Hydrogen-Atom Transfer Photochemistry of Tetrakis(μ-pyrophosphito)diplatinate(II)

Thesis by Robert J. Sweeney

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All my life I've been a blade of grass in the wind
Or like a stubborn tree I let the wind shape me
But now, I'm feeling bold enough to let go my hold
And I'll not be a blade of grass again
I'm gonna be the wind

-Laurie Lewis

Acknowledgements

Harry Gray provided me with options, which at times are more valuable than almost anything else. Of course, Harry's also a great source of humor and perspective and he's taught me a lot of what I thought I came to Caltech to learn. Jack Beauchamp helped me learn lessons which I never intended to learn, but as it turns out, I'm glad I did. Tom Dunn seems like my third advisor. For four years, he was a most accessible and helpful guide through what I often thought of as a swamp of electronics and design.

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and he also deserves a lot of thanks for when things were going well, too.

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Of course, Erica's filled all the roles I've mentioned so far. I look forward to our future collaborations.

Abstract

In many senses, the hydrogen-atom transfer reactions observed with the triplet excited state of pyrophosphito-bridged platinum(II) dimers resemble the reactions of organic ketone $n\pi^*$ states. The first two chapters describe our attempts to understand the reactivity differences between these two chromophores. Reactivity of the metal dimers is strongly regulated by the detailed nature of the ligands that ring the axial site, the hydrogen-abstraction center. A hydrogen-bonded network linking the ligands facilitates H-atom transfer quenching with alcohols through the formation of a hydrogen-bonded complex between the alcohol and a dimer. For substrates of equal C-H bond strength that lack a hydroxyl group (e.g., benzyl hydrocarbons), the quenching rate is several orders of magnitude slower.

The shape and size of the axial site, as determined by the ligands, also discriminate among quenchers by their steric characteristics. Very small quenchers quench slowly because of high entropies of activation, while very large ones have large enthalpic barriers. The two effects find a balance with quenchers of "just the right size."

The third chapter discusses the design of a mass spectrometer that uses positron annihilation to ionize neutral molecules. The mass spectrometer creates positron-molecule adducts whose annihilation produces fragmentation products that may yield information on the bonding of positrons in such complexes.

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Hydrogen-Atom Transfer Reactions of $^3Pt_2^*$ with Alcohols and Aromatic Hydrocarbons

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Introduction

The triplet excited state of tetrakis(μ-pyrophosphito) diplatinate(II) (Figure 1, ground state abbreviated Pt_2) is deactivated by reaction with a variety of hydrogen-donating organic species,[1, 2] including alcohols,[3-5] benzyl hydrocarbons,[4] alkenes[3, 6] and main-group hydrides.[7] The initial photoproducts are organic radicals, and the monohydride Pt_2H;[3, 5, 8] subsequent, poorly understood, steps lead to formation of the stable axial dihydride Pt_2H_2[9] and typical organic radical products (e.g., dimers from alkanes, ketones from alcohols).[4] In contrast to other hydrogen-abstraction reactions, the hydrogenated product Pt_2H_2 is efficiently photoconverted back to Pt_2 with the evolution of H_2, thus completing a catalytic cycle.[9]

$$Pt_2 \xrightarrow[372\ nm]{h\nu} {}^3Pt_2^* \qquad (1)$$

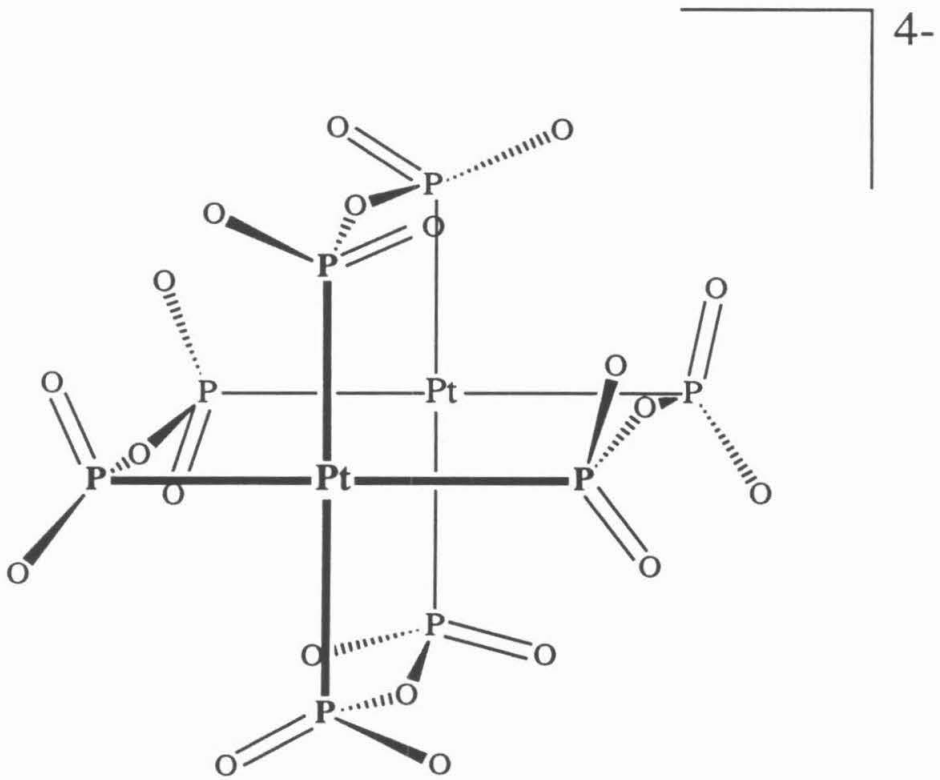
$${}^3Pt_2^* + RH \xrightarrow{k_q} Pt_2H + R\cdot \qquad (2)$$

$$Pt_2H \longrightarrow Pt_2H_2 \qquad (3)$$

$$Pt_2H_2 \xrightarrow[313\ nm]{h\nu} Pt_2 + H_2 \qquad (4)$$

The vast range of rate constants[3] for the C-H activation step (2) suggests that Pt_2 may be useful in selective functionalization of organic substrates. The utility of Pt_2 as a photo-dehydrogenation catalyst depends on several factors that are not well understood,

Figure 1. The structure of the tetrakis(μ-pyrophosphito) diplatinate(II) tetraanion.



Note: Protons (not shown) bridge neighboring P=O and P-O groups

namely, dehydrogenation selectivity and overall reaction efficiencies.

In an effort to address these questions, we have examined in detail the reactions of alcohols and aromatic hydrocarbons with $^3Pt_2^*$. In contrast to previous work on $^3Pt_2^*$ dehydrogenations, the rates of both the initial abstraction step and the stable product formation have been determined.

Several excellent reviews of Pt_2[1, 2] and its photochemistry[10] have recently been published. An extensive background will not be presented here, and readers are referred to these articles for further information.

Experimental Details

Materials. The tetra-*n*-butylammonium (TBA) salt of Pt_2 was prepared from the potassium salt as described previously.[11] The tetra-*n*-octylammonium (TOA) salt is prepared by vigorous mixing of ethyl ether with an aqueous mixture of K_4Pt_2 and TOABr (Aldrich 98%), followed by drying and evaporation of the ether phase. $[TOA]_4Pt_2$ is a yellow, viscous oil that resisted attempts at crystallization. Calculated 54.1%C, 9.88%H, 2.0%N. Found 54.4%C, 9.81%H, 1.55%N. $[TOA]_4Pt_2$ dissolves in diethyl ether, toluene, methylene chloride and acetonitrile, but not in water.

Burdick and Jackson High-Purity, UV grade acetonitrile was used as received as solvent for all experiments. Isopropanol, 2-butanol (Aldrich Gold Label 99+%), 3-methyl-2-butanol (Aldrich 99%), toluene (Burdick and Jackson High-Purity Solvent) and ethylene glycol (Aldrich 99+%) were used as received. Benzyl alcohol, 1-phenyl-1-ethanol (methylbenzyl alcohol), 1-phenyl-1-propanol and diphenylmethane were purchased from Aldrich, reagent grade; 2-methyl-1-phenyl-1-propanol was purchased from Wiley, 97%. Purification of ethylbenzene, cumene and *tert*-butylbenzene is detailed elsewhere.[12] The liquid alcohols and hydrocarbons were purified by fractional distillation under vacuum or a nitrogen atmosphere and stored under nitrogen or argon. The solid quencher 2,2-dimethyl-1-phenyl-1-propanol (Wiley 97%) was sublimed under vacuum two times immediately prior to use. The monodeuterated alcohol $PhCD(OH)CH_3$ was synthesized by reducing acetophenone with $NaBD_4$ and quenching the reaction with H_2O.

Quenching studies. Acetonitrile solutions containing $[TBA]_4Pt_2$ (1-3 $x10^{-4}$ M) plus incrementally varied quencher concentrations were degassed with at least 5 freeze-pump-thaw cycles on a vacuum line with a limiting pressure of ~10^{-5} torr. Quenchers were added directly to the quenching cell (roundbottom flask connected by two arms to 1 mm and 1 cm cuvettes and sealed by teflon vacuum valves), using a syringe of the appropriate volume (between 10 μL and 1 mL); the solution was opened to air for the addition of each quencher aliquot. Alternatively, relatively concentrated quencher solutions were successively diluted by additions of acetonitrile. Excited-state lifetimes (τ) were measured with a Quanta Ray Nd:YAG (8 ns fwhm; 355 nm excitation) laser system described elsewhere.[13] Emission was monitored at 518 nm. Quenching rate constants and the quantities derived from them have estimated associated errors of <10%.

Cumene and ethylbenzene react rapidly with Pt_2 in the presence of air with loss of Pt_2, requiring mixing of the two during quenching studies only after degassing. $[TOA]_4Pt_2$ in neat toluene also degrades rapidly in the presence of air.

Normal quenching studies were performed at room temperature. For activation parameter studies, temperature was controlled in the range 6°C to 80°C through immersion of the quenching cell in a water bath. The lifetime of $^3Pt_2^*$ in CH_3CN remains constant throughout the temperature range studied. Thus, changes in the $^3Pt_2^*$ lifetime as temperature varies, in the presence of a given quencher concentration, directly reflect changes in the quenching rate.

Kinetic data were analyzed by either linear Stern-Volmer plots of $(1/\tau-1/\tau_o)$ versus quencher concentration [Q], or linear Michaelis-Menten plots of $(1/\tau-1/\tau_o)^{-1}$ versus $[Q]^{-1}$.

The lifetime τ of $[TOA]_4Pt_2$ phosphorescence in toluene is 7.3 μsec. An unquenched τ_o of 10.3 μsec in toluene is calculated if k_q is assumed to be the same as that found in CH_3CN solutions ($k_q=4.2x10^3M^{-1}s^{-1}$). Therefore, τ_o is approximately invariant in acetonitrile, methanol and toluene! In quenching studies that employ high quencher concentrations, the quenchers may begin to alter the solvent's properties and therefore may change the unquenched lifetime of excited states, which may be sensitive to solvent viscosity or other properties. Since changes in the solvent medium do not significantly alter the natural lifetime τ_o of Pt_2, such effects are negligible and lifetime changes can be attributed solely to changes in the quenching rate.

Bulk photolyses. Acetonitrile solutions of $[TBA]_4Pt_2$ ($\sim3x10^{-4}M$) were degassed with at least 5 freeze-pump-thaw cycles. Solutions were irradiated in a 1 cm cell, and the absorption changes were measured in an attached 1 mm cell. Cary 14 and Shimadzu UV-260 absorption spectrometers were used. For the irradiation source, a 1000W Hg-Xe lamp with cutoff and band-pass optical filters provided a photon flux of $\sim10^{-7}$ Ei s^{-1} for the wavelength range 340 nm to 400 nm. Actinometry was performed with Aberchrome 540, or *trans*-2-(2,5-dimethyl-3-furanyl)ethylidene-3-(1-methylethylidene)succinic anhydride, dissolved in degassed toluene (Burdick and Jackson High-Purity Solvent). Absorptions of both the actinometer and Pt_2 solutions are

sufficiently high that all photons reaching the solutions are absorbed.

Product Identification. Products were identified by gas chromatography and their retention times compared to those of authentic samples. In some cases the products were also identified through ^1H NMR. Prior to GC analysis, KPF_6 was added to photolyzed solutions to precipitate the platinum complex. Both Carbowax and glass columns were used with a flame ionization detector on the Hewlett-Packard 8410 GC. GC peak areas are proportional to moles of carbon detected; this relationship was verified for the bibenzyl/biphenyl system. Biphenyl was used as the internal standard. Although the k_q for biphenyl with Pt_2 is $\sim 10^5 M^{-1}s^{-1}$, quenching does not lead to product formation and biphenyl is present at such low concentrations (less than 0.01 M) that its quenching is not significant.

Results and Discussion

H-atom transfer quenching of $^3Pt_2^*$

The reaction between $^3Pt_2^*$ and organic substrates has typically been monitored by determining the rate with which the organic compound (Q) quenches the luminescence of the $^3Pt_2^*$ excited state. The Stern-Volmer equation (Equation 1) describes the dependence of the excited state lifetime on the quencher concentration when deactivation of the excited state occurs via bimolecular reactions with a quencher.

$$1/\tau - 1/\tau_0 = k_q[Q] \qquad (1)$$

The quenched and unquenched lifetimes of the luminescent excited state are given by τ and τ_0, respectively; k_q is the Stern-Volmer quenching rate constant determined from the slope of a linear plot of $(1/\tau - 1/\tau_0)$ versus [Q].

The rate of hydrogen-atom abstraction by $^3Pt_2^*$, as measured by the quenching rate k_q, is given for a variety of organic H-atom donors in Table 1. Figure 2 shows the correlation of quenching rate constants with C-H homolytic bond strength.

Benzyl alcohols quench $^3Pt_2^*$ mainly through H-atom transfer, as demonstrated by the large kinetic isotope effect observed for quenching with methylbenzyl alcohol (k_H/k_D=5) and the observation of ketones and Pt_2H_2 as photolysis products in reasonably high yields (*vide infra*). Also, k_q tends to decrease with increasing D(C-H) for the alcohols, as observed in photoabstraction reactions by the $n\pi^*$ excited states of ketones.[14-16]

Figure 2. The dependence of the $^3Pt_2^*$ quenching rate constant on the C-H bond strength for a variety of organic H-atom donor quenchers. Squares represent data for sterically hindered alcohols.

