066(10) | 0.056(9) | -0.019(8) | -0.012(7) | 0.016(8) |
| C(6) | 0.052(10) | 0.11(2) | 0.07(1) | -0.019(10) | -0.010(8) | 0.03(1) |
| C(7) | 0.07(1) | 0.10(1) | 0.09(1) | -0.03(1) | -0.04(1) | 0.05(1) |
| C(8) | 0.10(1) | 0.06(1) | 0.09(1) | -0.02(1) | -0.05(1) | 0.020(9) |
| C(9) | 0.053(9) | 0.046(8) | 0.057(9) | -0.014(7) | -0.015(7) | 0.005(7) |
| C(10) | 0.051(8) | 0.034(7) | 0.034(7) | -0.015(6) | -0.006(5) | 0.007(5) |
| C(11) | 0.048(8) | 0.049(8) | 0.036(7) | -0.016(6) | 0.004(6) | 0.004(6) |
| C(12) | 0.063(9) | 0.045(8) | 0.045(8) | -0.018(7) | -0.007(6) | 0.016(6) |
| C(13) | 0.059(9) | 0.048(8) | 0.051(9) | -0.011(7) | -0.007(7) | 0.012(7) |
| C(14) | 0.045(8) | 0.053(9) | 0.053(8) | -0.012(7) | -0.003(6) | 0.003(7) |
| C(15) | 0.044(8) | 0.045(8) | 0.048(8) | -0.015(6) | -0.002(6) | 0.009(6) |
| C(16) | 0.044(7) | 0.049(8) | 0.035(7) | -0.017(6) | 0.001(5) | 0.005(6) |
| C(17) | 0.062(9) | 0.057(9) | 0.023(7) | -0.008(7) | -0.006(6) | 0.003(6) |
| C(18) | 0.038(7) | 0.052(8) | 0.041(7) | 0.002(6) | 0.005(6) | 0.016(6) |
| C(19) | 0.051(9) | 0.043(8) | 0.056(9) | 0.002(7) | 0.010(6) | 0.009(6) |
| C(20) | 0.08(1) | 0.063(10) | 0.07(1) | 0.001(9) | 0.024(8) | 0.013(8) |
| C(21) | 0.07(1) | 0.09(1) | 0.07(1) | 0.011(10) | 0.014(9) | 0.030(10) |
| C(22) | 0.041(9) | 0.10(1) | 0.08(1) | -0.014(9) | -0.004(7) | 0.034(10) |
| C(23) | 0.053(9) | 0.053(9) | 0.047(8) | -0.012(7) | 0.000(6) | 0.008(7) |
| C(24) | 0.038(7) | 0.040(7) | 0.031(7) | -0.005(5) | 0.011(5) | 0.004(5) |
| C(25) | 0.036(7) | 0.046(8) | 0.047(8) | -0.011(6) | -0.004(6) | 0.008(6) |
| C(26) | 0.052(8) | 0.047(8) | 0.053(8) | -0.016(7) | 0.002(6) | 0.003(7) |
| C(27) | 0.054(8) | 0.042(8) | 0.049(8) | -0.007(6) | -0.001(6) | 0.013(6) |
| C(28) | 0.049(8) | 0.045(8) | 0.046(8) | 0.003(6) | 0.002(6) | 0.009(6) |
| C(29) | 0.046(8) | 0.046(8) | 0.039(7) | -0.008(6) | -0.001(6) | 0.009(6) |
| C(30) | 0.08(1) | 0.038(8) | 0.039(8) | -0.013(7) | -0.008(7) | -0.007(6) |
| C(31) | 0.09(1) | 0.09(1) | 0.09(2) | -0.02(1) | -0.01(1) | 0.01(1) |
| C(32) | 0.16(2) | 0.10(2) | 0.10(2) | -0.01(1) | -0.06(2) | 0.00(1) |
| C(33) | 0.15(2) | 0.07(1) | 0.08(1) | -0.01(1) | -0.03(1) | 0.005(10) |

Table 5-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(16) | 1.40(1) | N(1) | C(24) | 1.41(1) |
| N(1) | C(30) | 1.46(2) | N(2) | C(16) | 1.39(1) |
| N(2) | C(17) | 1.48(1) | N(2) | C(18) | 1.43(1) |
| N(3) | C(16) | 1.26(1) | N(4) | C(1) | 1.40(1) |
| N(4) | C(3) | 1.47(2) | N(4) | C(10) | 1.40(1) |
| N(5) | C(1) | 1.40(1) | N(5) | C(2) | 1.47(1) |
| N(5) | C(4) | 1.41(1) | N(6) | C(1) | 1.27(1) |
| C(4) | C(5) | 1.38(2) | C(4) | C(9) | 1.39(2) |
| C(5) | C(6) | 1.43(2) | C(6) | C(7) | 1.40(2) |
| C(7) | C(8) | 1.41(2) | C(8) | C(9) | 1.41(2) |
| C(10) | C(11) | 1.42(2) | C(10) | C(15) | 1.38(2) |
| C(11) | C(12) | 1.38(2) | C(12) | C(13) | 1.38(2) |
| C(13) | C(14) | 1.40(2) | C(14) | C(15) | 1.41(2) |
| C(18) | C(19) | 1.40(2) | C(18) | C(23) | 1.38(2) |
| C(19) | C(20) | 1.40(2) | C(20) | C(21) | 1.41(2) |
| C(21) | C(22) | 1.42(2) | C(22) | C(23) | 1.41(2) |
| C(24) | C(25) | 1.40(2) | C(24) | C(29) | 1.42(2) |
| C(25) | C(26) | 1.39(2) | C(26) | C(27) | 1.38(2) |
| C(27) | C(28) | 1.41(2) | C(28) | C(29) | 1.38(2) |
| C(31) | C(32) | 1.48(3) | C(32) | C(33) | 1.45(3) |
| C(33) | C(33) | 1.51(3) | | | |

Table 5-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|-----------|
| C(16) | N(1) | C(24) | 121.9(9) | C(16) | N(1) | C(30) | 118(1) |
| C(24) | N(1) | C(30) | 118.7(9) | C(16) | N(2) | C(17) | 116(1) |
| C(16) | N(2) | C(18) | 123.0(10) | C(17) | N(2) | C(18) | 117(1) |
| C(1) | N(4) | C(3) | 117(1) | C(1) | N(4) | C(10) | 123.0(10) |
| C(3) | N(4) | C(10) | 119(1) | C(1) | N(5) | C(2) | 115(1) |
| C(1) | N(5) | C(4) | 123.2(9) | C(2) | N(5) | C(4) | 119(1) |
| N(4) | C(1) | N(5) | 112(1) | N(4) | C(1) | N(6) | 123(1) |
| N(5) | C(1) | N(6) | 124(1) | N(5) | C(4) | C(5) | 119(1) |
| N(5) | C(4) | C(9) | 118(1) | C(5) | C(4) | C(9) | 122(1) |
| C(4) | C(5) | C(6) | 119(1) | C(5) | C(6) | C(7) | 120(1) |
| C(6) | C(7) | C(8) | 117(1) | C(7) | C(8) | C(9) | 122(1) |
| C(4) | C(9) | C(8) | 118(1) | N(4) | C(10) | C(11) | 120(1) |
| N(4) | C(10) | C(15) | 120(1) | C(11) | C(10) | C(15) | 119(1) |
| C(10) | C(11) | C(12) | 120(1) | C(11) | C(12) | C(13) | 120(1) |
| C(12) | C(13) | C(14) | 120(1) | C(13) | C(14) | C(15) | 120(1) |
| C(10) | C(15) | C(14) | 119(1) | N(1) | C(16) | N(2) | 113(1) |
| N(1) | C(16) | N(3) | 121(1) | N(2) | C(16) | N(3) | 125(1) |
| N(2) | C(18) | C(19) | 117(1) | N(2) | C(18) | C(23) | 118(1) |
| C(19) | C(18) | C(23) | 123(1) | C(18) | C(19) | C(20) | 117(1) |
| C(19) | C(20) | C(21) | 120(1) | C(20) | C(21) | C(22) | 119(1) |
| C(21) | C(22) | C(23) | 120(1) | C(18) | C(23) | C(22) | 118(1) |
| N(1) | C(24) | C(25) | 120(1) | N(1) | C(24) | C(29) | 119(1) |
| C(25) | C(24) | C(29) | 120(1) | C(24) | C(25) | C(26) | 118(1) |
| C(25) | C(26) | C(27) | 122(1) | C(26) | C(27) | C(28) | 118(1) |
| C(27) | C(28) | C(29) | 121(1) | C(24) | C(29) | C(28) | 119(1) |
| C(31) | C(32) | C(33) | 118(2) | C(32) | C(33) | C(33) | 118(2) |

Table S-5. Least Squares Planes

| | | | | | |
|--------------------------------------|--------------|----------------------|------------------|-------|-------|
| Plane number 1 | | Plane number 4 | | | |
| Atoms defining plane | Distance | Atoms defining plane | Distance | | |
| N(1) | -0.0009(97) | C(1) | 0.083(111) | | |
| N(2) | -0.0008(97) | N(4) | -0.0022(97) | | |
| N(3) | -0.0012(103) | N(5) | -0.0020(99) | | |
| C(16) | 0.0037(112) | N(6) | -0.0027(103) | | |
| Plane number 2 | | Plane number 5 | | | |
| Atoms defining plane | Distance | Atoms defining plane | Distance | | |
| C(18) | -0.0026(113) | C(4) | -0.052(110) | | |
| C(19) | 0.0126(126) | C(5) | 0.0125(127) | | |
| C(20) | -0.0140(141) | C(6) | -0.0149(148) | | |
| C(21) | 0.0009(152) | C(7) | 0.0055(150) | | |
| C(22) | 0.0110(142) | C(8) | 0.0024(150) | | |
| C(23) | -0.0073(129) | C(9) | 0.0000(127) | | |
| Plane number 3 | | Plane number 6 | | | |
| Atoms defining plane | Distance | Atoms defining plane | Distance | | |
| C(24) | 0.0080(102) | C(10) | -0.047(109) | | |
| C(25) | -0.0013(120) | C(11) | 0.0035(120) | | |
| C(26) | -0.0099(129) | C(12) | 0.0028(126) | | |
| C(27) | 0.0083(129) | C(13) | -0.0072(130) | | |
| C(28) | 0.0029(123) | C(14) | 0.0039(122) | | |
| C(29) | -0.0121(120) | C(15) | 0.0020(117) | | |
| Summary | plane | mean deviation | CHI ² | | |
| | 1 | 0.0017 | 0.1 | | |
| | 2 | 0.0081 | 2.9 | | |
| | 3 | 0.0071 | 2.4 | | |
| | 4 | 0.0038 | 0.7 | | |
| | 5 | 0.0067 | 2.2 | | |
| | 6 | 0.0040 | 0.7 | | |
| Dihedral angles between planes (deg) | | | | | |
| plane | 1 | 2 | 3 | 4 | 5 |
| 2 | 62.45 | | | | |
| 3 | 62.13 | 38.25 | | | |
| 4 | 56.59 | 69.78 | 34.24 | | |
| 5 | 68.94 | 124.61 | 95.86 | 62.01 | |
| 6 | 35.09 | 97.28 | 86.40 | 62.94 | 37.01 |

***N,N'*-Dimethyl-*N,N'*-diphenylguanidinium bromide (4b)**

| | |
|--|--|
| A. Crystal Data | $C_{15}H_{18}N_3Br$ |
| Empirical Formula | 320.23 |
| Formula Weight | colorless, prismatic |
| Crystal Color, Habit | 0.20 X 0.10 X 0.45 mm |
| Crystal Dimensions | triclinic |
| Crystal System | Primitive |
| Lattice Type | |
| No. of Reflections Used for Unit | 25 (40.1 - 43.6°) |
| Cell Determination (2 θ range) | 0.23° |
| Omega Scan Peak Width at Half-height | $a = 13.034(3) \text{ \AA}$ |
| Lattice Parameters | $b = 13.216(4) \text{ \AA}$ |
| | $c = 9.711(2) \text{ \AA}$ |
| | $\alpha = 91.85(2)^\circ, \beta = 94.99(2)^\circ, \gamma = 65.14(1)^\circ$ |
| | $V = 1512.1(6) \text{ \AA}^3$ |
| Space Group | PT(#2) |
| Z value | 4 |
| D_{calc} | 1.407 g/cm ³ |
| F_{000} | 656.00 |
| $\mu(\text{CuK}\alpha)$ | 36.21 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuK α ($\lambda = 1.54178 \text{ \AA}$) |
| | graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 3.57, 12.70, 45.11) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal |
| | 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 32.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.42 + 0.30 tan θ)° |
| 2 θ_{max} | 120.2° |
| No. of Reflections Measured | Total: 4723 Unique: 4493 (Rint = 0.054) |
| Corrections | Lorentz-polarization |
| | Absorption |
| | (trans. factors: 0.6299 - 1.3013) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w(F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0010 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 3.00 σ (I)) | 3427 |
| No. Variables | 471 |
| Reflection/Parameter Ratio | 7.28 |
| Residuals: R; Rw | 0.079; 0.100 |
| Goodness of Fit Indicator | 5.87 |
| Max Shift/Error in Final Cycle | 7.57 |
| Maximum peak in Final Diff. Map | 2.76 e-/Å ³ |
| Minimum peak in Final Diff. Map | -1.03 e-/Å ³ |

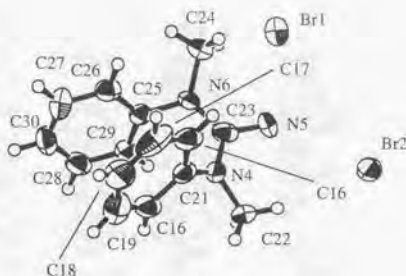
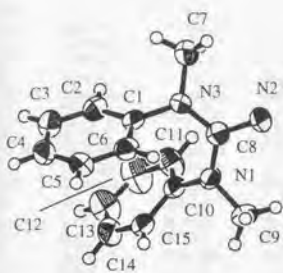


Table 6-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|------------|---------|
| Br(1) | 0.4097(1) | 0.2575(2) | 0.6476(2) | 5.71(5) |
| Br(2) | 0.1796(1) | 0.1576(1) | 0.2356(1) | 4.57(4) |
| N(1) | 0.9417(8) | 0.6820(9) | 0.2546(10) | 3.8(3) |
| N(2) | 0.8633(8) | 0.6989(8) | 0.4663(10) | 3.7(3) |
| N(3) | 1.0522(8) | 0.6691(8) | 0.4597(10) | 3.3(2) |
| N(4) | 0.4932(8) | 0.1623(10) | 0.1501(10) | 3.9(3) |
| N(5) | 0.4717(9) | 0.0173(10) | 0.262(1) | 4.4(3) |
| N(6) | 0.6360(8) | 0.0477(9) | 0.3075(10) | 3.7(3) |
| C(1) | 1.125(1) | 0.711(1) | 0.403(1) | 3.8(3) |
| C(2) | 1.238(1) | 0.646(1) | 0.389(2) | 4.4(4) |
| C(3) | 1.307(1) | 0.686(1) | 0.338(1) | 5.1(4) |
| C(4) | 1.257(1) | 0.802(2) | 0.296(1) | 5.0(4) |
| C(5) | 1.144(1) | 0.871(1) | 0.306(1) | 4.7(4) |
| C(6) | 1.077(1) | 0.825(1) | 0.360(1) | 3.9(3) |
| C(7) | 1.089(2) | 0.618(2) | 0.594(2) | 5.3(5) |
| C(8) | 0.952(1) | 0.6830(10) | 0.395(1) | 3.3(3) |
| C(9) | 0.827(1) | 0.735(2) | 0.180(2) | 5.3(5) |
| C(10) | 1.039(1) | 0.613(1) | 0.178(1) | 3.7(3) |
| C(11) | 1.103(1) | 0.508(1) | 0.208(2) | 5.0(4) |
| C(12) | 1.190(2) | 0.451(1) | 0.130(2) | 7.0(6) |
| C(13) | 1.224(2) | 0.488(1) | 0.030(2) | 6.0(5) |
| C(14) | 1.158(2) | 0.590(2) | -0.004(2) | 7.0(6) |
| C(15) | 1.063(1) | 0.664(1) | 0.067(1) | 4.7(4) |
| C(16) | 0.510(1) | 0.309(1) | 0.299(1) | 5.4(4) |
| C(17) | 0.542(1) | 0.403(1) | 0.314(2) | 6.8(5) |
| C(18) | 0.579(1) | 0.445(2) | 0.208(2) | 7.6(5) |
| C(19) | 0.588(1) | 0.389(1) | 0.080(2) | 6.1(5) |
| C(20) | 0.561(1) | 0.299(2) | 0.065(2) | 5.5(4) |
| C(21) | 0.521(1) | 0.254(1) | 0.170(1) | 3.7(3) |
| C(22) | 0.411(1) | 0.162(2) | 0.034(2) | 5.2(4) |
| C(23) | 0.532(1) | 0.073(1) | 0.240(1) | 3.6(3) |
| C(24) | 0.662(2) | -0.003(2) | 0.446(2) | 4.7(4) |
| C(25) | 0.7237(10) | 0.0642(10) | 0.246(1) | 3.2(3) |
| C(26) | 0.787(1) | 0.111(1) | 0.321(1) | 4.0(3) |
| C(27) | 0.873(1) | 0.125(1) | 0.260(2) | 4.6(4) |
| C(28) | 0.833(1) | 0.044(1) | 0.052(1) | 4.6(4) |
| C(29) | 0.748(1) | 0.026(1) | 0.111(1) | 3.8(3) |
| C(30) | 0.894(1) | 0.094(1) | 0.127(2) | 4.7(4) |

Table 6-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|------------|------------|------------|
| Br(1) | 0.054(1) | 0.099(1) | 0.072(1) | -0.038(10) | 0.0094(8) | 0.0106(10) |
| Br(2) | 0.0508(9) | 0.077(1) | 0.0442(9) | -0.0252(8) | 0.0065(7) | -0.0045(7) |
| N(1) | 0.035(6) | 0.071(8) | 0.038(6) | -0.023(6) | 0.004(5) | -0.006(5) |
| N(2) | 0.042(6) | 0.055(7) | 0.045(6) | -0.020(5) | 0.013(5) | -0.003(5) |
| N(3) | 0.042(6) | 0.051(7) | 0.035(6) | -0.021(5) | 0.001(5) | 0.010(5) |
| N(4) | 0.036(6) | 0.080(9) | 0.037(6) | -0.028(6) | 0.003(5) | 0.002(6) |
| N(5) | 0.050(7) | 0.084(9) | 0.049(7) | -0.040(7) | 0.014(6) | 0.007(6) |
| N(6) | 0.037(6) | 0.068(8) | 0.031(6) | -0.016(6) | 0.005(5) | 0.015(5) |
| C(1) | 0.043(8) | 0.07(1) | 0.031(7) | -0.028(7) | -0.004(6) | 0.001(7) |
| C(2) | 0.038(8) | 0.06(1) | 0.061(10) | -0.013(8) | -0.004(7) | 0.013(8) |
| C(3) | 0.050(9) | 0.09(1) | 0.059(10) | -0.033(9) | 0.006(8) | 0.000(9) |
| C(4) | 0.07(1) | 0.10(1) | 0.045(9) | -0.06(1) | 0.005(8) | -0.003(9) |
| C(5) | 0.06(1) | 0.07(1) | 0.053(9) | -0.036(9) | 0.003(8) | 0.013(8) |
| C(6) | 0.050(9) | 0.054(9) | 0.044(8) | -0.022(8) | 0.000(7) | -0.002(7) |
| C(7) | 0.05(1) | 0.09(1) | 0.06(1) | -0.03(1) | 0.003(9) | 0.019(10) |
| C(8) | 0.046(8) | 0.038(7) | 0.046(8) | -0.020(6) | 0.001(6) | 0.000(6) |
| C(9) | 0.05(1) | 0.09(2) | 0.06(1) | -0.02(1) | -0.012(8) | 0.02(1) |
| C(10) | 0.039(8) | 0.066(10) | 0.037(7) | -0.025(7) | 0.001(6) | -0.004(7) |
| C(11) | 0.07(1) | 0.048(9) | 0.07(1) | -0.025(9) | 0.027(9) | -0.004(8) |
| C(12) | 0.10(2) | 0.05(1) | 0.12(2) | -0.03(1) | 0.04(1) | -0.01(1) |
| C(13) | 0.08(1) | 0.05(1) | 0.09(1) | -0.020(10) | 0.03(1) | -0.003(10) |
| C(14) | 0.07(1) | 0.18(2) | 0.036(10) | -0.07(1) | 0.024(9) | -0.03(1) |
| C(15) | 0.046(9) | 0.10(1) | 0.041(8) | -0.035(9) | -0.001(7) | 0.000(8) |
| C(16) | 0.041(9) | 0.09(1) | 0.047(9) | -0.001(8) | 0.003(7) | 0.007(9) |
| C(17) | 0.06(1) | 0.06(1) | 0.10(1) | -0.001(9) | -0.026(10) | -0.03(1) |
| C(18) | 0.07(1) | 0.11(1) | 0.09(1) | -0.02(1) | 0.00(1) | 0.03(1) |
| C(19) | 0.06(1) | 0.06(1) | 0.11(2) | -0.024(8) | -0.004(10) | 0.02(1) |
| C(20) | 0.047(9) | 0.10(1) | 0.039(9) | -0.012(9) | 0.009(7) | 0.004(9) |
| C(21) | 0.035(7) | 0.052(9) | 0.045(8) | -0.011(6) | -0.003(6) | 0.002(7) |
| C(22) | 0.05(1) | 0.10(1) | 0.046(9) | -0.04(1) | -0.017(8) | 0.030(9) |
| C(23) | 0.043(8) | 0.046(8) | 0.032(7) | -0.002(6) | 0.008(6) | 0.001(6) |
| C(24) | 0.06(1) | 0.09(1) | 0.036(8) | -0.04(1) | 0.004(7) | 0.012(8) |
| C(25) | 0.033(7) | 0.040(7) | 0.039(7) | -0.007(6) | 0.001(6) | 0.005(6) |
| C(26) | 0.048(9) | 0.053(9) | 0.039(8) | -0.011(7) | 0.002(7) | -0.002(7) |
| C(27) | 0.044(9) | 0.054(9) | 0.08(1) | -0.023(7) | 0.012(8) | -0.013(8) |
| C(28) | 0.051(9) | 0.07(1) | 0.046(8) | -0.011(8) | 0.010(7) | 0.008(7) |
| C(29) | 0.040(8) | 0.065(9) | 0.036(7) | -0.019(7) | 0.007(6) | 0.002(6) |
| C(30) | 0.041(9) | 0.061(10) | 0.08(1) | -0.018(7) | 0.019(8) | 0.007(8) |

Table 6-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(8) | 1.35(1) | N(1) | C(9) | 1.50(2) |
| N(1) | C(10) | 1.47(2) | N(2) | C(8) | 1.33(1) |
| N(3) | C(1) | 1.44(2) | N(3) | C(7) | 1.44(2) |
| N(3) | C(8) | 1.34(2) | N(4) | C(21) | 1.40(2) |
| N(4) | C(22) | 1.47(2) | N(4) | C(23) | 1.38(2) |
| N(5) | C(23) | 1.33(2) | N(6) | C(23) | 1.35(2) |
| N(6) | C(24) | 1.47(2) | N(6) | C(25) | 1.43(1) |
| C(1) | C(2) | 1.38(2) | C(1) | C(6) | 1.43(2) |
| C(2) | C(3) | 1.37(2) | C(3) | C(4) | 1.44(2) |
| C(4) | C(5) | 1.37(2) | C(5) | C(6) | 1.39(2) |
| C(10) | C(11) | 1.30(2) | C(10) | C(15) | 1.41(2) |
| C(11) | C(12) | 1.40(2) | C(12) | C(13) | 1.24(2) |
| C(13) | C(14) | 1.34(3) | C(14) | C(15) | 1.43(2) |
| C(16) | C(17) | 1.48(2) | C(16) | C(21) | 1.42(2) |
| C(17) | C(18) | 1.39(3) | C(18) | C(19) | 1.39(2) |
| C(19) | C(20) | 1.38(4) | C(20) | C(21) | 1.41(3) |
| C(25) | C(26) | 1.37(2) | C(25) | C(29) | 1.40(2) |
| C(26) | C(27) | 1.40(2) | C(27) | C(30) | 1.36(2) |
| C(28) | C(29) | 1.40(2) | C(28) | C(30) | 1.39(2) |

Table 6-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|--------|-------|-------|-------|--------|
| C(8) | N(1) | C(9) | 120(1) | C(8) | N(1) | C(10) | 120(1) |
| C(9) | N(1) | C(10) | 117(1) | C(1) | N(3) | C(7) | 116(1) |
| C(1) | N(3) | C(8) | 122(1) | C(7) | N(3) | C(8) | 120(1) |
| C(21) | N(4) | C(22) | 121(1) | C(21) | N(4) | C(23) | 122(1) |
| C(22) | N(4) | C(23) | 115(1) | C(23) | N(6) | C(24) | 119(1) |
| C(23) | N(6) | C(25) | 122(1) | C(24) | N(6) | C(25) | 118(1) |
| N(3) | C(1) | C(2) | 121(1) | N(3) | C(1) | C(6) | 118(1) |
| C(2) | C(1) | C(6) | 119(1) | C(1) | C(2) | C(3) | 121(1) |
| C(2) | C(3) | C(4) | 117(1) | C(3) | C(4) | C(5) | 123(1) |
| C(4) | C(5) | C(6) | 117(1) | C(1) | C(6) | C(5) | 120(1) |
| N(1) | C(8) | N(2) | 120(1) | N(1) | C(8) | N(3) | 118(1) |
| N(2) | C(8) | N(3) | 121(1) | N(1) | C(10) | C(11) | 122(1) |
| N(1) | C(10) | C(15) | 117(1) | C(11) | C(10) | C(15) | 120(1) |
| C(10) | C(11) | C(12) | 117(1) | C(11) | C(12) | C(13) | 127(1) |
| C(12) | C(13) | C(14) | 116(2) | C(13) | C(14) | C(15) | 121(2) |
| C(10) | C(15) | C(14) | 116(1) | C(17) | C(16) | C(21) | 118(1) |
| C(16) | C(17) | C(18) | 125(1) | C(17) | C(18) | C(19) | 113(1) |
| C(18) | C(19) | C(20) | 122(1) | C(19) | C(20) | C(21) | 126(2) |
| N(4) | C(21) | C(16) | 121(1) | N(4) | C(21) | C(20) | 125(1) |
| C(16) | C(21) | C(20) | 113(1) | N(4) | C(23) | N(5) | 121(1) |
| N(4) | C(23) | N(6) | 116(1) | N(5) | C(23) | N(6) | 122(1) |
| N(6) | C(25) | C(26) | 120(1) | N(6) | C(25) | C(29) | 118(1) |
| C(26) | C(25) | C(29) | 120(1) | C(25) | C(26) | C(27) | 119(1) |
| C(26) | C(27) | C(30) | 120(1) | C(29) | C(28) | C(30) | 120(1) |
| C(25) | C(29) | C(28) | 118(1) | C(27) | C(30) | C(28) | 119(1) |

Table 6-5. Least Squares Planes

| Plane number 1 | | | Plane number 4 | | |
|----------------------|----------------|------------------|----------------------|----------------|------------------|
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(1) | 0.0058(121) | | C(25) | -0.0211(120) | |
| C(2) | -0.0111(172) | | C(26) | 0.0095(145) | |
| C(3) | 0.0019(151) | | C(27) | 0.0171(161) | |
| C(4) | 0.0056(158) | | C(28) | -0.0032(146) | |
| C(5) | -0.0043(148) | | C(29) | 0.0239(137) | |
| C(6) | -0.0021(139) | | C(30) | -0.0197(154) | |
| Plane number 2 | | | Plane number 5 | | |
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(10) | 0.0027(126) | | C(16) | -0.0142(145) | |
| C(11) | 0.0106(179) | | C(17) | 0.0126(160) | |
| C(12) | -0.0479(227) | | C(18) | -0.0014(162) | |
| C(13) | 0.0421(207) | | C(19) | -0.0063(168) | |
| C(14) | -0.0206(220) | | C(20) | 0.0005(271) | |
| C(15) | -0.0024(143) | | C(21) | 0.0067(124) | |
| Plane number 3 | | | Plane number 6 | | |
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(8) | 0.0058(124) | | C(23) | 0.0104(120) | |
| N(1) | -0.0018(115) | | N(4) | -0.0030(109) | |
| N(2) | -0.0018(107) | | N(5) | -0.0038(115) | |
| N(3) | -0.0018(107) | | N(6) | -0.0031(106) | |
| Summary | | | | | |
| plane | mean deviation | CHI ² | plane | mean deviation | CHI ² |
| 1 | 0.0052 | 0.8 | 4 | 0.0158 | 8.8 |
| 2 | 0.0211 | 8.5 | 5 | 0.0070 | 1.8 |
| 3 | 0.0028 | 0.3 | 6 | 0.0051 | 0.9 |

Dihedral angles between planes (deg)

| plane | 1 | 2 | 3 | 4 | 5 |
|-------|--------|--------|-------|-------|-------|
| 2 | 31.11 | | | | |
| 3 | 106.94 | 111.73 | | | |
| 4 | 81.19 | 79.87 | 31.98 | | |
| 5 | 72.00 | 56.80 | 59.80 | 30.67 | |
| 6 | 141.14 | 117.01 | 55.25 | 67.51 | 69.33 |

N,N,N'-Trimethyl-*N',N''*-diphenylguanidine (5)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{16}H_{19}N_3$ |
| Formula Weight | 253.35 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.50 X 0.40 X 0.25 mm |
| Crystal System | monoclinic |
| Lattice Type | C-centered |
| No. of Reflections Used for Unit | |
| Cell Determination (2 θ range) | 19 (49.0 - 50.9°) |
| Omega Scan Peak Width at Half-height | 0.18° |
| Lattice Parameters | $a = 18.532(2) \text{ \AA}$ $b = 7.736(2) \text{ \AA}$ $c = 20.462(2) \text{ \AA}$ $\beta = 104.273(9)^\circ$ $V = 2842(1) \text{ \AA}^3$ |
| Space Group | C2/c (#15) |
| Z value | 8 |
| D_{calc} | 1.184 g/cm ³ |
| $F_{(000)}$ | 1088.00 |
| μ (CuK α) | 5.55 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuK α ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated Ni foil (factors = 1.00, 3.57, 12.70, 45.11) 6.0° |
| Attenuator | |
| Take-off Angle | |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 32.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.37 + 0.30 tan θ)° |
| 2 θ max | 120.9° |
| No. of Reflections Measured | Total: 2390 Unique: 2304 (Rint = 0.014) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.6783 - 1.1041) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/(\sigma^2(F_o^2) + P^2 + P)$ |
| p-factor | 0.0030 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 1532 |
| No. Variables | 248 |
| Reflection/Parameter Ratio | 6.18 |
| Residuals: R; Rw | 0.069; 0.066 |
| Goodness of Fit Indicator | 4.61 |
| Max Shift/Error in Final Cycle | 4.61 |
| Maximum peak in Final Diff. Map | 0.30 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.26 e-/Å ³ |