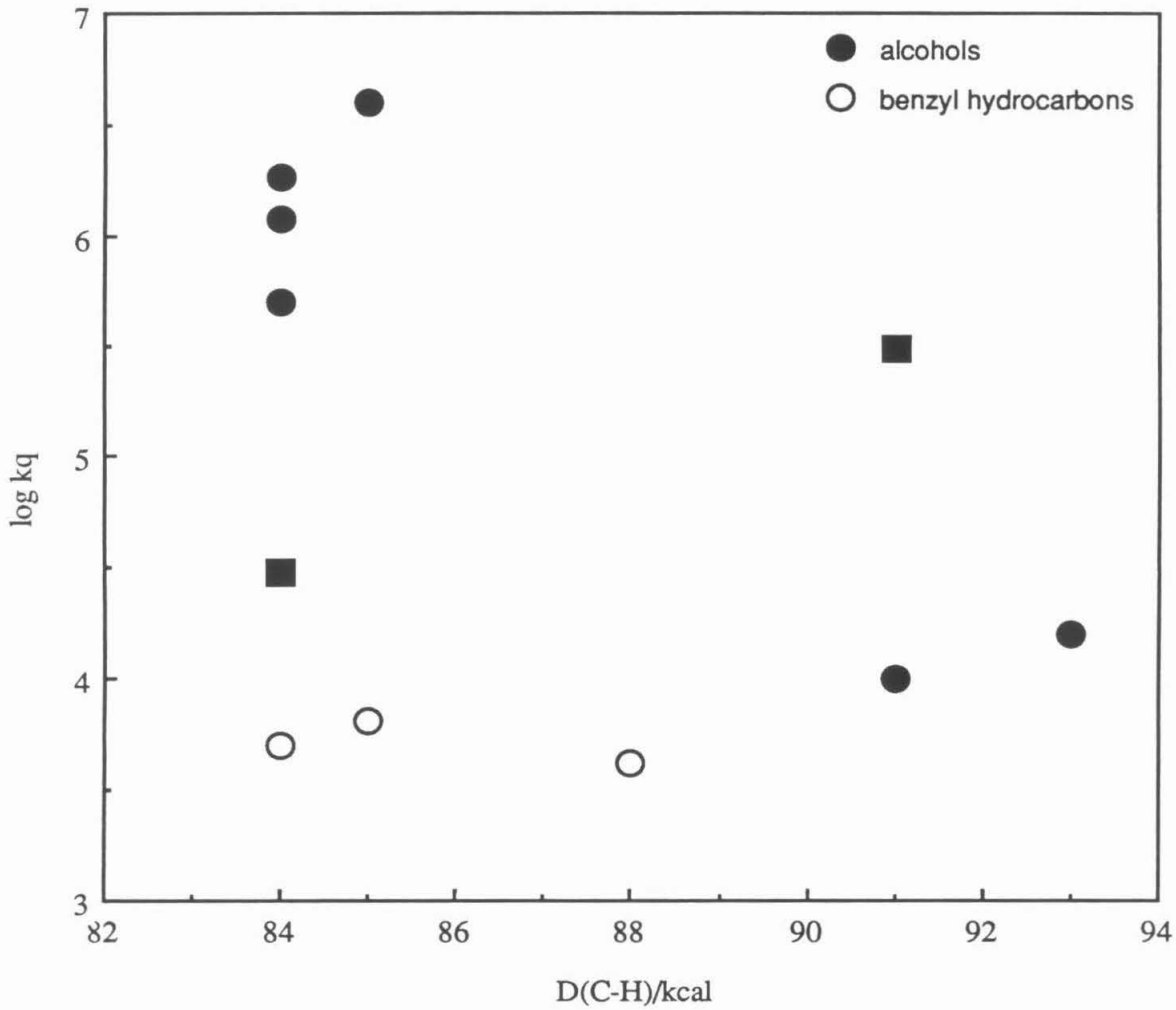


Table 1 $^3Pt_2^*$ Stern-Volmer quenching rate constants for organic H-atom donors Alcohols RR'CHOH[17]

R	R'	k_q ($M^{-1}s^{-1}$)	D(C-H) (kcal/mol)
Ph	H	4×10^6	85
Ph	CH_3	1.8×10^6	84
Ph α-D	CH_3	3.6×10^5	
Ph	CH_2CH_3	1.2×10^6	84
Ph	$CH(CH_3)_2$	5×10^5	84
Ph	$C(CH_3)_3$	3×10^4	84
CH_3	CH_3	$\sim 10^4$	91
CH_3	CH_2CH_3	$\sim 10^4$	91
CH_3	$CH(CH_3)_2$	3×10^5	91
CH_2OH	H	1.6×10^4	93
Benzyl Hydrocarbons			
$PhCH_3$		4.2×10^3	88
$PhCD_3$		2.8×10^3	
$PhCH_2CH_3$		6.4×10^3	85
$PhCH(CH_3)_2$		5.0×10^3	84
$PhC(CH_3)_3$		7.4×10^3	

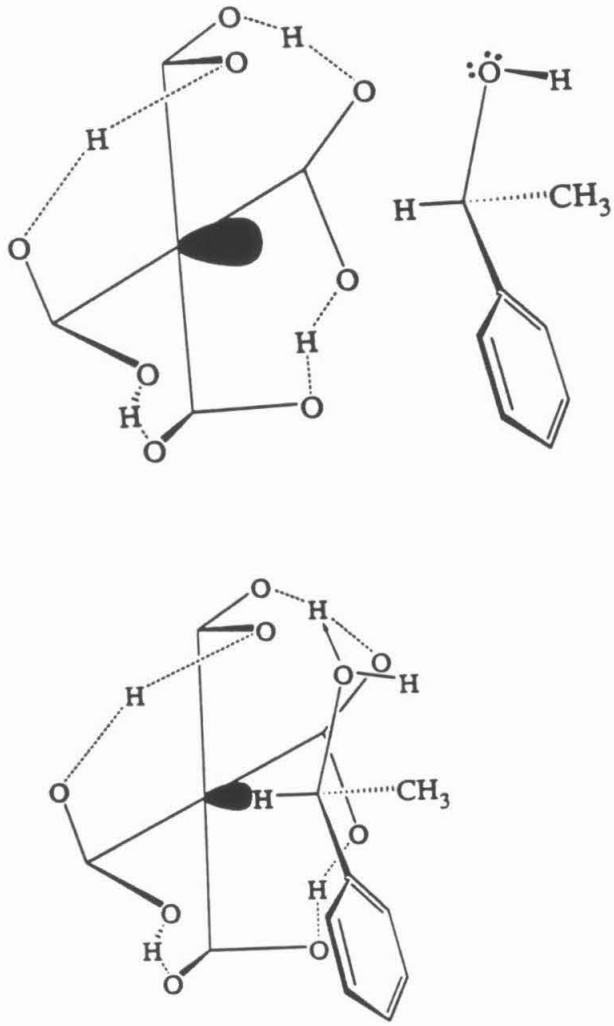
Benzyl hydrocarbons also quench $^3Pt_2^*$ through H-atom abstraction, as confirmed by the formation of Pt_2H_2 and radical coupling products (e.g., bibenzyl from toluene). However, the main route of quenching by benzyl hydrocarbons apparently is <u>not</u> H-atom transfer, since the quenching rate remains approximately constant from toluene to *tert*-butylbenzene, although the latter has no easily abstractable hydrogen atoms. Also, radical coupling products are detected in low yield (*vide infra*) and the isotope effect for toluene (k_H/k_D = 1.5) is much lower than for the alcohols. Therefore, we report the k_q values as upper limits on the actual H-atom-transfer

quenching rate for these substrates. Clearly, atom-transfer quenching rates for $^3Pt_2^*$ with benzyl alcohols are much faster than the rates for hydrocarbons with comparable benzylic C-H bond strengths.

Steric interactions are a very plausible source of the unusual reactivity patterns observed for reactions of $^3Pt_2^*$ with organic substrates. In the triplet excited state of Pt_2 responsible for H-atom transfer reactions, an electron has been promoted from a $d\sigma^*$ orbital directed out along the Pt-Pt axis to a $p\sigma$ orbital localized between the two platinum atoms.[11, 18] This leaves a hole/radical in the $d\sigma^*$ orbital, localized in the axial site. This situation is similar to the hole left in the oxygen-localized n orbital in the $n\pi^*$ state of organic ketones, which also abstract H atoms from suitable substrates.[14] The high kinetic isotope effect for H-atom transfer suggests that the C-H bond forms a linear transition state along the Pt-H-C coordinate during H-atom transfer. The presence of OH moieties in alcohols gives rise to the possibility of H-bonding interactions between the substrate and the H-bonded terminal oxygens on the Pt_2 ligands. Such interactions may specifically facilitate the approach of alcohol substrates to the axial sites on the metal complex, preparatory to abstraction by the metal center (Figure 3).

Alcohols exhibit unusual quenching behavior when present at high concentrations. The rate of quenching, $1/\tau - 1/\tau_o$, reaches a limiting value as more alcohol is added (i.e., the Stern-Volmer plot becomes horizontal, Figure 4). The initial linear region is used to extract k_q. Nonlinearity has previously been attributed to self-

Figure 3. A proposed view of alcohol "docking" onto Pt_2 ligands.



dimerization of alcohol quenchers,[19] but this model does not predict the limiting quenching rate observed.

A hydrogen-bonded intermediate alters the previously assumed bimolecular reaction model by dividing the quenching reaction into two steps. The first step is formation of an H-bonded precursor complex between the metal dimer and the alcohol substrate, followed by unimolecular H-atom transfer.

Scheme 2

$$^3Pt_2^* + RR'CHOH \underset{}{\overset{K_{eq}}{\rightleftharpoons}} {}^3[Pt_2{}^{\cdot\cdot}HCOHRR']^*$$

$$^3[Pt_2{}^{\cdot\cdot}HCOHRR']^* \xrightarrow{k_1} Pt_2H + RR'\dot{C}OH$$

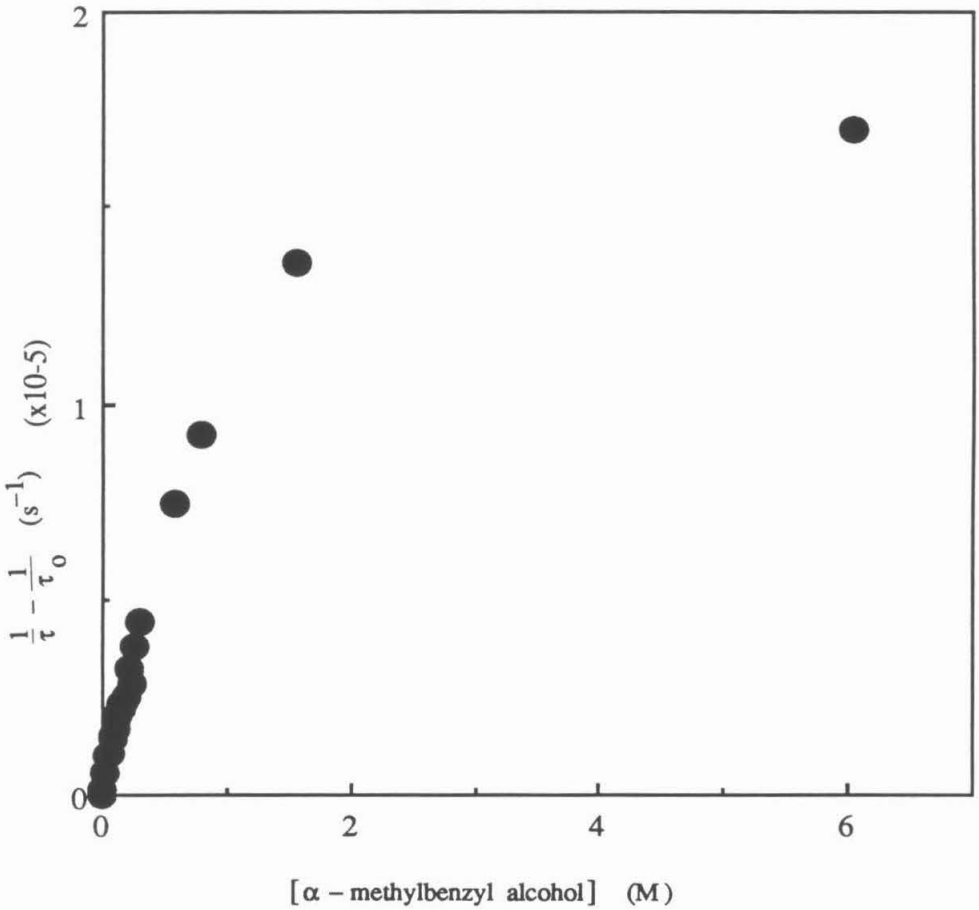
The pre-equilibrium step is consistent with pressure-dependent quenching studies that find a large negative $\Delta V^{\ddagger}$ for the reaction of $^3Pt_2^*$ with benzyl alcohols.[19]

The kinetic treatment for this pre-equilibrium model, which is directly analogous to Michaelis-Menten enzyme catalysis kinetics, predicts Equation 2.

$$1/\tau_0 - 1/\tau = \frac{K_{eq}k_1}{K_{eq} + 1/[ROH]} \qquad (2)$$

In contrast to Stern-Volmer bimolecular kinetics, quenching of the excited state should not be linear with quencher concentration except in the low-concentration limit where k_q experiments are normally performed. At high concentrations, the Stern-Volmer plot should begin to flatten out, as observed (Figure 4). Similar pre-

Figure 4. The Stern-Volmer quenching plot for the quenching of $^3Pt_2^*$ phosphorescence with α-methylbenzyl alcohol.



equilibrium reactions are important in electron-transfer reactions between bipyridyl complexes and copper proteins.[20]

Rearrangement of Equation 2 predicts a linear relationship between $1/k_q$ and 1/[ROH] for quenchers that form a precursor complex (Equation 3).

$$(1/\tau - 1/\tau_0)^{-1} = 1/k_1 + 1/K_{eq}k_1[ROH] \qquad (3)$$

Plotting alcohol quenching data in this manner does indeed give a straight line (Figure 5).

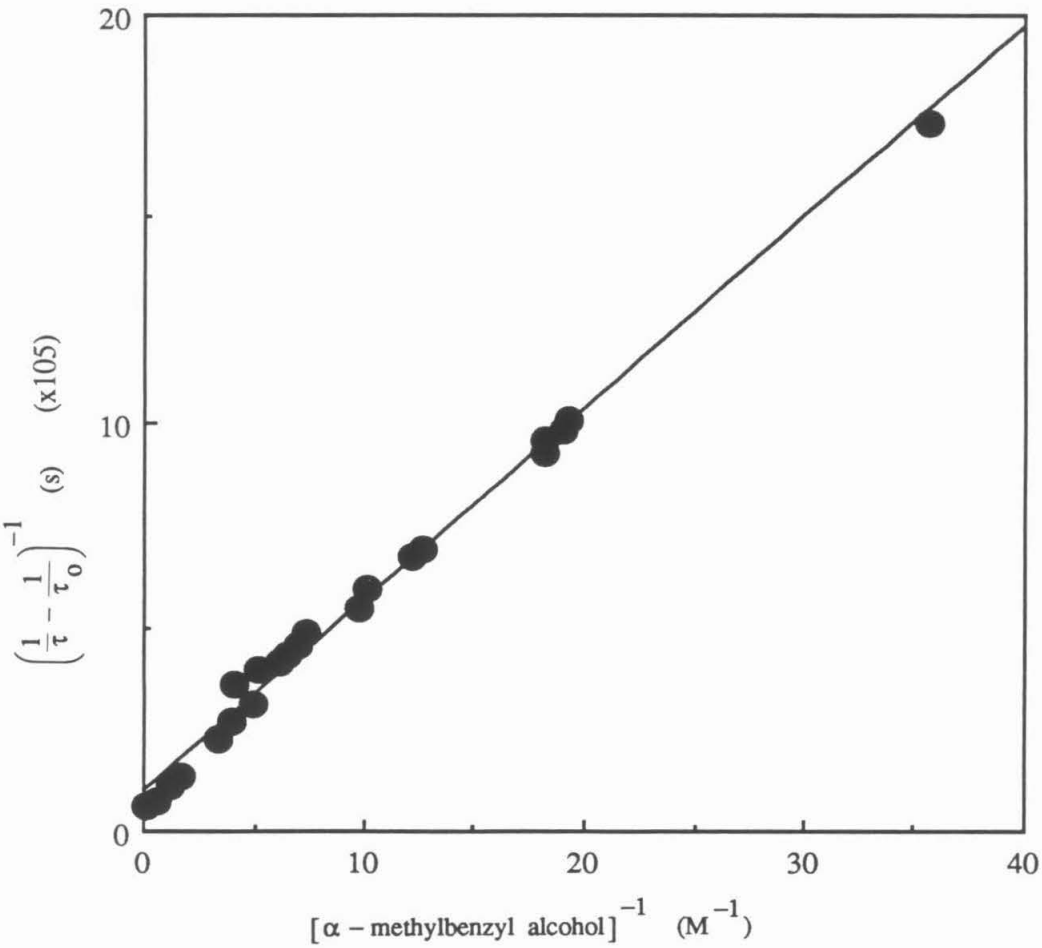
Values of K_{eq} and k_1 can be extracted from both types of plots. The slope of the Stern-Volmer plot at low alcohol concentrations is equal to $K_{eq}k_1$, which corresponds to the k_q reported previously. At high concentrations, k_q reaches a limiting value equivalent to the unimolecular rate constant, k_1. The slope of the linear Michaelis-Menten plot equals $(K_{eq}k_1)^{-1}$; the high-concentration intercept is k_1^{-1}.

Table 2 $^3Pt_2^*$ phosphorescence quenching parameters for selected alcohols RR'CHOH

R	R'	K_{eq} (M^{-1})	k_1 (s^{-1})
Ph	CH_3	1.0	2.1×10^6
Ph	$CH(CH_3)_2$	0.2	2.1×10^6
CH_2OH	H	0.5	3.5×10^4
CH_3	$CH(CH_3)_2$	0.5	5.0×10^5

K_{eq} and k_1 values were determined for a series of alcohols (Table 2). The fact that K_{eq} is relatively invariant with respect to substitution on the α carbon is consistent with a docking interaction

Figure 5. Quenching data for the reaction of α-methylbenzyl alcohol with $^3Pt_2^*$ plotted according to Equation (3).



involving only the hydroxyl group, since variation of alkyl groups on the α carbon should not affect the hydroxyl group significantly. The ΔS_{rxn} associated with K_{eq} is -66 e.u., as determined by variable-temperature quenching experiments with methylbenzyl alcohol. The high degree of organization implied agrees with our formulation of this step as a bimolecular association. The ΔH_{rxn} of -1.8 kcal/mol is reasonable for the strength of a hydrogen bond.

Since K_{eq} varies little, large changes in k_q are due mainly to differences in the unimolecular rate k_1. Therefore, in order to understand and predict the relative reactivities of alcohols with $^3Pt_2^*$, the factors that determine k_1 must be understood. As alcohol substituents are varied, the effect of such substitutions on k_1 can be determined by following changes in k_1's activation parameters. Arrhenius parameters for the k_1 constants of selected alcohols are listed in Table 3.

Table 3. Arrhenius parameters for $^3Pt_2^*$ phosphorescence quenching by alcohols RR'CHOH

R	R'	$\Delta S^{\ddagger}$ (e.u.)	E_a (kcal/mol)
Ph	CH_3	-20	2.9
Ph	$CH(CH_3)_2$	-12	5.5
CH_2OH	H	-23	4.4
CH_3	$CH(CH_3)_2$	-10	6.8

Entropic barriers in this unimolecular quenching step are reasonably large and reflect the highly organized nature of the presumably linear H-atom-transfer transition state. For comparison,

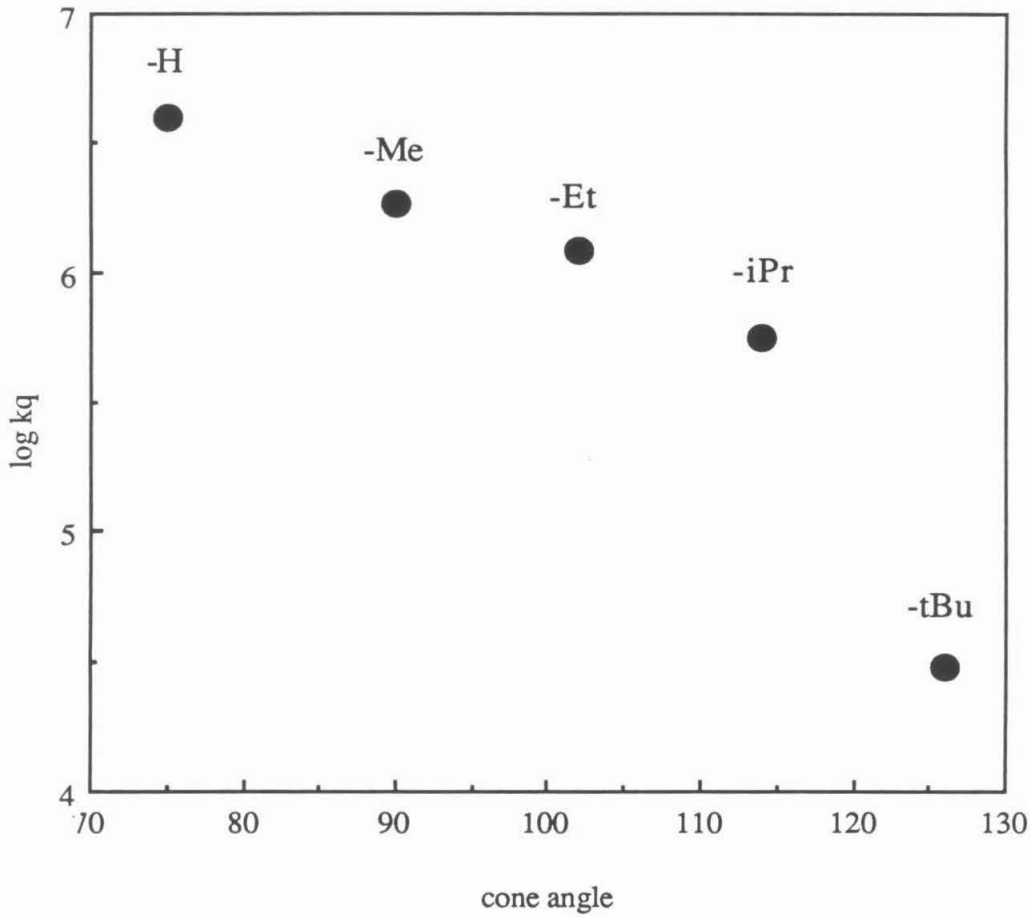
the $\Delta S^{\ddagger}$ for cyclopentadiene dimerization, is -34 e.u.[21] and corresponds to a highly ordered bimolecular condensation. The primary variable responsible for the range in $\Delta S^{\ddagger}$ appears to be steric bulk of substituents α to the hydroxyl group. Being anchored to Pt_2 via the hydroxyl group, alcohols have a limited number of available orientations that are further limited by steric requirements of the substituents. The entropy of activation reflects the proportion of these conformations that can lead to atom transfer. Large substituents reduce the number of nonreactive conformations and therefore make the reaction more facile entropically. For example, replacement of an α-methyl group with an *iso*-propyl group drastically decreases the magnitude of $\Delta S^{\ddagger}$ for both benzyl and aliphatic alcohols.

For compounds with similar $\Delta S^{\ddagger}$ values, the activation energy E_a follows the αC-H bond strength, as expected. E_a increases ~1.5 kcal/mol between benzyl and aliphatic alcohols. For both types of alcohols, increasing steric bulk actually increases E_a. Presumably, the transition state for atom transfer is not a low-energy conformation and the measured E_a is some combination of the barrier to atom abstraction and the energy required to reach the linear transition state. Thus, the overall contribution of increased steric bulk depends on the balance between changes in $\Delta S^{\ddagger}$ and E_a.

For the series of aliphatic alcohols including isopropanol, 2-butanol and 3-methyl-2-butanol, the increase in substituent size dramatically increases the quenching rate from the technique's lower measurement limits (10^4 $M^{-1}s^{-1}$) to rates near those of the benzyl alcohols. Within a series of benzyl alcohols (Figure 6),

increasing substituent size decreases the quenching rate k_q. In the case of *tert*-butyl benzyl alcohol, the reactive transition state itself is one of the conformations disallowed by sterics and k_q plummets.

Figure 6. The variation of the Stern-Volmer quenching rate k_q as a function of the cone angle of α-substituents on benzyl alcohols.



Product formation rates

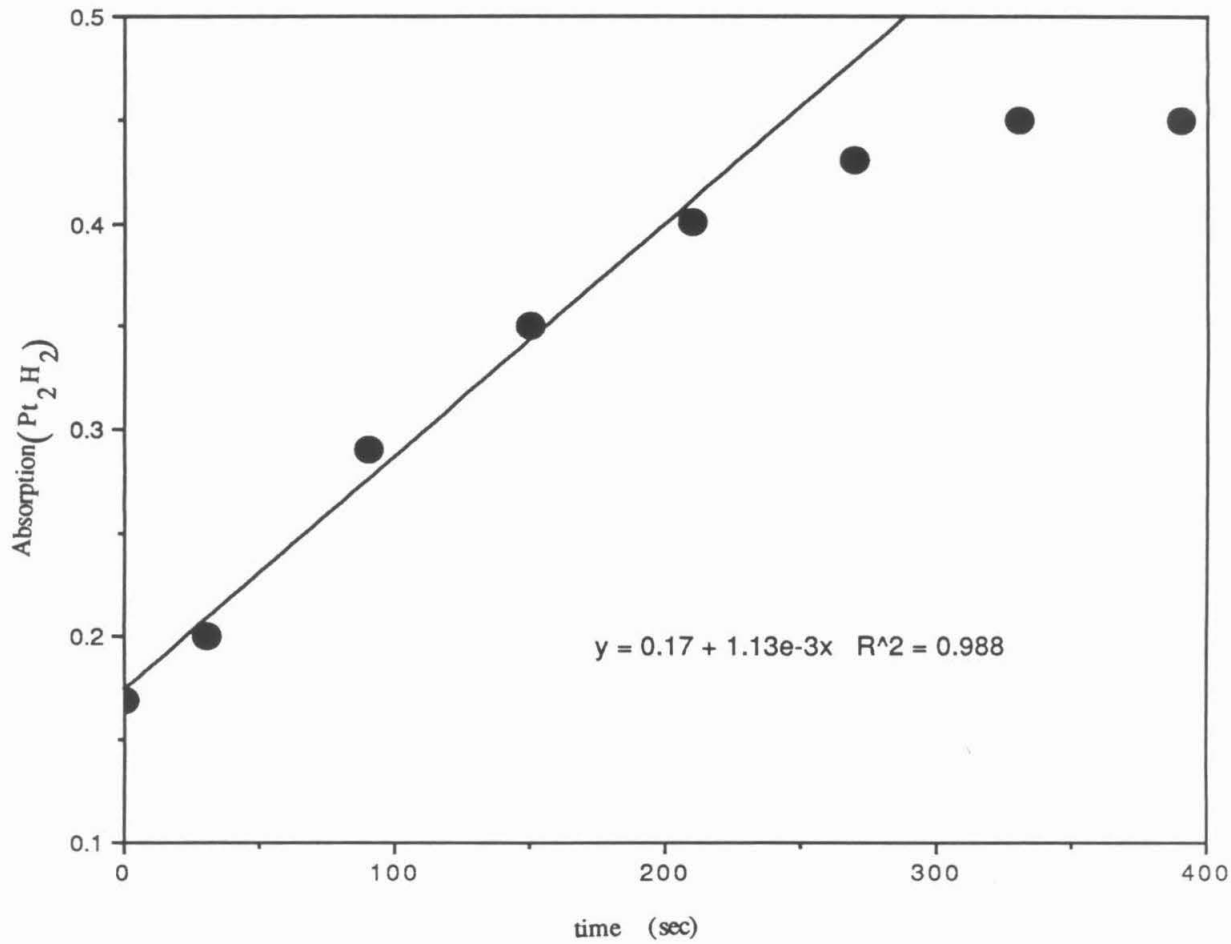
Stern-Volmer quenching constants provide useful information about factors that control the selectivity of the initial H-atom abstraction by $^3Pt_2^*$, but yield no information regarding formation of the eventual stable products. Although the quenching of $^3Pt_2^*$ with alcohols has been studied thoroughly, deactivation of the excited state is only the first step in a sequence of reactions that leads to the observed stable products Pt_2H_2, H_2, and ketones. The relationship between effective rate constants for product formation (k_p) and the rate constant of the quenching step (k_q) can be expressed through the efficiency parameter Φ_p, where Φ_p is necessarily less than 1.

$$k_p/k_q = \Phi_p \qquad (4)$$

A Φ_p value of unity (100%) implies that every deactivation reaction leads to the formation of one molecule of a stable atom-transfer product. The growth of the distinctive ultraviolet absorption band for Pt_2H_2 at 313 nm proved to be a useful handle for following product formation with alcohols in CH_3CN.

At high conversions to Pt_2H_2, the system appeared to approach a photostationary state; i.e., the absorption spectrum showed no change upon further irradiation (Figure 7). The low-energy tail of the Pt_2H_2 band presumably absorbs some of the excitation light (λ>350 nm) and photoeliminates dihydrogen. When the growth in Pt_2H_2 that is due to abstraction from alcohols is exactly balanced by its photochemical decomposition, a steady state of the dihydride is established.

Figure 7. Absorption of the 313 nm Pt_2H_2 band as a function of the time of irradiation into the Pt_2 absorption band at 372 nm. The H-atom donor quencher is benzyl alcohol (0.077M).



For reactions with benzyl hydrocarbons, long-term photolyses yielded benzyl dimers as products, which were quantitatively analyzed by gas chromatography. The amount of product formed and the photon flux (I) combine to give k_p, through the equation

moles RH consumed = 2(moles dimer R_2 produced) = $It\tau k_p[RH]$.

A small amount of the dihydride was also formed in photolyses with cumene and ethylbenzene, but the k_p values were not determined. Toluene solutions were not found to yield the dihydride. This may merely reflect the slow hydrogen-transfer rate of toluene relative to cumene and ethylbenzene. Photolyses of $[TOA]_4Pt_2$ in tert-butylbenzene yielded only trioctylamine, presumably via electron-transfer reactions from $^3Pt_2^*$ to the tetraoctylammonium cation.