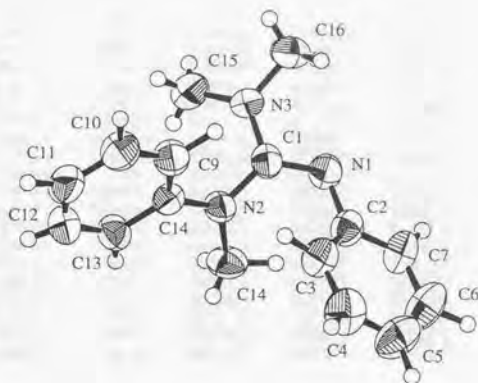


Table 7-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|-------------|-----------|----------|
| N(1) | 0.6061(2) | 0.1231(5) | 0.2691(2) | 4.71(10) |
| N(2) | 0.6692(2) | -0.0166(5) | 0.1941(2) | 4.04(9) |
| N(3) | 0.6007(2) | 0.2364(5) | 0.1651(2) | 4.79(10) |
| C(1) | 0.6239(2) | 0.1127(6) | 0.2117(2) | 4.1(1) |
| C(2) | 0.6165(2) | -0.0187(7) | 0.3145(2) | 4.6(1) |
| C(3) | 0.6006(3) | -0.1902(7) | 0.2950(3) | 5.3(1) |
| C(4) | 0.6124(4) | -0.3167(9) | 0.3433(4) | 6.7(2) |
| C(5) | 0.6391(3) | -0.2783(10) | 0.4105(3) | 7.2(2) |
| C(6) | 0.6512(3) | -0.1095(10) | 0.4293(3) | 6.9(2) |
| C(7) | 0.6390(3) | 0.0185(8) | 0.3816(3) | 5.6(1) |
| C(8) | 0.6452(2) | -0.1103(6) | 0.1350(2) | 4.0(1) |
| C(9) | 0.5686(3) | -0.1214(7) | 0.1037(2) | 5.1(1) |
| C(10) | 0.5456(3) | -0.2166(8) | 0.0454(2) | 5.8(1) |
| C(11) | 0.5956(3) | -0.3023(7) | 0.0172(3) | 6.0(2) |
| C(12) | 0.6698(4) | -0.2934(7) | 0.0486(3) | 5.8(2) |
| C(13) | 0.6945(3) | -0.2004(7) | 0.1061(2) | 4.8(1) |
| C(14) | 0.7407(3) | -0.0517(10) | 0.2395(3) | 5.2(1) |
| C(15) | 0.6394(4) | 0.278(1) | 0.1138(3) | 6.0(2) |
| C(16) | 0.5428(4) | 0.3561(9) | 0.1739(3) | 6.2(2) |

Table 7-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| N(1) | 0.061(3) | 0.063(3) | 0.056(2) | 0.001(2) | 0.015(2) | 0.000(2) |
| N(2) | 0.043(2) | 0.059(2) | 0.049(2) | 0.006(2) | 0.006(2) | -0.005(2) |
| N(3) | 0.067(3) | 0.064(3) | 0.052(2) | 0.018(2) | 0.015(2) | 0.013(2) |
| C(1) | 0.042(3) | 0.064(3) | 0.049(2) | -0.001(2) | 0.009(2) | -0.007(3) |
| C(2) | 0.054(3) | 0.070(4) | 0.053(3) | -0.004(3) | 0.016(2) | 0.002(3) |
| C(3) | 0.074(4) | 0.065(4) | 0.063(3) | -0.013(3) | 0.018(3) | 0.001(3) |
| C(4) | 0.095(5) | 0.075(5) | 0.094(5) | -0.023(4) | 0.038(4) | 0.003(4) |
| C(5) | 0.097(5) | 0.098(5) | 0.080(4) | -0.014(4) | 0.026(4) | 0.032(4) |
| C(6) | 0.093(5) | 0.109(6) | 0.059(4) | -0.034(4) | 0.017(3) | 0.013(4) |
| C(7) | 0.082(4) | 0.079(4) | 0.052(3) | -0.016(3) | 0.018(3) | -0.005(3) |
| C(8) | 0.051(3) | 0.055(3) | 0.046(2) | 0.000(2) | 0.010(2) | 0.003(2) |
| C(9) | 0.055(3) | 0.075(4) | 0.062(3) | 0.004(3) | 0.009(3) | -0.003(3) |
| C(10) | 0.064(4) | 0.088(4) | 0.061(3) | -0.002(3) | -0.003(3) | -0.010(3) |
| C(11) | 0.096(5) | 0.073(4) | 0.053(3) | 0.006(4) | 0.011(3) | -0.006(3) |
| C(12) | 0.088(5) | 0.074(4) | 0.064(3) | 0.014(3) | 0.030(3) | -0.006(3) |
| C(13) | 0.053(3) | 0.069(4) | 0.063(3) | 0.004(3) | 0.018(3) | -0.003(3) |
| C(14) | 0.044(3) | 0.074(4) | 0.071(4) | 0.008(3) | -0.003(3) | 0.000(3) |
| C(15) | 0.082(5) | 0.084(5) | 0.063(3) | 0.008(4) | 0.020(3) | 0.014(4) |
| C(16) | 0.085(5) | 0.074(4) | 0.071(4) | 0.027(4) | 0.007(4) | 0.004(4) |

Table 7-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.298(5) | N(1) | C(2) | 1.419(6) |
| N(2) | C(1) | 1.409(5) | N(2) | C(8) | 1.387(5) |
| N(2) | C(14) | 1.443(6) | N(3) | C(1) | 1.345(5) |
| N(3) | C(15) | 1.444(7) | N(3) | C(16) | 1.462(6) |
| C(2) | C(3) | 1.396(6) | C(2) | C(7) | 1.365(6) |
| C(3) | C(4) | 1.369(8) | C(4) | C(5) | 1.375(8) |
| C(5) | C(6) | 1.364(9) | C(6) | C(7) | 1.368(8) |
| C(8) | C(9) | 1.409(6) | C(8) | C(13) | 1.390(6) |
| C(9) | C(10) | 1.378(6) | C(10) | C(11) | 1.375(7) |
| C(11) | C(12) | 1.370(7) | C(12) | C(13) | 1.359(7) |

Table 7-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(1) | C(2) | 121.3(4) | C(1) | N(2) | C(8) | 120.7(3) |
| C(1) | N(2) | C(14) | 118.6(4) | C(8) | N(2) | C(14) | 120.6(4) |
| C(1) | N(3) | C(15) | 122.9(5) | C(1) | N(3) | C(16) | 118.6(4) |
| C(15) | N(3) | C(16) | 117.4(5) | N(1) | C(1) | N(2) | 125.2(4) |
| N(1) | C(1) | N(3) | 119.3(4) | N(2) | C(1) | N(3) | 115.5(4) |
| N(1) | C(2) | C(3) | 124.3(4) | N(1) | C(2) | C(7) | 117.0(5) |
| C(3) | C(2) | C(7) | 118.6(5) | C(2) | C(3) | C(4) | 119.2(5) |
| C(3) | C(4) | C(5) | 121.4(7) | C(4) | C(5) | C(6) | 118.8(6) |
| C(5) | C(6) | C(7) | 120.4(6) | C(2) | C(7) | C(6) | 121.3(6) |
| N(2) | C(8) | C(9) | 119.9(4) | N(2) | C(8) | C(13) | 122.0(4) |
| C(9) | C(8) | C(13) | 118.1(5) | C(8) | C(9) | C(10) | 119.2(5) |
| C(9) | C(10) | C(11) | 121.6(5) | C(10) | C(11) | C(12) | 118.8(6) |
| C(11) | C(12) | C(13) | 121.2(6) | C(8) | C(13) | C(12) | 121.1(5) |

Table 7-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-------------|----------------------|-------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(2) | 0.0205(44) | C(8) | 0.0075(42) |
| C(3) | -0.0153(51) | C(9) | -0.0075(51) |
| C(4) | -0.0095(64) | C(10) | -0.0016(55) |
| C(5) | 0.0215(63) | C(11) | 0.0069(54) |
| C(6) | -0.0058(60) | C(12) | -0.0028(56) |
| C(7) | -0.0225(57) | C(13) | -0.0059(50) |

| Plane number 3 | |
|----------------------|-------------|
| Atoms defining plane | Distance |
| C(1) | -0.0137(41) |
| N(1) | 0.0044(36) |
| N(2) | 0.0032(34) |
| N(3) | 0.0047(39) |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0158 | 55.9 |
| | 2 | 0.0054 | 8.0 |
| | 3 | 0.0065 | 13.5 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|-------|
| 2 | 79.56 | |
| 3 | 48.64 | 66.63 |

N,N,N',N''-Tetramethyl-*N',N''*-diphenylguanidinium iodide (6)
(+)-Crystal

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | C ₁₇ H ₂₄ N ₃ IO |
| Formula Weight | 413.30 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.30 X 0.20 X 0.40 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2 θ range) | 20 (53.7 - 56.0°) |
| Omega Scan Peak Width at Half-height | 0.17° |
| Lattice Parameters | a = 12.044(2) Å b = 14.786(4) Å c = 10.444(1) Å V = 1860.0(5) Å ³ |
| Space Group | P2 ₁ 2 ₁ 2 ₁ (#19) |
| Z value | 4 |
| D _{calc} | 1.476 g/cm ³ |
| F ₀₀₀ | 832.00 |
| μ (CuK α) | 135.60 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffraction | Rigaku AFC5S |
| Radiation | CuK α (λ = 1.54178 Å) |
| | graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 2.37, 6.13, 15.65) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.21 + 0.30 tan θ)° |
| 2 θ _{max} | 135.2° |
| No. of Reflections Measured | Total: 3867 Unique: 1935 (Rint = 0.063) |
| Corrections | Lorentz-polarization Secondary Extinction (coefficient: 2.19084e-06) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0200 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 3.00 σ (I)) | 3283 |
| No. Variables | 200 |
| Reflection/Parameter Ratio | 16.42 |
| Residuals: R, Rw | 0.063 ; 0.075 |
| Goodness of Fit Indicator | 2.79 |
| Max Shift/Error in Final Cycle | 0.17 |
| Maximum peak in Final Diff. Map | 1.38 e-/Å ³ |
| Minimum peak in Final Diff. Map | -1.99 e-/Å ³ |

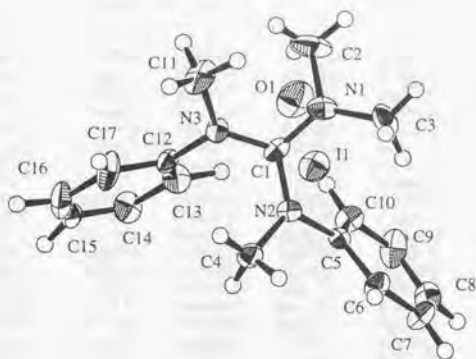


Table 8-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-------------|-------------|-------------|----------|
| I(1) | -1.30469(4) | -0.46405(3) | -0.34451(4) | 3.351(9) |
| O(1) | -0.7643(4) | -0.1533(3) | -0.3587(5) | 4.8(1) |
| N(1) | -1.0522(4) | -0.2727(4) | -0.3806(5) | 2.6(1) |
| N(2) | -1.0055(4) | -0.3746(3) | -0.2206(4) | 1.90(9) |
| N(3) | -0.9563(4) | -0.4021(4) | -0.4316(5) | 2.3(1) |
| C(1) | -1.0043(4) | -0.3484(4) | -0.3435(6) | 1.90(9) |
| C(2) | -1.0081(7) | -0.2209(5) | -0.4930(8) | 4.5(2) |
| C(3) | -1.1429(6) | -0.2315(5) | -0.3121(7) | 3.7(2) |
| C(4) | -1.0076(5) | -0.4708(4) | -0.1843(5) | 2.5(1) |
| C(5) | -0.9968(4) | -0.3123(4) | -0.1151(5) | 1.6(1) |
| C(6) | -1.0599(5) | -0.3219(4) | -0.0058(6) | 2.5(1) |
| C(7) | -1.0430(7) | -0.2657(5) | 0.0995(7) | 3.6(2) |
| C(8) | -0.9642(6) | -0.1994(5) | 0.0942(7) | 3.5(2) |
| C(9) | -0.9047(5) | -0.1855(5) | -0.0159(7) | 3.3(1) |
| C(10) | -0.9185(5) | -0.2404(4) | -0.1206(6) | 2.3(1) |
| C(11) | -1.0085(6) | -0.4174(6) | -0.5585(6) | 4.3(2) |
| C(12) | -0.8520(5) | -0.4454(4) | -0.4056(5) | 2.0(1) |
| C(13) | -0.7678(5) | -0.3993(4) | -0.3443(7) | 2.7(1) |
| C(14) | -0.6661(5) | -0.4418(4) | -0.3220(7) | 3.1(1) |
| C(15) | -0.6477(5) | -0.5253(5) | -0.3634(6) | 3.1(1) |
| C(16) | -0.7290(6) | -0.5734(5) | -0.4222(8) | 3.9(2) |
| C(17) | -0.8336(5) | -0.5349(5) | -0.4479(7) | 3.4(1) |

Table 8-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|------------|------------|------------|
| I(1) | 0.0378(2) | 0.0508(2) | 0.0386(2) | -0.0022(2) | -0.0059(2) | -0.0073(2) |
| O(1) | 0.060(3) | 0.060(3) | 0.064(4) | -0.015(3) | 0.020(3) | 0.002(3) |
| N(1) | 0.026(3) | 0.043(3) | 0.028(3) | -0.003(2) | -0.012(2) | 0.004(2) |
| N(2) | 0.026(2) | 0.023(2) | 0.023(2) | -0.006(2) | -0.003(2) | 0.001(2) |
| N(3) | 0.024(2) | 0.040(3) | 0.024(2) | 0.009(2) | -0.011(2) | -0.010(2) |
| C(1) | 0.014(2) | 0.039(3) | 0.018(2) | -0.008(2) | -0.003(3) | -0.006(2) |
| C(2) | 0.056(5) | 0.063(6) | 0.050(5) | -0.005(4) | 0.000(4) | 0.038(4) |
| C(3) | 0.038(4) | 0.046(4) | 0.057(5) | 0.022(3) | -0.006(3) | 0.001(4) |
| C(4) | 0.041(3) | 0.024(2) | 0.029(3) | -0.005(3) | 0.008(3) | 0.003(3) |
| C(5) | 0.016(3) | 0.024(3) | 0.022(2) | -0.001(2) | -0.005(2) | 0.000(2) |
| C(6) | 0.031(4) | 0.031(3) | 0.032(3) | -0.008(3) | 0.012(3) | 0.001(2) |
| C(7) | 0.055(5) | 0.055(5) | 0.026(3) | 0.007(3) | 0.007(4) | -0.006(3) |
| C(8) | 0.048(4) | 0.048(4) | 0.037(3) | 0.014(3) | -0.019(3) | -0.016(4) |
| C(9) | 0.029(3) | 0.038(4) | 0.059(4) | -0.011(3) | -0.002(3) | -0.024(3) |
| C(10) | 0.020(3) | 0.032(3) | 0.034(3) | -0.013(2) | 0.006(3) | 0.003(2) |
| C(11) | 0.042(4) | 0.091(6) | 0.029(3) | 0.012(4) | -0.022(3) | -0.028(4) |
| C(12) | 0.021(2) | 0.035(3) | 0.021(3) | 0.003(2) | 0.003(2) | -0.004(2) |
| C(13) | 0.026(3) | 0.039(3) | 0.038(3) | -0.001(2) | -0.011(3) | -0.008(3) |
| C(14) | 0.022(3) | 0.048(4) | 0.047(4) | -0.001(2) | -0.001(3) | -0.002(3) |
| C(15) | 0.034(3) | 0.057(4) | 0.026(3) | 0.027(3) | 0.008(2) | 0.003(3) |
| C(16) | 0.044(3) | 0.041(4) | 0.062(5) | 0.011(3) | 0.020(3) | -0.012(4) |
| C(17) | 0.036(3) | 0.039(3) | 0.055(4) | -0.007(3) | 0.007(3) | -0.030(4) |

Table 8-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.32(1) | N(1) | C(2) | 1.50(1) |
| N(1) | C(3) | 1.44(1) | N(2) | C(1) | 1.34(1) |
| N(2) | C(4) | 1.47(1) | N(2) | C(5) | 1.44(1) |
| N(3) | C(1) | 1.35(1) | N(3) | C(11) | 1.48(1) |
| N(3) | C(12) | 1.44(1) | C(5) | C(6) | 1.38(1) |
| C(5) | C(10) | 1.42(1) | C(6) | C(7) | 1.39(1) |
| C(7) | C(8) | 1.37(2) | C(8) | C(9) | 1.37(2) |
| C(9) | C(10) | 1.37(1) | C(12) | C(13) | 1.38(1) |
| C(12) | C(17) | 1.41(1) | C(13) | C(14) | 1.40(1) |
| C(14) | C(15) | 1.33(2) | C(15) | C(16) | 1.36(2) |
| C(16) | C(17) | 1.41(2) | | | |

Table 8-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|-----------|
| C(1) | N(1) | C(2) | 120.6(10) | C(1) | N(1) | C(3) | 123.1(9) |
| C(2) | N(1) | C(3) | 116.2(10) | C(1) | N(2) | C(4) | 121.7(8) |
| C(1) | N(2) | C(5) | 123.2(8) | C(4) | N(2) | C(5) | 115.0(7) |
| C(1) | N(3) | C(11) | 121.2(9) | C(1) | N(3) | C(12) | 120.6(8) |
| C(11) | N(3) | C(12) | 118.1(8) | N(1) | C(1) | N(2) | 121.4(9) |
| N(1) | C(1) | N(3) | 119.3(10) | N(2) | C(1) | N(3) | 119.3(9) |
| N(2) | C(5) | C(6) | 121.9(8) | N(2) | C(5) | C(10) | 119.7(8) |
| C(6) | C(5) | C(10) | 118.4(9) | C(5) | C(6) | C(7) | 120.8(10) |
| C(6) | C(7) | C(8) | 119(1) | C(7) | C(8) | C(9) | 120(1) |
| C(8) | C(9) | C(10) | 121.1(10) | C(5) | C(10) | C(9) | 119.4(9) |
| N(3) | C(12) | C(13) | 120.7(9) | N(3) | C(12) | C(17) | 119.7(9) |
| C(13) | C(12) | C(17) | 119.5(9) | C(12) | C(13) | C(14) | 119.9(10) |
| C(13) | C(14) | C(15) | 120(1) | C(14) | C(15) | C(16) | 120(1) |
| C(15) | C(16) | C(17) | 121(1) | C(12) | C(17) | C(16) | 117(1) |

Table 8-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|--------------|----------------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(5) | 0.0188(91) | C(12) | -0.0010(95) |
| C(6) | -0.0187(107) | C(13) | 0.0052(122) |
| C(7) | -0.0073(130) | C(14) | -0.0127(114) |
| C(8) | 0.0216(113) | C(15) | 0.0142(106) |
| C(9) | -0.0140(120) | C(16) | -0.0142(128) |
| C(10) | -0.0096(103) | C(17) | 0.0036(123) |
| Plane number 3 | | | |
| Atoms defining plane | Distance | | |
| C(1) | 0.0107(80) | | |
| N(1) | -0.0042(86) | | |
| N(2) | -0.0040(79) | | |
| N(3) | -0.0041(83) | | |
| Summary | plane | mean deviation | CHI ² |
| | 1 | 0.0150 | 12.7 |
| | 2 | 0.0085 | 4.4 |
| | 3 | 0.0057 | 2.3 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|--------|-------|
| 2 | 107.26 | |
| 3 | 69.44 | 71.03 |

N,N,N',N''-Tetramethyl-*N',N''*-diphenylguanidinium iodide (6)
(-)-Crystal

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | C ₁₇ H ₂₄ N ₃ IO |
| Formula Weight | 413.30 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.30 X 0.15 X 0.40 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2 θ range) | 20 (144.4 - 49.0°) |
| Omega Scan Peak Width at Half-height | 0.22° |
| Lattice Parameters | a = 12.055(3) Å b = 14.776(3) Å c = 10.466(4) Å V = 1864.3(7) Å ³ |
| Space Group | P2 ₁ 2 ₁ 2 ₁ (#19) |
| Z value | 4 |
| D _{calc} | 1.472 g/cm ³ |
| F ₀₀₀ | 832.00 |
| μ (CuK α) | 135.29 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuK α (λ = 1.54178 Å) graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 2.37, 6.13, 15.65) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.37 + 0.30 tan θ)° |
| 2 θ _{max} | 135.1° |
| No. of Reflections Measured | Total: 3872 Unique: 1938 (Rint = 0.090) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.8578 - 1.5304) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0000 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 3.00 σ (I)) | 3107 |
| No. Variables | 199 |
| Reflection/Parameter Ratio | 15.61 |
| Residuals: R; Rw | 0.065; 0.075 |
| Goodness of Fit Indicator | 1.95 |
| Max Shift/Error in Final Cycle | 0.38 |
| Maximum peak in Final Diff. Map | 3.86 e-/Å ³ |
| Minimum peak in Final Diff. Map | -1.28 e-/Å ³ |

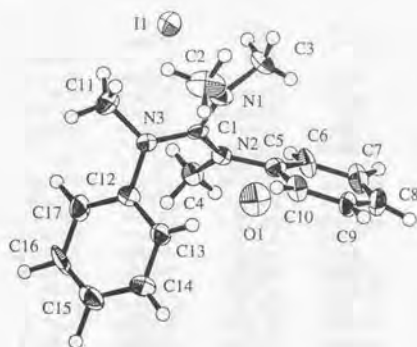


Table 8-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-------------|-------------|-------------|---------|
| I(1) | -0.19457(5) | -0.46471(4) | -0.84484(6) | 3.50(1) |
| O(1) | -0.7372(6) | -0.1532(4) | -0.8590(8) | 5.0(2) |
| N(1) | -0.4487(6) | -0.2730(5) | -0.8800(7) | 3.0(2) |
| N(2) | -0.4944(5) | -0.3739(4) | -0.7208(6) | 2.0(1) |
| N(3) | -0.5431(6) | -0.4026(5) | -0.9314(7) | 2.7(1) |
| C(1) | -0.4956(6) | -0.3481(5) | -0.8401(9) | 2.0(1) |
| C(2) | -0.4880(9) | -0.2221(8) | -0.994(1) | 4.8(3) |
| C(3) | -0.3547(8) | -0.2315(6) | -0.8131(10) | 3.7(2) |
| C(4) | -0.4922(7) | -0.4709(6) | -0.6847(8) | 2.8(2) |
| C(5) | -0.5024(7) | -0.3107(5) | -0.6189(8) | 2.2(1) |
| C(6) | -0.4402(8) | -0.3212(6) | -0.5070(9) | 3.1(2) |
| C(7) | -0.4538(10) | -0.2658(7) | -0.4020(9) | 3.8(2) |
| C(8) | -0.5379(9) | -0.1989(7) | -0.4095(10) | 4.0(2) |
| C(9) | -0.5944(8) | -0.1846(6) | -0.5192(10) | 3.4(2) |
| C(10) | -0.5800(7) | -0.2401(6) | -0.6235(8) | 2.7(2) |
| C(11) | -0.4934(9) | -0.4187(8) | -1.0568(9) | 4.7(3) |
| C(12) | -0.6483(7) | -0.4463(5) | -0.9052(8) | 2.3(1) |
| C(13) | -0.7323(6) | -0.3980(5) | -0.844(1) | 2.9(2) |
| C(14) | -0.8352(7) | -0.4406(6) | -0.8213(9) | 3.3(2) |
| C(15) | -0.8513(7) | -0.5309(8) | -0.8654(8) | 3.6(2) |
| C(16) | -0.7692(9) | -0.5767(6) | -0.925(1) | 4.2(2) |
| C(17) | -0.6655(7) | -0.5338(7) | -0.9466(10) | 3.7(2) |

Table 8-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|-----------|-----------|------------|
| I(1) | 0.0428(3) | 0.0422(3) | 0.0479(3) | 0.0011(3) | 0.0046(3) | -0.0072(3) |
| O(1) | 0.064(4) | 0.054(4) | 0.072(5) | 0.017(3) | -0.010(4) | 0.006(4) |
| N(1) | 0.035(4) | 0.031(4) | 0.047(4) | -0.007(3) | 0.006(3) | 0.005(3) |
| N(2) | 0.021(3) | 0.020(3) | 0.035(3) | 0.002(3) | -0.001(3) | 0.001(2) |
| N(3) | 0.026(3) | 0.043(4) | 0.034(3) | -0.006(3) | 0.006(3) | -0.010(3) |
| C(1) | 0.015(3) | 0.029(3) | 0.032(3) | 0.005(3) | 0.008(4) | 0.000(3) |
| C(2) | 0.056(7) | 0.067(7) | 0.061(6) | 0.002(6) | 0.000(6) | 0.043(6) |
| C(3) | 0.044(5) | 0.039(5) | 0.059(7) | -0.021(4) | 0.003(4) | -0.005(5) |
| C(4) | 0.043(4) | 0.018(3) | 0.044(5) | 0.000(4) | 0.005(4) | 0.002(4) |
| C(5) | 0.031(4) | 0.022(3) | 0.033(4) | 0.000(3) | 0.005(3) | 0.003(3) |
| C(6) | 0.046(6) | 0.031(5) | 0.042(5) | -0.001(4) | -0.022(4) | -0.008(4) |
| C(7) | 0.072(7) | 0.039(5) | 0.034(4) | -0.016(4) | -0.009(5) | -0.004(4) |
| C(8) | 0.069(7) | 0.040(5) | 0.044(5) | -0.013(4) | 0.013(4) | -0.021(5) |
| C(9) | 0.037(5) | 0.033(5) | 0.061(5) | 0.002(4) | 0.006(4) | -0.027(4) |
| C(10) | 0.033(4) | 0.030(4) | 0.040(5) | 0.009(3) | -0.015(4) | -0.002(3) |
| C(11) | 0.057(7) | 0.091(9) | 0.033(5) | -0.021(6) | 0.017(5) | -0.023(6) |
| C(12) | 0.026(3) | 0.030(4) | 0.033(4) | 0.001(3) | -0.004(3) | 0.005(3) |
| C(13) | 0.030(4) | 0.030(4) | 0.051(5) | 0.000(3) | 0.004(4) | -0.013(5) |
| C(14) | 0.025(4) | 0.051(5) | 0.051(6) | -0.005(3) | 0.000(4) | -0.002(4) |
| C(15) | 0.043(4) | 0.058(5) | 0.036(5) | -0.023(4) | -0.010(4) | 0.001(5) |
| C(16) | 0.047(5) | 0.032(5) | 0.082(8) | -0.017(4) | -0.016(5) | -0.021(5) |
| C(17) | 0.037(4) | 0.036(4) | 0.066(6) | 0.008(4) | 0.002(4) | -0.027(5) |

Table 8-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.31(1) | N(1) | C(2) | 1.49(2) |
| N(1) | C(3) | 1.47(2) | N(2) | C(1) | 1.30(2) |
| N(2) | C(4) | 1.48(1) | N(2) | C(5) | 1.42(1) |
| N(3) | C(1) | 1.37(1) | N(3) | C(11) | 1.46(2) |
| N(3) | C(12) | 1.45(1) | C(5) | C(6) | 1.40(2) |
| C(5) | C(10) | 1.40(1) | C(6) | C(7) | 1.38(2) |
| C(7) | C(8) | 1.42(2) | C(8) | C(9) | 1.35(2) |
| C(9) | C(10) | 1.38(2) | C(12) | C(13) | 1.40(2) |
| C(12) | C(17) | 1.38(2) | C(13) | C(14) | 1.41(2) |
| C(14) | C(15) | 1.43(2) | C(15) | C(16) | 1.35(2) |
| C(16) | C(17) | 1.42(2) | | | |

Table 8-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|-----------|
| C(1) | N(1) | C(2) | 123(1) | C(1) | N(1) | C(3) | 122(1) |
| C(2) | N(1) | C(3) | 114(1) | C(1) | N(2) | C(4) | 121.8(9) |
| C(1) | N(2) | C(5) | 121.7(9) | C(4) | N(2) | C(5) | 116.4(9) |
| C(1) | N(3) | C(11) | 123(1) | C(1) | N(3) | C(12) | 119.5(9) |
| C(11) | N(3) | C(12) | 117(1) | N(1) | C(1) | N(2) | 123(1) |
| N(1) | C(1) | N(3) | 116(1) | N(2) | C(1) | N(3) | 119.8(10) |
| N(2) | C(5) | C(6) | 121.3(10) | N(2) | C(5) | C(10) | 120.6(10) |
| C(6) | C(5) | C(10) | 117(1) | C(5) | C(6) | C(7) | 122(1) |
| C(6) | C(7) | C(8) | 117(1) | C(7) | C(8) | C(9) | 121(1) |
| C(8) | C(9) | C(10) | 121(1) | C(5) | C(10) | C(9) | 120(1) |
| N(3) | C(12) | C(13) | 119.7(10) | N(3) | C(12) | C(17) | 119(1) |
| C(13) | C(12) | C(17) | 121(1) | C(12) | C(13) | C(14) | 119(1) |
| C(13) | C(14) | C(15) | 118(1) | C(14) | C(15) | C(16) | 121(1) |
| C(15) | C(16) | C(17) | 119(1) | C(12) | C(17) | C(16) | 119(1) |

Table 8-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|--------------|----------------------|--------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(5) | -0.0125(111) | C(12) | 0.0033(111) |
| C(6) | 0.0062(132) | C(13) | -0.0083(151) |
| C(7) | 0.0242(148) | C(14) | 0.0076(135) |
| C(8) | -0.0361(142) | C(15) | -0.0052(127) |
| C(9) | 0.01930(133) | C(16) | 0.0052(160) |
| C(10) | 0.0056(125) | C(17) | -0.0026(148) |
| Plane number 3 | | | |
| Atoms defining plane | Distance | | |
| C(1) | -0.0145(92) | | |
| N(1) | 0.0063(108) | | |
| N(2) | 0.0055(88) | | |
| N(3) | 0.0053(97) | | |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0173 | 12.0 |
| | 2 | 0.0053 | 1.1 |
| | 3 | 0.079 | 3.4 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|--------|-------|
| 2 | 106.91 | |
| 3 | 69.19 | 70.96 |

N-Phenylbenzamidinium Chloride (7)

| | |
|--|--|
| A. Crystal Data | |
| Empirical Formula | $C_{12}H_{13}N_2Cl$ |
| Formula Weight | 232.71 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.20 X 0.20 X 0.20 mm |
| Crystal System | tetragonal |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2 θ range) | 20 (43.7 - 46.4°) |
| Omega Scan Peak Width at Half-height | 0.37° |
| Lattice Parameters | $a = 16.565(2) \text{ \AA}$ $c = 8.880(3) \text{ \AA}$ $V = 2436.6(5) \text{ \AA}^3$ |
| Space Group | P42/n (#86) |
| Z value | 8 |
| D_{calc} | 1.269 g/cm ³ |
| F_{000} | 976.00 |
| μ (CuK α) | 25.49 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC7S |
| Radiation | CuK α ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated Ni foil (factor = 8.99) |
| Attenuator | 6.0° |
| Take-off Angle | 9.0 mm horizontal |
| Detector Aperture | 13.0 mm vertical |
| Crystal to Detector Distance | 235 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in to) (up to 3 scans) |
| Scan Width | (1.21 + 0.30 tan θ)° |
| 2 θ_{max} | 135.1° |
| No. of Reflections Measured | Total: 2535; Unique: 2365 (Rint = 0.030) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.9314 - 0.9991) Secondary Extinction (coefficient: 2.36218e-06) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $S w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[s^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0020 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 2.00 σ (I)) | 1500 |
| No. Variables | 146 |
| Reflection/Parameter Ratio | 10.27 |
| Residuals: R; Rw | 0.043; 0.035 |
| Goodness of Fit Indicator | 1.66 |
| Max Shift/Error in Final Cycle | 0.05 |
| Maximum peak in Final Diff. Map | 0.16 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.16 e-/Å ³ |