Table 4 Product formation rates and reaction efficiencies for selected quenchers

Quencher	[ROH] (M)	k_p ($M^{-1}s^{-1}$)	Φ_p
		Pt_2H_2 product	
benzyl alcohol	0.058	5.9×10^5	0.15
	0.077	4.0×10^5	0.10
isopropanol	6.53	820	~0.08
		Dimer product	
toluene	4.7	25	0.006
ethylbenzene	4.1	400	0.06
cumene	3.6	600	0.1

The Φ_p (Table 4) values of about 10% reveal that the H-atom-transfer reaction is reasonably efficient for many substrates. However, the rates of product formation span nearly three orders of magnitude among the alcohols, demonstrating remarkable reaction selectivity. From these data, one would predict that given a choice of isopropanol and benzyl alcohol in the same solution, 99.8% of $^3Pt_2^*$ would dehydrogenate benzyl alcohol.

In a more practical test of dehydrogenation selectivity, Pt_2 was irradiated in the presence of two alcohols to compare the relative yields of the corresponding ketones. Photolysis of Pt_2 in an approximately equimolar (0.5M) solution of benzyl alcohol and cyclohexanol demonstrated a reaction selectivity for the benzyl alcohol over cyclohexanol of 15:1. A similar experiment with 2-cyclohexen-1-ol and cyclohexanol yielded no cyclohexenol but showed 365 turnovers in the dehydrogenation of the cyclohexanol to cyclohexanone.

Conclusions

The H-atom-transfer reaction selectivity of $^3Pt_2^*$ is governed more by the chemical and physical structure of its ligands than by the inherent activity of the abstraction center. The hydrophilic nature of the ligands selects alcohols preferentially over hydrophobic substrates, and the steric constraints of the ligands moderate reactivities according to the steric properties of the substrate.

Appendix 1

Extraction of Activation Parameter for a Complex Reaction

The pre-equilibrium quenching model requires the measurement of four activation parameters rather than two, as are needed for simple bimolecular reactions. The activation parameters for the equilibrium step are the enthalpy, ΔH^{eq}, and the entropy of the reaction, ΔS^{eq}. The unimolecular quenching step has an energy, E_a, and an entropy of activation, $\Delta S^{\ddagger}$, which describe the transition state of the reaction. These four terms can be extracted from the apparent Arrhenius parameters at high- and low-quencher concentrations, as determined by following the reaction at various temperatures.

The quenching of emission for the reaction

$$^3Pt_2^* + RR'CHOH \underset{}{\overset{K_{eq}}{\rightleftharpoons}} {}^3[Pt_2{}^{\cdot\cdot}HCOHRR']^*$$

$$^3[Pt_2{}^{\cdot\cdot}HCOHRR']^* \xrightarrow{k_1} Pt_2H + RR'\dot{C}OH$$

obeys the rate law

$$-\frac{d[^3Pt_2^*]}{dt} = \frac{K_{eq}\,k_1}{K_{eq} + 1/[ROH]} \qquad (1)$$

Equation (1) can be contrasted to the analogous Stern-Volmer equation

$$-\frac{d[^3Pt^*_2]}{dt} = \left(\frac{1}{\tau} - \frac{1}{\tau_o}\right) = k_q[Q] \quad . \qquad (2)$$

When coupled to the rate expressions

$$K_{eq} = A^{eq} \exp(-\Delta H^{eq}/RT) \qquad (3)$$

$$k_1 = A^1 \exp(-E_a/RT) \quad , \qquad (4)$$

the quenching rate can be expressed as

$$\left(\frac{1}{\tau} - \frac{1}{\tau_o}\right) = \frac{A^{eq} A^1 \exp(-E_a/RT)\exp(-\Delta H^{eq}/RT)}{A^{eq} \exp(-\Delta H^{eq}/RT) + 1/[ROH]} \quad . \qquad (5)$$

The two limiting cases of quencher concentrations simplify this equation considerably.

A) High-concentration limit, $[ROH]^{-1} >> K_{eq}$. Equations (1) and (5) reduce to

$$k_{obs} = k_1 = A^1 \exp(-E_a/RT) \quad , \qquad (6)$$

and k_{obs} can be treated as if it represented a simple, one-step reaction.

$$\log k_1 = \log A^1 - \frac{E_a}{2.303RT} \qquad (7)$$

$$\Delta S^{\neq} = R \ln\left(\frac{A^1 h c^o}{kT}\right) \qquad (8)$$

$R = 1.987$ cal mol^{-1} K^{-1}

$h = 6.626 \times 10^{-34}$ J sec

$c^o = 1$ M

$k = 1.38 \times 10^{-23}$ J K^{-1}

T = 298 K

B) Low-concentration limit, $[ROH]^{-1} << K_{eq}$. Equations (1) and (5) reduce to

$$k_{obs} = K_{eq} k_1 [ROH] = [ROH] A^{eq} A^1 \exp(-E_a/RT) \exp(-\Delta H^{eq}/RT), \quad (9)$$

which requires a more complicated but still reasonable treatment. We can still treat these data with equations similar to (7) and (8), but we find that

$$E_{obs} = E_a + \Delta H^{eq} \quad (10)$$

and

$$A_{obs} = A^1 A^{eq} [ROH]. \quad (11)$$

Equation (11) produces the sum of the entropic parameters through

$$\Delta S^{\neq} + \Delta S^{eq} = R \ln \left[\left(\frac{hc^o}{kT} \right)^2 A^1 A^{eq} \right]. \quad (12)$$

The activation parameters for the equilibrium follow from knowledge of results from the two limiting cases.

Appendix 2

Representative Data

Figure 8 Calibration plot for the quantitative determination of bibenzyl using biphenyl as an internal GC standard.

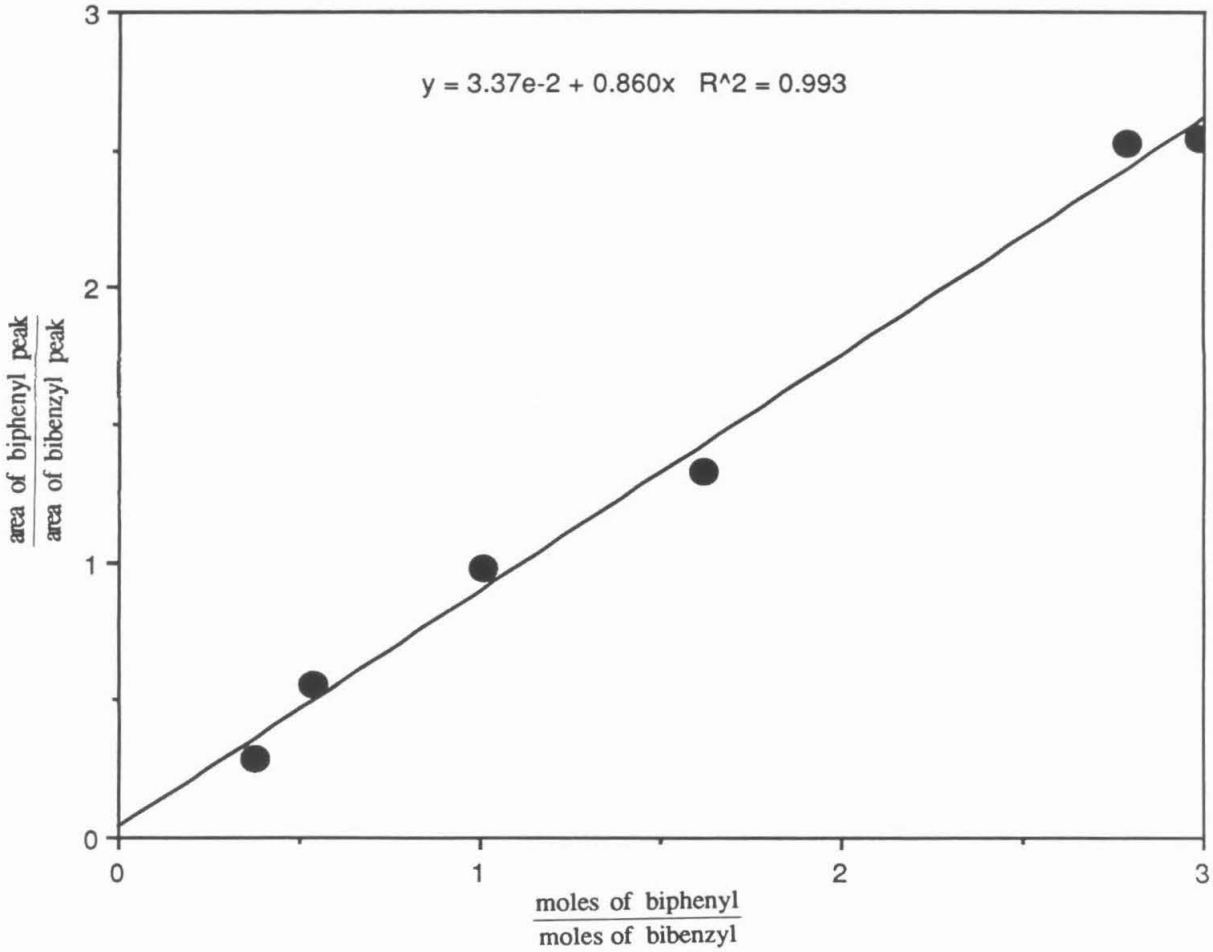


Figure 9 Stern-Volmer plot for the quenching of $^3Pt_2^*$ phosphorescence by ethylbenzene

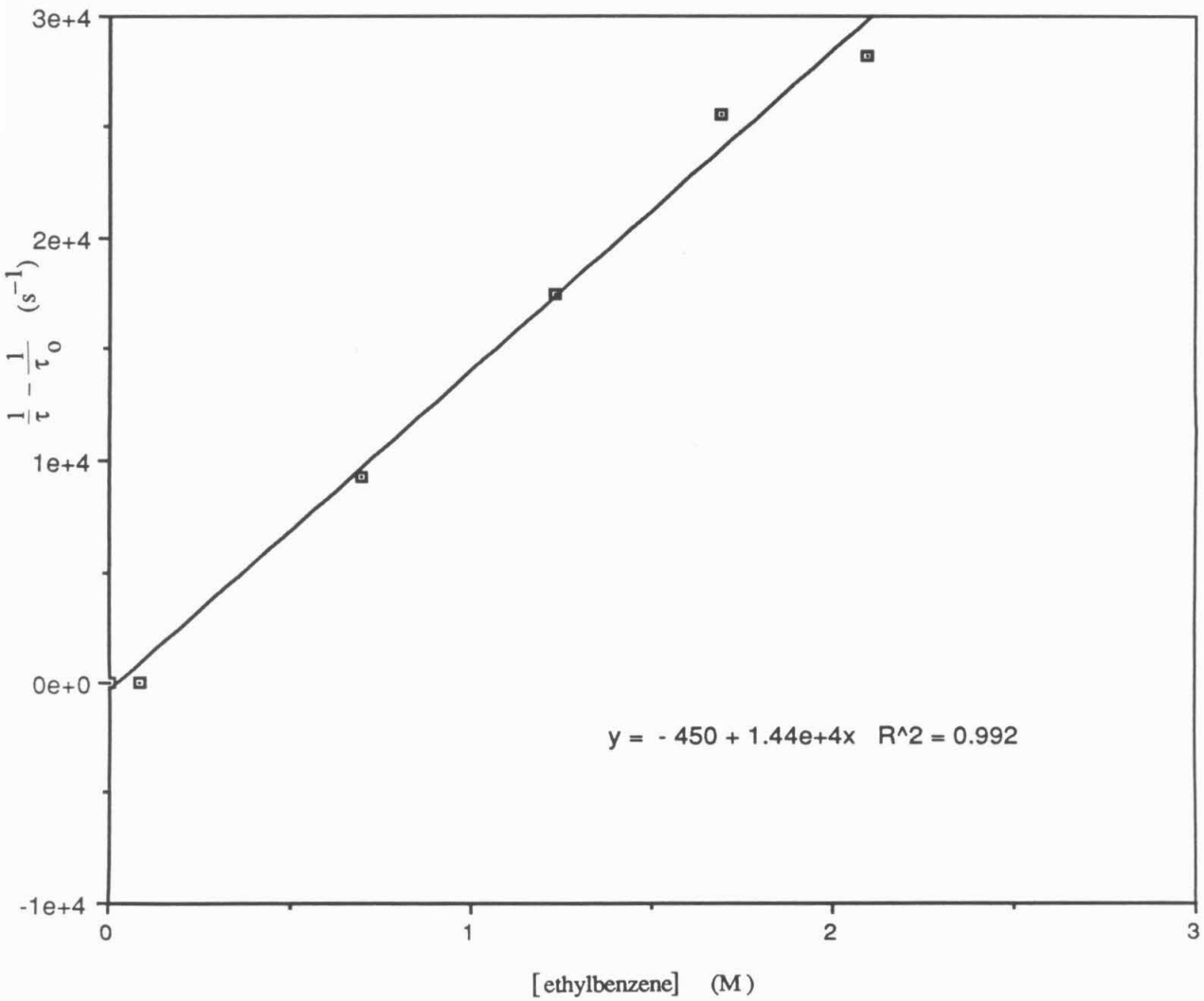


Figure 10 Stern-Volmer plot for the quenching of $^3Pt_2^*$ phosphorescence by α-deuterio-α-methylbenzyl alcohol

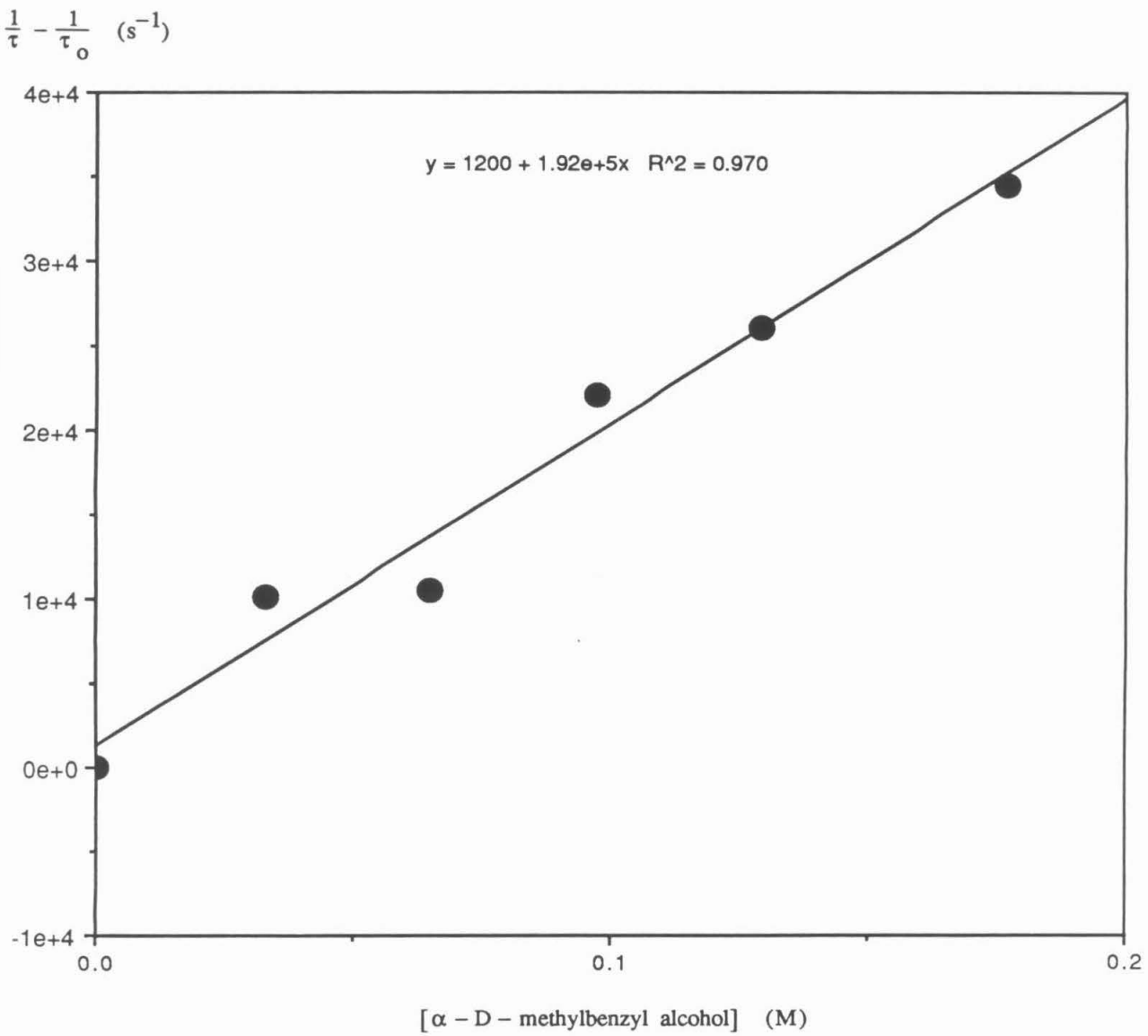


Figure 11 Stern-Volmer plot for the quenching of $^3Pt_2^*$ phosphorescence by ethylene glycol

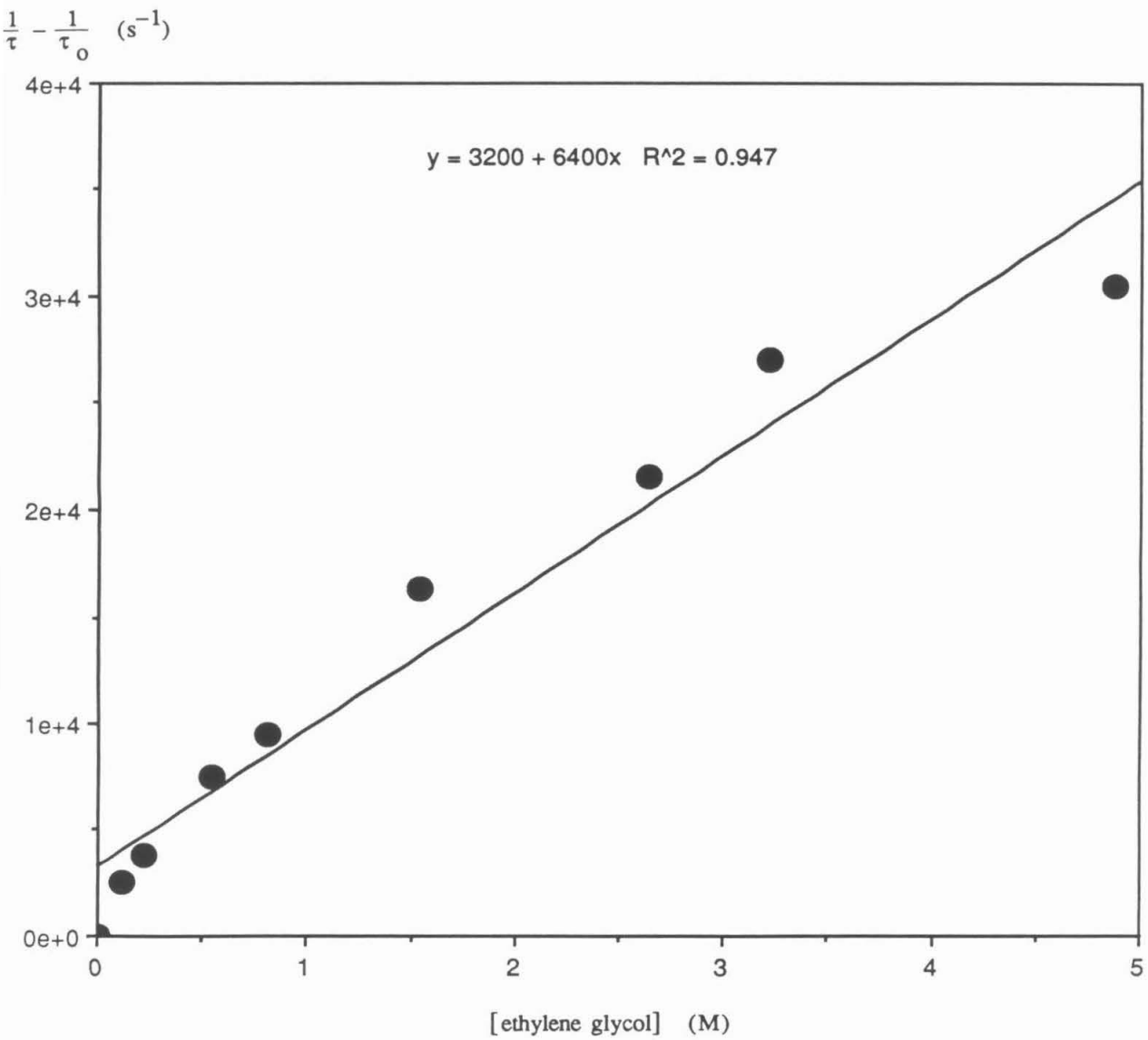


Figure 12 Michaelis-Menten plot for the quenching of $^3Pt_2^*$ phosphorescence by ethylene glycol

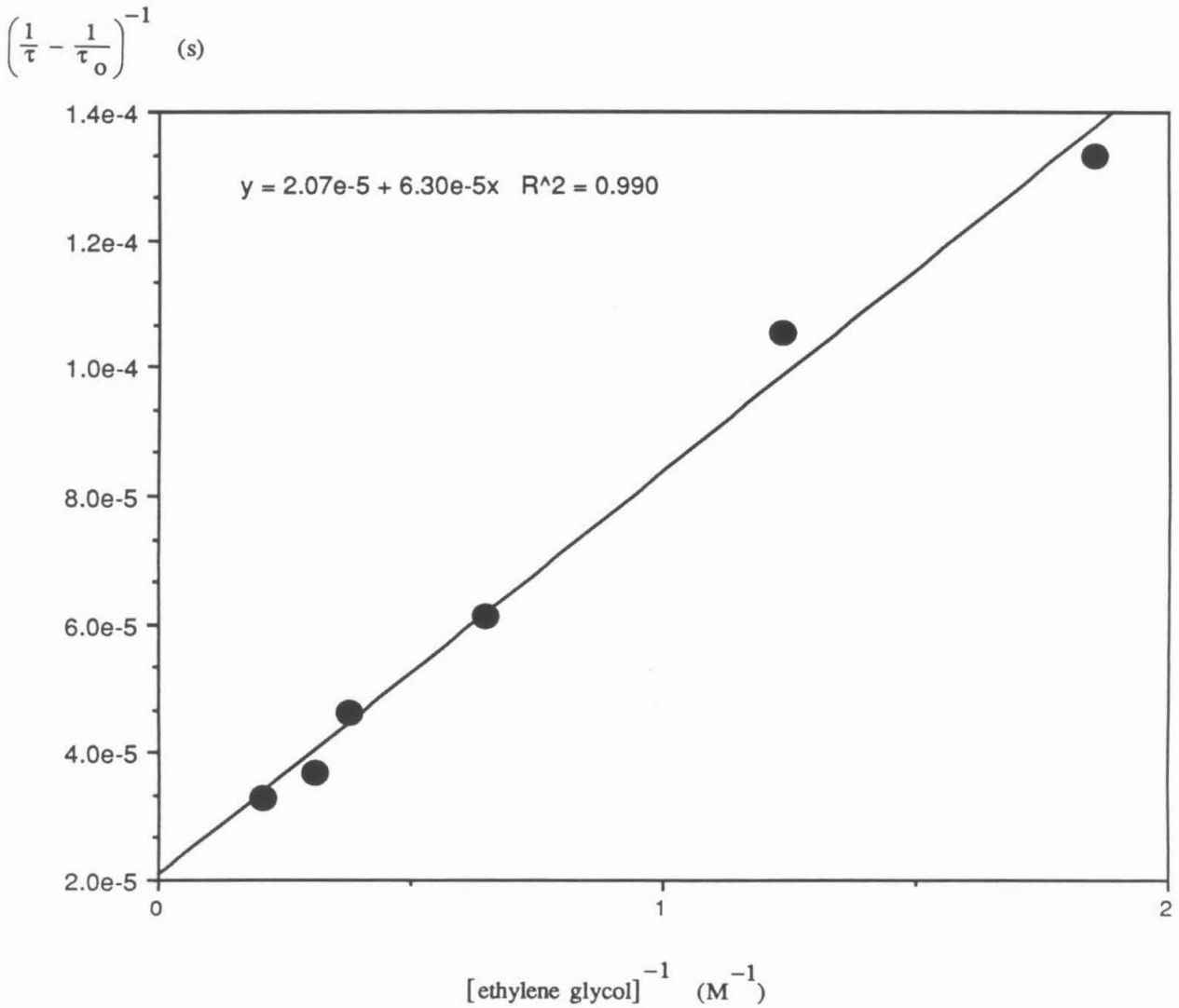


Figure 13 Temperature dependence of the rate of $^3Pt_2^*$ phosphorescence quenching by ethylene glycol (9.0M)

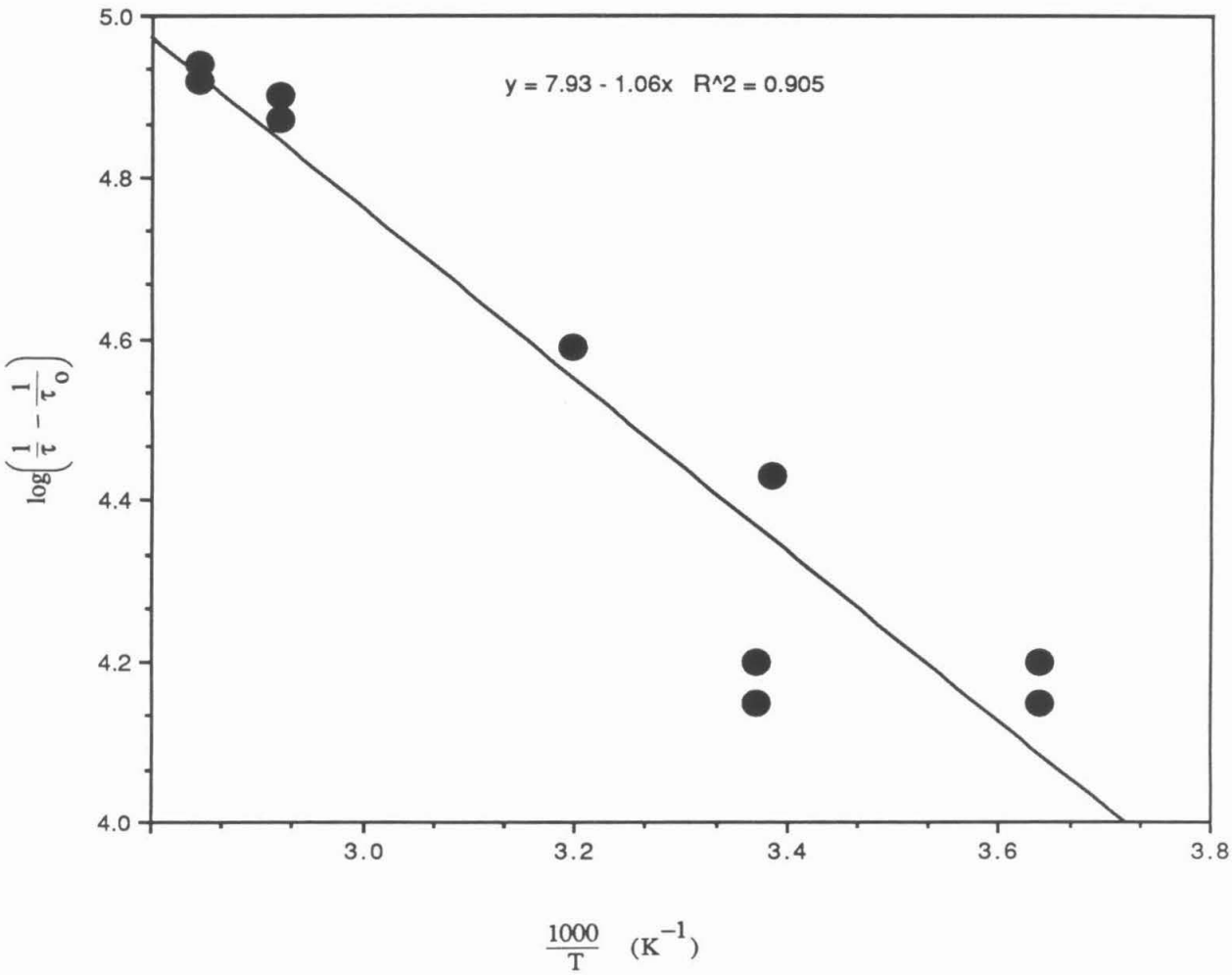


Figure 14 Temperature dependence of the rate of $^3Pt_2^*$ phosphorescence quenching by α-methylbenzyl alcohol (0.24M)