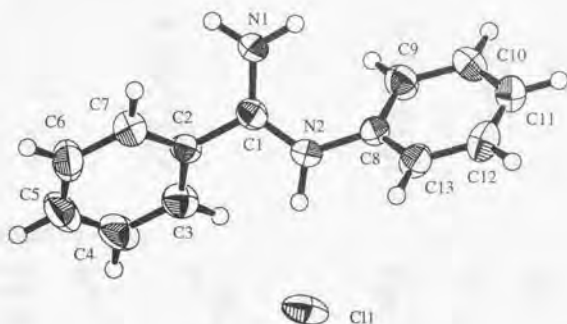


Table 10-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|-------------|-----------|----------|
| Cl(1) | 0.40354(5) | -0.04598(5) | 0.6729(1) | 4.74(2) |
| N(1) | 0.1207(1) | 0.0108(2) | 0.9160(3) | 3.84(6) |
| N(2) | 0.2565(1) | -0.0170(1) | 0.8813(3) | 3.19(6) |
| C(1) | 0.1872(2) | 0.0146(2) | 0.8371(3) | 3.03(6) |
| C(2) | 0.1859(2) | 0.0560(2) | 0.6891(3) | 3.08(6) |
| C(3) | 0.2498(2) | 0.1053(2) | 0.6484(4) | 3.96(8) |
| C(4) | 0.2480(2) | 0.1442(2) | 0.5114(4) | 5.17(10) |
| C(5) | 0.1834(3) | 0.1346(2) | 0.4160(4) | 5.5(1) |
| C(6) | 0.1202(2) | 0.0851(2) | 0.4551(4) | 4.97(10) |
| C(7) | 0.1215(2) | 0.0456(2) | 0.5926(4) | 4.08(8) |
| C(8) | 0.2721(2) | -0.0559(2) | 1.0216(3) | 3.03(7) |
| C(9) | 0.2554(2) | -0.0189(2) | 1.1575(4) | 3.90(8) |
| C(10) | 0.2751(2) | -0.0572(2) | 1.2908(4) | 4.33(9) |
| C(11) | 0.3110(2) | -0.1317(2) | 1.2883(4) | 4.40(9) |
| C(12) | 0.3274(2) | -0.1683(2) | 1.1530(4) | 4.53(9) |
| C(13) | 0.3089(2) | -0.1306(2) | 1.0188(4) | 3.73(7) |

Table 10-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|-----------|-----------|------------|
| Cl(1) | 0.0698(6) | 0.0465(5) | 0.0638(5) | 0.0006(4) | 0.0341(5) | -0.0065(4) |
| N(1) | 0.041(2) | 0.060(2) | 0.045(2) | 0.008(1) | 0.010(1) | 0.020(1) |
| N(2) | 0.037(1) | 0.047(2) | 0.037(1) | 0.000(1) | 0.006(1) | 0.004(1) |
| C(1) | 0.043(2) | 0.034(2) | 0.038(2) | -0.003(1) | 0.004(1) | 0.002(1) |
| C(2) | 0.044(2) | 0.035(2) | 0.037(2) | 0.005(1) | 0.008(1) | 0.003(1) |
| C(3) | 0.055(2) | 0.040(2) | 0.055(2) | -0.002(1) | 0.007(2) | 0.005(2) |
| C(4) | 0.079(3) | 0.051(2) | 0.066(3) | 0.002(2) | 0.023(2) | 0.021(2) |
| C(5) | 0.103(3) | 0.058(2) | 0.047(2) | 0.025(2) | 0.021(2) | 0.020(2) |
| C(6) | 0.074(3) | 0.071(3) | 0.044(2) | 0.017(2) | -0.010(2) | 0.006(2) |
| C(7) | 0.054(2) | 0.056(2) | 0.046(2) | 0.002(2) | 0.000(2) | 0.004(2) |
| C(8) | 0.031(2) | 0.046(2) | 0.038(2) | -0.002(1) | 0.000(1) | 0.004(1) |
| C(9) | 0.059(2) | 0.049(2) | 0.041(2) | 0.007(2) | 0.004(2) | 0.000(2) |
| C(10) | 0.061(2) | 0.069(2) | 0.034(2) | 0.004(2) | 0.005(2) | 0.002(2) |
| C(11) | 0.048(2) | 0.071(2) | 0.048(2) | 0.004(2) | -0.005(2) | 0.016(2) |
| C(12) | 0.054(2) | 0.053(2) | 0.065(3) | 0.011(2) | -0.012(2) | 0.006(2) |
| C(13) | 0.043(2) | 0.050(2) | 0.048(2) | 0.006(1) | -0.005(2) | -0.003(2) |

Table 10-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.308(3) | N(2) | C(1) | 1.321(3) |
| N(2) | C(8) | 1.426(4) | C(1) | C(2) | 1.482(4) |
| C(2) | C(3) | 1.386(4) | C(2) | C(7) | 1.379(4) |
| C(3) | C(4) | 1.377(4) | C(4) | C(5) | 1.374(5) |
| C(5) | C(6) | 1.375(5) | C(6) | C(7) | 1.385(4) |
| C(8) | C(9) | 1.382(4) | C(8) | C(13) | 1.379(4) |
| C(9) | C(10) | 1.382(4) | C(10) | C(11) | 1.370(4) |
| C(11) | C(12) | 1.373(4) | C(12) | C(13) | 1.379(4) |

Table 10-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(2) | C(8) | 126.7(2) | N(1) | C(1) | N(2) | 123.6(3) |
| N(1) | C(1) | C(2) | 119.0(3) | N(2) | C(1) | C(2) | 117.4(3) |
| C(1) | C(2) | C(3) | 119.5(3) | C(1) | C(2) | C(7) | 120.3(3) |
| C(3) | C(2) | C(7) | 120.2(3) | C(2) | C(3) | C(4) | 119.3(3) |
| C(3) | C(4) | C(5) | 120.5(3) | C(4) | C(5) | C(6) | 120.4(3) |
| C(5) | C(6) | C(7) | 119.5(3) | C(2) | C(7) | C(6) | 120.1(3) |
| N(2) | C(8) | C(9) | 121.7(3) | N(2) | C(8) | C(13) | 118.0(3) |
| C(9) | C(8) | C(13) | 120.2(3) | C(8) | C(9) | C(10) | 119.8(3) |
| C(9) | C(10) | C(11) | 120.1(3) | C(10) | C(11) | C(12) | 119.9(3) |
| C(11) | C(12) | C(13) | 120.8(3) | C(8) | C(13) | C(12) | 119.2(3) |

Table 10-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | | |
|----------------------|-------------|----------------------|----------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance | |
| C(2) | -0.0035(28) | C(8) | -0.0032(27) | |
| C(3) | 0.0017(31) | C(9) | -0.0003(32) | |
| C(4) | 0.0036(36) | C(10) | 0.0027(34) | |
| C(5) | -0.0067(38) | C(11) | 0.0003(34) | |
| C(6) | 0.0026(37) | C(12) | -0.0052(33) | |
| C(7) | 0.0029(33) | C(13) | 0.0062(30) | |
| Plane number 3 | | Summary | | |
| Atoms defining plane | Distance | plane | mean deviation | CHI ² |
| N(1) | 0.0 | 1 | 0.0035 | 7.1 |
| N(2) | 0.0 | 2 | 0.0030 | 8.6 |
| C(8) | 0.0 | 3 | 0.0000 | 0.0 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|--------|
| 2 | 85.39 | |
| 3 | 41.22 | 125.69 |

N-Methyl-N-phenylbenzamidinium Chloride (8)

| | |
|--|--|
| A. Crystal Data | $C_{11}H_{10}N_2ClO$ |
| Empirical Formula | 278.78 |
| Formula Weight | clear, prism |
| Crystal Color, Habit | 0.38 X 0.30 X 0.01 mm |
| Crystal Dimensions | monoclinic |
| Crystal System | Primitive |
| Lattice Type | 3 oscillations @ 5.0 minutes |
| Indexing Images | 86.33 mm |
| Detector Position | 0.00° |
| Detector Swing Angle | 0.203 mm |
| Pixel Size | $a = 6.91(2) \text{ \AA}$ |
| Lattice Parameters | $b = 22.13(5) \text{ \AA}$ |
| | $c = 9.918(8) \text{ \AA}$ |
| | $\beta = 94.8(2)^\circ$ |
| | $V = 1511.8 \text{ \AA}^3$ |
| | $P2_1/c$ (#14) |
| Space Group | 4 |
| Z value | 1.225 g/cm ³ |
| D_{calc} | 592.00 |
| F_{000} | 2.47 cm ⁻¹ |
| $\mu(\text{MoK}\alpha)$ | |
| B. Intensity Measurements | RAXIS-II |
| Diffractometer | MoK α ($\lambda = 0.71070 \text{ \AA}$) |
| Radiation | graphite monochromated |
| | 200 mm x 200 mm |
| | 15 exposures @ 5.0 minutes |
| Detector Aperture | 7.0° |
| Data Images | 86.33 mm |
| Oscillation Range | 0.00° |
| Detector Position | 0.203 mm |
| Detector Swing Angle | 54.2° |
| Pixel Size | Total: 2121 |
| $2\theta_{max}$ | Lorentz-polarization |
| No. of Reflections Measured | |
| Corrections | Direct Methods (SHELXS86) |
| C. Structure Solution and Refinement | Full-matrix least-squares |
| Structure Solution | $S w (F_o - F_c)^2$ |
| Refinement | $w = 1/[s^2(F_o^2) + P^2 + P]$ |
| Function Minimized | 0.020 |
| Least Squares Weights | All non-hydrogen atoms |
| p-factor | 1547 |
| Anomalous Dispersion | 172 |
| No. Observations ($I > 3.00\sigma(I)$) | 8.99 |
| No. Variables | 0.102 ; 0.118 |
| Reflection/Parameter Ratio | 5.39 |
| Residuals: R; Rw | 0.11 |
| Goodness of Fit Indicator | 0.41 e-/Å ³ |
| Max Shift/Error in Final Cycle | -0.43 e-/Å ³ |
| Maximum peak in Final Diff. Map | |
| Minimum peak in Final Diff. Map | |

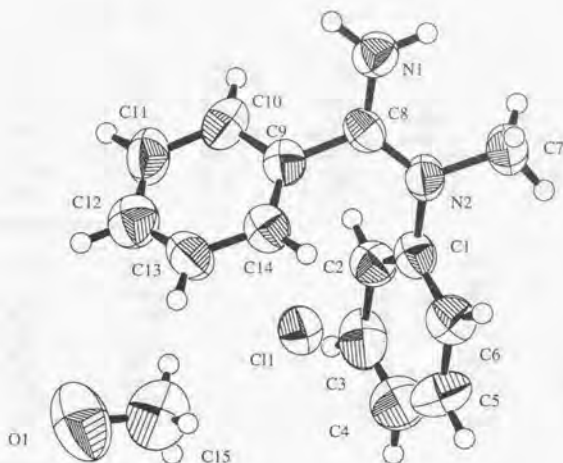


Table 11-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-------------|------------|------------|---------|
| Cl(1) | 0.3882(3) | 0.29327(9) | 0.2529(1) | 5.54(5) |
| O(1) | 0.297(1) | 0.0688(4) | 0.6966(6) | 11.0(3) |
| N(1) | -0.3983(10) | 0.2003(3) | 0.0596(5) | 5.0(1) |
| N(2) | -0.1332(8) | 0.1406(3) | 0.0254(4) | 4.5(1) |
| C(1) | 0.017(1) | 0.0986(3) | 0.0739(6) | 4.6(2) |
| C(2) | -0.029(1) | 0.0513(3) | 0.1571(6) | 5.1(2) |
| C(3) | 0.116(2) | 0.0116(4) | 0.2058(7) | 6.7(2) |
| C(4) | 0.299(2) | 0.0173(4) | 0.1642(9) | 7.3(3) |
| C(5) | 0.342(1) | 0.0637(4) | 0.0798(8) | 6.6(2) |
| C(6) | 0.201(1) | 0.1046(4) | 0.0320(7) | 5.5(2) |
| C(7) | -0.169(1) | 0.1477(4) | -0.1220(5) | 5.7(2) |
| C(8) | -0.240(1) | 0.1710(3) | 0.1073(5) | 4.2(2) |
| C(9) | -0.183(1) | 0.1728(3) | 0.2536(6) | 4.5(2) |
| C(10) | -0.318(1) | 0.1572(3) | 0.3457(6) | 5.7(2) |
| C(11) | -0.258(2) | 0.1600(4) | 0.4843(6) | 6.4(2) |
| C(12) | -0.074(2) | 0.1793(4) | 0.5253(8) | 6.5(2) |
| C(13) | 0.051(1) | 0.1956(4) | 0.4375(6) | 5.9(2) |
| C(14) | 0.003(1) | 0.1923(3) | 0.2994(6) | 5.1(2) |
| C(15) | 0.286(2) | 0.0502(5) | 0.570(1) | 9.9(4) |

Table 11-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|----------|-----------|------------|-----------|------------|
| Cl(1) | 0.073(2) | 0.075(1) | 0.0615(8) | 0.0034(10) | 0.0017(8) | -0.0043(8) |
| O(1) | 0.213(10) | 0.108(6) | 0.095(4) | 0.004(6) | -0.011(5) | 0.009(4) |
| N(1) | 0.062(4) | 0.062(4) | 0.068(3) | 0.001(3) | 0.007(3) | -0.005(3) |
| N(2) | 0.067(4) | 0.059(4) | 0.045(2) | 0.005(3) | 0.006(3) | 0.001(2) |
| C(1) | 0.071(6) | 0.049(4) | 0.054(3) | 0.001(4) | 0.001(3) | -0.002(3) |
| C(2) | 0.067(6) | 0.058(5) | 0.067(3) | 0.004(4) | 0.001(4) | -0.002(3) |
| C(3) | 0.129(10) | 0.055(5) | 0.070(4) | 0.015(5) | 0.009(5) | 0.003(4) |
| C(4) | 0.110(9) | 0.065(6) | 0.099(5) | 0.025(5) | 0.005(5) | -0.008(5) |
| C(5) | 0.063(7) | 0.070(6) | 0.118(6) | 0.008(5) | 0.018(5) | -0.006(5) |
| C(6) | 0.068(6) | 0.067(5) | 0.074(4) | -0.008(4) | 0.003(4) | 0.000(4) |
| C(7) | 0.088(7) | 0.078(6) | 0.051(3) | 0.013(4) | 0.003(3) | -0.003(3) |

Table 11-2. Anisotropic Displacement Parameters (Continued)

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| C(8) | 0.057(5) | 0.050(4) | 0.052(3) | -0.008(3) | -0.005(3) | 0.000(3) |
| C(9) | 0.066(5) | 0.049(4) | 0.056(3) | 0.001(3) | 0.006(3) | 0.000(3) |
| C(10) | 0.082(6) | 0.063(5) | 0.075(4) | 0.008(4) | 0.028(4) | 0.002(3) |
| C(11) | 0.106(8) | 0.084(6) | 0.055(3) | 0.015(5) | 0.019(4) | 0.009(3) |
| C(12) | 0.096(8) | 0.069(5) | 0.082(5) | 0.007(5) | 0.009(5) | -0.007(4) |
| C(13) | 0.081(7) | 0.077(6) | 0.063(3) | 0.010(4) | -0.013(4) | 0.000(3) |
| C(14) | 0.072(6) | 0.054(5) | 0.066(3) | -0.005(4) | 0.001(4) | -0.006(3) |
| C(15) | 0.15(1) | 0.102(9) | 0.127(7) | -0.002(7) | 0.029(7) | 0.004(7) |

Table 11-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| O(1) | C(15) | 1.32(1) | N(1) | C(8) | 1.327(9) |
| N(2) | C(1) | 1.444(9) | N(2) | C(7) | 1.470(7) |
| N(2) | C(8) | 1.324(8) | C(1) | C(2) | 1.387(9) |
| C(1) | C(6) | 1.38(1) | C(2) | C(3) | 1.39(1) |
| C(3) | C(4) | 1.37(1) | C(4) | C(5) | 1.37(1) |
| C(5) | C(6) | 1.38(1) | C(8) | C(9) | 1.472(8) |
| C(9) | C(10) | 1.406(9) | C(9) | C(14) | 1.39(1) |
| C(10) | C(11) | 1.40(1) | C(11) | C(12) | 1.37(1) |
| C(12) | C(13) | 1.33(1) | C(13) | C(14) | 1.384(9) |

Table 11-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(2) | C(7) | 117.1(5) | C(1) | N(2) | C(8) | 122.8(5) |
| C(7) | N(2) | C(8) | 120.0(6) | N(2) | C(1) | C(2) | 119.4(7) |
| N(2) | C(1) | C(6) | 119.6(6) | C(2) | C(1) | C(6) | 121.0(7) |
| C(1) | C(2) | C(3) | 119.3(8) | C(2) | C(3) | C(4) | 119.7(7) |
| C(3) | C(4) | C(5) | 120.2(8) | C(4) | C(5) | C(6) | 121.3(8) |
| C(1) | C(6) | C(5) | 118.4(7) | N(1) | C(8) | N(2) | 121.0(5) |
| N(1) | C(8) | C(9) | 118.9(6) | N(2) | C(8) | C(9) | 120.1(7) |
| C(8) | C(9) | C(10) | 119.7(7) | C(8) | C(9) | C(14) | 119.6(6) |
| C(10) | C(9) | C(14) | 120.7(6) | C(9) | C(10) | C(11) | 117.7(8) |
| C(10) | C(11) | C(12) | 119.8(8) | C(11) | C(12) | C(13) | 122.0(8) |
| C(12) | C(13) | C(14) | 121.2(9) | C(9) | C(14) | C(13) | 118.5(7) |

Table 11-5. Least Squares Planes

| Plane number 1 | | | Plane number 3 | | |
|----------------------|-------------|--|----------------------|----------------|------------------|
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(1) | 0.0133(63) | | C(9) | 0.0079(69) | |
| C(2) | -0.0180(66) | | C(10) | -0.0134(77) | |
| C(3) | 0.0170(78) | | C(11) | 0.0086(86) | |
| C(4) | -0.0058(82) | | C(12) | 0.0071(87) | |
| C(5) | -0.0002(83) | | C(13) | -0.0116(82) | |
| C(6) | -0.0074(72) | | C(14) | 0.0043(73) | |
| Plane number 2 | | | Summary | | |
| Atoms defining plane | Distance | | plane | mean deviation | CHI ² |
| N(1) | 0.0 | | 1 | 0.0103 | 18.2 |
| N(2) | 0.0 | | 2 | 0.0000 | 0.0 |
| C(8) | 0.0 | | 3 | 0.0088 | 7.9 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|--------|--------|
| 2 | 61.32 | |
| 3 | 120.44 | 126.00 |

meta-Diamidine (9)

| | |
|--|---|
| A. Crystal Data | $C_{12}H_{12}N_4$ |
| Empirical Formula | 342.44 |
| Formula Weight | clear, prismatic |
| Crystal Color, Habit | 0.30 X 0.30 X 0.30 mm |
| Crystal Dimensions | triclinic |
| Crystal System | Primitive |
| Lattice Type | 3 oscillations @ 5.0 minutes |
| Indexing Images | 86.33 mm |
| Detector Position | 0.00° |
| Detector Swing Angle | 0.203 mm |
| Pixel Size | a = 9.19(3) Å, b = 13.58(5) Å, c = 8.47(2) Å |
| Lattice Parameters | $\alpha = 93.74(8)^\circ$, $\beta = 117.1(2)^\circ$, $\gamma = 83.7(1)^\circ$ |
| | V = 935.7000 Å ³ |
| Space Group | P $\bar{1}$ (#2) |
| Z value | 2 |
| D _{calc} | 1.215 g/cm ³ |
| F ₀₀₀ | 364.00 |
| μ (MoK α) | 0.00 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | RAXIS-II |
| Radiation | MoK α ($\lambda = 0.71070$ Å) |
| | graphite monochromated |
| Detector Aperture | 200 mm x 200 mm |
| Data Images | 15 exposures @ 5.0 minutes |
| Oscillation Range | 7.0° |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| $2\theta_{max}$ | 50.3° |
| No. of Reflections Measured | Total: 2295 |
| Corrections | Lorentz-polarization |
| | Absorption |
| | (trans. factors: -1.4750 - 65.0260) |
| | Secondary Extinction |
| | (coefficient: 5.88973e-05) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0250 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 4.00\sigma(I)$) | 1572 |
| No. Variables | 236 |
| Reflection/Parameter Ratio | 6.66 |
| Residuals: R; Rw | 0.107; 0.129 |
| Goodness of Fit Indicator | 6.18 |
| Max Shift/Error in Final Cycle | 0.01 |
| Maximum peak in Final Diff. Map | 0.30 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.33 e-/Å ³ |

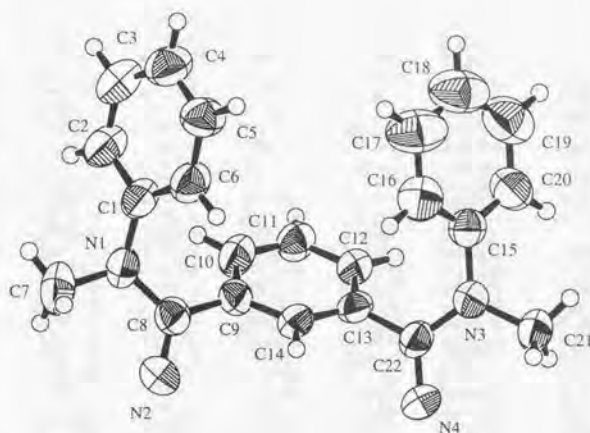


Table 12-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|------------|------------|--------|
| N(1) | 1.2435(6) | 0.3822(4) | 1.5346(7) | 5.4(1) |
| N(2) | 1.2484(7) | 0.2467(4) | 1.6915(7) | 6.0(1) |
| N(3) | 0.7194(6) | 0.0234(3) | 0.9979(7) | 5.1(1) |
| N(4) | 0.8128(7) | -0.0088(4) | 1.2936(7) | 6.0(1) |
| C(1) | 1.2293(8) | 0.4085(5) | 1.3659(9) | 5.2(2) |
| C(2) | 1.2099(9) | 0.5068(5) | 1.319(1) | 6.2(2) |
| C(3) | 1.2036(9) | 0.5327(5) | 1.165(1) | 6.7(2) |
| C(4) | 1.2149(9) | 0.4619(6) | 1.047(1) | 6.8(2) |
| C(5) | 1.2363(9) | 0.3645(5) | 1.0917(10) | 6.3(2) |
| C(6) | 1.2394(9) | 0.3370(5) | 1.2462(10) | 6.0(2) |
| C(7) | 1.3946(9) | 0.4080(5) | 1.686(1) | 7.1(2) |
| C(8) | 1.1744(8) | 0.2983(5) | 1.5475(9) | 5.1(2) |
| C(9) | 1.0120(7) | 0.2778(4) | 1.4008(8) | 4.6(1) |
| C(10) | 0.8866(8) | 0.3549(4) | 1.3167(9) | 5.3(2) |
| C(11) | 0.7348(8) | 0.3325(4) | 1.1874(8) | 5.1(2) |
| C(12) | 0.7036(7) | 0.2351(4) | 1.1353(8) | 4.6(1) |
| C(13) | 0.8235(7) | 0.1590(4) | 1.2140(8) | 4.4(1) |
| C(14) | 0.9763(7) | 0.1810(4) | 1.3461(8) | 4.6(1) |
| C(15) | 0.7213(8) | 0.0777(4) | 0.8602(8) | 5.0(2) |
| C(16) | 0.8645(9) | 0.1145(5) | 0.880(1) | 6.5(2) |
| C(17) | 0.862(1) | 0.1688(7) | 0.749(2) | 9.0(3) |
| C(18) | 0.724(2) | 0.1861(7) | 0.596(2) | 9.3(3) |
| C(19) | 0.580(1) | 0.1472(7) | 0.572(1) | 8.3(3) |
| C(20) | 0.5807(9) | 0.0936(5) | 0.7072(9) | 6.6(2) |
| C(21) | 0.6618(8) | -0.0744(5) | 0.9526(9) | 6.1(2) |
| C(22) | 0.7898(7) | 0.0525(4) | 1.1733(9) | 4.6(1) |

Table 12-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|----------|-----------|
| N(1) | 0.081(3) | 0.063(3) | 0.065(4) | -0.029(3) | 0.033(3) | -0.012(2) |
| N(2) | 0.089(4) | 0.083(4) | 0.054(3) | -0.017(3) | 0.028(3) | -0.002(3) |
| N(3) | 0.076(3) | 0.053(3) | 0.058(3) | -0.012(2) | 0.024(3) | -0.001(2) |
| N(4) | 0.099(4) | 0.055(3) | 0.071(4) | -0.018(3) | 0.032(3) | 0.012(3) |
| C(1) | 0.073(4) | 0.056(4) | 0.078(5) | -0.018(3) | 0.041(3) | -0.004(3) |
| C(2) | 0.097(5) | 0.059(4) | 0.099(6) | -0.015(3) | 0.058(5) | -0.001(3) |
| C(3) | 0.093(5) | 0.063(4) | 0.113(7) | -0.016(4) | 0.055(5) | 0.008(4) |
| C(4) | 0.094(5) | 0.091(6) | 0.094(6) | -0.019(4) | 0.053(4) | 0.013(4) |
| C(5) | 0.101(5) | 0.076(5) | 0.073(5) | -0.004(4) | 0.051(4) | 0.003(3) |
| C(6) | 0.101(5) | 0.057(4) | 0.083(5) | -0.015(3) | 0.053(4) | -0.007(3) |
| C(7) | 0.093(5) | 0.080(5) | 0.097(6) | -0.034(4) | 0.042(4) | -0.033(4) |
| C(8) | 0.078(4) | 0.064(4) | 0.059(4) | -0.017(3) | 0.037(4) | -0.013(3) |
| C(9) | 0.069(4) | 0.065(4) | 0.050(4) | -0.019(3) | 0.031(3) | -0.009(3) |
| C(10) | 0.077(4) | 0.051(4) | 0.080(5) | -0.015(3) | 0.040(4) | -0.006(3) |
| C(11) | 0.074(4) | 0.049(4) | 0.073(4) | -0.003(3) | 0.036(4) | 0.001(3) |
| C(12) | 0.063(4) | 0.052(4) | 0.057(4) | -0.009(3) | 0.023(3) | 0.004(3) |
| C(13) | 0.075(4) | 0.051(3) | 0.057(4) | -0.014(3) | 0.039(3) | 0.001(3) |
| C(14) | 0.068(4) | 0.046(3) | 0.064(4) | -0.008(3) | 0.031(3) | 0.004(3) |
| C(15) | 0.077(4) | 0.052(3) | 0.064(4) | -0.006(3) | 0.035(4) | -0.004(3) |
| C(16) | 0.081(4) | 0.089(5) | 0.089(6) | -0.006(4) | 0.047(4) | -0.003(4) |
| C(17) | 0.141(8) | 0.118(8) | 0.125(9) | 0.011(6) | 0.095(7) | 0.024(6) |
| C(18) | 0.19(1) | 0.097(7) | 0.101(8) | 0.019(7) | 0.096(8) | 0.011(5) |
| C(19) | 0.128(8) | 0.096(6) | 0.081(6) | 0.011(5) | 0.042(6) | 0.001(4) |
| C(20) | 0.096(5) | 0.082(5) | 0.064(5) | -0.008(4) | 0.028(4) | -0.001(4) |
| C(21) | 0.087(4) | 0.058(4) | 0.075(4) | -0.023(3) | 0.020(4) | -0.005(3) |
| C(22) | 0.068(4) | 0.046(3) | 0.066(4) | -0.012(3) | 0.032(3) | -0.003(3) |

Table 12-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|-----------|
| N(1) | C(1) | 1.442(8) | N(1) | C(7) | 1.458(9) |
| N(1) | C(8) | 1.396(8) | N(2) | C(8) | 1.301(8) |
| N(3) | C(15) | 1.429(8) | N(3) | C(21) | 1.446(7) |
| N(3) | C(22) | 1.374(8) | N(4) | C(22) | 1.286(7) |
| C(1) | C(2) | 1.387(9) | C(1) | C(6) | 1.384(10) |
| C(2) | C(3) | 1.35(1) | C(3) | C(4) | 1.37(1) |
| C(4) | C(5) | 1.37(1) | C(5) | C(6) | 1.372(9) |
| C(8) | C(9) | 1.487(9) | C(9) | C(10) | 1.420(9) |
| C(9) | C(14) | 1.388(8) | C(10) | C(11) | 1.378(9) |
| C(11) | C(12) | 1.385(8) | C(12) | C(13) | 1.377(8) |
| C(13) | C(14) | 1.390(9) | C(13) | C(22) | 1.497(7) |
| C(15) | C(16) | 1.39(1) | C(15) | C(20) | 1.359(9) |
| C(16) | C(17) | 1.36(1) | C(17) | C(18) | 1.35(1) |
| C(18) | C(19) | 1.40(2) | C(19) | C(20) | 1.39(1) |

Table 12-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|-----------|
| C(1) | N(1) | C(7) | 114.1(5) | C(1) | N(1) | C(8) | 120.0(5) |
| C(7) | N(1) | C(8) | 117.6(5) | C(15) | N(3) | C(21) | 117.3(5) |
| C(15) | N(3) | C(22) | 123.6(5) | C(21) | N(3) | C(22) | 118.4(5) |
| N(1) | C(1) | C(2) | 121.3(6) | N(1) | C(1) | C(6) | 121.5(6) |
| C(2) | C(1) | C(6) | 117.2(7) | C(1) | C(2) | C(3) | 121.9(7) |
| C(2) | C(3) | C(4) | 120.7(7) | C(3) | C(4) | C(5) | 118.4(8) |
| C(4) | C(5) | C(6) | 121.4(8) | C(1) | C(6) | C(5) | 120.2(6) |
| N(1) | C(8) | N(2) | 118.9(5) | N(1) | C(8) | C(9) | 117.6(6) |
| N(2) | C(8) | C(9) | 123.3(5) | C(8) | C(9) | C(10) | 121.8(5) |
| C(8) | C(9) | C(14) | 120.4(6) | C(10) | C(9) | C(14) | 117.7(5) |
| C(9) | C(10) | C(11) | 120.1(5) | C(10) | C(11) | C(12) | 120.7(5) |
| C(11) | C(12) | C(13) | 120.4(5) | C(12) | C(13) | C(14) | 119.3(5) |
| C(12) | C(13) | C(22) | 121.9(5) | C(14) | C(13) | C(22) | 118.6(5) |
| C(9) | C(14) | C(13) | 121.9(5) | N(3) | C(15) | C(16) | 121.2(6) |
| N(3) | C(15) | C(20) | 119.1(6) | C(16) | C(15) | C(20) | 119.6(7) |
| C(15) | C(16) | C(17) | 120.1(8) | C(16) | C(17) | C(18) | 121.6(10) |
| C(17) | C(18) | C(19) | 119.0(9) | C(18) | C(19) | C(20) | 119.8(8) |
| C(15) | C(20) | C(19) | 119.8(8) | N(3) | C(22) | N(4) | 120.1(5) |
| N(3) | C(22) | C(13) | 117.2(5) | N(4) | C(22) | C(13) | 122.5(6) |