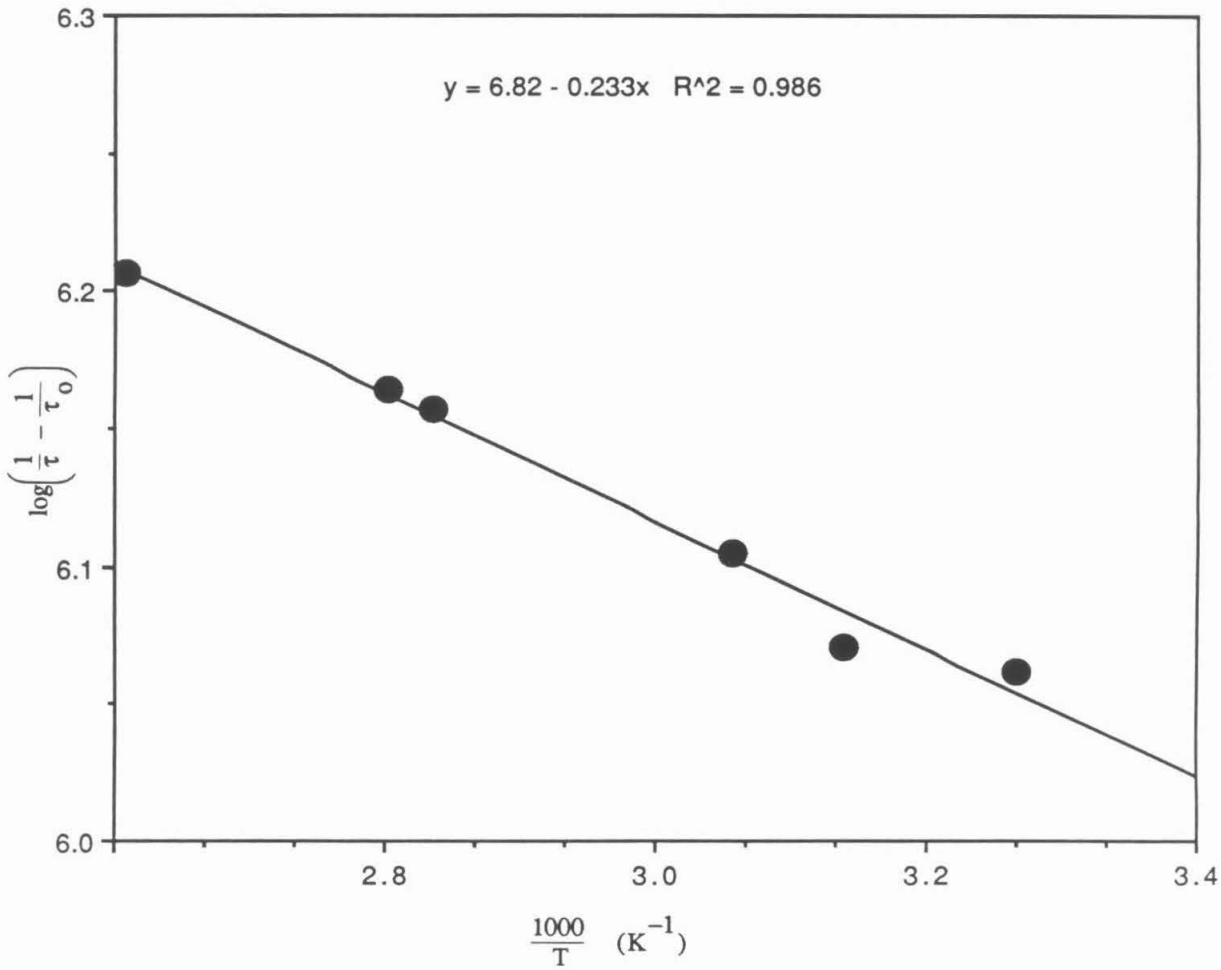


Figure 15 Temperature dependence of the rate of $^3Pt_2^*$ phosphorescence quenching by α-methylbenzyl alcohol (6.0M)

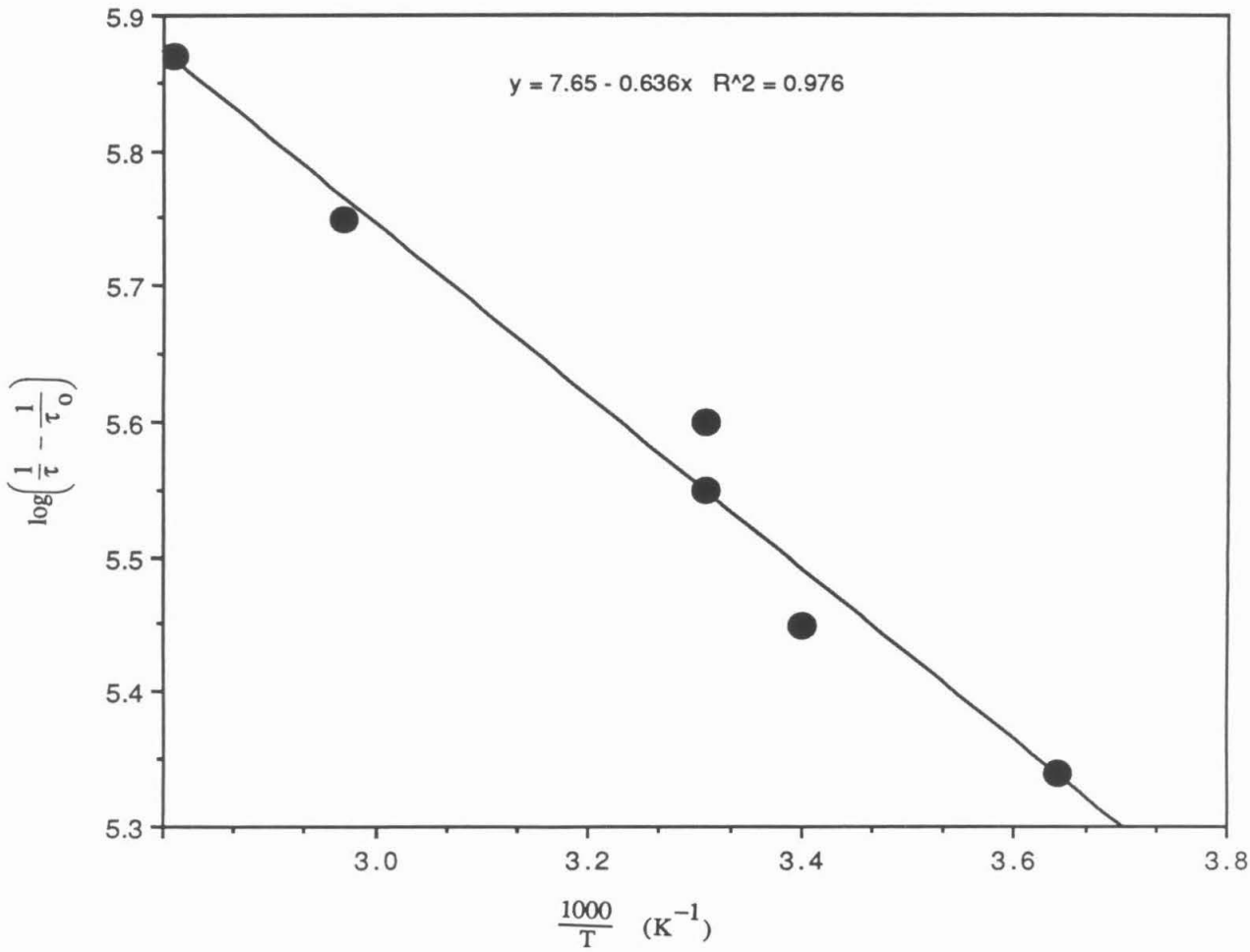


Figure 16 Stern-Volmer plot for the quenching of $^3Pt_2^*$ phosphorescence by 3-methyl-2-butanol

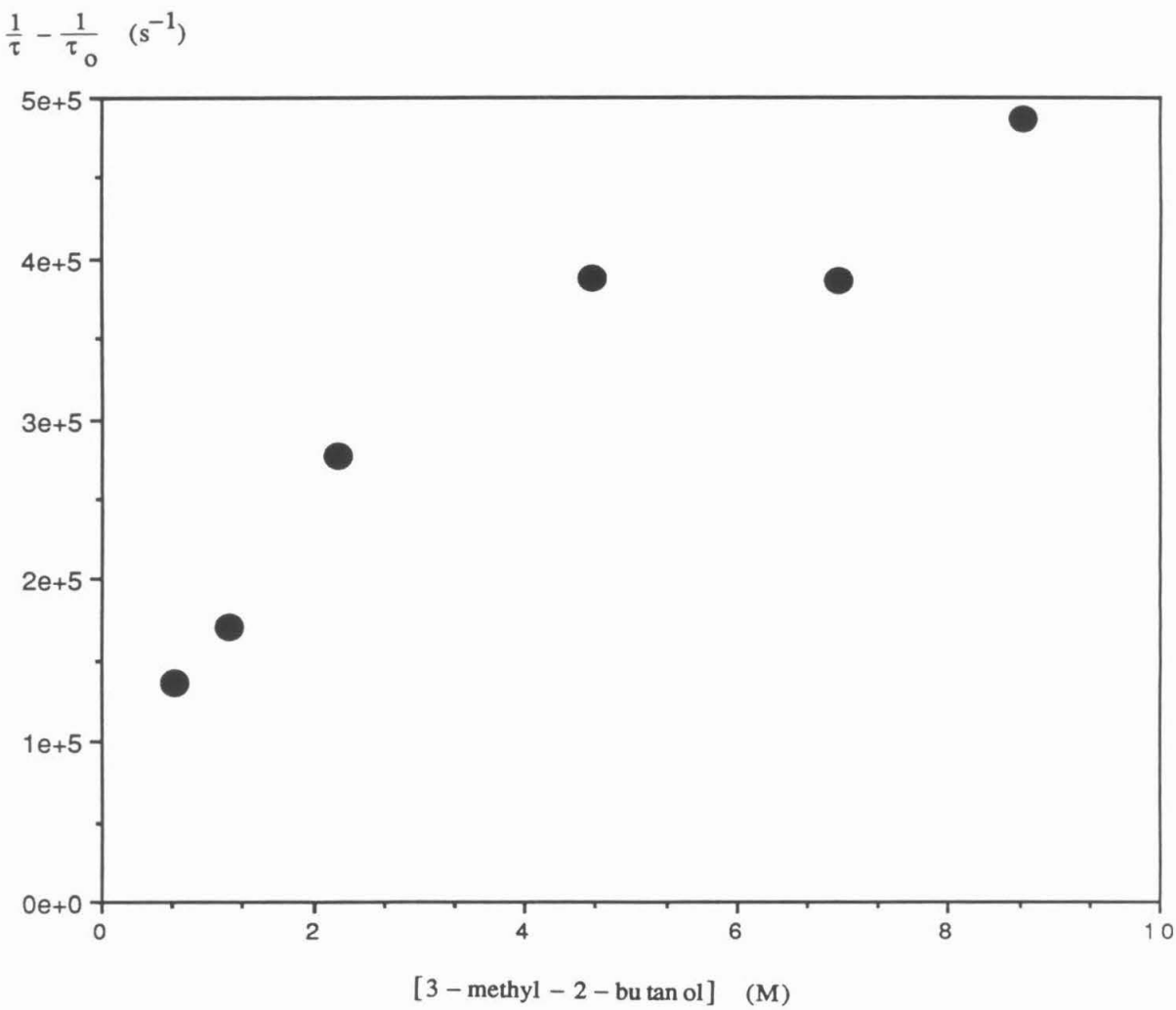


Figure 17 Michaelis-Menten plot for the quenching of $^3Pt_2^*$ phosphorescence by 3-methyl-2-butanol

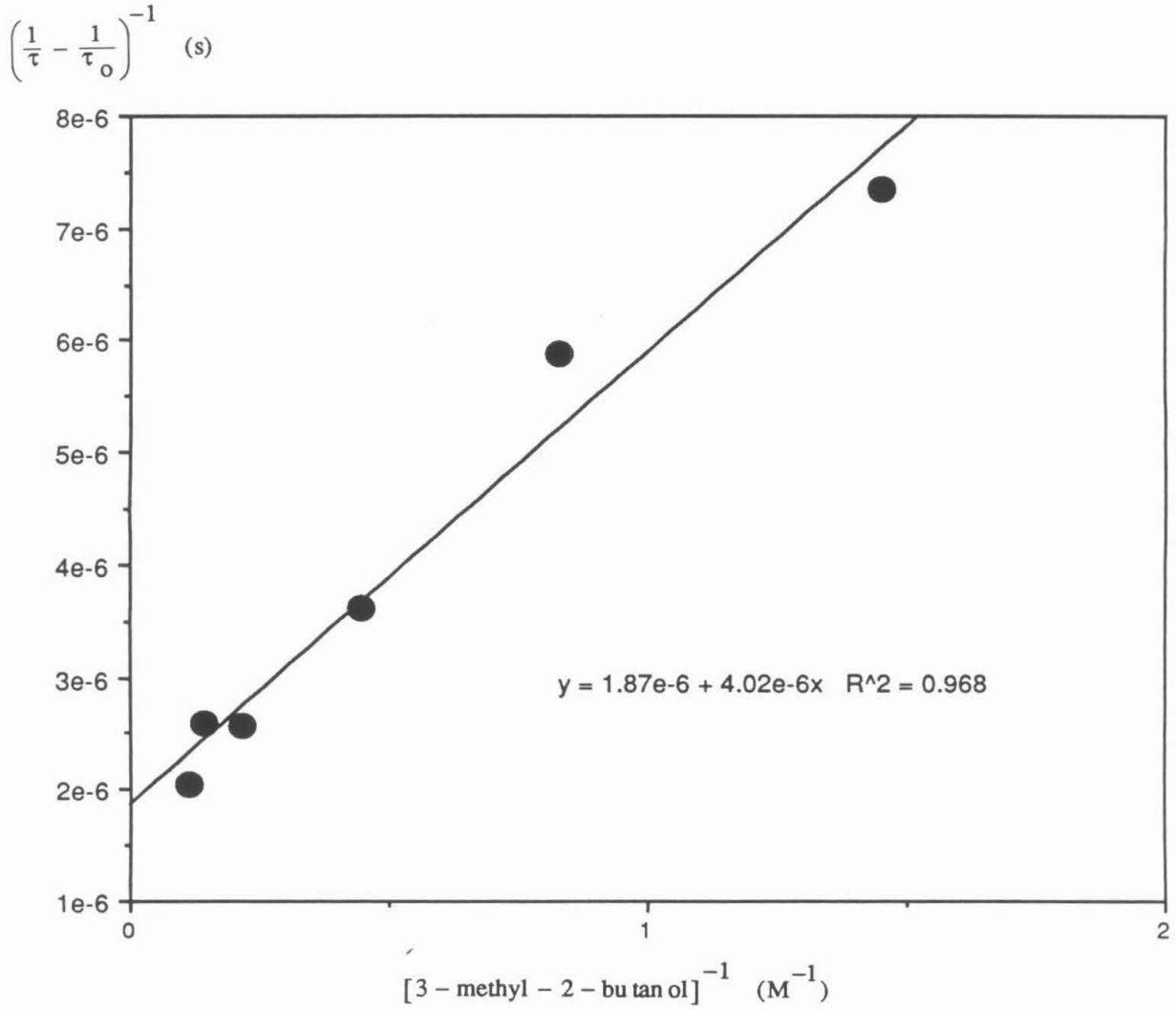
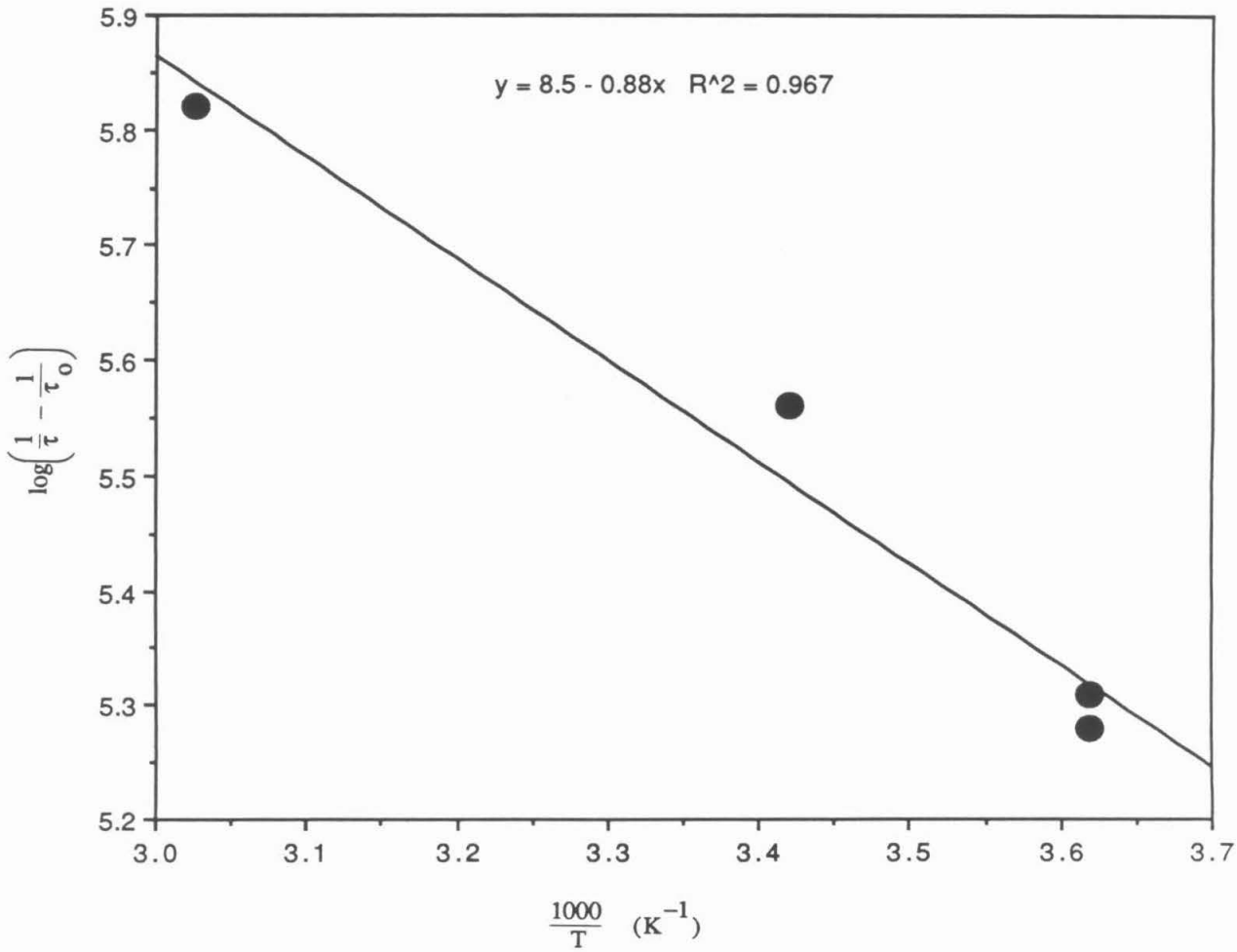