Table 12-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|--------------|----------------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(1) | 0.0052(61) | C(9) | -0.0014(59) |
| C(2) | -0.0001(70) | C(10) | 0.0066(67) |
| C(3) | -0.0009(72) | C(11) | -0.0063(68) |
| C(4) | -0.0080(74) | C(12) | 0.0009(63) |
| C(5) | 0.0148(72) | C(13) | 0.0011(57) |
| C(6) | -0.0135(72) | C(14) | -0.0020(62) |
| Plane number 3 | | Plane number 4 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(15) | -0.0058(62) | N(1) | 0.0 |
| C(16) | 0.0124(75) | N(2) | 0.0 |
| C(17) | -0.0090(100) | C(8) | 0.0 |
| C(18) | -0.0082(91) | | |
| C(19) | 0.0115(86) | | |
| C(20) | 0.0004(75) | | |
| Plane number 5 | | | |
| Atoms defining plane | Distance | | |
| N(3) | 0.0 | | |
| N(4) | 0.0 | | |
| C(22) | 0.0 | | |
| Summary | plane | mean deviation | CHI ² |
| | 1 | 0.0071 | 9.1 |
| | 2 | 0.0031 | 2.1 |
| | 3 | 0.0079 | 6.8 |
| | 4 | 0.0000 | 0.0 |
| | 5 | 0.0000 | 0.0 |

Dihedral angles between planes (deg)

| plane | 1 | 2 | 3 | 4 |
|-------|--------|--------|--------|--------|
| 2 | 70.60 | | | |
| 3 | 81.45 | 61.08 | | |
| 4 | 117.78 | 139.21 | 154.06 | |
| 5 | 28.64 | 52.78 | 54.13 | 146.39 |

para-Diamidine (10)

| | |
|--|---------------------------------------|
| A. Crystal Data | $C_{42}H_{42}N_4$ |
| Empirical Formula | 342.44 |
| Formula Weight | clear, prism |
| Crystal Color, Habit | 0.45 X 0.30 X 0.08 mm |
| Crystal Dimensions | monoclinic |
| Crystal System | Primitive |
| Lattice Type | 3 oscillations @ 5.0 minutes |
| Indexing Images | 86.33 mm |
| Detector Position | 0.00° |
| Detector Swing Angle | 0.203 mm |
| Pixel Size | a = 7.82(2) Å |
| Lattice Parameters | b = 12.63(3) Å |
| | c = 9.507(5) Å |
| | $\beta = 92.41(9)^\circ$ |
| | V = 938.2 Å ³ |
| | P2 ₁ /c (#14) |
| Space Group | 2 |
| Z value | 1.212 g/cm ³ |
| D _{calc} | 364.00 |
| F ₀₀₀ | 0.74 cm ⁻¹ |
| μ (MoK α) | RAXIS-II |
| B. Intensity Measurements | MoK α ($\lambda = 0.71070$ Å) |
| Diffractometer | graphite monochromated |
| Radiation | 200 mm x 200 mm |
| | 15 exposures @ 5.0 minutes |
| Detector Aperture | 7.0° |
| Data Images | 86.33 mm |
| Oscillation Range | 0.00° |
| Detector Position | 0.203 mm |
| Detector Swing Angle | 54.0° |
| Pixel Size | 0.203 mm |
| $2\theta_{max}$ | Total: 1352 |
| No. of Reflections Measured | Lorentz-polarization |
| Corrections | Absorption |
| | (trans. factors; -0.6420 - 1.7095) |
| C. Structure Solution and Refinement | Direct Methods (SHELXS86) |
| Structure Solution | Full-matrix least-squares |
| Refinement | $\sum w (F_o - F_c)^2$ |
| Function Minimized | $w = 1/[\sigma^2(F_o^2) + P]$ |
| Least Squares Weights | 0.0200 |
| p-factor | All non-hydrogen atoms |
| Anomalous Dispersion | 1007 |
| No. Observations (I > 3.50 σ (I)) | 118 |
| No. Variables | 8.53 |
| Reflection/Parameter Ratio | 0.076 ; 0.091 |
| Residuals; R; Rw | 4.41 |
| Goodness of Fit Indicator | 0.07 |
| Max Shift/Error in Final Cycle | 0.27 e-/Å ³ |
| Maximum peak in Final Diff. Map | -0.32 e-/Å ³ |
| Minimum peak in Final Diff. Map | |

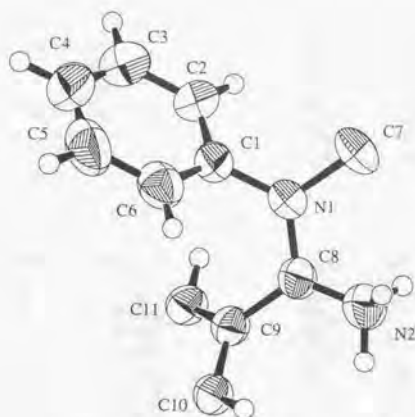


Table 13-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|-----------|------------|----------|
| N(1) | 0.8038(5) | 0.5173(3) | 0.1336(3) | 4.62(9) |
| N(2) | 0.9590(5) | 0.6664(3) | 0.1775(4) | 5.9(1) |
| C(1) | 0.7006(6) | 0.4315(3) | 0.1799(4) | 4.3(1) |
| C(2) | 0.7140(6) | 0.3344(4) | 0.1170(5) | 5.5(1) |
| C(3) | 0.6141(9) | 0.2510(5) | 0.1598(6) | 7.5(2) |
| C(4) | 0.5023(9) | 0.2638(6) | 0.2634(7) | 7.9(2) |
| C(5) | 0.4860(7) | 0.3610(6) | 0.3268(5) | 7.2(2) |
| C(6) | 0.5847(6) | 0.4462(4) | 0.2852(4) | 5.6(1) |
| C(7) | 0.7730(6) | 0.5539(4) | -0.0130(4) | 5.8(1) |
| C(8) | 0.9038(6) | 0.5789(3) | 0.2225(4) | 4.15(10) |
| C(9) | 0.9507(5) | 0.5363(3) | 0.3657(4) | 3.96(9) |
| C(10) | 0.9388(5) | 0.6016(3) | 0.4818(4) | 4.03(10) |
| C(11) | 1.0129(5) | 0.4339(3) | 0.3853(4) | 4.20(10) |

Table 13-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|-----------|-----------|
| N(1) | 0.069(2) | 0.062(2) | 0.044(2) | -0.010(2) | -0.005(2) | 0.005(2) |
| N(2) | 0.105(3) | 0.057(2) | 0.061(2) | -0.005(2) | -0.007(2) | 0.009(2) |
| C(1) | 0.055(3) | 0.058(3) | 0.049(2) | -0.007(2) | -0.002(2) | 0.005(2) |
| C(2) | 0.076(3) | 0.067(3) | 0.066(3) | -0.020(3) | -0.005(2) | -0.004(2) |
| C(3) | 0.116(5) | 0.083(4) | 0.083(4) | -0.033(4) | -0.014(3) | 0.000(3) |
| C(4) | 0.106(5) | 0.109(5) | 0.085(4) | -0.051(4) | -0.016(4) | 0.017(4) |
| C(5) | 0.067(4) | 0.142(6) | 0.065(3) | -0.020(4) | 0.004(2) | 0.024(3) |
| C(6) | 0.059(3) | 0.091(4) | 0.061(3) | -0.002(3) | 0.000(2) | 0.007(2) |
| C(7) | 0.092(4) | 0.089(4) | 0.040(2) | -0.003(3) | -0.010(2) | 0.013(2) |
| C(8) | 0.065(3) | 0.042(2) | 0.050(2) | 0.001(2) | -0.001(2) | 0.005(2) |
| C(9) | 0.056(3) | 0.043(2) | 0.052(2) | -0.001(2) | 0.000(2) | 0.002(2) |
| C(10) | 0.063(3) | 0.039(2) | 0.051(2) | 0.003(2) | -0.002(2) | 0.001(2) |
| C(11) | 0.063(3) | 0.040(2) | 0.056(2) | 0.004(2) | 0.001(2) | -0.004(2) |

Table 13-3. Bond Lengths(Å)

| atom | atom | distance | atom | atom | distance |
|------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.432(5) | N(1) | C(7) | 1.479(5) |
| N(1) | C(8) | 1.369(5) | N(2) | C(8) | 1.268(5) |
| C(1) | C(2) | 1.370(6) | C(1) | C(6) | 1.391(7) |
| C(2) | C(3) | 1.383(7) | C(3) | C(4) | 1.354(9) |
| C(4) | C(5) | 1.377(9) | C(5) | C(6) | 1.391(7) |
| C(8) | C(9) | 1.495(5) | C(9) | C(10) | 1.383(5) |
| C(9) | C(11) | 1.393(5) | C(10) | C(11) | 1.378(5) |

Table 13-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|------|-------|-------|----------|
| C(1) | N(1) | C(7) | 117.1(3) | C(1) | N(1) | C(8) | 123.7(3) |
| C(7) | N(1) | C(8) | 118.0(3) | N(1) | C(1) | C(2) | 119.3(4) |
| N(1) | C(1) | C(6) | 120.9(4) | C(2) | C(1) | C(6) | 119.9(4) |
| C(1) | C(2) | C(3) | 119.9(5) | C(2) | C(3) | C(4) | 120.9(6) |
| C(3) | C(4) | C(5) | 120.0(5) | C(4) | C(5) | C(6) | 120.2(5) |
| C(1) | C(6) | C(5) | 119.2(5) | N(1) | C(8) | N(2) | 118.8(3) |
| N(1) | C(8) | C(9) | 118.0(3) | N(2) | C(8) | C(9) | 123.1(4) |
| C(8) | C(9) | C(10) | 119.4(3) | C(8) | C(9) | C(11) | 121.8(3) |
| C(10) | C(9) | C(11) | 118.8(3) | C(9) | C(10) | C(11) | 120.9(3) |
| C(9) | C(11) | C(10) | 120.3(3) | | | | |

Table 13-5. Least Squares Planes

| Plane number 1 | | Plane number3 | | |
|----------------------|-------------|----------------------|----------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance | |
| C(1) | 0.0028(32) | C(9) | 0.0 | |
| C(2) | -0.0057(38) | C(10) | 0.0 | |
| C(3) | 0.0054(47) | C(11) | 0.0 | |
| C(4) | 0.0023(47) | | | |
| C(5) | -0.0043(43) | | | |
| C(6) | 0.0004(35) | | | |
| Plane number 2 | | Summary | | |
| Atoms defining plane | Distance | plane | mean deviation | CHI ² |
| N(1) | 0.0 | 1 | 0.0035 | 5.2 |
| N(2) | 0.0 | 2 | 0.0000 | 0.0 |
| C(8) | 0.0 | 3 | 0.0000 | 0.0 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|--------|-------|
| 2 | 117.68 | |
| 3 | 118.29 | 47.91 |

cyclic-Triamidine (11)

| | |
|---|--|
| A. Crystal Data | |
| Empirical Formula | $C_{14}H_{16}N_6O$ |
| Formula Weight | 414.51 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.45 X 0.45 X 0.40 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2θ range) | 20 (53.3–56.6°) |
| Omega Scan Peak Width at Half-height | 0.40° |
| Lattice Parameters | $a = 11.521(1) \text{ \AA}$, $b = 10.302(1) \text{ \AA}$ $c = 17.755(1) \text{ \AA}$ $\beta = 93.044(7)^\circ$ $V = 2104.3(4) \text{ \AA}^3$ |
| Space Group | $P2_1/c$ (#14) |
| Z value | 4 |
| D_{calc} | 1.308 g/cm ³ |
| F_{000} | 880.00 |
| $\mu(\text{CuK}\alpha)$ | 6.69 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC7S |
| Radiation | $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated |
| Attenuator | Ni foil (factor = 8.99) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 235 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | $(1.37 + 0.30 \tan \theta)^\circ$ |
| $2\theta_{max}$ | 135.2° |
| No. of Reflections Measured | Total: 4229; Unique: 4020 (Rint = 0.023) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.9224 - 0.9989) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0120 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 1.5\sigma(I)$) | 2646 |
| No. Variables | 280 |
| Reflection/Parameter Ratio | 9.45 |
| Residuals; R; Rw | 0.057; 0.061 |
| Goodness of Fit Indicator | 2.79 |
| Max Shift/Error in Final Cycle | 0.29 |
| Maximum peak in Final Diff. Map | 0.28 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.19 e-/Å ³ |

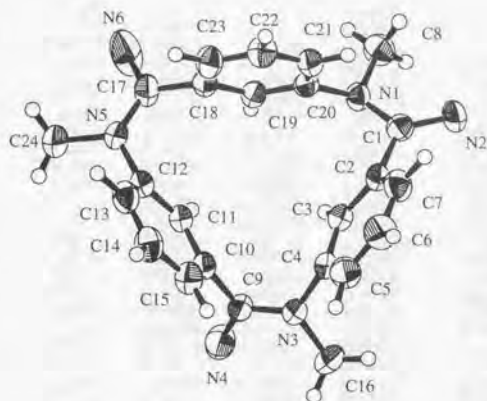


Table 14-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|------------|-----------|----------|
| O(1) | 0.2398(3) | 0.1297(3) | 0.4671(2) | 7.23(10) |
| N(1) | 1.0013(2) | 0.1931(3) | 0.7225(2) | 3.23(6) |
| N(2) | 1.1556(2) | 0.2685(3) | 0.8013(2) | 4.44(8) |
| N(3) | 0.7820(2) | 0.0068(3) | 0.9571(2) | 4.05(7) |
| N(4) | 0.6716(3) | -0.1736(3) | 0.9269(2) | 5.01(9) |
| N(5) | 0.5110(3) | 0.0768(3) | 0.6696(2) | 4.46(8) |
| N(6) | 0.5945(3) | 0.0741(5) | 0.5547(2) | 8.3(1) |
| C(1) | 1.0481(3) | 0.2369(3) | 0.7916(2) | 3.38(8) |
| C(2) | 0.9657(3) | 0.2366(3) | 0.8541(2) | 3.16(8) |
| C(3) | 0.9012(3) | 0.1268(3) | 0.8701(2) | 3.20(8) |
| C(4) | 0.8358(3) | 0.1254(4) | 0.9337(2) | 3.49(8) |
| C(5) | 0.8300(3) | 0.2344(4) | 0.9788(2) | 4.53(10) |
| C(6) | 0.8908(4) | 0.3440(4) | 0.9616(2) | 4.9(1) |
| C(7) | 0.9607(3) | 0.3442(4) | 0.9014(2) | 4.08(9) |
| C(8) | 1.0810(3) | 0.1909(4) | 0.6614(2) | 4.47(10) |
| C(9) | 0.6928(3) | -0.0524(4) | 0.9179(2) | 3.46(8) |
| C(10) | 0.6155(3) | 0.0344(3) | 0.8701(2) | 3.28(8) |
| C(11) | 0.6063(3) | 0.0208(4) | 0.7921(2) | 3.43(8) |
| C(12) | 0.5235(3) | 0.0927(4) | 0.7501(2) | 3.72(8) |
| C(13) | 0.4488(3) | 0.1742(4) | 0.7855(2) | 4.28(9) |
| C(14) | 0.4573(3) | 0.1871(4) | 0.8632(2) | 4.52(10) |
| C(15) | 0.5419(3) | 0.1187(4) | 0.9055(2) | 4.20(9) |
| C(16) | 0.8478(3) | -0.0685(4) | 1.0147(2) | 5.2(1) |
| C(17) | 0.5961(3) | 0.1085(4) | 0.6236(2) | 3.97(9) |
| C(18) | 0.6897(3) | 0.1972(4) | 0.6557(2) | 3.30(8) |
| C(19) | 0.8011(3) | 0.1521(3) | 0.6748(2) | 3.14(8) |
| C(20) | 0.8858(3) | 0.2383(3) | 0.7010(2) | 3.01(7) |
| C(21) | 0.8611(3) | 0.3698(4) | 0.7059(2) | 3.53(8) |
| C(22) | 0.7513(3) | 0.4145(4) | 0.6871(2) | 4.05(9) |
| C(23) | 0.6652(3) | 0.3283(4) | 0.6621(2) | 4.13(9) |
| C(24) | 0.4078(3) | 0.0069(4) | 0.6397(2) | 5.4(1) |

Table 14-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|----------|----------|-----------|-----------|-----------|
| O(1) | 0.114(3) | 0.075(2) | 0.081(2) | -0.003(2) | -0.029(2) | 0.001(2) |
| N(1) | 0.031(1) | 0.048(2) | 0.044(2) | 0.001(1) | 0.002(1) | -0.002(1) |
| N(2) | -0.030(2) | 0.068(2) | 0.069(2) | -0.006(2) | -0.002(1) | 0.010(2) |
| N(3) | 0.045(2) | 0.062(2) | 0.045(2) | -0.013(2) | -0.009(1) | 0.016(2) |
| N(4) | 0.065(2) | 0.048(2) | 0.075(2) | -0.005(2) | -0.015(2) | 0.009(2) |
| N(5) | 0.046(2) | 0.075(2) | 0.046(2) | -0.020(2) | -0.014(1) | 0.012(2) |
| N(6) | 0.079(3) | 0.169(5) | 0.070(3) | -0.054(3) | 0.024(2) | -0.061(3) |
| C(1) | 0.040(2) | 0.040(2) | 0.048(2) | 0.004(2) | -0.001(2) | 0.006(2) |
| C(2) | 0.031(2) | 0.044(2) | 0.044(2) | -0.002(2) | -0.004(1) | 0.004(2) |
| C(3) | 0.037(2) | 0.043(2) | 0.040(2) | 0.002(2) | -0.003(2) | 0.000(2) |
| C(4) | 0.035(2) | 0.055(2) | 0.042(2) | -0.006(2) | -0.005(2) | 0.006(2) |
| C(5) | 0.056(2) | 0.072(3) | 0.045(2) | -0.005(2) | 0.009(2) | -0.011(2) |
| C(6) | 0.067(3) | 0.057(3) | 0.060(3) | -0.003(2) | 0.007(2) | -0.017(2) |
| C(7) | 0.049(2) | 0.046(2) | 0.059(2) | -0.007(2) | -0.002(2) | -0.002(2) |
| C(8) | 0.046(2) | 0.068(3) | 0.057(2) | 0.004(2) | 0.012(2) | -0.003(2) |
| C(9) | 0.037(2) | 0.055(2) | 0.039(2) | 0.000(2) | -0.002(2) | 0.002(2) |
| C(10) | 0.034(2) | 0.044(2) | 0.046(2) | -0.006(2) | -0.003(2) | 0.001(2) |
| C(11) | 0.035(2) | 0.048(2) | 0.046(2) | -0.007(2) | -0.002(2) | 0.002(2) |
| C(12) | 0.039(2) | 0.053(2) | 0.048(2) | -0.014(2) | -0.005(2) | 0.010(2) |
| C(13) | 0.039(2) | 0.049(2) | 0.074(3) | 0.000(2) | -0.005(2) | 0.011(2) |
| C(14) | 0.045(2) | 0.053(3) | 0.074(3) | 0.003(2) | 0.002(2) | -0.007(2) |
| C(15) | 0.048(2) | 0.056(3) | 0.055(2) | -0.002(2) | -0.001(2) | -0.007(2) |
| C(16) | 0.066(3) | 0.077(3) | 0.053(3) | -0.009(2) | -0.020(2) | 0.021(2) |
| C(17) | 0.036(2) | 0.060(3) | 0.054(2) | -0.003(2) | -0.003(2) | -0.006(2) |
| C(18) | 0.036(2) | 0.053(2) | 0.036(2) | -0.002(2) | 0.004(1) | -0.005(2) |
| C(19) | 0.038(2) | 0.043(2) | 0.038(2) | 0.001(2) | 0.000(1) | -0.002(2) |
| C(20) | 0.034(2) | 0.044(2) | 0.037(2) | 0.002(2) | 0.003(1) | 0.003(2) |
| C(21) | 0.041(2) | 0.045(2) | 0.048(2) | -0.005(2) | -0.001(2) | 0.000(2) |
| C(22) | 0.049(2) | 0.044(2) | 0.061(2) | 0.008(2) | 0.001(2) | -0.002(2) |
| C(23) | 0.036(2) | 0.059(3) | 0.062(2) | 0.009(2) | 0.001(2) | -0.001(2) |
| C(24) | 0.055(2) | 0.081(3) | 0.066(3) | -0.024(2) | -0.017(2) | 0.011(2) |

Table 14-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(1) | 1.390(4) | N(1) | C(8) | 1.458(4) |
| N(1) | C(20) | 1.442(4) | N(2) | C(1) | 1.283(4) |
| N(3) | C(4) | 1.441(4) | N(3) | C(9) | 1.355(4) |
| N(3) | C(16) | 1.463(4) | N(4) | C(9) | 1.284(4) |
| N(5) | C(12) | 1.439(4) | N(5) | C(17) | 1.348(4) |
| N(5) | C(24) | 1.465(4) | N(6) | C(17) | 1.273(5) |
| C(1) | C(2) | 1.498(5) | C(2) | C(3) | 1.391(4) |
| C(2) | C(7) | 1.393(5) | C(3) | C(4) | 1.391(4) |
| C(4) | C(5) | 1.383(5) | C(5) | C(6) | 1.371(5) |
| C(6) | C(7) | 1.373(5) | C(9) | C(10) | 1.495(4) |
| C(10) | C(11) | 1.389(4) | C(10) | C(15) | 1.387(5) |
| C(11) | C(12) | 1.393(4) | C(12) | C(13) | 1.377(5) |
| C(13) | C(14) | 1.385(5) | C(14) | C(15) | 1.391(5) |
| C(17) | C(18) | 1.503(5) | C(18) | C(19) | 1.390(4) |
| C(18) | C(23) | 1.386(5) | C(19) | C(20) | 1.382(4) |
| C(20) | C(21) | 1.388(5) | C(21) | C(22) | 1.370(4) |
| C(22) | C(23) | 1.387(5) | | | |

Table 14-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|------|-------|----------|-------|------|-------|----------|
| C(1) | N(1) | C(8) | 115.6(3) | C(1) | N(1) | C(20) | 116.0(3) |
| C(8) | N(1) | C(20) | 114.6(3) | C(4) | N(3) | C(9) | 124.1(3) |
| C(4) | N(3) | C(16) | 115.8(3) | C(9) | N(3) | C(16) | 118.1(3) |
| C(12) | N(5) | C(17) | 122.4(3) | C(12) | N(5) | C(24) | 116.9(3) |
| C(17) | N(5) | C(24) | 120.1(3) | N(1) | C(1) | N(2) | 121.8(3) |
| N(1) | C(1) | C(2) | 114.9(3) | N(2) | C(1) | C(2) | 123.1(3) |

Table 14-4. Bond Angles (deg) (Continued)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | C(2) | C(3) | 121.3(3) | C(1) | C(2) | C(7) | 119.5(3) |
| C(3) | C(2) | C(7) | 119.0(3) | C(2) | C(3) | C(4) | 119.5(3) |
| N(3) | C(4) | C(3) | 120.2(3) | N(3) | C(4) | C(5) | 119.2(3) |
| C(3) | C(4) | C(5) | 120.4(3) | C(4) | C(5) | C(6) | 119.9(3) |
| C(5) | C(6) | C(7) | 120.2(4) | C(2) | C(7) | C(6) | 120.8(4) |
| N(3) | C(9) | N(4) | 121.2(3) | N(3) | C(9) | C(10) | 115.8(3) |
| N(4) | C(9) | C(10) | 122.8(3) | C(9) | C(10) | C(11) | 121.2(3) |
| C(9) | C(10) | C(15) | 118.5(3) | C(11) | C(10) | C(15) | 119.9(3) |
| C(10) | C(11) | C(12) | 119.6(3) | N(5) | C(12) | C(11) | 120.1(4) |
| N(5) | C(12) | C(13) | 119.4(3) | C(11) | C(12) | C(13) | 120.4(4) |
| C(12) | C(13) | C(14) | 120.1(3) | C(13) | C(14) | C(15) | 119.9(4) |
| C(10) | C(15) | C(14) | 120.0(4) | N(5) | C(17) | N(6) | 122.8(4) |
| N(5) | C(17) | C(18) | 116.6(3) | N(6) | C(17) | C(18) | 120.4(4) |
| C(17) | C(18) | C(19) | 121.6(3) | C(17) | C(18) | C(23) | 118.6(3) |
| C(19) | C(18) | C(23) | 119.7(3) | C(18) | C(19) | C(20) | 119.6(3) |
| N(1) | C(20) | C(19) | 120.5(3) | N(1) | C(20) | C(21) | 119.2(3) |
| C(19) | C(20) | C(21) | 120.3(3) | C(20) | C(21) | C(22) | 120.2(3) |
| C(21) | C(22) | C(23) | 119.9(3) | C(18) | C(23) | C(22) | 120.3(3) |

Table 14-5. Least Squares Planes

| Plane number 1 | | | Plane number 2 | | |
|----------------------|-----------|----------------|----------------------|-----------|--|
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(2) | 0.002(3) | | C(10) | -0.003(3) | |
| C(3) | -0.015(3) | | C(11) | -0.007(3) | |
| C(4) | 0.016(3) | | C(12) | 0.011(3) | |
| C(5) | 0.000(4) | | C(13) | -0.004(4) | |
| C(6) | -0.025(4) | | C(14) | -0.009(4) | |
| C(7) | 0.018(4) | | C(15) | 0.013(4) | |
| Plane number 3 | | | Plane number 4 | | |
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| C(18) | 0.000(3) | | N(1) | 0.0 | |
| C(19) | 0.007(3) | | C(1) | 0.0 | |
| C(20) | -0.010(3) | | N(2) | 0.0 | |
| C(21) | 0.009(4) | | | | |
| C(22) | 0.001(4) | | | | |
| C(23) | -0.006(4) | | | | |
| Plane number 5 | | | Plane number 6 | | |
| Atoms defining plane | Distance | | Atoms defining plane | Distance | |
| N(3) | 0.0 | | N(5) | 0.0 | |
| N(4) | 0.0 | | N(6) | 0.0 | |
| C(9) | 0.0 | | C(17) | 0.0 | |
| Summary | plane | mean deviation | CHI ² | | |
| | 1 | 0.0128 | 103.0 | | |
| | 2 | 0.0079 | 32.7 | | |
| | 3 | 0.0055 | 21.1 | | |
| | 4 | 0.0000 | 0.0 | | |
| | 5 | 0.0000 | 0.0 | | |
| | 6 | 0.0000 | 0.0 | | |

Dihedral angles between planes (deg)

| plane | 1 | 2 | 3 | 4 | 5 |
|-------|--------|--------|--------|--------|-------|
| 2 | 79.31 | | | | |
| 3 | 110.35 | 66.98 | | | |
| 4 | 50.76 | 126.02 | 108.42 | | |
| 5 | 98.76 | 108.80 | 148.58 | 98.93 | |
| 6 | 142.56 | 70.24 | 77.51 | 163.71 | 72.12 |

N,N'-Diphenylthiourea (12)

| | |
|--|--|
| A. Crystal Data | $C_{12}H_{12}N_2S$ |
| Empirical Formula | 228.31 |
| Formula Weight | colorless, prismatic |
| Crystal Color, Habit | 0.30 X 0.05 X 0.48 mm |
| Crystal Dimensions | orthorhombic |
| Crystal System | Primitive |
| Lattice Type | |
| No. of Reflections Used for Unit | 16 (44.1 - 49.1°) |
| Cell Determination (2 θ range) | 0.28° |
| Omega Scan Peak Width at Half-height | $a = 7.946(2) \text{ \AA}$ |
| Lattice Parameters | $b = 25.588(4) \text{ \AA}$ |
| | $c = 5.689(1) \text{ \AA}$ |
| | $V = 1156.7(4) \text{ \AA}^3$ |
| | Pnma (#62) |
| Space Group | 4 |
| Z value | 1.311 g/cm ³ |
| D_{calc} | 480.00 |
| $F_{(0)}$ | 22.44 cm ⁻¹ |
| $\mu(\text{CuK}\alpha)$ | |
| B. Intensity Measurements | Rigaku AFC5S |
| Diffractometer | CuK α ($\lambda = 1.54178 \text{ \AA}$) |
| Radiation | graphite monochromated |
| | Ni foil (factors = 1.00, 3.57, 12.70, 45.11) |
| Attenuator | 6.0° |
| Take-off Angle | 9.0 mm horizontal |
| Detector Aperture | 13.0 mm vertical |
| | 258 mm |
| Crystal to Detector Distance | 23.0°C |
| Temperature | ω -2 θ |
| Scan Type | 32.0°/min (in ω) (up to 3 scans) |
| Scan Rate | (1.47 + 0.30 tan θ)° |
| Scan Width | 119.9° |
| $2\theta_{\text{max}}$ | Total: 1062 |
| No. of Reflections Measured | Lorentz-polarization |
| Corrections | Absorption |
| | (trans. factors: 0.6742 - 1.2281) |
| C. Structure Solution and Refinement | Direct Methods (SHELXS-86) |
| Structure Solution | Full-matrix least-squares |
| Refinement | $\sum w (F_o - F_c)^2$ |
| Function Minimized | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| Least Squares Weights | 0.0070 |
| p-factor | All non-hydrogen atoms |
| Anomalous Dispersion | 641 |
| No. Observations ($I > 3.00\sigma(I)$) | 100 |
| No. Variables | 6.41 |
| Reflection/Parameter Ratio | 0.062 ; 0.065 |
| Residuals: R; Rw | 3.81 |
| Goodness of Fit Indicator | 1.89 |
| Max Shift/Error in Final Cycle | 0.45 e-/Å ³ |
| Maximum peak in Final Diff. Map | -0.39 e-/Å ³ |
| Minimum peak in Final Diff. Map | |

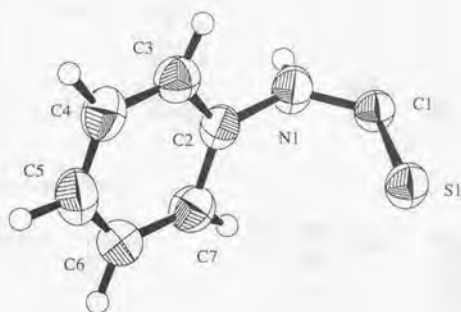


Table 15-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|------|------------|-----------|-----------|---------|
| S(1) | 0.0860(3) | 0.7500 | 0.1128(4) | 4.02(5) |
| N(1) | 0.3103(8) | 0.7064(2) | -0.168(1) | 4.4(1) |
| C(1) | 0.2459(10) | 0.7500 | -0.085(2) | 3.3(2) |
| C(2) | 0.2667(8) | 0.6542(2) | -0.103(1) | 3.7(1) |
| C(3) | 0.1762(10) | 0.6241(2) | -0.260(1) | 4.3(2) |
| C(4) | 0.1346(9) | 0.5722(2) | -0.203(1) | 4.7(2) |
| C(5) | 0.1848(10) | 0.5526(3) | 0.013(1) | 5.1(2) |
| C(6) | 0.2763(10) | 0.5829(3) | 0.165(1) | 4.7(2) |
| C(7) | 0.3154(9) | 0.6341(2) | 0.110(1) | 4.3(2) |