Figure 18 Temperature dependence of the rate of $^3Pt_2^*$ phosphorescence quenching by 3-methyl-2-butanol (7.4M)



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Chapter 2

Characterization and Reactivity of Tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

Robert J. Sweeney, Larry Henling, Harry B. Gray

Introduction

To test the postulate that H-atom abstraction reactivity of the triplet state of tetrakis(μ-pyrophosphito)diplatinate(II) $^3Pt_2^*$ with alcohol substrates is governed by interaction of the substrate with the Pt_2 ligands, an attempt was made to perturb the interligand OH network in the metal complex. Close examination of the H-bonding arrangement around an axial site in Pt_2 reveals four 6-membered rings fused together around a central Pt atom (Figure 1). The arrangement of atoms within each 6-membered ring resembles the arrangement of atoms in the enol tautomer of a β-diketone complex. In analogy to β-diketonates, the bridging protons in Pt_2 are susceptible to replacement with BF_2^+.

Reaction of $[TBA]_4Pt_2$ with BF_3 or $BF_3{\cdot}OEt_2$ produces a new compound that bears a striking physical and photophysical resemblance to Pt_2, but is much harder to oxidize.[1] This new complex, tetrakis(bis(difluoroborato)-μ-pyrophosphito) diplatinate(II), has the structure shown in Figure 2; the complex will be abbreviated as BF_2Pt_2 .

In analogy to the products of oxidative addition to Pt_2, a series of axially substituted $BF_2Pt_2X_2$ (X=Cl, Br, I) complexes are avilable through direct reaction of BF_2Pt_2 and X_2. H-atom-transfer quenching reactivity of $^3BF_2Pt_2^*$ is also similar to that of the parent compound.

Figure 1. Structure of one face of the tetrakis(μ-pyrophosphito)diplatinate(II) tetraanion.

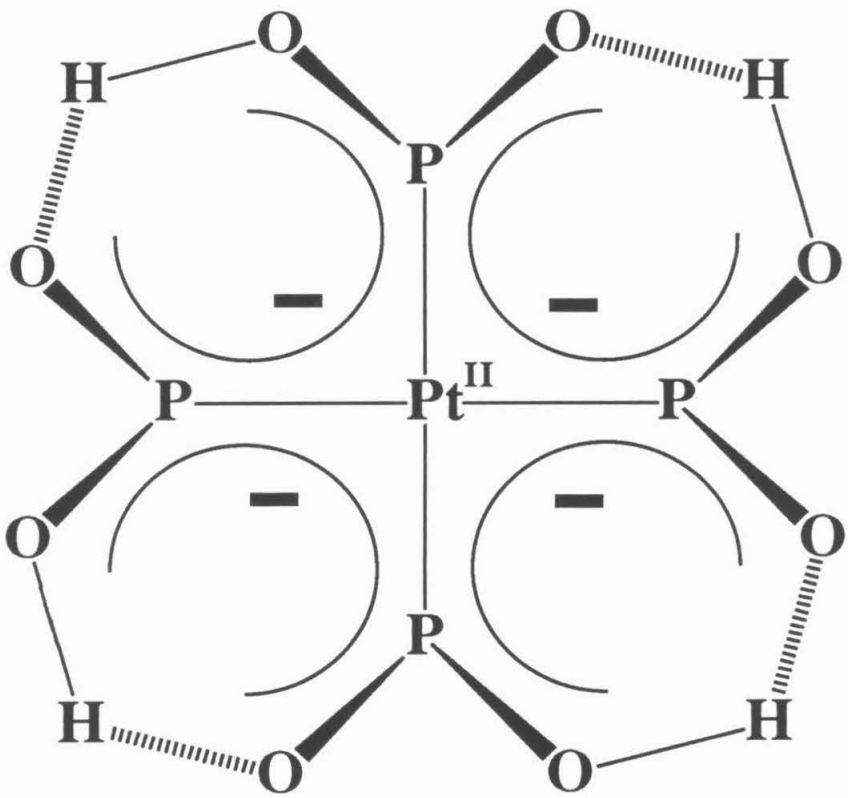
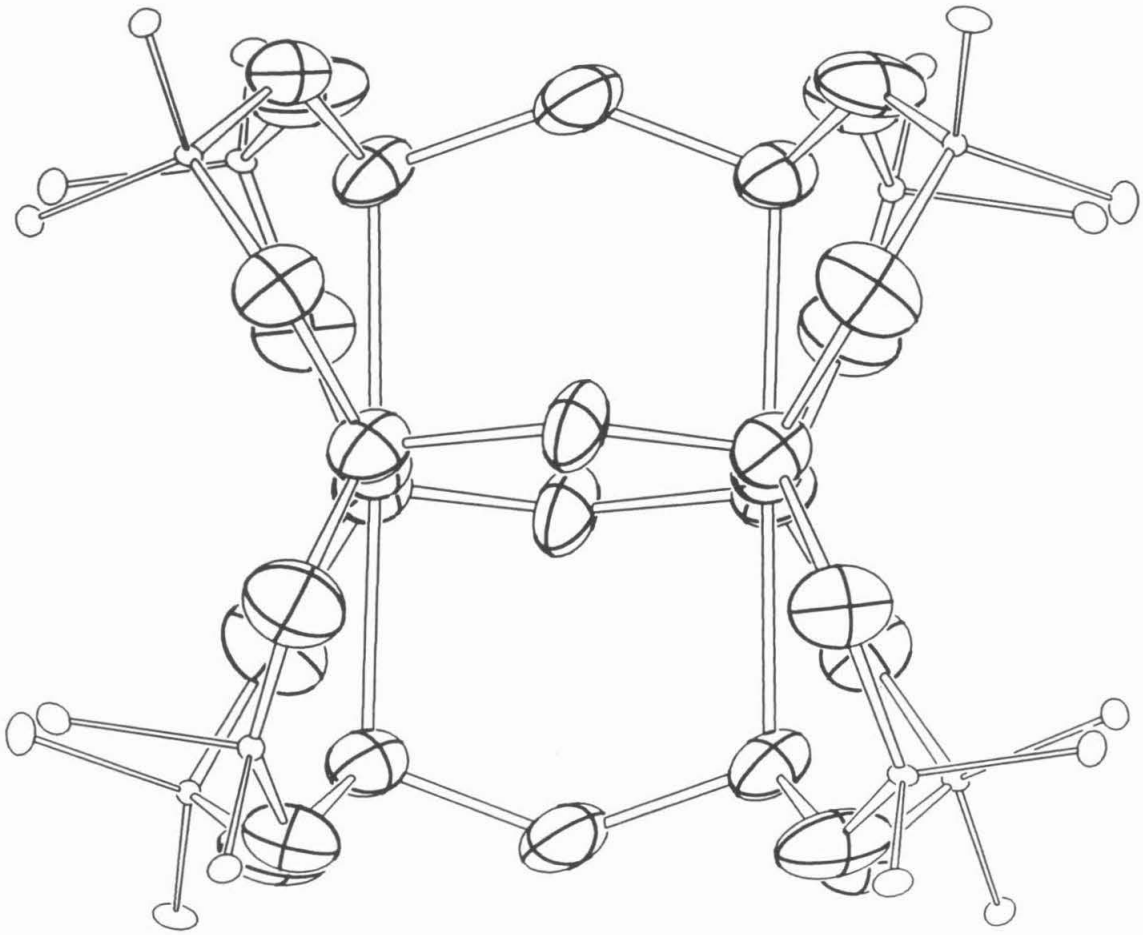


Figure 2 An ORTEP drawing of tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II). Thermal ellipsoids are shown at the 20% probability level; the BF_2 groups are one-tenth scale.



Experimental Details

Instrumentation

All spectroscopic measurements were made in Burdick and Jackson High-Purity acetonitrile.

UV-Visible absorption spectra were measured on a Cary 14 UV-Visible spectrometer; all spectra were run against solvent baselines.

Emission spectra were recorded on a previously described[2] emission spectrometer; 366 nm excitation light from an Oriel 200W Hg/Xe lamp was selected with a Spex 1670 monochromator and an Oriel 366 nm(#5643) interference filter. Emitted light was sent through a cutoff filter into a Spex 1870 monochromator connected to a Hamamatsu R955 photomultiplier tube and EG & G 182-A lock-in amplifier. Uncorrected spectra were printed out on a chart recorder. Quantum yields were measured relative to quinine sulfate in 1M H_2SO_4 as a standard (Φ_f=0.546).[3] Relative emission intensities were measured by cutting out the emission bands from photocopies of emission spectra and weighing the paper.

Excited-state lifetimes (τ) were measured with a Quanta Ray Nd:YAG (8 ns fwhm; 355 nm excitation) laser system described elsewhere.[4] $^3Pt_2^*$ emission was monitored at 518 nm. Quenching rate constants k_q were determined using the Stern-Volmer kinetics outlined in Chapter 1. Quenching rate constants and the quantities derived from them have estimated associated errors of <10%.

Synthesis and Purification

Alcohol and hydrocarbon quenchers and solvents were purified as described in Chapter 1. $[TBA]_4BF_2Pt_2$ and $TBA]_4BF_2Pt_2X_2$ (X=Cl, Br, I) were prepared as previously described.[1]

In an attempt to synthesize the BCl_2^+-substituted compound, 1 ml of BCl_3 in hexanes (1M, Aldrich) was added to 11 mg $[TBA]_4Pt_2$ under an argon atmosphere. After a few minutes, all volatiles were removed under vacuum, leaving behind a yellow powder that demonstrated a bright yellow emission under a black light. UV-Vis spectra were taken of this solid dissolved in 10 ml acetonitrile and exposed to air. The yellow solution had UV λ_{max} values of 239 and 367 nm. From comparison with the BF_2^+-substituted dimer, this could well be "BCl_2Pt_2." Exposed to air overnight, a new UV spectrum appeared, with λ_{max} values similar to those for Pt_2Cl_2 (283 and 356 nm). A yellow precipitate also began to form, and the emission turned greener. Hydrolysis by atmospheric moisture probably accounted for the decomposition.

Crystal Structure

Small, transparent, green crystals of $[TBA]_4BF_2Pt_2$ were obtained by enclosing an open vial containing an acetonitrile solution of $[TBA]_4BF_2Pt_2$ in a larger chamber of ethyl ether. As the ether transferred onto the acetonitrile solution, a yellow-green oil came out of the solution, and crystals began to form slowly on the walls of the vial. Several crystals were examined and found to be inadequate before a twinned but usable crystal was found. Crystals also formed from methylene chloride/diethyl ether solutions, but

these samples clouded and lost order rapidly, once they were removed from the solution.

All crystallographic measurements and calculations were performed by Larry Henling at Caltech.

A flat fragment was broken off a twinned crystal, mounted on a fiber and centered on a CAD-4 diffractometer. Unit cell parameters and an orientation cell matrix were obtained by a least-squares calculation from the setting angles of 24 reflections with $26°<2\theta<31°$. Two equivalent data sets out to a 2θ of 45° were collected at a Y angle calculated to minimize absorption. The data were corrected for absorption and decay. An average background as a function of 2θ was calculated but not used. Lorentz and polarization factors were applied and the two data sets were then merged to yield the final data set. Preliminary Weissenberg photographs and absences in the diffractometer data revealed the space group to be $P2_1/n$. The platinum dimer has a center of symmetry and therefore only one half of the dimer was located in a unit cell.

A Patterson map gave the platinum atom coordinates. The remaining non-hydrogen atoms in the dianion were located via successive structure factor-Fourier calculations. One of the two tetra-*n*-butyl ammonium cations was disordered and defied attempts at construction of a refinable model. As a result, four of the carbon atoms (the last two atoms on two of the arms) were fixed in positions derived from electron density maps calculated from the end of the least-squares refinement process. One terminal atom was placed in three sites with populations based on relative peak heights. Isotropic temperature factors were estimated from

the refined atoms. All parameters for these four atoms were then held constant for the remainder of the refinement.