Table 15-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|------|----------|----------|----------|-----------|-----------|-----------|
| S(1) | 0.051(1) | 0.048(1) | 0.054(1) | 0.0000 | 0.015(1) | 0.0000 |
| N(1) | 0.064(4) | 0.041(3) | 0.062(4) | -0.002(3) | 0.029(4) | 0.001(3) |
| C(1) | 0.039(5) | 0.042(4) | 0.045(5) | 0.0000 | 0.010(5) | 0.0000 |
| C(2) | 0.047(4) | 0.042(3) | 0.049(4) | -0.001(3) | 0.005(4) | -0.004(3) |
| C(3) | 0.051(4) | 0.059(4) | 0.054(4) | 0.005(4) | 0.002(4) | -0.002(4) |
| C(4) | 0.053(5) | 0.054(4) | 0.073(6) | 0.001(4) | -0.005(4) | -0.012(4) |
| C(5) | 0.065(5) | 0.046(4) | 0.082(5) | 0.003(4) | 0.016(5) | 0.003(4) |
| C(6) | 0.072(5) | 0.052(4) | 0.054(5) | 0.004(4) | 0.002(4) | 0.002(4) |
| C(7) | 0.061(5) | 0.052(4) | 0.051(4) | -0.007(4) | -0.007(4) | -0.007(4) |

Table 15-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|------|------|----------|------|------|----------|
| S(1) | C(1) | 1.696(8) | N(1) | C(1) | 1.315(7) |
| N(1) | C(2) | 1.428(8) | C(2) | C(3) | 1.381(8) |
| C(2) | C(7) | 1.375(9) | C(3) | C(4) | 1.405(8) |
| C(4) | C(5) | 1.388(9) | C(5) | C(6) | 1.370(9) |
| C(6) | C(7) | 1.383(8) | | | |

Table 15-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|------|------|------|----------|------|------|------|----------|
| C(1) | N(1) | C(2) | 127.2(6) | S(1) | C(1) | N(1) | 122.1(4) |
| S(1) | C(1) | N(1) | 122.1(4) | N(1) | C(1) | N(1) | 115.9(8) |
| N(1) | C(2) | C(3) | 118.9(6) | N(1) | C(2) | C(7) | 120.7(6) |
| C(3) | C(2) | C(7) | 120.5(6) | C(2) | C(3) | C(4) | 120.2(7) |
| C(3) | C(4) | C(5) | 118.5(7) | C(4) | C(5) | C(6) | 120.4(7) |
| C(5) | C(6) | C(7) | 121.0(7) | C(2) | C(7) | C(6) | 119.3(7) |

Table 15-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-----------|----------------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| S(1) | 0.0 | C(2) | 0.002(6) |
| N(1) | 0.0 | C(3) | -0.001(7) |
| C(1) | 0.0 | C(4) | 0.002(7) |
| | | C(5) | -0.008(7) |
| | | C(6) | 0.011(7) |
| C(7) | -0.008(7) | | |
| Summary | plane | mean deviation | CHI ² |
| | 1 | 0.0000 | 0.0 |
| | 2 | 0.0053 | 4.6 |

Dihedral angles between planes (deg): 105.10

N,N'-Dimethyl-*N,N'*-diphenylthiourea (13)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{15}H_{14}N_2S$ |
| Formula Weight | 256.36 |
| Crystal Color, Habit | clear, prismatic |
| Crystal Dimensions | 0.30 X 0.30 X 0.30 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2θ range) | $0^\circ (0.0 - 0.0^\circ)$ |
| Omega Scan Peak Width at Half-height | 0.00° |
| Lattice Parameters | $a = 15.911(7) \text{ \AA}$ $b = 11.611(3) \text{ \AA}$ $c = 7.539(7) \text{ \AA}$ $\beta = 96.93(1)^\circ$ $V = 1382(1) \text{ \AA}^3$ |
| Space Group | $P2_1/n$ (#14) |
| Z value | 4 |
| D_{calc} | 1.232 g/cm^3 |
| F_{000} | 544.00 |
| $\mu(\text{CuK}\alpha)$ | 19.30 cm^{-1} |
| B. Intensity Measurements | |
| Diffractionmeter | Rigaku AFC5S |
| Radiation | $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated |
| Take-off Angle | 2.8° |
| Detector Aperture | 2.0 - 2.5 mm horizontal 2.0 mm vertical |
| Crystal to Detector Distance | 21 mm |
| Temperature | 0.0°C |
| Scan Type | ω |
| Scan Rate | $0.0^\circ/\text{min}$ (in ω) (up to 0 scans) |
| Scan Width | $(0.00 + 0.00 \tan \theta)^\circ$ |
| $2\theta_{\text{max}}$ | 120.3° |
| No. of Reflections Measured | Total: 2371; Unique: 2189 (Rint = 0.026) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.9077 - 1.2880) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0400 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 1848 |
| No. Variables | 227 |
| Reflection/Parameter Ratio | 8.14 |
| Residuals: R; Rw | 0.049; 0.054 |
| Goodness of Fit Indicator | 4.71 |
| Max Shift/Error in Final Cycle | 6.73 |
| Maximum peak in Final Diff. Map | $0.25 \text{ e}/\text{\AA}^3$ |
| Minimum peak in Final Diff. Map | $-0.31 \text{ e}/\text{\AA}^3$ |

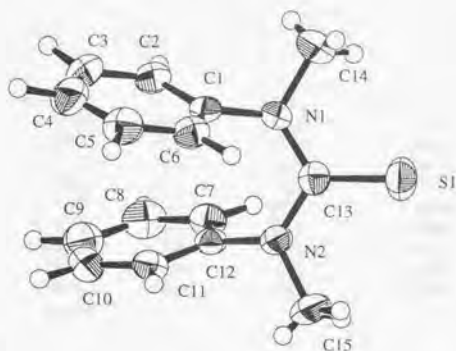


Table 16-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-------------|-------------|------------|---------|
| S(1) | -0.56387(5) | -0.82879(8) | -0.1970(1) | 4.76(2) |
| N(1) | -0.4461(1) | -0.6948(2) | -0.3104(3) | 3.03(5) |
| N(2) | -0.4157(1) | -0.8895(2) | -0.2950(3) | 3.15(6) |
| C(1) | -0.4029(2) | -0.6733(2) | -0.4636(3) | 2.70(6) |
| C(2) | -0.3317(2) | -0.6054(3) | -0.4515(4) | 3.45(7) |
| C(3) | -0.2916(2) | -0.5858(3) | -0.6011(5) | 4.44(9) |
| C(4) | -0.3228(3) | -0.6334(3) | -0.7627(5) | 4.86(9) |
| C(5) | -0.3953(2) | -0.6997(3) | -0.7772(4) | 4.21(8) |
| C(6) | -0.4357(2) | -0.7195(3) | -0.6272(4) | 3.38(7) |
| C(7) | -0.2772(2) | -0.8227(3) | -0.1591(4) | 3.56(7) |
| C(8) | -0.1931(2) | -0.8004(3) | -0.1699(5) | 4.31(8) |
| C(9) | -0.1586(2) | -0.8261(3) | -0.3241(5) | 4.51(9) |
| C(10) | -0.2076(2) | -0.8768(3) | -0.4658(5) | 4.03(8) |
| C(11) | -0.2914(2) | -0.8999(2) | -0.4550(4) | 3.32(7) |
| C(12) | -0.3275(2) | -0.8696(2) | -0.3035(4) | 2.75(6) |
| C(13) | -0.4712(2) | -0.8035(2) | -0.2699(3) | 2.95(6) |
| C(14) | -0.4942(3) | -0.5959(4) | -0.2552(6) | 4.7(1) |
| C(15) | -0.4399(3) | -1.0098(3) | -0.2719(8) | 4.9(1) |

Table 16-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| S(1) | 0.0455(5) | 0.0705(6) | 0.0686(6) | 0.0003(4) | 0.0222(4) | 0.0115(5) |
| N(1) | 0.042(1) | 0.030(1) | 0.045(1) | 0.007(1) | 0.012(1) | 0.001(1) |
| N(2) | 0.036(1) | 0.030(1) | 0.055(2) | -0.001(1) | 0.007(1) | 0.004(1) |
| C(1) | 0.037(2) | 0.025(1) | 0.040(2) | 0.006(1) | 0.004(1) | 0.005(1) |
| C(2) | 0.049(2) | 0.033(2) | 0.049(2) | -0.005(1) | 0.004(2) | -0.004(1) |
| C(3) | 0.061(2) | 0.038(2) | 0.073(2) | -0.014(2) | 0.019(2) | 0.000(2) |
| C(4) | 0.086(3) | 0.049(2) | 0.055(2) | -0.001(2) | 0.028(2) | 0.008(2) |
| C(5) | 0.068(2) | 0.051(2) | 0.040(2) | 0.004(2) | 0.003(2) | 0.003(2) |
| C(6) | 0.041(2) | 0.039(2) | 0.047(2) | 0.000(1) | -0.004(1) | 0.003(1) |
| C(7) | 0.049(2) | 0.041(2) | 0.044(2) | 0.004(2) | 0.002(2) | 0.000(1) |
| C(8) | 0.049(2) | 0.050(2) | 0.060(2) | -0.002(2) | -0.015(2) | -0.003(2) |
| C(9) | 0.039(2) | 0.051(2) | 0.080(3) | 0.001(2) | 0.001(2) | 0.003(2) |
| C(10) | 0.046(2) | 0.048(2) | 0.060(2) | 0.005(2) | 0.013(2) | -0.003(2) |
| C(11) | 0.040(2) | 0.035(2) | 0.049(2) | 0.003(1) | 0.001(1) | -0.005(1) |
| C(12) | 0.035(2) | 0.025(2) | 0.044(2) | 0.004(1) | 0.003(1) | 0.004(1) |

Table 16-2. Anisotropic Displacement Parameters (Continued)

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|----------|----------|----------|-----------|----------|-----------|
| C(13) | 0.038(2) | 0.042(2) | 0.032(1) | 0.000(1) | 0.003(1) | 0.002(1) |
| C(14) | 0.066(3) | 0.046(2) | 0.070(3) | 0.015(2) | 0.024(2) | -0.004(2) |
| C(15) | 0.062(3) | 0.032(2) | 0.095(4) | -0.007(2) | 0.018(3) | 0.008(2) |

Table 16-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| S(1) | C(13) | 1.660(3) | N(1) | C(1) | 1.434(3) |
| N(1) | C(13) | 1.370(4) | N(1) | C(14) | 1.468(4) |
| N(2) | C(12) | 1.432(3) | N(2) | C(13) | 1.361(4) |
| N(2) | C(15) | 1.465(4) | C(1) | C(2) | 1.375(4) |
| C(1) | C(6) | 1.387(4) | C(2) | C(3) | 1.380(4) |
| C(3) | C(4) | 1.375(5) | C(4) | C(5) | 1.380(5) |
| C(5) | C(6) | 1.386(4) | C(7) | C(8) | 1.375(4) |
| C(7) | C(12) | 1.383(4) | C(8) | C(9) | 1.376(5) |
| C(9) | C(10) | 1.377(5) | C(10) | C(11) | 1.372(4) |
| C(11) | C(12) | 1.384(4) | | | |

Table 16-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(1) | C(13) | 121.4(2) | C(1) | N(1) | C(14) | 114.2(3) |
| C(13) | N(1) | C(14) | 118.7(3) | C(12) | N(2) | C(13) | 123.0(2) |
| C(12) | N(2) | C(15) | 115.6(3) | C(13) | N(2) | C(15) | 119.9(3) |
| N(1) | C(1) | C(2) | 121.1(3) | N(1) | C(1) | C(6) | 118.9(3) |
| C(2) | C(1) | C(6) | 120.0(3) | C(1) | C(2) | C(3) | 119.9(3) |
| C(2) | C(3) | C(4) | 120.3(3) | C(3) | C(4) | C(5) | 120.2(3) |
| C(4) | C(5) | C(6) | 119.6(3) | C(1) | C(6) | C(5) | 120.0(3) |
| C(8) | C(7) | C(12) | 120.2(3) | C(7) | C(8) | C(9) | 119.9(3) |
| C(8) | C(9) | C(10) | 120.2(3) | C(9) | C(10) | C(11) | 120.0(3) |
| C(10) | C(11) | C(12) | 120.2(3) | N(2) | C(12) | C(7) | 120.4(3) |
| N(2) | C(12) | C(11) | 120.1(3) | C(7) | C(12) | C(11) | 119.4(3) |
| S(1) | C(13) | N(1) | 122.1(2) | S(1) | C(13) | N(2) | 122.2(2) |
| N(1) | C(13) | N(2) | 115.6(3) | | | | |

Table 16-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|----------------|----------------------|-------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(1) | -0.0087(26) | C(7) | -0.0135(31) |
| C(2) | 0.0075(32) | C(8) | -0.0069(35) |
| C(3) | 0.0036(36) | C(9) | 0.0170(35) |
| C(4) | -0.0101(37) | C(10) | -0.0019(34) |
| C(5) | 0.0025(34) | C(11) | -0.0174(30) |
| C(6) | 0.0070(30) | C(12) | 0.0191(27) |
| Plane number 3 | | | |
| Atoms defining plane | Distance | | |
| N(1) | 0.0012(24) | | |
| N(2) | 0.0012(24) | | |
| S(1) | 0.0001(10) | | |
| C(13) | -0.0040(27) | | |
| Summary | | CHI ² | |
| plane | mean deviation | 1 | 30.4 |
| 2 | 0.0066 | 2 | 126.1 |
| 3 | 0.0126 | 3 | 2.5 |
| | 0.0016 | | |

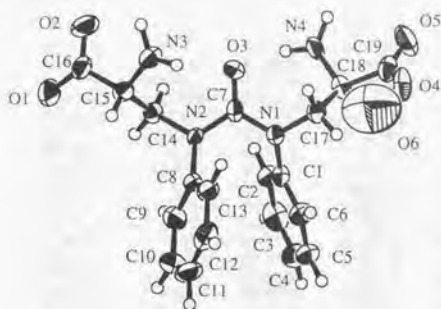
Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|-------|
| 2 | 22.96 | |
| 3 | 74.27 | 72.19 |

(±)-N,N'-Bis(β-alanyl)-N,N'-diphenylurea (14)

| | |
|--------------------------------------|---|
| A. Crystal Data | |
| Empirical Formula | $C_{16}H_{22}N_2O_5$ |
| Formula Weight | 386.41 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.30 X 0.30 X 0.10 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2θ range) | 20 (33.8 - 36.1°) |
| Omega Scan Peak Width at Half-height | 0.12° |
| Lattice Parameters | a = 15.820(2) Å b = 24.639(2) Å c = 11.732(1) Å V = 4573.1(9) Å ³ |
| Space Group | Pbca (#61) |
| Z value | 8 |
| D _{calc} | 1.122 g/cm ³ |
| F ₀₀₀ | 1632.00 |
| μ(CuKα) | 6.90 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuKα (λ = 1.54178 Å) graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 2.37, 6.13, 15.65) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω-2θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.10 + 0.30 tan θ)° |
| 2θ _{max} | 135.2° |
| No. of Reflections Measured | Total: 4554 |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.8489 - 0.9992) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/(\sigma^2(F_o^2) + P^2 + P)$ |
| p-factor | 0.020 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 2.00σ(I)) | 1784 |
| No. Variables | 290 |
| Reflection/Parameter Ratio | 6.15 |
| Residuals: R; Rw | 0.084 ; 0.081 |
| Goodness of Fit Indicator | 2.39 |
| Max Shift/Error in Final Cycle | 0.17 |
| Maximum peak in Final Diff. Map | 0.42 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.38 e-/Å ³ |

Appendix



O7

Table 17-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|-----------|-----------|------------|---------|
| O(1) | 0.9375(5) | 0.0966(3) | -0.2892(6) | 6.5(2) |
| O(2) | 0.8712(5) | 0.0207(3) | -0.2503(6) | 5.3(2) |
| O(3) | 0.7261(4) | 0.0647(2) | 0.0674(5) | 3.4(2) |
| O(4) | 0.5447(4) | 0.0745(3) | 0.4191(6) | 5.2(2) |
| O(5) | 0.4417(5) | 0.0471(3) | 0.3029(6) | 5.9(2) |
| O(6) | 0.713(1) | 0.0694(6) | 0.524(1) | 22.0(7) |
| O(7) | 0.3897(5) | 0.4368(4) | 0.5157(6) | 8.1(3) |
| O(8) | 0.0906(4) | 0.0934(3) | 0.6047(5) | 4.7(2) |
| O(9) | 0.1899(5) | 0.0146(4) | 0.7231(9) | 11.9(4) |
| N(1) | 0.6878(4) | 0.1431(3) | 0.1575(6) | 2.8(2) |
| N(2) | 0.7914(4) | 0.1441(3) | 0.0145(6) | 2.5(2) |
| N(3) | 0.8772(5) | 0.0360(3) | -0.0253(6) | 3.6(2) |
| N(4) | 0.5488(5) | 0.0586(3) | 0.1232(6) | 3.6(2) |
| C(1) | 0.6642(5) | 0.1988(4) | 0.1452(7) | 2.8(2) |
| C(2) | 0.6222(6) | 0.2152(4) | 0.0485(8) | 3.6(3) |
| C(3) | 0.5958(7) | 0.2693(5) | 0.0383(9) | 4.9(3) |
| C(4) | 0.6115(7) | 0.3060(4) | 0.125(1) | 5.3(3) |
| C(5) | 0.6531(7) | 0.2886(4) | 0.2204(9) | 4.4(3) |
| C(6) | 0.6790(6) | 0.2347(4) | 0.2313(8) | 3.8(3) |
| C(7) | 0.7339(5) | 0.1142(4) | 0.0782(7) | 2.8(2) |
| C(8) | 0.8363(6) | 0.1893(4) | 0.0606(8) | 2.9(2) |
| C(9) | 0.8388(6) | 0.2379(4) | 0.0025(9) | 4.0(3) |
| C(10) | 0.8842(7) | 0.2814(4) | 0.051(1) | 5.3(3) |
| C(11) | 0.9236(7) | 0.2762(5) | 0.155(1) | 5.1(3) |
| C(12) | 0.9205(7) | 0.2270(5) | 0.2105(9) | 4.9(3) |
| C(13) | 0.8769(6) | 0.1829(4) | 0.1642(8) | 3.4(2) |
| C(14) | 0.8139(5) | 0.1222(3) | -0.0980(7) | 2.7(2) |
| C(15) | 0.8908(5) | 0.0840(4) | -0.1002(7) | 3.1(2) |
| C(16) | 0.9018(6) | 0.0645(4) | -0.2244(8) | 3.5(2) |
| C(17) | 0.6466(6) | 0.1116(4) | 0.2483(8) | 3.3(2) |
| C(18) | 0.5554(6) | 0.0963(4) | 0.2206(8) | 3.3(2) |
| C(19) | 0.5100(7) | 0.0695(4) | 0.3247(9) | 3.9(3) |

Table 17-2. Anisotropic Displacement Parameters

| atom | U ₁₁ | U ₂₂ | U ₃₃ | U ₁₂ | U ₁₃ | U ₂₃ |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| O(1) | 0.119(7) | 0.056(5) | 0.071(5) | 0.004(5) | 0.050(5) | 0.008(4) |
| O(2) | 0.109(6) | 0.047(4) | 0.045(4) | -0.009(5) | 0.006(4) | -0.017(4) |
| O(3) | 0.041(4) | 0.035(4) | 0.052(4) | -0.009(3) | 0.007(3) | -0.004(4) |
| O(4) | 0.060(5) | 0.098(6) | 0.041(4) | 0.010(5) | 0.021(4) | 0.019(5) |
| O(5) | 0.056(5) | 0.092(6) | 0.074(6) | -0.028(5) | 0.018(5) | 0.009(5) |
| O(6) | 0.29(2) | 0.24(2) | 0.31(2) | -0.02(2) | -0.03(2) | -0.03(2) |
| O(7) | 0.068(5) | 0.172(9) | 0.068(5) | 0.015(6) | -0.016(5) | -0.023(6) |
| O(8) | 0.061(5) | 0.074(5) | 0.045(4) | -0.006(4) | 0.005(4) | -0.001(4) |
| O(9) | 0.078(6) | 0.172(10) | 0.20(1) | -0.030(7) | -0.023(7) | 0.132(9) |
| N(1) | 0.040(5) | 0.035(5) | 0.032(4) | 0.000(4) | 0.008(4) | 0.002(4) |
| N(2) | 0.030(4) | 0.036(5) | 0.028(4) | -0.006(4) | 0.007(4) | -0.012(4) |
| N(3) | 0.062(6) | 0.039(5) | 0.035(4) | 0.008(5) | 0.000(4) | -0.003(4) |
| N(4) | 0.052(5) | 0.054(6) | 0.029(4) | -0.022(4) | 0.011(4) | 0.002(4) |
| C(1) | 0.032(5) | 0.041(6) | 0.032(5) | 0.003(5) | 0.006(5) | 0.002(5) |
| C(2) | 0.048(6) | 0.042(6) | 0.048(6) | -0.002(6) | 0.005(6) | -0.010(5) |
| C(3) | 0.053(7) | 0.073(9) | 0.062(8) | 0.002(7) | -0.001(6) | 0.015(7) |
| C(4) | 0.069(8) | 0.046(7) | 0.086(9) | 0.007(7) | 0.011(8) | -0.007(7) |
| C(5) | 0.060(7) | 0.048(7) | 0.060(8) | -0.010(6) | 0.009(6) | -0.021(6) |
| C(6) | 0.055(7) | 0.047(6) | 0.043(6) | -0.001(5) | -0.002(6) | -0.010(6) |
| C(7) | 0.028(5) | 0.051(6) | 0.026(5) | -0.003(5) | 0.003(5) | -0.002(5) |
| C(8) | 0.035(5) | 0.033(5) | 0.042(6) | -0.005(5) | 0.009(5) | -0.010(5) |
| C(9) | 0.052(6) | 0.049(7) | 0.050(6) | -0.008(6) | 0.002(6) | -0.001(6) |
| C(10) | 0.079(9) | 0.038(7) | 0.083(9) | -0.011(7) | 0.017(8) | 0.001(6) |
| C(11) | 0.058(8) | 0.051(8) | 0.086(9) | -0.008(7) | 0.004(7) | -0.033(8) |
| C(12) | 0.047(7) | 0.078(9) | 0.062(7) | 0.003(7) | 0.003(6) | -0.025(7) |
| C(13) | 0.039(6) | 0.042(6) | 0.049(6) | -0.001(5) | 0.002(6) | -0.012(5) |
| C(14) | 0.036(6) | 0.039(5) | 0.028(5) | -0.001(5) | -0.002(5) | -0.001(5) |
| C(15) | 0.027(5) | 0.042(6) | 0.046(6) | -0.002(5) | -0.002(5) | -0.012(5) |
| C(16) | 0.049(6) | 0.043(6) | 0.041(6) | 0.014(6) | 0.012(5) | 0.000(6) |
| C(17) | 0.050(6) | 0.046(6) | 0.029(5) | -0.002(5) | 0.005(5) | 0.004(5) |
| C(18) | 0.034(5) | 0.047(6) | 0.042(6) | 0.001(5) | 0.003(5) | 0.010(5) |
| C(19) | 0.060(7) | 0.051(7) | 0.038(6) | 0.015(6) | 0.016(6) | 0.011(6) |

Table 17-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|-----------|-------|-------|-----------|
| O(1) | C(9) | 1.229(10) | O(2) | C(9) | 1.225(10) |
| O(3) | C(10) | 1.227(9) | O(4) | C(18) | 1.25(1) |
| O(5) | C(18) | 1.24(1) | N(1) | C(6) | 1.426(9) |
| N(1) | C(7) | 1.472(9) | N(1) | C(10) | 1.390(9) |
| N(2) | C(8) | 1.485(10) | N(3) | C(10) | 1.380(9) |
| N(3) | C(11) | 1.432(9) | N(3) | C(16) | 1.467(9) |
| N(4) | C(17) | 1.469(10) | C | C(11) | 1.36(1) |
| C | C(12) | 1.39(1) | C(1) | C(2) | 1.39(1) |
| C(1) | C(6) | 1.38(1) | C(2) | C(3) | 1.37(1) |
| C(3) | C(4) | 1.38(1) | C(4) | C(5) | 1.40(1) |
| C(5) | C(6) | 1.38(1) | C(7) | C(8) | 1.53(1) |
| C(8) | C(9) | 1.54(1) | C(11) | C(15) | 1.37(1) |
| C(12) | C(13) | 1.37(1) | C(13) | C(14) | 1.39(1) |
| C(14) | C(15) | 1.39(1) | C(16) | C(17) | 1.52(1) |
| C(17) | C(18) | 1.56(1) | | | |

Table 17-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|-----------|
| C(6) | N(1) | C(7) | 120.3(6) | C(6) | N(1) | C(10) | 122.7(6) |
| C(7) | N(1) | C(10) | 116.4(6) | C(10) | N(3) | C(11) | 124.5(7) |
| C(10) | N(3) | C(16) | 116.5(7) | C(11) | N(3) | C(16) | 117.9(7) |
| C(11) | C | C(12) | 120.1(9) | C(2) | C(1) | C(6) | 119.0(9) |
| C(1) | C(2) | C(3) | 121.1(10) | C(2) | C(3) | C(4) | 119.1(10) |
| C(3) | C(4) | C(5) | 121.1(10) | C(4) | C(5) | C(6) | 118.6(9) |
| N(1) | C(6) | C(1) | 118.4(8) | N(1) | C(6) | C(5) | 120.6(8) |
| C(1) | C(6) | C(5) | 121.0(8) | N(1) | C(7) | C(8) | 116.0(6) |
| N(2) | C(8) | C(7) | 111.1(7) | N(2) | C(8) | C(9) | 109.5(7) |
| C(7) | C(8) | C(9) | 107.3(7) | O(1) | C(9) | O(2) | 126.0(9) |
| O(1) | C(9) | C(8) | 116.5(9) | O(2) | C(9) | C(8) | 117.3(9) |
| O(3) | C(10) | N(1) | 122.5(8) | O(3) | C(10) | N(3) | 121.8(8) |
| N(1) | C(10) | N(3) | 115.7(8) | N(3) | C(11) | C | 120.2(8) |
| N(3) | C(11) | C(15) | 119.5(8) | C | C(11) | C(15) | 120.2(8) |
| C | C(12) | C(13) | 120.8(9) | C(12) | C(13) | C(14) | 119.0(9) |
| C(13) | C(14) | C(15) | 120.2(9) | C(11) | C(15) | C(14) | 119.8(8) |
| N(3) | C(16) | C(17) | 113.2(7) | N(4) | C(17) | C(16) | 112.7(7) |
| N(4) | C(17) | C(18) | 108.1(7) | C(16) | C(17) | C(18) | 111.7(7) |
| O(4) | C(18) | O(5) | 127.5(9) | O(4) | C(18) | C(17) | 115.0(9) |
| O(5) | C(18) | C(17) | 117.4(9) | | | | |

Table 17-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-------------|----------------------|------------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(1) | 0.0048(77) | C(10) | -0.0032(77) |
| C(2) | -0.0029(86) | C(11) | -0.0030(91) |
| C(3) | -0.0024(95) | C(12) | 0.0105(102) |
| C(4) | 0.0040(102) | C(13) | -0.0075(100) |
| C(5) | 0.0004(95) | C(14) | -0.0011(94) |
| C(6) | -0.0054(90) | C(15) | 0.0051(80) |
| Plane number 3 | | | |
| Atoms defining plane | Distance | | |
| N(1) | 0.0029(65) | | |
| N(2) | 0.0026(62) | | |
| C(7) | -0.0116(76) | | |
| O(3) | 0.0037(55) | | |
| Summary | plane | mean deviation | CHI ² |
| | 1 | 0.0033 | 0.9 |
| | 2 | 0.0051 | 2.2 |
| | 3 | 0.0052 | 2.8 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|-------|
| 2 | 31.02 | |
| 3 | 72.97 | 72.06 |

***N,N'*-Dimethyl-*N,N'*-diphenylurea Bis[(tricarbonyl)chromium] Complex (15)**

| | |
|---------------------------------------|---|
| A. Crystal Data | |
| Empirical Formula | $C_{21}H_{16}N_2O_3Cr_2$ |
| Formula Weight | 512.36 |
| Crystal Color, Habit | Yellow, Prismatic |
| Crystal Dimensions | 0.30 X 0.30 X 0.30 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| Indexing Images | 3 oscillations @ 5.0 minutes |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| Lattice Parameters | $a = 13.483(3) \text{ \AA}$ $b = 17.416(3) \text{ \AA}$ $c = 18.08(1) \text{ \AA}$ $V = 4245(4) \text{ \AA}^3$ |
| Space Group | Pbcn (#60) |
| Z value | 8 |
| D_{calc} | 1.603 g/cm ³ |
| $F_{(000)}$ | 2080.00 |
| $\mu(\text{MoK}\alpha)$ | 0.00 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractionmeter | RAXIS-II |
| Radiation | MoK α ($\lambda = 0.71070 \text{ \AA}$) graphite monochromated |
| Detector Aperture | 200 mm x 200 mm |
| Data Images | 15 exposures @ 5.0 minutes |
| Oscillation Range | 7.0° |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| $2\theta_{max}$ | 44.0° |
| No. of Reflections Measured | Total: 2005 |
| Corrections | Lorentz-polarization |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o) + P^2 + P]$ |
| p-factor | 0.0100 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($>3.00\sigma(I)$) | 1230 |
| No. Variables | 353 |
| Reflection/Parameter Ratio | 3.48 |
| Residuals: R; Rw | 0.047 ; 0.048 |
| Goodness of Fit Indicator | 1.30 |
| Max Shift/Error in Final Cycle | 2.24 |
| Maximum peak in Final Diff. Map | 0.37 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.48 e-/Å ³ |

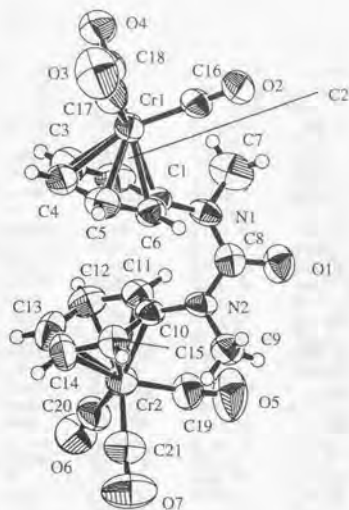


Table 18-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|-------------|------------|---------|
| Cr(1) | 0.1927(1) | 0.03644(9) | 0.34985(9) | 4.70(4) |
| Cr(2) | 0.2671(1) | -0.25602(9) | 0.61096(9) | 4.96(4) |
| O(1) | 0.5168(5) | -0.0991(4) | 0.4577(4) | 6.3(2) |
| O(2) | 0.3815(6) | 0.0842(4) | 0.2798(4) | 7.0(2) |
| O(3) | 0.1098(7) | 0.1936(5) | 0.3390(6) | 10.3(3) |
| O(4) | 0.1080(6) | 0.0034(5) | 0.2013(5) | 7.8(3) |
| O(5) | 0.4754(7) | -0.3022(5) | 0.5866(6) | 11.4(3) |
| O(6) | 0.2064(6) | -0.4175(5) | 0.6407(5) | 8.3(3) |
| O(7) | 0.3135(8) | -0.2525(5) | 0.7722(5) | 10.0(3) |
| N(1) | 0.3654(7) | -0.0897(4) | 0.4064(5) | 4.6(2) |
| N(2) | 0.3851(6) | -0.1091(4) | 0.5338(5) | 4.5(2) |
| C(1) | 0.2706(8) | -0.0550(6) | 0.4150(5) | 4.5(3) |
| C(2) | 0.188(1) | -0.0853(6) | 0.3815(7) | 6.3(4) |
| C(3) | 0.096(1) | -0.0516(10) | 0.3892(10) | 7.7(5) |
| C(4) | 0.085(1) | 0.009(1) | 0.4335(9) | 7.4(5) |
| C(5) | 0.1658(10) | 0.0424(7) | 0.4693(7) | 6.1(4) |
| C(6) | 0.2587(8) | 0.0096(6) | 0.4582(5) | 4.7(3) |
| C(7) | 0.403(1) | -0.1062(8) | 0.3330(8) | 7.7(5) |
| C(8) | 0.4257(9) | -0.0991(5) | 0.4651(7) | 4.7(3) |
| C(9) | 0.4466(9) | -0.0933(8) | 0.5988(7) | 5.7(4) |
| C(10) | 0.2944(7) | -0.1499(6) | 0.5443(6) | 4.1(3) |
| C(11) | 0.2691(8) | -0.2097(6) | 0.4981(6) | 4.9(3) |
| C(12) | 0.1803(10) | -0.2483(7) | 0.5081(7) | 5.7(3) |
| C(13) | 0.1198(8) | -0.2273(8) | 0.5680(9) | 6.6(4) |
| C(14) | 0.1472(8) | -0.1719(8) | 0.6165(8) | 6.0(4) |
| C(15) | 0.2354(8) | -0.1313(6) | 0.6035(6) | 4.9(3) |
| C(16) | 0.3093(8) | 0.0667(6) | 0.3075(6) | 5.2(3) |
| C(17) | 0.1435(8) | 0.1339(8) | 0.3421(7) | 6.7(4) |
| C(18) | 0.1422(7) | 0.0164(6) | 0.2582(7) | 5.6(3) |
| C(19) | 0.3948(8) | -0.2854(6) | 0.5987(6) | 6.3(3) |
| C(20) | 0.2307(8) | -0.3564(8) | 0.6288(6) | 6.3(4) |
| C(21) | 0.2925(8) | -0.2531(6) | 0.7094(7) | 6.4(3) |

Table 18-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|------------|-----------|-----------|------------|------------|-----------|
| Cr(1) | 0.0607(10) | 0.055(1) | 0.063(1) | -0.0021(8) | 0.0019(9) | 0.0095(9) |
| Cr(2) | 0.069(1) | 0.047(1) | 0.072(1) | 0.0005(9) | -0.0003(9) | 0.0087(9) |
| O(1) | 0.067(5) | 0.070(6) | 0.103(7) | 0.013(4) | 0.012(4) | 0.009(4) |
| O(2) | 0.075(5) | 0.095(6) | 0.095(6) | -0.014(4) | 0.004(5) | 0.038(5) |
| O(3) | 0.130(8) | 0.070(7) | 0.19(1) | 0.028(6) | 0.034(7) | 0.013(7) |
| O(4) | 0.093(6) | 0.126(8) | 0.075(6) | -0.020(5) | -0.011(5) | 0.006(6) |
| O(5) | 0.080(6) | 0.110(8) | 0.24(1) | 0.036(6) | 0.028(7) | 0.056(8) |
| O(6) | 0.119(7) | 0.060(6) | 0.138(8) | -0.024(5) | -0.016(5) | 0.023(5) |
| O(7) | 0.207(10) | 0.092(7) | 0.079(7) | -0.003(7) | -0.031(6) | -0.005(6) |
| N(1) | 0.080(7) | 0.049(6) | 0.044(7) | 0.010(4) | 0.014(5) | 0.000(4) |
| N(2) | 0.074(6) | 0.047(6) | 0.052(6) | -0.006(4) | -0.003(5) | 0.015(4) |
| C(1) | 0.058(7) | 0.066(8) | 0.047(6) | -0.010(7) | -0.008(5) | 0.001(6) |
| C(2) | 0.11(1) | 0.045(8) | 0.080(9) | 0.001(9) | -0.010(9) | 0.027(6) |
| C(3) | 0.09(1) | 0.08(1) | 0.12(1) | -0.03(1) | -0.014(10) | 0.04(1) |
| C(4) | 0.067(9) | 0.12(2) | 0.09(1) | 0.02(1) | 0.007(8) | 0.057(10) |
| C(5) | 0.084(9) | 0.08(1) | 0.071(9) | 0.034(8) | 0.012(7) | 0.008(7) |
| C(6) | 0.062(7) | 0.063(8) | 0.054(7) | -0.004(6) | -0.008(6) | 0.001(6) |
| C(7) | 0.14(1) | 0.07(1) | 0.08(1) | 0.02(1) | 0.018(9) | -0.003(9) |
| C(8) | 0.065(7) | 0.038(7) | 0.076(9) | -0.002(5) | 0.004(8) | 0.002(6) |
| C(9) | 0.076(8) | 0.085(10) | 0.056(9) | -0.018(7) | -0.005(7) | -0.003(8) |
| C(10) | 0.060(7) | 0.046(7) | 0.051(7) | -0.002(6) | -0.002(6) | 0.011(5) |
| C(11) | 0.070(8) | 0.045(8) | 0.070(8) | -0.006(6) | -0.003(6) | 0.011(6) |
| C(12) | 0.091(9) | 0.048(8) | 0.077(9) | 0.006(8) | -0.016(7) | 0.003(6) |
| C(13) | 0.058(7) | 0.06(1) | 0.13(1) | -0.007(7) | -0.020(9) | 0.021(9) |
| C(14) | 0.056(8) | 0.08(1) | 0.10(1) | 0.000(7) | 0.017(6) | 0.014(9) |
| C(15) | 0.064(7) | 0.048(7) | 0.075(8) | 0.003(6) | 0.002(7) | -0.002(6) |
| C(16) | 0.075(8) | 0.057(8) | 0.067(8) | -0.013(6) | -0.001(6) | 0.021(6) |
| C(17) | 0.083(9) | 0.066(9) | 0.10(1) | 0.025(7) | 0.024(7) | 0.000(8) |
| C(18) | 0.068(7) | 0.070(8) | 0.073(9) | -0.015(6) | 0.008(6) | 0.019(7) |
| C(19) | 0.066(8) | 0.064(8) | 0.108(10) | 0.014(6) | 0.008(7) | 0.022(7) |
| C(20) | 0.082(8) | 0.068(9) | 0.089(10) | -0.007(7) | 0.008(6) | 0.020(7) |
| C(21) | 0.119(10) | 0.052(8) | 0.072(9) | -0.010(7) | -0.008(7) | -0.004(7) |

Table 18-3. Bond Lengths(Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|-----------|
| Cr(1) | C(1) | 2.24(1) | Cr(1) | C(2) | 2.20(1) |
| Cr(1) | C(3) | 2.14(1) | Cr(1) | C(4) | 2.15(1) |
| Cr(1) | C(5) | 2.19(1) | Cr(1) | C(6) | 2.20(1) |
| Cr(1) | C(16) | 1.83(1) | Cr(1) | C(17) | 1.83(1) |
| Cr(1) | C(18) | 1.82(1) | Cr(2) | C(10) | 2.238(10) |
| Cr(2) | C(11) | 2.19(1) | Cr(2) | C(12) | 2.20(1) |
| Cr(2) | C(13) | 2.19(1) | Cr(2) | C(14) | 2.18(1) |
| Cr(2) | C(15) | 2.22(1) | Cr(2) | C(19) | 1.81(1) |
| Cr(2) | C(20) | 1.84(1) | Cr(2) | C(21) | 1.81(1) |
| O(1) | C(8) | 1.24(1) | O(2) | C(16) | 1.14(1) |
| O(3) | C(17) | 1.14(1) | O(4) | C(18) | 1.15(1) |
| O(5) | C(19) | 1.15(1) | O(6) | C(20) | 1.13(1) |
| O(7) | C(21) | 1.17(1) | N(1) | C(1) | 1.42(1) |
| N(1) | C(7) | 1.45(2) | N(1) | C(8) | 1.35(1) |
| N(2) | C(8) | 1.37(1) | N(2) | C(9) | 1.46(1) |
| N(2) | C(10) | 1.43(1) | C(1) | C(2) | 1.38(2) |
| C(1) | C(6) | 1.38(1) | C(2) | C(3) | 1.38(2) |
| C(3) | C(4) | 1.33(2) | C(4) | C(5) | 1.39(2) |
| C(5) | C(6) | 1.39(1) | C(10) | C(11) | 1.38(1) |
| C(10) | C(15) | 1.37(1) | C(11) | C(12) | 1.38(1) |
| C(12) | C(13) | 1.40(2) | C(13) | C(14) | 1.36(2) |
| C(14) | C(15) | 1.40(1) | | | |

Table 18-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|--------|-------|-------|-----------|--------|-------|-------|-----------|
| Cr(1) | Cr(1) | C(2) | 36.2(4) | Cr(1) | Cr(1) | C(3) | 66.5(5) |
| Cr(1) | Cr(1) | C(4) | 77.8(4) | Cr(1) | Cr(1) | C(5) | 66.0(4) |
| Cr(1) | Cr(1) | C(6) | 36.1(3) | Cr(1) | Cr(1) | C(16) | 91.3(4) |
| Cr(1) | Cr(1) | C(17) | 150.4(5) | Cr(1) | Cr(1) | C(18) | 121.0(5) |
| Cr(2) | Cr(1) | C(3) | 37.0(5) | Cr(2) | Cr(1) | C(4) | 65.2(5) |
| Cr(2) | Cr(1) | C(5) | 77.5(5) | Cr(2) | Cr(1) | C(6) | 64.9(5) |
| Cr(2) | Cr(1) | C(16) | 114.5(5) | Cr(2) | Cr(1) | C(17) | 154.7(6) |
| Cr(2) | Cr(1) | C(18) | 92.2(5) | Cr(3) | Cr(1) | C(4) | 36.2(5) |
| Cr(3) | Cr(1) | C(5) | 66.7(6) | Cr(3) | Cr(1) | C(6) | 78.3(5) |
| Cr(3) | Cr(1) | C(16) | 150.8(7) | Cr(3) | Cr(1) | C(17) | 118.0(7) |
| Cr(3) | Cr(1) | C(18) | 86.4(6) | Cr(4) | Cr(1) | C(5) | 37.5(5) |
| Cr(4) | Cr(1) | C(6) | 66.4(5) | Cr(4) | Cr(1) | C(16) | 160.1(6) |
| Cr(4) | Cr(1) | C(17) | 90.9(6) | Cr(4) | Cr(1) | C(18) | 110.1(6) |
| Cr(5) | Cr(1) | C(6) | 36.9(4) | Cr(5) | Cr(1) | C(16) | 122.8(5) |
| Cr(5) | Cr(1) | C(17) | 88.4(5) | Cr(5) | Cr(1) | C(18) | 147.3(5) |
| Cr(6) | Cr(1) | C(16) | 95.0(4) | Cr(6) | Cr(1) | C(17) | 114.3(5) |
| Cr(6) | Cr(1) | C(18) | 156.6(5) | Cr(6) | Cr(1) | C(17) | 90.7(5) |
| Cr(16) | Cr(1) | C(18) | 89.8(5) | Cr(17) | Cr(1) | C(18) | 88.5(6) |
| Cr(10) | Cr(2) | C(11) | 36.2(3) | Cr(10) | Cr(2) | C(12) | 65.3(4) |
| Cr(10) | Cr(2) | C(13) | 76.7(4) | Cr(10) | Cr(2) | C(14) | 65.9(4) |
| Cr(10) | Cr(2) | C(15) | 35.9(3) | Cr(10) | Cr(2) | C(19) | 90.6(4) |
| Cr(10) | Cr(2) | C(20) | 157.1(5) | Cr(10) | Cr(2) | C(21) | 118.3(5) |
| Cr(11) | Cr(2) | C(12) | 36.7(4) | Cr(11) | Cr(2) | C(13) | 66.2(5) |
| Cr(11) | Cr(2) | C(14) | 78.8(4) | Cr(11) | Cr(2) | C(15) | 65.5(4) |
| Cr(11) | Cr(2) | C(19) | 88.8(5) | Cr(11) | Cr(2) | C(20) | 121.0(5) |
| Cr(11) | Cr(2) | C(21) | 154.2(5) | Cr(12) | Cr(2) | C(13) | 37.3(5) |
| Cr(12) | Cr(2) | C(14) | 66.7(5) | Cr(12) | Cr(2) | C(15) | 77.7(5) |
| Cr(12) | Cr(2) | C(19) | 114.8(5) | Cr(12) | Cr(2) | C(20) | 93.7(5) |
| Cr(12) | Cr(2) | C(21) | 158.1(5) | Cr(13) | Cr(2) | C(14) | 36.1(5) |
| Cr(13) | Cr(2) | C(15) | 65.2(5) | Cr(13) | Cr(2) | C(19) | 152.1(6) |
| Cr(13) | Cr(2) | C(20) | 92.1(5) | Cr(13) | Cr(2) | C(21) | 120.9(6) |
| Cr(14) | Cr(2) | C(15) | 37.2(4) | Cr(14) | Cr(2) | C(19) | 154.1(5) |
| Cr(14) | Cr(2) | C(20) | 115.5(5) | Cr(14) | Cr(2) | C(21) | 94.4(5) |
| Cr(15) | Cr(2) | C(19) | 116.9(5) | Cr(15) | Cr(2) | C(20) | 152.6(5) |
| Cr(15) | Cr(2) | C(21) | 93.9(5) | Cr(19) | Cr(2) | C(20) | 90.4(5) |
| Cr(19) | Cr(2) | C(21) | 87.0(5) | Cr(20) | Cr(2) | C(21) | 84.6(5) |
| Cr(1) | N(1) | C(7) | 119(1) | Cr(1) | N(1) | C(8) | 120.5(9) |
| Cr(7) | N(1) | C(8) | 119(1) | Cr(8) | N(2) | C(9) | 118.5(9) |
| Cr(8) | N(2) | C(10) | 121.8(9) | Cr(9) | N(2) | C(10) | 118.2(9) |
| Cr(1) | C(1) | N(1) | 131.7(7) | Cr(1) | C(1) | C(2) | 70.1(6) |
| Cr(1) | C(1) | C(6) | 70.3(6) | N(1) | C(1) | C(2) | 121(1) |
| N(1) | C(1) | C(6) | 120.9(10) | Cr(2) | C(1) | C(6) | 117(1) |
| Cr(1) | C(2) | C(1) | 73.7(7) | Cr(1) | C(2) | C(3) | 69.1(7) |
| Cr(1) | C(2) | C(3) | 121(1) | Cr(1) | C(3) | C(2) | 74.0(7) |
| Cr(1) | C(3) | C(4) | 72.6(8) | Cr(2) | C(3) | C(4) | 119(1) |
| Cr(1) | C(4) | C(3) | 71.3(8) | Cr(1) | C(4) | C(5) | 72.9(8) |
| Cr(3) | C(4) | C(5) | 121(1) | Cr(1) | C(5) | C(4) | 69.7(8) |
| Cr(1) | C(5) | C(6) | 71.9(6) | Cr(4) | C(5) | C(6) | 117(1) |
| Cr(1) | C(6) | C(1) | 73.6(6) | Cr(1) | C(6) | C(5) | 71.2(7) |
| Cr(1) | C(6) | C(5) | 121(1) | O(1) | C(8) | N(1) | 120(1) |
| O(1) | C(8) | N(2) | 119(1) | N(1) | C(8) | N(2) | 119(1) |
| Cr(2) | C(10) | N(2) | 128.6(6) | Cr(2) | C(10) | C(11) | 70.2(6) |
| Cr(2) | C(10) | C(15) | 71.3(6) | N(2) | C(10) | C(11) | 120.6(10) |
| N(2) | C(10) | C(15) | 118(1) | Cr(11) | C(10) | C(15) | 120.4(10) |
| Cr(2) | C(11) | C(10) | 73.6(6) | Cr(2) | C(11) | C(12) | 72.0(7) |
| Cr(10) | C(11) | C(12) | 120(1) | Cr(2) | C(12) | C(11) | 71.3(6) |
| Cr(2) | C(12) | C(13) | 70.9(7) | Cr(11) | C(12) | C(13) | 118(1) |
| Cr(2) | C(13) | C(12) | 71.8(7) | Cr(2) | C(13) | C(14) | 71.7(7) |
| Cr(12) | C(13) | C(14) | 121(1) | Cr(2) | C(14) | C(13) | 72.2(7) |
| Cr(2) | C(14) | C(15) | 72.7(6) | Cr(13) | C(14) | C(15) | 118(1) |
| Cr(2) | C(15) | C(10) | 72.8(6) | Cr(2) | C(15) | C(14) | 70.1(7) |
| Cr(10) | C(15) | C(14) | 120(1) | Cr(1) | C(16) | O(2) | 178(1) |

Table 18-4. Bond Angles (deg) (Continued)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|------|--------|-------|-------|------|-----------|
| Cr(1) | C(17) | O(3) | 177(1) | Cr(1) | C(18) | O(4) | 178.2(10) |
| Cr(2) | C(19) | O(5) | 175(1) | Cr(2) | C(20) | O(6) | 178(1) |
| Cr(2) | C(21) | O(7) | 176(1) | | | | |

Table 18-5. Least Squares Planes

| Plane number 1 | | | Plane number 2 | | |
|----------------------|-------|----------------|----------------------|--|-----------|
| Atoms defining plane | | Distance | Atoms defining plane | | Distance |
| C(1) | | -0.004(10) | C(10) | | -0.017(9) |
| C(2) | | -0.01(1) | C(11) | | 0.025(10) |
| C(3) | | 0.03(1) | C(12) | | -0.01(1) |
| C(4) | | -0.01(1) | C(13) | | -0.02(1) |
| C(5) | | -0.01(1) | C(14) | | 0.03(1) |
| C(6) | | 0.013(10) | C(15) | | 0.00(1) |
| Plane number 3 | | | | | |
| Atoms defining plane | | Distance | | | |
| N(1) | | -0.001(8) | | | |
| N(2) | | -0.001(8) | | | |
| O(1) | | -0.001(7) | | | |
| C(8) | | 0.002(10) | | | |
| Summary | plane | mean deviation | CHI ² | | |
| | 1 | 0.0127 | 8.4 | | |
| | 2 | 0.0162 | 18.2 | | |
| | 3 | 0.0009 | 0.1 | | |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|-------|--------|
| 2 | | 140.09 |
| 3 | 61.96 | 124.30 |

meta-Substituted Diguandinium iodide (19)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{12}H_{10}N_8I_2$ |
| Formula Weight | 656.35 |
| Crystal Color, Habit | brown, prismatic |
| Crystal Dimensions | 0.50 X 0.40 X 0.60 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2θ range) | 2θ (48.9 - 51.0°) |
| Omega Scan Peak Width at Half-height | 0.16° |
| Lattice Parameters | $a = 11.312(2) \text{ \AA}$ $b = 15.420(2) \text{ \AA}$ $c = 16.236(3) \text{ \AA}$ $\beta = 101.33(1)^\circ$ $V = 2776.9(8) \text{ \AA}^3$ |
| Space Group | $P2_1/a$ (#14) |
| Z value | 4 |
| D_{calc} | 1.570 g/cm ³ |
| $F_{(00)}$ | 1288.00 |
| μ (CuK α) | 179.47 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractionmeter | Rigaku AFC5S |
| Radiation | CuK α ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 3.57, 12.70, 45.11) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | $(1.47 + 0.30 \tan \theta)^\circ$ |
| $2\theta_{max}$ | 120.1° |
| No. of Reflections Measured | Total: 4566 Unique: 4325 (Rint = 0.181) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.8384 - 1.1060) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0080 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 2696 |
| No. Variables | 409 |
| Reflection/Parameter Ratio | 6.59 |
| Residuals: R; Rw | 0.057; 0.057 |
| Goodness of Fit Indicator | 2.67 |
| Max Shift/Error in Final Cycle | 3.06 |
| Maximum peak in Final Diff. Map | 1.21 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.93 e-/Å ³ |

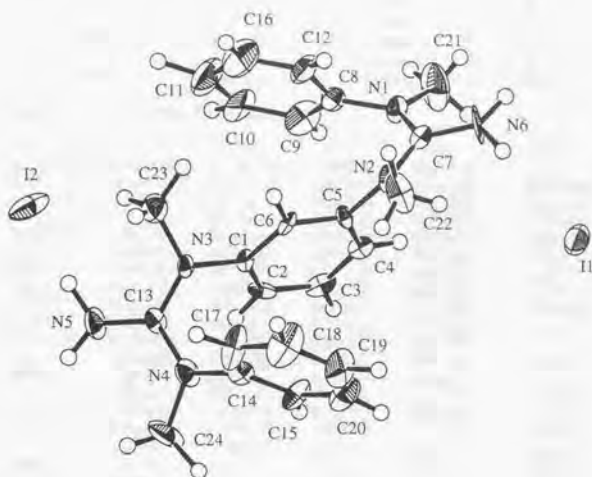


Table 19-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|------------|---------|
| I(1) | 0.23156(9) | 0.21340(6) | 0.94260(6) | 3.55(2) |
| I(2) | 0.3404(1) | 0.73059(8) | 1.54510(6) | 4.92(3) |
| N(1) | 0.0108(10) | 0.3864(7) | 1.1734(7) | 2.5(3) |
| N(2) | 0.1819(10) | 0.4213(7) | 1.1214(6) | 2.0(3) |
| N(3) | 0.4314(9) | 0.6037(6) | 1.3285(6) | 1.6(2) |
| N(4) | 0.630(1) | 0.5599(8) | 1.3548(7) | 2.7(3) |
| N(5) | 0.570(1) | 0.6695(9) | 1.4345(7) | 3.2(3) |
| N(6) | 0.034(1) | 0.3347(9) | 1.0430(9) | 4.4(4) |
| C(1) | 0.382(1) | 0.5218(8) | 1.3038(7) | 1.3(3) |
| C(2) | 0.404(1) | 0.4518(9) | 1.3572(8) | 1.8(3) |
| C(3) | 0.355(1) | 0.3700(9) | 1.3334(9) | 2.4(3) |
| C(4) | 0.281(1) | 0.3617(8) | 1.2562(9) | 1.8(3) |
| C(5) | 0.257(1) | 0.4316(8) | 1.2021(7) | 1.5(3) |
| C(6) | 0.308(1) | 0.5121(8) | 1.2242(7) | 1.4(3) |
| C(7) | 0.075(1) | 0.3811(9) | 1.1111(9) | 2.7(4) |
| C(8) | 0.020(1) | 0.4614(9) | 1.2253(8) | 2.5(4) |
| C(9) | 0.045(2) | 0.451(1) | 1.312(1) | 4.3(5) |
| C(10) | 0.050(2) | 0.525(1) | 1.364(1) | 4.8(5) |
| C(11) | 0.035(2) | 0.608(1) | 1.331(1) | 5.7(6) |
| C(12) | 0.002(2) | 0.542(1) | 1.187(1) | 3.9(4) |
| C(13) | 0.544(1) | 0.6120(9) | 1.3726(8) | 1.9(3) |
| C(14) | 0.625(1) | 0.5278(10) | 1.2680(8) | 2.5(3) |
| C(15) | 0.629(1) | 0.4396(10) | 1.2548(9) | 2.9(4) |
| C(16) | 0.007(2) | 0.613(1) | 1.244(2) | 6.9(7) |
| C(17) | 0.609(2) | 0.5876(10) | 1.2041(9) | 3.9(4) |
| C(18) | 0.599(2) | 0.557(1) | 1.122(1) | 5.0(5) |
| C(19) | 0.605(2) | 0.468(1) | 1.109(1) | 4.6(5) |

Table 19-1. Atomic coordinates and Biso/Beq (Continued)

| atom | x | y | z | Beq |
|-------|-----------|----------|------------|--------|
| C(20) | 0.624(2) | 0.411(1) | 1.175(1) | 4.2(5) |
| C(21) | -0.073(2) | 0.317(1) | 1.188(1) | 5.9(7) |
| C(22) | 0.232(2) | 0.446(1) | 1.0468(10) | 3.7(5) |
| C(23) | 0.347(2) | 0.678(1) | 1.313(1) | 3.6(4) |
| C(24) | 0.743(1) | 0.542(2) | 1.416(1) | 4.8(5) |

Table 19-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|------------|-----------|------------|-----------|------------|
| I(1) | 0.0566(7) | 0.0366(6) | 0.0401(6) | 0.0081(6) | 0.0058(5) | -0.0092(5) |
| I(2) | 0.0681(8) | 0.0883(10) | 0.0316(6) | 0.0539(7) | 0.0127(5) | 0.0025(6) |
| N(1) | 0.028(7) | 0.037(7) | 0.038(7) | -0.008(6) | 0.021(6) | -0.016(6) |
| N(2) | 0.032(7) | 0.024(7) | 0.026(6) | -0.013(5) | 0.016(6) | -0.011(5) |
| N(3) | 0.024(6) | 0.022(6) | 0.016(6) | -0.004(5) | 0.010(5) | -0.008(5) |
| N(4) | 0.034(7) | 0.050(8) | 0.020(6) | -0.004(6) | 0.005(6) | -0.009(6) |
| N(5) | 0.040(9) | 0.052(9) | 0.032(7) | -0.011(7) | 0.012(7) | -0.023(7) |
| N(6) | 0.06(1) | 0.054(10) | 0.052(10) | -0.028(8) | 0.007(8) | -0.046(8) |
| C(1) | 0.021(7) | 0.021(8) | 0.011(6) | -0.005(6) | 0.015(6) | -0.003(6) |
| C(2) | 0.015(7) | 0.040(9) | 0.013(7) | 0.004(6) | 0.002(6) | 0.013(6) |
| C(3) | 0.032(9) | 0.029(9) | 0.035(9) | 0.010(7) | 0.019(7) | 0.016(7) |
| C(4) | 0.020(8) | 0.016(8) | 0.037(9) | -0.005(6) | 0.018(7) | 0.009(7) |
| C(5) | 0.021(7) | 0.024(8) | 0.013(6) | -0.008(6) | 0.005(6) | -0.004(6) |
| C(6) | 0.028(8) | 0.013(7) | 0.016(7) | 0.001(6) | 0.021(6) | 0.000(6) |
| C(7) | 0.032(9) | 0.028(9) | 0.042(10) | 0.008(7) | 0.004(8) | -0.012(7) |
| C(8) | 0.027(8) | 0.043(10) | 0.029(9) | 0.003(7) | 0.012(7) | -0.009(7) |
| C(9) | 0.07(1) | 0.06(1) | 0.04(1) | 0.01(1) | 0.02(1) | 0.010(9) |
| C(10) | 0.06(1) | 0.08(2) | 0.04(1) | 0.03(1) | 0.03(1) | -0.03(1) |
| C(11) | 0.09(2) | 0.07(2) | 0.05(1) | 0.03(1) | 0.01(1) | -0.02(1) |
| C(12) | 0.06(1) | 0.04(1) | 0.04(1) | 0.026(9) | 0.000(10) | -0.011(9) |
| C(13) | 0.024(8) | 0.038(9) | 0.011(7) | -0.007(7) | 0.010(6) | -0.005(6) |
| C(14) | 0.022(8) | 0.05(1) | 0.028(8) | -0.001(7) | 0.018(7) | -0.011(7) |
| C(15) | 0.05(1) | 0.035(10) | 0.032(9) | 0.012(8) | 0.032(9) | 0.001(7) |
| C(16) | 0.10(2) | 0.03(1) | 0.12(2) | 0.03(1) | 0.00(2) | 0.01(1) |
| C(17) | 0.10(1) | 0.026(9) | 0.036(10) | -0.012(10) | 0.05(1) | 0.000(8) |
| C(18) | 0.10(2) | 0.06(1) | 0.04(1) | 0.00(1) | 0.05(1) | 0.008(10) |
| C(19) | 0.07(1) | 0.07(1) | 0.04(1) | 0.00(1) | 0.04(1) | -0.022(10) |
| C(20) | 0.06(1) | 0.04(1) | 0.08(1) | 0.002(10) | 0.04(1) | -0.01(1) |
| C(21) | 0.08(2) | 0.07(1) | 0.09(2) | -0.05(1) | 0.04(1) | -0.03(1) |
| C(22) | 0.06(1) | 0.06(1) | 0.021(9) | -0.03(1) | 0.018(9) | 0.000(8) |
| C(23) | 0.05(1) | 0.03(1) | 0.05(1) | 0.007(9) | -0.007(9) | -0.004(9) |
| C(24) | 0.03(1) | 0.12(2) | 0.03(1) | 0.00(1) | -0.008(8) | -0.03(1) |

Table 19-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(1) | C(7) | 1.36(2) | N(1) | C(8) | 1.42(2) |
| N(1) | C(21) | 1.48(2) | N(2) | C(5) | 1.42(1) |
| N(2) | C(7) | 1.34(2) | N(2) | C(22) | 1.49(2) |
| N(3) | C(1) | 1.41(1) | N(3) | C(13) | 1.34(1) |
| N(3) | C(23) | 1.49(2) | N(4) | C(13) | 1.33(2) |
| N(4) | C(14) | 1.48(2) | N(4) | C(24) | 1.49(2) |
| N(5) | C(13) | 1.33(2) | N(6) | C(7) | 1.33(2) |
| C(1) | C(2) | 1.38(2) | C(1) | C(6) | 1.40(2) |
| C(2) | C(3) | 1.40(2) | C(3) | C(4) | 1.37(2) |
| C(4) | C(5) | 1.38(2) | C(5) | C(6) | 1.39(2) |
| C(8) | C(9) | 1.39(2) | C(8) | C(12) | 1.38(2) |
| C(9) | C(10) | 1.42(2) | C(10) | C(11) | 1.39(2) |
| C(11) | C(16) | 1.37(3) | C(12) | C(16) | 1.45(3) |
| C(14) | C(15) | 1.38(2) | C(14) | C(17) | 1.37(2) |
| C(15) | C(20) | 1.36(2) | C(17) | C(18) | 1.39(2) |
| C(18) | C(19) | 1.38(2) | C(19) | C(20) | 1.38(2) |

Table 19-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|--------|-------|-------|-------|--------|
| C(7) | N(1) | C(8) | 119(1) | C(7) | N(1) | C(21) | 121(1) |
| C(8) | N(1) | C(21) | 118(1) | C(5) | N(2) | C(7) | 121(1) |
| C(5) | N(2) | C(22) | 117(1) | C(7) | N(2) | C(22) | 119(1) |
| C(1) | N(3) | C(13) | 121(1) | C(1) | N(3) | C(23) | 116(1) |
| C(13) | N(3) | C(23) | 122(1) | C(13) | N(4) | C(14) | 120(1) |
| C(13) | N(4) | C(24) | 122(1) | C(14) | N(4) | C(24) | 115(1) |
| N(3) | C(1) | C(2) | 120(1) | N(3) | C(1) | C(6) | 119(1) |
| C(2) | C(1) | C(6) | 120(1) | C(1) | C(2) | C(3) | 120(1) |
| C(2) | C(3) | C(4) | 118(1) | C(3) | C(4) | C(5) | 121(1) |
| N(2) | C(5) | C(4) | 120(1) | N(2) | C(5) | C(6) | 118(1) |
| C(4) | C(5) | C(6) | 120(1) | C(1) | C(6) | C(5) | 118(1) |
| N(1) | C(7) | N(2) | 118(1) | N(1) | C(7) | N(6) | 120(1) |
| N(2) | C(7) | N(6) | 120(1) | N(1) | C(8) | C(9) | 118(1) |
| N(1) | C(8) | C(12) | 118(1) | C(9) | C(8) | C(12) | 122(1) |
| C(8) | C(9) | C(10) | 118(1) | C(9) | C(10) | C(11) | 121(1) |
| C(10) | C(11) | C(16) | 116(1) | C(8) | C(12) | C(16) | 115(1) |
| N(3) | C(13) | N(4) | 118(1) | N(3) | C(13) | N(5) | 120(1) |
| N(4) | C(13) | N(5) | 120(1) | N(4) | C(14) | C(15) | 118(1) |
| N(4) | C(14) | C(17) | 117(1) | C(15) | C(14) | C(17) | 123(1) |
| C(14) | C(15) | C(20) | 118(1) | C(11) | C(16) | C(12) | 125(1) |
| C(14) | C(17) | C(18) | 117(1) | C(17) | C(18) | C(19) | 119(1) |
| C(18) | C(19) | C(20) | 121(1) | C(15) | C(20) | C(19) | 119(1) |

Table 19-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | | |
|--------------------------------------|----------|----------------------|------------------|-------|
| Atoms defining plane | Distance | Atoms defining plane | Distance | |
| N(1) | 0.00(1) | N(3) | -0.002(10) | |
| N(2) | 0.00(1) | N(4) | 0.00(1) | |
| N(6) | 0.01(2) | N(5) | 0.00(1) | |
| C(7) | -0.01(1) | C(13) | 0.01(1) | |
| Plane number 3 | | Plane number 4 | | |
| Atoms defining plane | Distance | Atoms defining plane | Distance | |
| C(8) | 0.00(1) | C(1) | 0.00(1) | |
| C(9) | 0.00(2) | C(2) | -0.01(1) | |
| C(10) | -0.01(2) | C(3) | 0.01(1) | |
| C(11) | 0.02(2) | C(4) | 0.00(1) | |
| C(12) | 0.00(2) | C(5) | -0.01(1) | |
| C(16) | -0.03(3) | C(6) | 0.01(1) | |
| Plane number 5 | | | | |
| Atoms defining plane | Distance | | | |
| C(14) | 0.01(1) | | | |
| C(15) | -0.02(2) | | | |
| C(17) | 0.00(2) | | | |
| C(18) | -0.01(2) | | | |
| C(19) | -0.01(2) | | | |
| C(20) | 0.03(2) | | | |
| Summary | plane | mean deviation | CHI ² | |
| | 1 | 0.0060 | 1.0 | |
| | 2 | 0.0039 | 0.5 | |
| | 3 | 0.0118 | 2.7 | |
| | 4 | 0.0082 | 3.3 | |
| | 5 | 0.0138 | 5.0 | |
| Dihedral angles between planes (deg) | | | | |
| plane | 1 | 2 | 3 | 4 |
| 2 | 135.16 | | | |
| 3 | 71.64 | 67.17 | | |
| 4 | 68.92 | 66.67 | 30.51 | |
| 5 | 68.93 | 71.03 | 4.78 | 34.00 |

para-Substituted Diguanidinium iodide (20)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{12}H_{10}N_4I_2$ |
| Formula Weight | 656.35 |
| Crystal Color, Habit | brown, prismatic |
| Crystal Dimensions | 0.60 X 0.20 X 0.20 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2θ range) | 20 (43.9 - 48.9°) |
| Omega Scan Peak Width at Half-height | 0.14° |
| Lattice Parameters | $a = 10.929(2) \text{ \AA}$ $b = 11.173(2) \text{ \AA}$ $c = 11.895(2) \text{ \AA}$ $\beta = 113.56(1)^\circ$ $V = 1331.3(5) \text{ \AA}^3$ |
| Space Group | $P2_1/c$ (#14) |
| Z value | 2 |
| D_{calc} | 1.637 g/cm ³ |
| $F_{(00)}$ | 644.00 |
| $\mu(\text{CuK}\alpha)$ | 187.16 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC5S |
| Radiation | CuK α ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated |
| Attenuator | Ni foil (factors = 1.00, 3.57, 12.70, 45.11) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 258 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | $(1.37 + 0.30 \tan \theta)^\circ$ |
| $2\theta_{\text{max}}$ | 120.1° |
| No. of Reflections Measured | Total: 2226 Unique: 2105 (Rint = 0.079) |
| Corrections | Lorentz-polarization Absorption (trans. factors: 0.9396 - 1.0326) |
| C. Structure Solution and Refinement | |
| Structure Solution | Patterson Methods (SAPI) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0050 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 1555 |
| No. Variables | 205 |
| Reflection/Parameter Ratio | 7.59 |
| Residuals: R ; R_w | 0.041 ; 0.044 |
| Goodness of Fit Indicator | 2.91 |
| Max Shift/Error in Final Cycle | 5.63 |
| Maximum peak in Final Diff. Map | 0.64 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.43 e-/Å ³ |

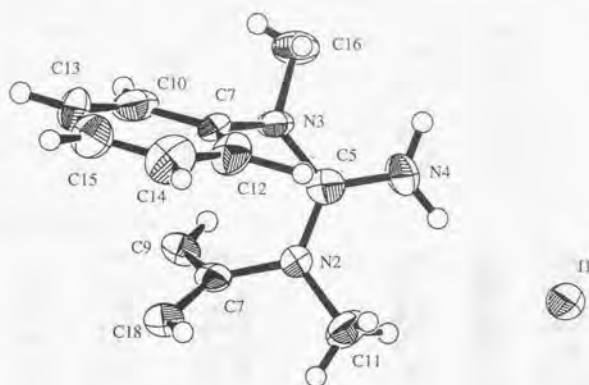


Table 20-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|------------|---------|
| I(1) | 0.37859(7) | 0.31187(6) | 0.51120(6) | 3.75(2) |
| N(2) | 0.7263(7) | 0.4360(7) | 0.8860(6) | 2.8(2) |
| N(3) | 0.7503(8) | 0.2863(7) | 1.0302(7) | 2.9(2) |
| N(4) | 0.5734(8) | 0.2779(8) | 0.8369(7) | 4.4(2) |
| C(5) | 0.6819(10) | 0.3327(9) | 0.9159(9) | 3.2(2) |
| C(7) | 0.8010(10) | 0.3624(9) | 1.1336(8) | 2.9(2) |
| C(8) | 0.904(1) | 0.5829(9) | 0.9978(9) | 2.8(3) |
| C(9) | 0.967(1) | 0.3869(9) | 0.9470(9) | 2.7(2) |
| C(10) | 0.932(1) | 0.352(1) | 1.220(1) | 4.0(3) |
| C(11) | 0.637(1) | 0.514(1) | 0.790(1) | 4.4(3) |
| C(12) | 0.721(1) | 0.452(1) | 1.1490(9) | 4.0(3) |
| C(13) | 0.985(1) | 0.425(1) | 1.3206(9) | 4.2(3) |
| C(14) | 0.773(1) | 0.530(1) | 1.249(1) | 5.2(4) |
| C(15) | 0.906(1) | 0.514(1) | 1.334(1) | 4.6(3) |
| C(16) | 0.744(1) | 0.157(1) | 1.045(1) | 4.6(4) |
| C(17) | 0.8669(10) | 0.4694(8) | 0.9439(7) | 2.7(2) |

Table 20-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|-----------|-----------|-----------|------------|-----------|-----------|
| I(1) | 0.0532(4) | 0.0466(4) | 0.0382(4) | -0.0081(4) | 0.0138(3) | 0.0012(4) |
| N(2) | 0.033(4) | 0.034(5) | 0.033(4) | -0.002(4) | 0.009(4) | 0.004(4) |
| N(3) | 0.050(5) | 0.028(5) | 0.030(4) | -0.004(4) | 0.013(4) | 0.007(4) |
| N(4) | 0.061(6) | 0.048(6) | 0.043(5) | -0.025(5) | 0.004(4) | -0.010(4) |
| C(5) | 0.044(6) | 0.039(7) | 0.041(6) | 0.002(5) | 0.018(5) | 0.002(5) |
| C(7) | 0.041(6) | 0.040(6) | 0.023(5) | -0.005(5) | 0.006(5) | 0.010(5) |
| C(8) | 0.046(7) | 0.023(6) | 0.042(6) | 0.008(5) | 0.021(5) | -0.001(5) |
| C(9) | 0.048(7) | 0.022(6) | 0.040(6) | -0.003(5) | 0.025(5) | -0.007(5) |
| C(10) | 0.052(8) | 0.046(8) | 0.059(8) | 0.012(6) | 0.026(6) | 0.025(6) |
| C(11) | 0.061(9) | 0.041(8) | 0.047(8) | 0.008(7) | 0.002(6) | 0.010(6) |
| C(12) | 0.053(7) | 0.073(9) | 0.029(6) | -0.001(7) | 0.019(5) | -0.001(6) |
| C(13) | 0.058(8) | 0.060(9) | 0.023(6) | -0.015(7) | -0.004(5) | -0.004(6) |
| C(14) | 0.075(9) | 0.08(1) | 0.051(8) | 0.010(8) | 0.033(7) | -0.004(7) |
| C(15) | 0.072(9) | 0.066(10) | 0.033(7) | -0.012(7) | 0.017(6) | -0.007(6) |
| C(16) | 0.07(1) | 0.024(8) | 0.072(10) | 0.007(6) | 0.021(7) | 0.015(6) |
| C(17) | 0.051(6) | 0.034(6) | 0.019(5) | -0.010(5) | 0.016(4) | 0.000(4) |

Table 20-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(2) | C(5) | 1.34(1) | N(2) | C(11) | 1.45(1) |
| N(2) | C(17) | 1.46(1) | N(3) | C(5) | 1.36(1) |
| N(3) | C(7) | 1.42(1) | N(3) | C(16) | 1.45(1) |
| N(4) | C(5) | 1.31(1) | C(7) | C(10) | 1.40(1) |
| C(7) | C(12) | 1.38(1) | C(8) | C(9) | 1.34(1) |
| C(8) | C(17) | 1.40(1) | C(9) | C(17) | 1.41(1) |
| C(10) | C(13) | 1.36(2) | C(12) | C(14) | 1.39(2) |
| C(13) | C(15) | 1.36(2) | C(14) | C(15) | 1.39(2) |

Table 20-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|-----------|-------|-------|-------|----------|
| C(5) | N(2) | C(11) | 121.2(9) | C(5) | N(2) | C(17) | 120.6(8) |
| C(11) | N(2) | C(17) | 118.1(8) | C(5) | N(3) | C(7) | 119.7(8) |
| C(5) | N(3) | C(16) | 118.1(9) | C(7) | N(3) | C(16) | 121.0(9) |
| N(2) | C(5) | N(3) | 119.6(9) | N(2) | C(5) | N(4) | 120.0(9) |
| N(3) | C(5) | N(4) | 120.4(10) | N(3) | C(7) | C(10) | 121(1) |
| N(3) | C(7) | C(12) | 120.3(9) | C(10) | C(7) | C(12) | 118(1) |
| C(9) | C(8) | C(17) | 121.1(10) | C(8) | C(9) | C(17) | 119.6(9) |
| C(7) | C(10) | C(13) | 123(1) | C(7) | C(12) | C(14) | 119(1) |
| C(10) | C(13) | C(15) | 117(1) | C(12) | C(14) | C(15) | 120(1) |
| C(13) | C(15) | C(14) | 121(1) | N(2) | C(17) | C(8) | 120.7(9) |
| N(2) | C(17) | C(9) | 120.0(8) | C(8) | C(17) | C(9) | 119.3(9) |

Table 20-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-------------|----------------------|--------------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(5) | -0.035(96) | C(7) | -0.0019(89) |
| N(2) | 0.0008(75) | C(10) | 0.0067(104) |
| N(3) | 0.0009(80) | C(13) | -0.0058(117) |
| N(4) | 0.0018(112) | C(15) | -0.0019(120) |
| | | C(14) | 0.0079(129) |
| | | C(12) | -0.0032(104) |

| Plane number 3 | |
|----------------------|----------|
| Atoms defining plane | Distance |
| C(8) | 0.0000 |
| C(9) | 0.0000 |
| C(17) | 0.0000 |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0018 | 0.2 |
| | 2 | 0.0046 | 1.1 |
| | 3 | 0.0000 | 0.0 |

Dihedral angles between planes (deg)

| plane | 1 | 2 |
|-------|--------|--------|
| 2 | 72.30 | |
| 3 | 111.82 | 152.03 |

meta-Substituted Tetraguanidinium Chloride (21)

| | |
|--|--|
| A. Crystal Data | |
| Empirical Formula | $C_{24}H_{36}N_{12}Cl_4O_2$ |
| Formula Weight | 904.81 |
| Crystal Color, Habit | clear, needle |
| Crystal Dimensions | 0.35 X 0.30 X 0.30 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| Indexing Images | 3 oscillations @ 5.0 minutes |
| Detector Position | 86.33 mm |
| Detector Swing Angle | 0.00° |
| Pixel Size | 0.203 mm |
| Lattice Parameters | $a = 11.647(2) \text{ \AA}$ $b = 25.027(3) \text{ \AA}$ $c = 15.866(2) \text{ \AA}$ $\beta = 93.52(1)^\circ$ $V = 4616.1099 \text{ \AA}^3$ $P2_1/c$ (#14) |
| Space Group | 4 |
| Z value | 1,302 g/cm ³ |
| D_{calc} | 1912.00 |
| $F_{(00)}$ | 3.06 cm ⁻¹ |
| $\mu(\text{MoK}\alpha)$ | |
| B. Intensity Measurements | |
| Diffractometer | RAXIS-II |
| Radiation | MoK α ($\lambda = 0.71070 \text{ \AA}$) graphite monochromated 200 mm x 200 mm 15 exposures @ 5.0 minutes |
| Detector Aperture | 7.0° |
| Data Images | 86.33 mm |
| Oscillation Range | 0.00° |
| Detector Position | 0.203 mm |
| Detector Swing Angle | 44.0° |
| Pixel Size | Total: 5313 |
| 2 θ_{max} | Lorentz-polarization |
| No. of Reflections Measured | Absorption |
| Corrections | (trans. factors: 0.8384 - 1.0905) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/[\sigma^2(F_o^2) + P^2 + P]$ |
| p-factor | 0.0200 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations ($I > 3.00\sigma(I)$) | 4814 |
| No. Variables | 541 |
| Reflection/Parameter Ratio | 8.90 |
| Residuals: R; Rw | 0.066 ; 0.081 |
| Goodness of Fit Indicator | 4.23 |
| Max Shift/Error in Final Cycle | 0.06 |
| Maximum peak in Final Diff. Map | 0.47 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.53 e-/Å ³ |

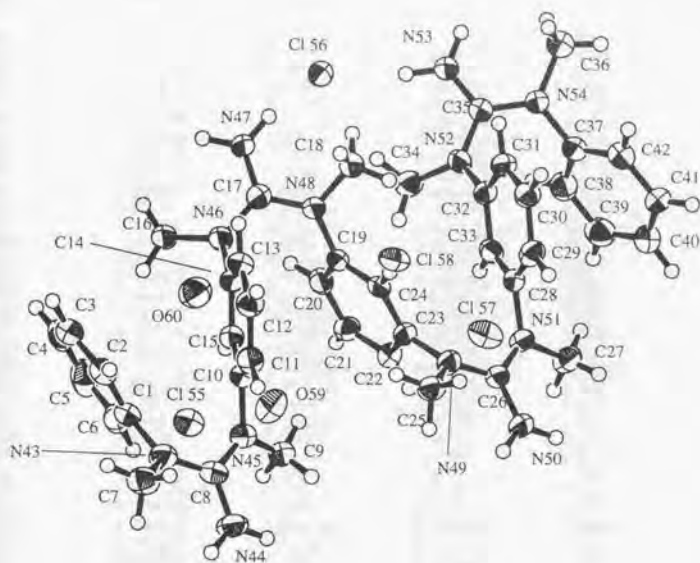


Table 21-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|--------|------------|------------|------------|----------|
| Cl(55) | 0.8881(1) | 0.61303(5) | 0.41598(8) | 4.21(3) |
| Cl(56) | 0.38638(9) | 0.43210(5) | 0.08798(7) | 3.25(3) |
| Cl(57) | 0.5304(1) | 0.37524(6) | 0.56308(8) | 4.52(3) |
| Cl(58) | 1.00060(9) | 0.31340(5) | 0.12776(7) | 3.65(3) |
| O(59) | 0.6926(3) | 0.5737(2) | 0.5256(2) | 4.97(9) |
| O(60) | 0.6538(3) | 0.5964(2) | 0.3031(2) | 4.92(9) |
| N(43) | 1.2707(3) | 0.5649(2) | 0.2597(2) | 3.51(9) |
| N(44) | 1.3205(3) | 0.5240(2) | 0.3884(2) | 3.93(10) |
| N(45) | 1.1383(3) | 0.5116(2) | 0.3250(2) | 3.25(9) |
| N(46) | 0.7907(3) | 0.5141(1) | 0.1362(2) | 3.05(9) |
| N(47) | 0.6238(3) | 0.4864(2) | 0.0625(3) | 3.75(10) |
| N(48) | 0.7213(3) | 0.4280(1) | 0.1539(2) | 2.81(9) |
| N(49) | 0.9229(3) | 0.3327(2) | 0.3866(2) | 3.00(8) |
| N(50) | 0.9711(3) | 0.2856(2) | 0.5085(2) | 3.34(9) |
| N(51) | 0.7808(3) | 0.2861(1) | 0.4521(2) | 2.91(9) |
| N(52) | 0.4336(3) | 0.3350(1) | 0.2802(2) | 3.04(9) |
| N(53) | 0.2663(3) | 0.3398(1) | 0.1924(2) | 3.16(9) |
| N(54) | 0.3069(3) | 0.2626(1) | 0.2689(2) | 3.23(9) |

Table 21-1. Atomic coordinates and Biso/Beq (Continued)

| atom | x | y | z | Beq |
|-------|-----------|-----------|-----------|----------|
| C(1) | 1.1847(4) | 0.5969(2) | 0.2146(3) | 3.4(1) |
| C(2) | 1.1791(4) | 0.5991(2) | 0.1266(3) | 3.9(1) |
| C(3) | 1.0958(5) | 0.6298(2) | 0.0844(3) | 4.5(1) |
| C(4) | 1.0182(5) | 0.6589(2) | 0.1294(4) | 5.1(2) |
| C(5) | 1.0249(4) | 0.6557(2) | 0.2157(4) | 5.2(2) |
| C(6) | 1.1086(4) | 0.6261(2) | 0.2592(3) | 3.9(1) |
| C(7) | 1.3890(4) | 0.5679(2) | 0.2322(3) | 4.3(1) |
| C(8) | 1.2433(4) | 0.5330(2) | 0.3249(3) | 3.4(1) |
| C(9) | 1.0853(4) | 0.4966(2) | 0.4037(3) | 3.4(1) |
| C(10) | 1.0778(4) | 0.4975(2) | 0.2464(3) | 3.0(1) |
| C(11) | 1.1329(4) | 0.4681(2) | 0.1886(3) | 3.3(1) |
| C(12) | 1.0761(4) | 0.4535(2) | 0.1137(3) | 3.4(1) |
| C(13) | 0.9628(4) | 0.4685(2) | 0.0968(3) | 3.2(1) |
| C(14) | 0.9078(3) | 0.4983(2) | 0.1560(3) | 2.8(1) |
| C(15) | 0.9640(4) | 0.5132(2) | 0.2310(3) | 2.9(1) |
| C(16) | 0.7662(4) | 0.5710(2) | 0.1247(3) | 3.3(1) |
| C(17) | 0.7111(4) | 0.4766(2) | 0.1166(3) | 3.1(1) |
| C(18) | 0.6818(4) | 0.3800(2) | 0.1090(3) | 3.5(1) |
| C(19) | 0.7553(3) | 0.4235(2) | 0.2420(3) | 2.69(10) |
| C(20) | 0.7121(4) | 0.4599(2) | 0.2992(3) | 3.3(1) |
| C(21) | 0.7381(4) | 0.4533(2) | 0.3839(3) | 3.2(1) |
| C(22) | 0.8057(4) | 0.4110(2) | 0.4134(3) | 3.1(1) |
| C(23) | 0.8486(3) | 0.3762(2) | 0.3562(3) | 2.8(1) |
| C(24) | 0.8253(3) | 0.3819(2) | 0.2704(3) | 2.6(1) |
| C(25) | 1.0431(4) | 0.3341(2) | 0.3630(3) | 3.5(1) |
| C(26) | 0.8918(4) | 0.3014(2) | 0.4500(3) | 2.9(1) |
| C(27) | 0.7379(4) | 0.2634(2) | 0.5299(3) | 3.8(1) |
| C(28) | 0.7078(3) | 0.2801(2) | 0.3755(3) | 2.67(10) |
| C(29) | 0.7354(4) | 0.2433(2) | 0.3165(3) | 3.2(1) |
| C(30) | 0.6617(4) | 0.2355(2) | 0.2454(3) | 3.1(1) |
| C(31) | 0.5615(4) | 0.2659(2) | 0.2341(3) | 3.1(1) |
| C(32) | 0.5355(3) | 0.3032(2) | 0.2939(3) | 2.8(1) |
| C(33) | 0.6065(3) | 0.3101(2) | 0.3668(3) | 2.9(1) |
| C(34) | 0.4386(4) | 0.3922(2) | 0.3001(3) | 3.6(1) |
| C(35) | 0.3343(4) | 0.3128(2) | 0.2465(3) | 2.9(1) |
| C(36) | 0.2277(4) | 0.2306(2) | 0.2141(3) | 4.2(1) |
| C(37) | 0.3462(4) | 0.2420(2) | 0.3506(3) | 3.2(1) |
| C(38) | 0.3371(4) | 0.2729(2) | 0.4220(3) | 3.8(1) |
| C(39) | 0.3772(4) | 0.2528(2) | 0.5005(3) | 4.2(1) |
| C(40) | 0.4243(4) | 0.2025(2) | 0.5064(3) | 4.2(1) |
| C(41) | 0.4313(4) | 0.1718(2) | 0.4347(3) | 4.0(1) |
| C(42) | 0.3940(4) | 0.1914(2) | 0.3560(3) | 3.7(1) |

Table 21-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|--------|-----------|-----------|-----------|------------|------------|------------|
| Cl(55) | 0.0480(7) | 0.0560(8) | 0.0552(8) | -0.0071(6) | -0.0040(6) | 0.0008(6) |
| Cl(56) | 0.0394(6) | 0.0424(7) | 0.0412(7) | -0.0030(5) | -0.0013(5) | 0.0060(5) |
| Cl(57) | 0.0478(7) | 0.0635(9) | 0.0599(9) | -0.0016(6) | -0.0005(6) | -0.0170(7) |
| Cl(58) | 0.0408(6) | 0.0478(8) | 0.0488(7) | 0.0014(5) | -0.0071(5) | -0.0121(6) |
| O(59) | 0.061(2) | 0.071(3) | 0.057(2) | 0.008(2) | 0.005(2) | 0.015(2) |
| O(60) | 0.060(2) | 0.071(3) | 0.056(2) | -0.003(2) | 0.000(2) | 0.006(2) |
| N(43) | 0.036(2) | 0.051(3) | 0.046(2) | -0.003(2) | -0.003(2) | 0.003(2) |
| N(44) | 0.039(2) | 0.067(3) | 0.042(2) | -0.005(2) | -0.010(2) | 0.005(2) |
| N(45) | 0.041(2) | 0.044(2) | 0.037(2) | -0.002(2) | -0.003(2) | -0.001(2) |
| N(46) | 0.032(2) | 0.033(2) | 0.050(2) | -0.002(2) | -0.007(2) | 0.004(2) |
| N(47) | 0.040(2) | 0.042(3) | 0.057(3) | -0.009(2) | -0.020(2) | 0.016(2) |
| N(48) | 0.034(2) | 0.033(2) | 0.039(2) | -0.001(2) | -0.008(2) | 0.003(2) |
| N(49) | 0.033(2) | 0.039(2) | 0.041(2) | 0.002(2) | -0.001(2) | 0.007(2) |
| N(50) | 0.037(2) | 0.045(2) | 0.043(2) | -0.001(2) | -0.008(2) | 0.011(2) |
| N(51) | 0.038(2) | 0.039(2) | 0.033(2) | 0.003(2) | -0.006(2) | 0.003(2) |
| N(52) | 0.033(2) | 0.032(2) | 0.049(2) | -0.003(2) | -0.005(2) | 0.001(2) |
| N(53) | 0.037(2) | 0.036(2) | 0.046(2) | -0.003(2) | -0.009(2) | 0.005(2) |
| N(54) | 0.039(2) | 0.037(2) | 0.045(2) | -0.005(2) | -0.011(2) | 0.007(2) |
| C(1) | 0.038(3) | 0.043(3) | 0.049(3) | -0.010(2) | -0.007(2) | 0.000(2) |
| C(2) | 0.055(3) | 0.041(3) | 0.052(3) | -0.008(3) | -0.005(3) | -0.002(2) |
| C(3) | 0.065(4) | 0.044(3) | 0.060(4) | -0.010(3) | -0.019(3) | 0.001(3) |
| C(4) | 0.053(3) | 0.039(3) | 0.099(5) | -0.012(3) | -0.017(3) | 0.017(3) |
| C(5) | 0.048(3) | 0.051(4) | 0.098(5) | -0.006(3) | 0.015(3) | 0.015(3) |
| C(6) | 0.049(3) | 0.043(3) | 0.055(3) | -0.002(3) | 0.003(3) | 0.002(3) |
| C(7) | 0.035(3) | 0.070(4) | 0.057(3) | -0.005(2) | 0.000(2) | 0.000(3) |
| C(8) | 0.035(3) | 0.048(3) | 0.045(3) | -0.005(2) | -0.006(2) | -0.003(2) |
| C(9) | 0.039(3) | 0.045(3) | 0.046(3) | 0.000(2) | -0.006(2) | 0.004(2) |
| C(10) | 0.037(3) | 0.037(3) | 0.039(3) | -0.008(2) | -0.007(2) | 0.003(2) |
| C(11) | 0.032(2) | 0.041(3) | 0.052(3) | 0.002(2) | 0.003(2) | 0.002(2) |
| C(12) | 0.045(3) | 0.044(3) | 0.041(3) | 0.000(2) | 0.001(2) | -0.004(2) |
| C(13) | 0.037(3) | 0.042(3) | 0.043(3) | -0.007(2) | -0.006(2) | 0.000(2) |
| C(14) | 0.029(2) | 0.037(3) | 0.039(3) | -0.004(2) | -0.005(2) | 0.005(2) |
| C(15) | 0.035(3) | 0.035(3) | 0.041(3) | -0.001(2) | -0.003(2) | 0.002(2) |
| C(16) | 0.033(2) | 0.041(3) | 0.051(3) | -0.002(2) | -0.007(2) | 0.004(2) |
| C(17) | 0.039(3) | 0.041(3) | 0.039(3) | -0.002(2) | -0.001(2) | 0.004(2) |
| C(18) | 0.045(3) | 0.037(3) | 0.050(3) | -0.002(2) | -0.009(2) | 0.003(2) |
| C(19) | 0.030(2) | 0.036(3) | 0.035(3) | -0.010(2) | -0.003(2) | 0.005(2) |
| C(20) | 0.039(3) | 0.034(3) | 0.052(3) | -0.003(2) | -0.002(2) | 0.003(2) |
| C(21) | 0.046(3) | 0.042(3) | 0.034(3) | 0.000(2) | -0.002(2) | -0.003(2) |
| C(22) | 0.043(3) | 0.037(3) | 0.035(3) | 0.000(2) | -0.001(2) | 0.005(2) |
| C(23) | 0.031(2) | 0.034(3) | 0.040(3) | 0.001(2) | -0.006(2) | 0.006(2) |
| C(24) | 0.029(2) | 0.030(3) | 0.039(3) | -0.004(2) | -0.004(2) | -0.001(2) |
| C(25) | 0.038(3) | 0.050(3) | 0.043(3) | -0.001(2) | -0.004(2) | 0.004(2) |
| C(26) | 0.038(3) | 0.034(3) | 0.039(3) | 0.001(2) | -0.006(2) | 0.000(2) |
| C(27) | 0.045(3) | 0.058(3) | 0.039(3) | 0.001(2) | 0.000(2) | 0.009(2) |
| C(28) | 0.035(2) | 0.031(3) | 0.036(3) | -0.003(2) | -0.003(2) | 0.005(2) |
| C(29) | 0.039(2) | 0.042(3) | 0.042(3) | 0.005(2) | 0.000(2) | 0.005(2) |
| C(30) | 0.044(3) | 0.037(3) | 0.038(3) | 0.003(2) | 0.000(2) | -0.004(2) |
| C(31) | 0.036(2) | 0.043(3) | 0.037(3) | -0.002(2) | -0.003(2) | 0.002(2) |
| C(32) | 0.030(2) | 0.037(3) | 0.041(3) | 0.000(2) | -0.004(2) | 0.007(2) |
| C(33) | 0.035(2) | 0.033(3) | 0.043(3) | -0.003(2) | -0.002(2) | -0.003(2) |
| C(34) | 0.046(3) | 0.044(3) | 0.046(3) | 0.004(2) | -0.004(2) | 0.000(2) |
| C(35) | 0.037(3) | 0.035(3) | 0.039(3) | -0.003(2) | -0.002(2) | 0.002(2) |
| C(36) | 0.051(3) | 0.050(3) | 0.055(3) | -0.010(2) | -0.009(2) | 0.006(3) |
| C(37) | 0.036(2) | 0.042(3) | 0.044(3) | -0.008(2) | -0.003(2) | 0.004(2) |
| C(38) | 0.047(3) | 0.045(3) | 0.053(3) | -0.001(2) | 0.003(2) | 0.002(3) |
| C(39) | 0.056(3) | 0.061(4) | 0.044(3) | -0.014(3) | 0.005(2) | -0.003(3) |
| C(40) | 0.061(3) | 0.047(4) | 0.051(3) | -0.012(3) | -0.006(2) | 0.010(3) |
| C(41) | 0.058(3) | 0.044(3) | 0.048(3) | -0.007(2) | -0.015(2) | 0.011(3) |
| C(42) | 0.048(3) | 0.041(3) | 0.053(3) | -0.007(2) | -0.002(2) | 0.000(3) |

Table 21-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|----------|
| N(43) | C(1) | 1.439(6) | N(43) | C(7) | 1.473(6) |
| N(43) | C(8) | 1.360(6) | N(44) | C(8) | 1.328(6) |
| N(45) | C(8) | 1.335(6) | N(45) | C(9) | 1.475(6) |
| N(45) | C(10) | 1.438(6) | N(46) | C(14) | 1.436(5) |
| N(46) | C(16) | 1.463(6) | N(46) | C(17) | 1.342(6) |
| N(47) | C(17) | 1.313(6) | N(48) | C(17) | 1.355(6) |
| N(48) | C(18) | 1.458(6) | N(48) | C(19) | 1.433(5) |
| N(49) | C(23) | 1.454(6) | N(49) | C(25) | 1.471(5) |
| N(49) | C(26) | 1.344(6) | N(50) | C(26) | 1.328(6) |
| N(51) | C(26) | 1.350(5) | N(51) | C(27) | 1.474(6) |
| N(51) | C(28) | 1.447(6) | N(52) | C(32) | 1.435(6) |
| N(52) | C(34) | 1.466(6) | N(52) | C(35) | 1.362(6) |
| N(53) | C(35) | 1.319(6) | N(54) | C(35) | 1.349(6) |
| N(54) | C(36) | 1.466(6) | N(54) | C(37) | 1.443(6) |
| C(1) | C(2) | 1.395(7) | C(1) | C(6) | 1.379(7) |
| C(2) | C(3) | 1.377(7) | C(3) | C(4) | 1.391(8) |
| C(4) | C(5) | 1.368(8) | C(5) | C(6) | 1.376(8) |
| C(10) | C(11) | 1.365(6) | C(10) | C(15) | 1.389(6) |
| C(11) | C(12) | 1.374(7) | C(12) | C(13) | 1.381(6) |
| C(13) | C(14) | 1.386(6) | C(14) | C(15) | 1.374(6) |
| C(19) | C(20) | 1.400(6) | C(19) | C(24) | 1.380(6) |
| C(20) | C(21) | 1.370(6) | C(21) | C(22) | 1.383(6) |
| C(22) | C(23) | 1.373(6) | C(23) | C(24) | 1.379(6) |
| C(28) | C(29) | 1.366(6) | C(28) | C(33) | 1.399(6) |
| C(29) | C(30) | 1.389(6) | C(30) | C(31) | 1.395(6) |
| C(31) | C(32) | 1.378(6) | C(32) | C(33) | 1.391(6) |
| C(37) | C(38) | 1.382(7) | C(37) | C(42) | 1.383(7) |
| C(38) | C(39) | 1.397(7) | C(39) | C(40) | 1.374(7) |
| C(40) | C(41) | 1.378(7) | C(41) | C(42) | 1.387(7) |

Table 21-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(43) | C(7) | 117.3(4) | C(1) | N(43) | C(8) | 121.1(4) |
| C(7) | N(43) | C(8) | 121.6(4) | C(8) | N(45) | C(9) | 122.3(4) |
| C(8) | N(45) | C(10) | 119.8(3) | C(9) | N(45) | C(10) | 117.6(3) |
| C(14) | N(46) | C(16) | 118.1(3) | C(14) | N(46) | C(17) | 119.4(4) |
| C(16) | N(46) | C(17) | 121.7(4) | C(17) | N(48) | C(18) | 120.7(4) |
| C(17) | N(48) | C(19) | 120.5(4) | C(18) | N(48) | C(19) | 118.1(4) |
| C(23) | N(49) | C(25) | 117.1(3) | C(23) | N(49) | C(26) | 120.2(4) |
| C(25) | N(49) | C(26) | 120.6(4) | C(26) | N(51) | C(27) | 120.2(4) |
| C(26) | N(51) | C(28) | 121.5(3) | C(27) | N(51) | C(28) | 116.9(3) |
| C(32) | N(52) | C(34) | 119.1(3) | C(32) | N(52) | C(35) | 120.5(4) |
| C(34) | N(52) | C(35) | 120.3(4) | C(35) | N(54) | C(36) | 120.2(4) |
| C(35) | N(54) | C(37) | 120.1(4) | C(36) | N(54) | C(37) | 119.4(4) |
| N(43) | C(1) | C(2) | 120.7(4) | N(43) | C(1) | C(6) | 119.3(4) |
| C(2) | C(1) | C(6) | 120.0(5) | C(1) | C(2) | C(3) | 119.8(5) |
| C(2) | C(3) | C(4) | 120.2(5) | C(3) | C(4) | C(5) | 119.0(5) |
| C(4) | C(5) | C(6) | 121.9(5) | C(1) | C(6) | C(5) | 119.1(5) |
| N(43) | C(8) | N(44) | 119.7(4) | N(43) | C(8) | N(45) | 119.7(4) |
| N(44) | C(8) | N(45) | 120.6(4) | C(10) | C(10) | C(11) | 119.3(4) |
| N(45) | C(10) | C(15) | 119.7(4) | C(11) | C(10) | C(15) | 121.1(4) |
| C(10) | C(11) | C(12) | 120.2(4) | C(11) | C(12) | C(13) | 119.9(4) |
| C(12) | C(13) | C(14) | 119.3(4) | N(46) | C(14) | C(13) | 118.2(4) |
| N(46) | C(14) | C(15) | 120.7(4) | C(13) | C(14) | C(15) | 121.2(4) |
| C(10) | C(15) | C(14) | 118.3(4) | N(46) | C(17) | N(47) | 121.1(4) |
| N(46) | C(17) | N(48) | 119.1(4) | N(47) | C(17) | N(48) | 119.8(4) |
| N(48) | C(19) | C(20) | 119.5(4) | N(48) | C(19) | C(24) | 120.0(4) |
| C(20) | C(19) | C(24) | 120.5(4) | C(19) | C(20) | C(21) | 119.4(4) |
| C(20) | C(21) | C(22) | 120.8(4) | C(21) | C(22) | C(23) | 119.0(4) |
| N(49) | C(23) | C(22) | 119.3(4) | N(49) | C(23) | C(24) | 118.8(4) |
| C(22) | C(23) | C(24) | 121.9(4) | C(19) | C(24) | C(23) | 118.5(4) |

Table 21-4. Bond Angles (deg) (continued)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| N(49) | C(26) | N(50) | 119.2(4) | N(49) | C(26) | N(51) | 119.1(4) |
| N(50) | C(26) | N(51) | 121.7(4) | N(51) | C(28) | C(29) | 119.6(4) |
| N(51) | C(28) | C(33) | 118.5(4) | C(29) | C(28) | C(33) | 121.8(4) |
| C(28) | C(29) | C(30) | 119.5(4) | C(29) | C(30) | C(31) | 119.9(4) |
| C(30) | C(31) | C(32) | 119.9(4) | N(52) | C(32) | C(31) | 119.1(4) |
| N(52) | C(32) | C(33) | 120.0(4) | C(31) | C(32) | C(33) | 120.9(4) |
| C(28) | C(33) | C(32) | 118.0(4) | N(52) | C(35) | N(53) | 120.5(4) |
| N(52) | C(35) | N(54) | 119.1(4) | N(53) | C(35) | N(54) | 120.4(4) |
| N(54) | C(37) | C(38) | 120.0(4) | N(54) | C(37) | C(42) | 119.2(4) |
| C(38) | C(37) | C(42) | 120.8(4) | C(37) | C(38) | C(39) | 119.3(5) |
| C(38) | C(39) | C(40) | 120.1(5) | C(39) | C(40) | C(41) | 119.8(5) |
| C(40) | C(41) | C(42) | 121.0(5) | C(37) | C(42) | C(41) | 118.9(4) |

Table 21-5. Least Squares Planes

| Plane number 1 | | Plane number 2 | |
|----------------------|-----------|----------------------|-----------|
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(1) | -0.007(5) | C(10) | -0.001(5) |
| C(2) | 0.002(5) | C(11) | -0.001(5) |
| C(3) | 0.000(5) | C(12) | 0.001(5) |
| C(4) | 0.006(5) | C(13) | 0.000(5) |
| C(5) | -0.013(6) | C(14) | -0.002(4) |
| C(6) | 0.013(5) | C(15) | 0.002(5) |
| Plane number 3 | | Plane number 4 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(19) | -0.008(4) | C(28) | 0.006(4) |
| C(20) | 0.003(4) | C(29) | 0.007(5) |
| C(21) | 0.007(5) | C(30) | -0.010(5) |
| C(22) | -0.007(5) | C(31) | -0.002(4) |
| C(23) | -0.001(4) | C(32) | 0.014(4) |
| C(24) | 0.008(4) | C(33) | -0.017(4) |
| Plane number 5 | | Plane number 6 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(37) | -0.001(4) | C(8) | 0.005(5) |
| C(38) | -0.003(5) | N(43) | -0.001(4) |
| C(39) | 0.002(5) | N(44) | -0.001(4) |
| C(40) | 0.005(5) | N(45) | -0.001(4) |
| C(41) | -0.010(5) | | |
| C(42) | 0.007(5) | | |
| Plane number 7 | | Plane number 8 | |
| Atoms defining plane | Distance | Atoms defining plane | Distance |
| C(17) | 0.002(4) | C(26) | -0.006(5) |
| N(46) | -0.001(4) | N(49) | 0.002(4) |
| N(47) | -0.001(4) | N(50) | 0.002(4) |
| N(48) | 0.000(4) | N(51) | 0.001(4) |

Table 11-5. Least Squares Planes (Continued)

Plane number 9

| Atoms defining plane | Distance |
|----------------------|-----------|
| C(35) | -0.002(4) |
| N(52) | 0.001(4) |
| N(53) | 0.001(4) |
| N(54) | 0.001(4) |

| Summary | plane | mean deviation | CHI ² |
|---------|-------|----------------|------------------|
| | 1 | 0.0067 | 14.6 |
| | 2 | 0.0011 | 0.4 |
| | 3 | 0.0055 | 12.2 |
| | 4 | 0.0092 | 34.1 |
| | 5 | 0.0049 | 8.2 |
| | 6 | 0.0021 | 1.1 |
| | 7 | 0.0011 | 0.4 |
| | 8 | 0.0025 | 1.8 |
| | 9 | 0.0010 | 0.3 |

Dihedral angles between planes (deg)

| plane | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-------|--------|--------|--------|--------|-------|-------|-------|
| 8 | | | | | | | |
| 2 | 31.74 | | | | | | |
| 3 | 17.31 | 38.79 | | | | | |
| 4 | 30.52 | 14.19 | 30.35 | | | | |
| 5 | 30.11 | 47.23 | 12.81 | 35.72 | | | |
| 6 | 115.02 | 110.74 | 98.10 | 98.44 | 85.58 | | |
| 7 | 85.03 | 76.15 | 70.23 | 64.00 | 59.72 | 34.60 | |
| 8 | 121.00 | 112.23 | 104.56 | 101.13 | 92.37 | 8.55 | 37.42 |
| 9 | 88.48 | 78.80 | 73.74 | 66.94 | 63.21 | 31.96 | 3.51 |
| | 34.29 | | | | | | |

para-Substituted Tetraguanidinium Chloride (22)

| | |
|--|---|
| A. Crystal Data | |
| Empirical Formula | $C_{12}H_{12}N_{12}Cl_4O_4$ |
| Formula Weight | 940.84 |
| Crystal Color, Habit | colorless, prismatic |
| Crystal Dimensions | 0.40 X 0.20 X 0.06 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| No. of Reflections Used for Unit | |
| Cell Determination (2 θ range) | 20 (38.5 - 41.6°) |
| Omega Scan Peak Width at Half-height | 0.26° |
| Lattice Parameters | a = 10.854(2) Å b = 20.205(2) Å c = 13.388(2) Å β = 113.59(1)° V = 2690.7(6) Å ³ |
| Space Group | P2 ₁ /n (#14) |
| Z value | 2 |
| D _{calc} | 1.161 g/cm ³ |
| F ₀₀₀ | 996.00 |
| μ (CuK α) | 23.84 cm ⁻¹ |
| B. Intensity Measurements | |
| Diffractometer | Rigaku AFC7S |
| Radiation | CuK α (λ = 1.54178 Å) |
| | graphite monochromated |
| Attenuator | Ni foil (factor = 8.99) |
| Take-off Angle | 6.0° |
| Detector Aperture | 9.0 mm horizontal 13.0 mm vertical |
| Crystal to Detector Distance | 235 mm |
| Temperature | 23.0°C |
| Scan Type | ω -2 θ |
| Scan Rate | 16.0°/min (in ω) (up to 3 scans) |
| Scan Width | (1.26 + 0.30 tan θ)° |
| 2 θ max | 135.2° |
| No. of Reflections Measured | Total: 5258 Unique: 4992 (Rint = 0.054) |
| Corrections | Lorentz-polarization Secondary Extinction (coefficient: 3.57980e-07) |
| C. Structure Solution and Refinement | |
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\sum w (F_o - F_c)^2$ |
| Least Squares Weights | $w = 1/(\sigma^2(F_o^2) + P^2 + P)$ |
| p-factor | 0.0080 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I > 3.00 σ (I)) | 2929 |
| No. Variables | 407 |
| Reflection/Parameter Ratio | 7.20 |
| Residuals: R; Rw | 0.069; 0.079 |
| Goodness of Fit Indicator | 3.29 |
| Max Shift/Error in Final Cycle | 0.01 |
| Maximum peak in Final Diff. Map | 0.54 e-/Å ³ |
| Minimum peak in Final Diff. Map | -0.50 e-/Å ³ |

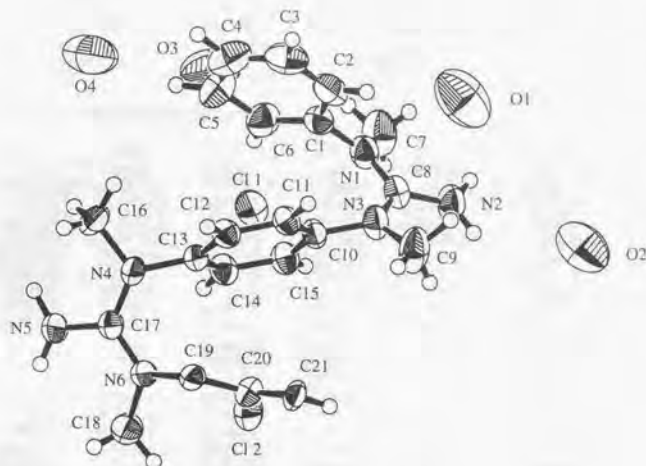


Table 12-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|--------------|-----------|---------|
| Cl(1) | 0.2245(2) | 0.04140(10) | 0.6167(2) | 5.66(5) |
| Cl(2) | 0.5576(2) | -0.12959(10) | 0.8122(1) | 4.66(4) |
| O(1) | 0.8514(7) | 0.2523(4) | 0.4837(6) | 12.3(3) |
| O(2) | 0.9817(8) | 0.0723(4) | 0.3782(6) | 11.3(3) |
| O(3) | 0.0970(7) | 0.1889(3) | 0.5958(7) | 10.6(3) |
| O(4) | 0.1105(7) | 0.2386(3) | 0.7977(6) | 10.5(2) |
| N(1) | 0.5079(6) | 0.1406(3) | 0.5255(4) | 4.4(1) |
| N(2) | 0.6045(7) | 0.0776(4) | 0.4311(5) | 5.3(2) |
| N(3) | 0.7251(5) | 0.0986(3) | 0.6142(4) | 4.1(1) |
| N(4) | 0.7203(5) | 0.0982(3) | 1.0333(4) | 3.4(1) |
| N(5) | 0.6672(6) | 0.0382(3) | 1.1570(5) | 4.1(1) |
| N(6) | 0.7903(5) | -0.0117(2) | 1.0716(4) | 3.2(1) |
| C(1) | 0.5259(6) | 0.1933(3) | 0.6017(5) | 3.8(2) |
| C(2) | 0.6104(8) | 0.2445(4) | 0.6088(7) | 5.0(2) |
| C(3) | 0.6273(9) | 0.2949(4) | 0.6816(8) | 6.0(2) |
| C(4) | 0.5555(10) | 0.2934(5) | 0.7477(8) | 6.6(3) |
| C(5) | 0.4686(9) | 0.2421(5) | 0.7411(8) | 5.9(2) |
| C(6) | 0.4524(7) | 0.1916(4) | 0.6665(7) | 4.8(2) |
| C(7) | 0.3731(10) | 0.1316(7) | 0.4393(8) | 6.6(3) |
| C(8) | 0.6128(7) | 0.1066(4) | 0.5237(5) | 4.0(2) |
| C(9) | 0.8543(10) | 0.0830(7) | 0.6083(8) | 6.7(3) |
| C(10) | 0.7229(6) | 0.0992(3) | 0.7215(5) | 3.5(1) |
| C(11) | 0.8110(6) | 0.1395(3) | 0.8011(5) | 3.4(1) |
| C(12) | 0.8110(6) | 0.1388(3) | 0.9051(5) | 3.5(2) |
| C(13) | 0.7204(6) | 0.0984(3) | 0.9249(5) | 3.0(1) |
| C(14) | 0.6316(7) | 0.0591(3) | 0.8455(5) | 3.7(2) |
| C(15) | 0.6335(7) | 0.0583(3) | 0.7413(5) | 3.8(2) |

Table 22-1. Atomic coordinates and Biso/Beq

| atom | x | y | z | Beq |
|-------|------------|------------|-----------|--------|
| C(16) | 0.686(1) | 0.1609(4) | 1.0699(8) | 5.2(2) |
| C(17) | 0.7274(6) | 0.0413(3) | 1.0873(5) | 3.2(1) |
| C(18) | 0.7630(10) | -0.0779(4) | 1.1030(8) | 4.7(2) |
| C(19) | 0.8986(6) | -0.0052(3) | 1.0355(5) | 3.1(1) |
| C(20) | 0.8889(6) | -0.0379(3) | 0.9413(5) | 3.3(1) |
| C(21) | 0.9918(7) | -0.0316(3) | 0.9078(5) | 3.4(1) |

Table 22-2. Anisotropic Displacement Parameters

| atom | U11 | U22 | U33 | U12 | U13 | U23 |
|-------|------------|----------|------------|-----------|-----------|-------------|
| Cl(1) | 0.096(2) | 0.066(1) | 0.059(1) | 0.001(1) | 0.037(1) | 0.0029(10) |
| Cl(2) | 0.0533(10) | 0.077(1) | 0.0528(10) | 0.0008(9) | 0.0281(8) | -0.0026(10) |
| O(1) | 0.115(6) | 0.205(9) | 0.143(7) | -0.020(6) | 0.046(5) | 0.048(6) |
| O(2) | 0.155(7) | 0.140(7) | 0.134(7) | -0.022(6) | 0.055(6) | 0.032(5) |
| O(3) | 0.109(6) | 0.085(5) | 0.207(9) | -0.005(4) | 0.063(6) | 0.011(5) |
| O(4) | 0.152(7) | 0.094(5) | 0.135(6) | 0.018(5) | 0.040(5) | 0.027(5) |
| N(1) | 0.049(3) | 0.073(4) | 0.042(3) | 0.007(3) | 0.016(3) | 0.003(3) |
| N(2) | 0.069(5) | 0.094(6) | 0.037(3) | 0.015(4) | 0.019(3) | -0.002(4) |
| N(3) | 0.045(3) | 0.074(4) | 0.037(3) | 0.004(3) | 0.017(3) | -0.001(3) |
| N(4) | 0.054(3) | 0.042(3) | 0.046(3) | 0.004(3) | 0.032(3) | -0.001(3) |
| N(5) | 0.058(4) | 0.056(4) | 0.056(4) | 0.011(3) | 0.039(3) | 0.011(3) |
| N(6) | 0.045(3) | 0.039(3) | 0.046(3) | 0.005(2) | 0.025(3) | 0.006(2) |
| C(1) | 0.048(4) | 0.048(4) | 0.047(4) | 0.005(3) | 0.018(3) | 0.006(3) |
| C(2) | 0.062(5) | 0.066(5) | 0.064(5) | 0.006(4) | 0.027(4) | 0.022(4) |
| C(3) | 0.076(6) | 0.050(5) | 0.094(7) | -0.008(5) | 0.025(5) | 0.010(5) |
| C(4) | 0.084(7) | 0.061(6) | 0.099(8) | 0.008(5) | 0.028(6) | -0.015(5) |
| C(5) | 0.073(6) | 0.070(6) | 0.089(7) | 0.006(5) | 0.041(5) | -0.015(5) |
| C(6) | 0.052(5) | 0.062(5) | 0.075(5) | 0.004(4) | 0.033(4) | 0.000(4) |
| C(7) | 0.054(5) | 0.13(1) | 0.052(5) | 0.005(6) | 0.008(4) | -0.006(6) |
| C(8) | 0.055(4) | 0.062(5) | 0.038(4) | -0.002(4) | 0.021(3) | 0.002(3) |
| C(9) | 0.053(5) | 0.14(1) | 0.060(6) | 0.026(6) | 0.026(5) | -0.005(7) |
| C(10) | 0.046(4) | 0.055(4) | 0.035(3) | 0.006(3) | 0.019(3) | 0.005(3) |
| C(11) | 0.044(4) | 0.045(4) | 0.044(4) | -0.006(3) | 0.021(3) | 0.004(3) |
| C(12) | 0.046(4) | 0.044(4) | 0.043(4) | -0.004(3) | 0.017(3) | 0.001(3) |
| C(13) | 0.045(4) | 0.038(3) | 0.038(3) | 0.002(3) | 0.022(3) | 0.002(3) |
| C(14) | 0.049(4) | 0.047(4) | 0.049(4) | -0.009(3) | 0.026(3) | 0.001(3) |
| C(15) | 0.048(4) | 0.055(4) | 0.037(4) | -0.005(3) | 0.012(3) | -0.005(3) |
| C(16) | 0.097(7) | 0.043(5) | 0.085(7) | 0.011(5) | 0.063(6) | -0.004(5) |
| C(17) | 0.039(3) | 0.046(4) | 0.040(3) | -0.001(3) | 0.021(3) | 0.000(3) |
| C(18) | 0.077(6) | 0.043(4) | 0.072(6) | -0.002(4) | 0.044(5) | 0.002(4) |
| C(19) | 0.041(4) | 0.036(3) | 0.045(4) | 0.004(3) | 0.023(3) | 0.002(3) |
| C(20) | 0.039(4) | 0.041(4) | 0.046(4) | -0.003(3) | 0.020(3) | -0.008(3) |
| C(21) | 0.051(4) | 0.045(4) | 0.037(3) | 0.004(3) | 0.022(3) | -0.012(3) |

Table 22-3. Bond Lengths (Å)

| atom | atom | distance | atom | atom | distance |
|-------|-------|----------|-------|-------|-----------|
| N(1) | C(1) | 1.431(8) | N(1) | C(7) | 1.464(8) |
| N(1) | C(8) | 1.338(8) | N(2) | C(8) | 1.339(8) |
| N(3) | C(8) | 1.341(8) | N(3) | C(9) | 1.474(8) |
| N(3) | C(10) | 1.444(7) | N(4) | C(13) | 1.452(7) |
| N(4) | C(16) | 1.464(8) | N(4) | C(17) | 1.344(7) |
| N(5) | C(17) | 1.334(7) | N(6) | C(17) | 1.330(7) |
| N(6) | C(18) | 1.468(8) | N(6) | C(19) | 1.446(7) |
| C(1) | C(2) | 1.361(9) | C(1) | C(6) | 1.396(9) |
| C(2) | C(3) | 1.37(1) | C(3) | C(4) | 1.40(1) |
| C(4) | C(5) | 1.37(1) | C(5) | C(6) | 1.386(10) |
| C(10) | C(11) | 1.378(8) | C(10) | C(15) | 1.380(8) |
| C(11) | C(12) | 1.389(8) | C(12) | C(13) | 1.382(8) |
| C(13) | C(14) | 1.368(8) | C(14) | C(15) | 1.402(8) |
| C(19) | C(20) | 1.392(8) | C(19) | C(21) | 1.351(8) |
| C(20) | C(21) | 1.369(8) | | | |

Table 22-4. Bond Angles (deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|-------|-------|-------|----------|-------|-------|-------|----------|
| C(1) | N(1) | C(7) | 117.4(6) | C(1) | N(1) | C(8) | 121.3(6) |
| C(7) | N(1) | C(8) | 120.7(6) | C(8) | N(3) | C(9) | 121.6(6) |
| C(8) | N(3) | C(10) | 121.8(5) | C(9) | N(3) | C(10) | 116.3(5) |
| C(13) | N(4) | C(16) | 115.7(5) | C(13) | N(4) | C(17) | 121.2(5) |
| C(16) | N(4) | C(17) | 122.0(5) | C(17) | N(6) | C(18) | 121.0(5) |
| C(17) | N(6) | C(19) | 121.2(5) | C(18) | N(6) | C(19) | 117.4(5) |
| N(1) | C(1) | C(2) | 120.6(6) | N(1) | C(1) | C(6) | 118.3(6) |
| C(2) | C(1) | C(6) | 121.0(7) | C(1) | C(2) | C(3) | 120.4(7) |
| C(2) | C(3) | C(4) | 119.3(8) | C(3) | C(4) | C(5) | 120.6(8) |
| C(4) | C(5) | C(6) | 119.7(8) | C(1) | C(6) | C(5) | 118.9(7) |
| N(1) | C(8) | N(2) | 119.9(6) | N(1) | C(8) | N(3) | 121.1(6) |
| N(2) | C(8) | N(3) | 118.9(6) | N(3) | C(10) | C(11) | 119.5(6) |
| N(3) | C(10) | C(15) | 118.7(6) | C(11) | C(10) | C(15) | 121.8(5) |
| C(10) | C(11) | C(12) | 119.5(6) | C(11) | C(12) | C(13) | 118.8(6) |
| N(4) | C(13) | C(12) | 118.7(5) | N(4) | C(13) | C(14) | 119.4(5) |
| C(12) | C(13) | C(14) | 121.9(6) | C(13) | C(14) | C(15) | 119.5(6) |
| C(10) | C(15) | C(14) | 118.5(6) | N(4) | C(17) | N(5) | 118.4(6) |
| N(4) | C(17) | N(6) | 121.7(5) | N(5) | C(17) | N(6) | 119.8(6) |
| N(6) | C(19) | C(20) | 118.8(5) | N(6) | C(19) | C(21) | 120.8(5) |
| C(20) | C(19) | C(21) | 120.4(5) | C(19) | C(20) | C(21) | 118.6(5) |
| C(19) | C(21) | C(20) | 121.0(5) | | | | |

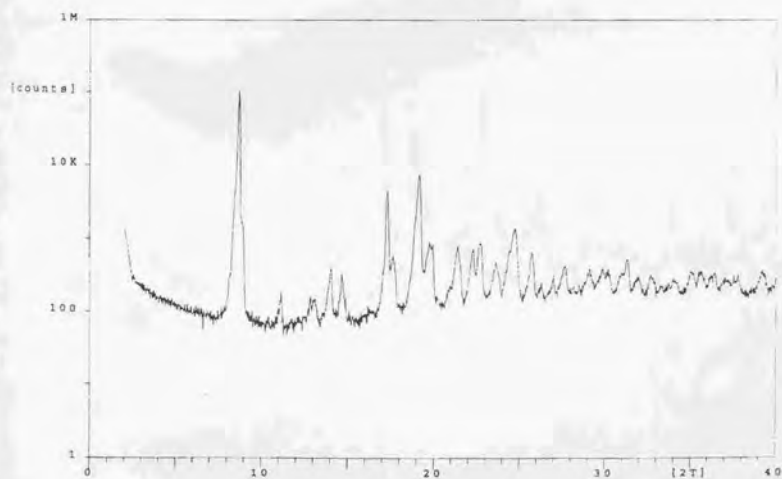
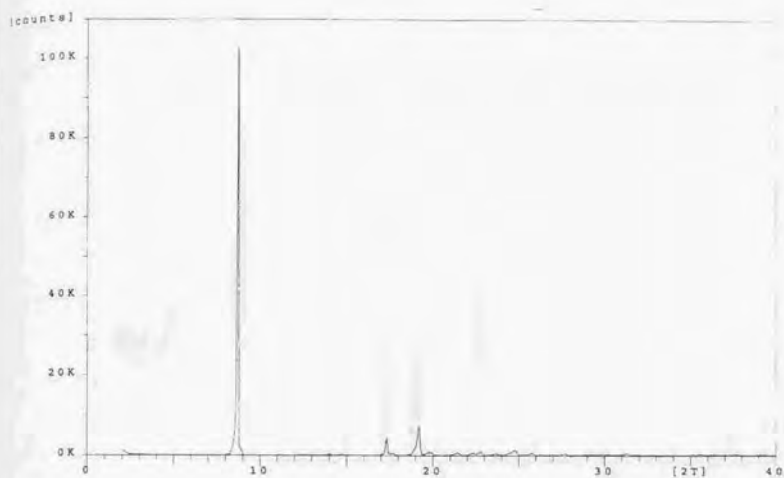
Table 22-5. Least Squares Planes

| Plane number 1 | | | Plane number 2 | | |
|----------------------|--|-----------|----------------------|------------------|-----------|
| Atoms defining plane | | Distance | Atoms defining plane | | Distance |
| N(1) | | -0.004(6) | N(4) | | -0.002(5) |
| N(2) | | -0.004(7) | N(5) | | -0.002(6) |
| N(3) | | -0.003(6) | N(6) | | -0.002(5) |
| C(8) | | 0.012(7) | C(17) | | 0.006(6) |
| Plane number 3 | | | Plane number 4 | | |
| Atoms defining plane | | Distance | Atoms defining plane | | Distance |
| C(1) | | 0.006(6) | C(10) | | 0.000(6) |
| C(2) | | -0.005(7) | C(11) | | -0.009(6) |
| C(3) | | 0.000(8) | C(12) | | 0.009(6) |
| C(4) | | 0.002(9) | C(13) | | 0.000(6) |
| C(5) | | 0.002(8) | C(14) | | -0.009(7) |
| C(6) | | -0.006(7) | C(15) | | 0.009(6) |
| Plane number 5 | | | | | |
| Atoms defining plane | | Distance | | | |
| C(19) | | 0.0 | | | |
| C(20) | | 0.0 | | | |
| C(21) | | 0.0 | | | |
| Summary | | plane | mean deviation | CHI ² | |
| | | 1 | 0.0055 | 3.7 | |
| | | 2 | 0.0028 | 1.3 | |
| | | 3 | 0.0034 | 1.9 | |
| | | 4 | 0.0060 | 7.4 | |
| | | 5 | 0.0000 | 0.0 | |

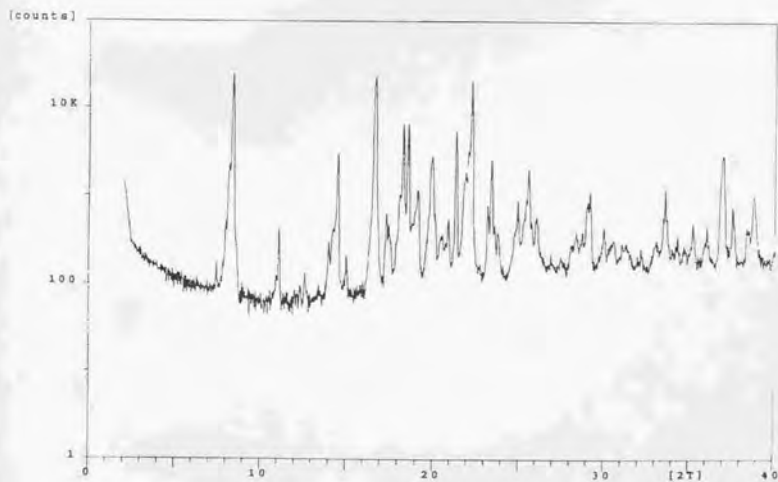
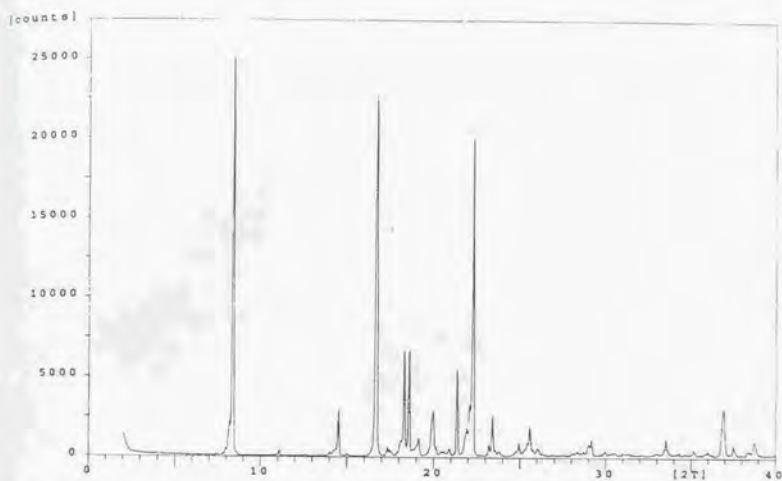
Dihedral angles between planes (deg)

| plane | 1 | 2 | 3 | 4 |
|-------|--------|--------|--------|--------|
| 2 | 67.02 | | | |
| 3 | 108.67 | 48.18 | | |
| 4 | 111.20 | 69.80 | 28.89 | |
| 5 | 48.39 | 107.74 | 155.47 | 153.28 |

Powder X-ray Crystallographical Data of Chiral Crystal of 1



Powder X-ray Crystallographical Data of Racemic Crystal of 1



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