In the early stages of refinement, the thermal parameters of the BF_2 group adjacent to the disordered cation were larger than those of the other three groups. Additionally, the BF_2 and the cation were unusually close. On the assumption that this site was partially occupied by both a BF_2 bridge and a hydrogen atom, population factors were introduced for all four BF_2 groups, with the three atoms in each group constrained to the same population. In the final cycle of least squares, the populations of three of the groups converged to within 2σ ($\sigma<0.02$) of unity. However, the site near the cation had a population of only 0.73(2). The boron atom in this group, and all refined carbon atoms, were treated isotropically. Anisotropic displacement parameters were used for the remaining non-hydrogen atoms. The fractional hydrogen atom was ignored in the calculations.

The position of the tetra-*n*-butyl ammonium cation apparently depends on the nature of the bridging group. The hydrogen atoms of the cations were introduced as constant contributions of the structure factors at calculated positions (C-H=0.95Å), assuming staggered geometry. They were repositioned before the final three cycles. The complete least-squares full matrix, consisting of coordinates, displacement parameters, and a scale factor, contained 373 variables. A final difference Fourier map showed deviations ranging from $-2.41 e Å^{-3}$ to $+3.44 e Å^{-3}$. The largest features were near the platinum and were attributed to deficiencies in the absorption correction. The refinement converged with an R-factor of 0.1196 (0.0774 for $F_o^2>3\sigma(F_o^2)$) and a goodness of fit of 2.00 for all

6557 reflections. The R-factors for various subsets of reflections revealed nothing unusual. Crystallographic data, including associated error estimates, are given in the appendix.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference. $R=\Sigma||F_o|-|F_c||/\Sigma F_o$, for only $F_o^2>0$, and goodness of fit=$[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\Sigma w(F_o^2-F_c^2)^2$, where $w=1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned based on counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. The absorption correction was done by Gaussian integration over an 8x8x8 grid. Transmission factors varied from 0.56 to 0.79.

Results and Discussion

Crystal Structure

Like the parent compound Pt_2, BF_2Pt_2 consists of two rigorously eclipsed, square-planar platinum(II) ions bridged by four bidentate pyrophosphito ligands (Figure 3). Difluoroborato groups replace the protons between terminal oxygen atoms in the parent compound Pt_2. The two halves of the dimer are related by a center of symmetry. The eclipsed phosphorus atoms have tortional angles of 0.1(2) and 0.3(2)°. The platinum atom lies 0.04Å from the plane that passes closest to the four coordinated phosphorus atoms, and the Pt-Pt-P angles range from 90.6(1) to 91.4(1)°. There are no significant interactions between different ions in the crystal.

Tables 1 and 2 contain selected distances and angles for both BF_2Pt_2 and Pt_2.[5-7]

As predicted by Harvey and Gray[1] from UV absorption data, the Pt-P bond distances shorten in BF_2Pt_2. The electron-withdrawing BF_2^+ groups increase the π-acidity of the phosphorus atoms, strengthening the backbonding interactions. Electron density transfers from the π/π^* Pt-Pt orbitals to the phosphorus centers, leading to less repulsive interactions between the metals. The decrease in intermetallic repulsion shortens the Pt-Pt bond (by 0.041Å), and the increase in backbonding shortens the Pt-P bond (by 0.015-0.040Å).

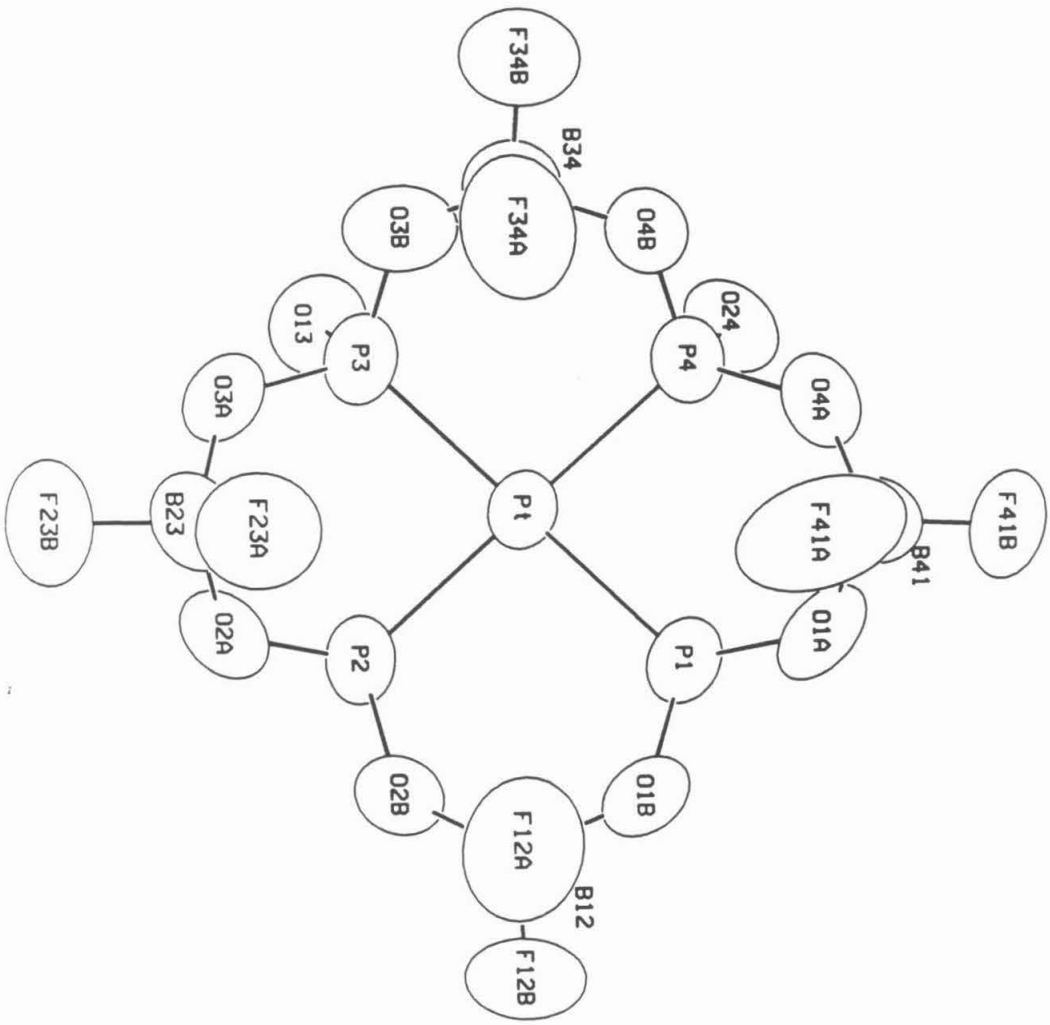
Table 1. Selected bond distances for BF_2Pt_2 and Pt_2.

Bond Distance (Å)	$[TBA]_4BF_2Pt_2$	K_4Pt_2
Pt-Pt	2.884	2.925
Pt-P	2.278-2.305	2.320
P-O_{term}	1.51-1.56	1.52, 1.58
P-O_{bridge}	1.56-1.64	1.62

Table 2. Selected bond angles for BF_2Pt_2 and Pt_2.

Bond Angle (°)	$[TBA]_4BF_2Pt_2$	K_4Pt_2
Pt-Pt-P	90.6, 91.4	90.7
P-Pt-P	90.8, 88.9	
P-O-P_{bridge}	137	133
O-P-O_{term}	107	

Figure 3 An ORTEP drawing of one face of the tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II) tetraanion shown at the 10% probability level.



The terminal P-O bonds, which alternate between double and single bonds in hydrogen-bonded Pt_2, have equivalent lengths in BF_2Pt_2, reflecting the covalent nature of B-O bonds.

Table 3 Selected geometric parameters for BF_2Pt_2 and other BF_2-bridged square-planar, platinum phosphito complexes.

	$[TBA]_4BF_2Pt_2$	Reference Compounds
Bond Distance (Å)		
B-F	1.33-1.43	1.31-1.40
B-O	1.44	1.46-1.49
Bond Angle (°)		
O-B-O	116-119	107-110
F-B-F	103-110	112

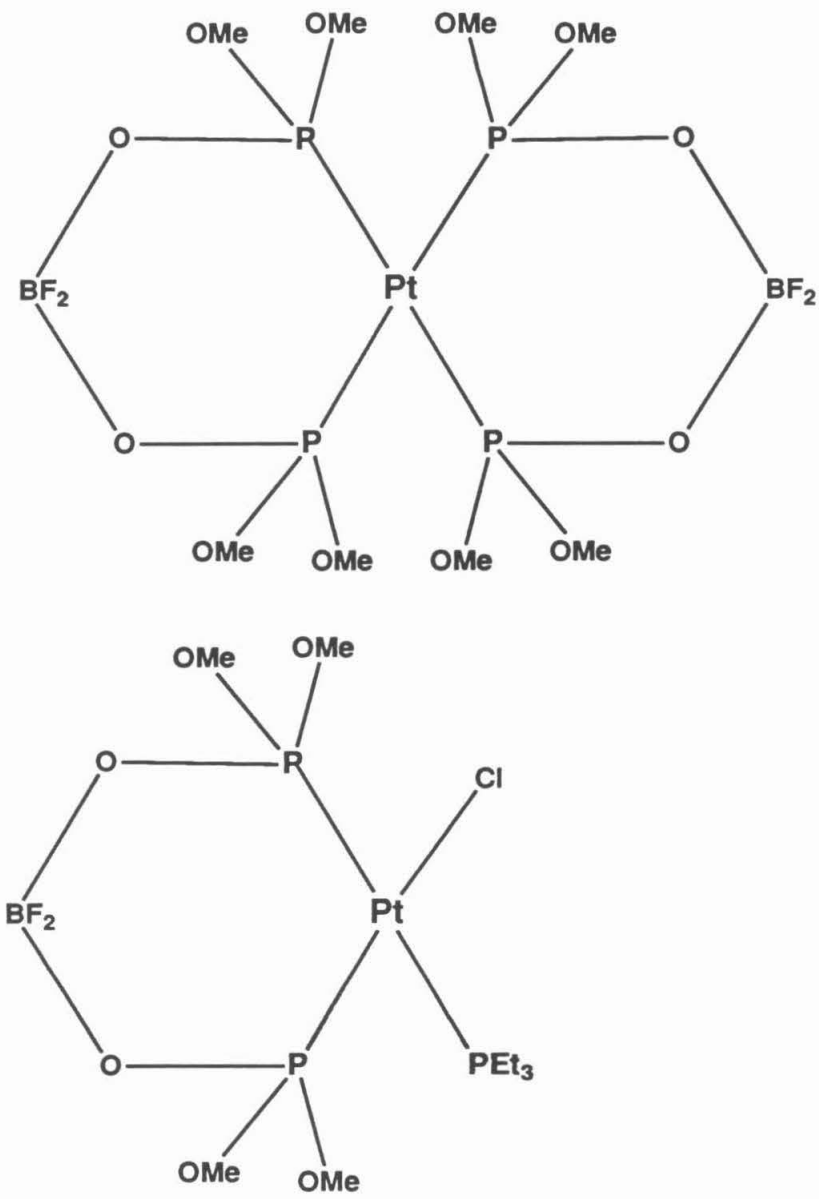
The O-B and B-F bond lengths (Table 3) are in agreement with those found for other BF_2-bridged phosphito ligands on square-planar platinum centers[8, 9] (Figure 4). The O-B-O angles in BF_2Pt_2 are larger, and the F-B-F angles smaller, than in those same compounds, a difference that may reflect ring strain in BF_2Pt_2.

On average, the crystal structure predicts 7.5 BF_2 groups per platinum dimer unit. This population may reflect either the actual solution composition of BF_2Pt_2 or merely the fraction of solution species that crystallize. Either way, reaction with $BF_3{\cdot}OEt_2$ effectively replaces all eight protons on the original dimer with BF_2^+ groups. The dimers pack in the crystal so that any protons left on the dimer concentrate in the cramped region of the unit cell

where the TBA cation is very close to the ligands, since protons take up less space than BF_2 groups. This accounts for the reduced population in only one crystallographic BF_2 site.

The BF_2 group with a low population density is excluded from Tables 1,2 and 3. The bond angles ($\angle$O-B-O=132°, $\angle$F-B-F=97°) and distances (d(B-F)=1.36Å, 1.53Å, d(B-O)=1.23Å, 1.43Å) for this group are not within the range of values found for the other BF_2 groups. Because crystallographic calculations ignore the (assumed) partial population of the proton in that position when the BF_2 is absent, the position of the boron atom is subject to errors in excess of the calculated standard deviations. Therefore, the strange distances and angles may or may not reflect the actual geometry of the BF_2 moiety. If the geometry is accurate, it indicates that ring-induced strain could account for the difficulty in fully populating this position.

Figure 4 Structures of previously reported difluoroborato-substituted, square-planar, phosphito platinum complexes.



Photophysics

Photophysical properties of BF_2Pt_2 are startlingly similar to those of Pt_2. The emission band maxima, excited triplet-state lifetime (10 μsec) and phosphorescence quantum yields are nearly identical within experimental resolution. In contrast, a large increase is observed in the fluorescence quantum yield of BF_2Pt_2 (Table 4). This increase may reflect the extra rigidity forced on BF_2Pt_2 by the new 6-membered covalently bound rings introduced through BF_2 substitution. A decrease in the the number of accessible vibrational modes may eliminate deactivational motions important to the singlet state. High-energy O-H vibrational modes, which are eliminated in the modified complex, may be responsible for this effect.

Heuer, et al.[10] reported the phosphorescence quantum yield for Pt_2 in water as 0.52, but they report the unquenched lifetime to be only 6.2 msec. Assuming that the decrease in lifetime is due to quenching, the unquenched quantum yield can be calculated, using τ_0=10 msec. The resulting value of 0.83 agrees with our results.

The axial dihalides $BF_2Pt_2X_2$ (X=Cl, Br, I) have electronic absorption spectra that closely resemble those of the Pt_2 derivatives. Absorption and emission data for the dihalides are presented in Table 5.

Table 4 Emission parameters for BF_2Pt_2 and Pt_2

Emission	$[TBA]_4Pt_2$	$[TBA]_4BF_2Pt_2$
Phosphorescence λ_{max} (nm), 77K	518	521
Fluorescence λ_{max} (nm), 77K	409	409
Phosphorescence λ_{max} (nm), RT	524	521
Φ_p, RT	0.8	0.8
Fluorescence λ_{max} (nm), RT	416	413
Φ_f, RT	$1x10^{-4}$	$7x10^{-3}$

Table 5 Photophysical parameters for axial dihydrides

X_2	Pt_2X_2 absorption λ_{max} (nm)	$BF_2Pt_2X_2$ absorption λ_{max} (nm)[a]	Pt_2X_2 emission λ_{max} (nm)[b]	$BF_2Pt_2X_2$ emission λ_{max} (nm)[c]
Cl_2	285	276 (4.66)	685	628
	349	321 (4.05)		
Br_2	308	301 (4.64)	715	685
	349	336 (4.43)		
I_2	338	364 (4.60)	-----	-----
	438	455 (3.73)		

a log(ε) is in parentheses

b Ph_4As^+ salt in ethanol/methanol glass[11]

c measured in acetonitrile solutions at 77K.

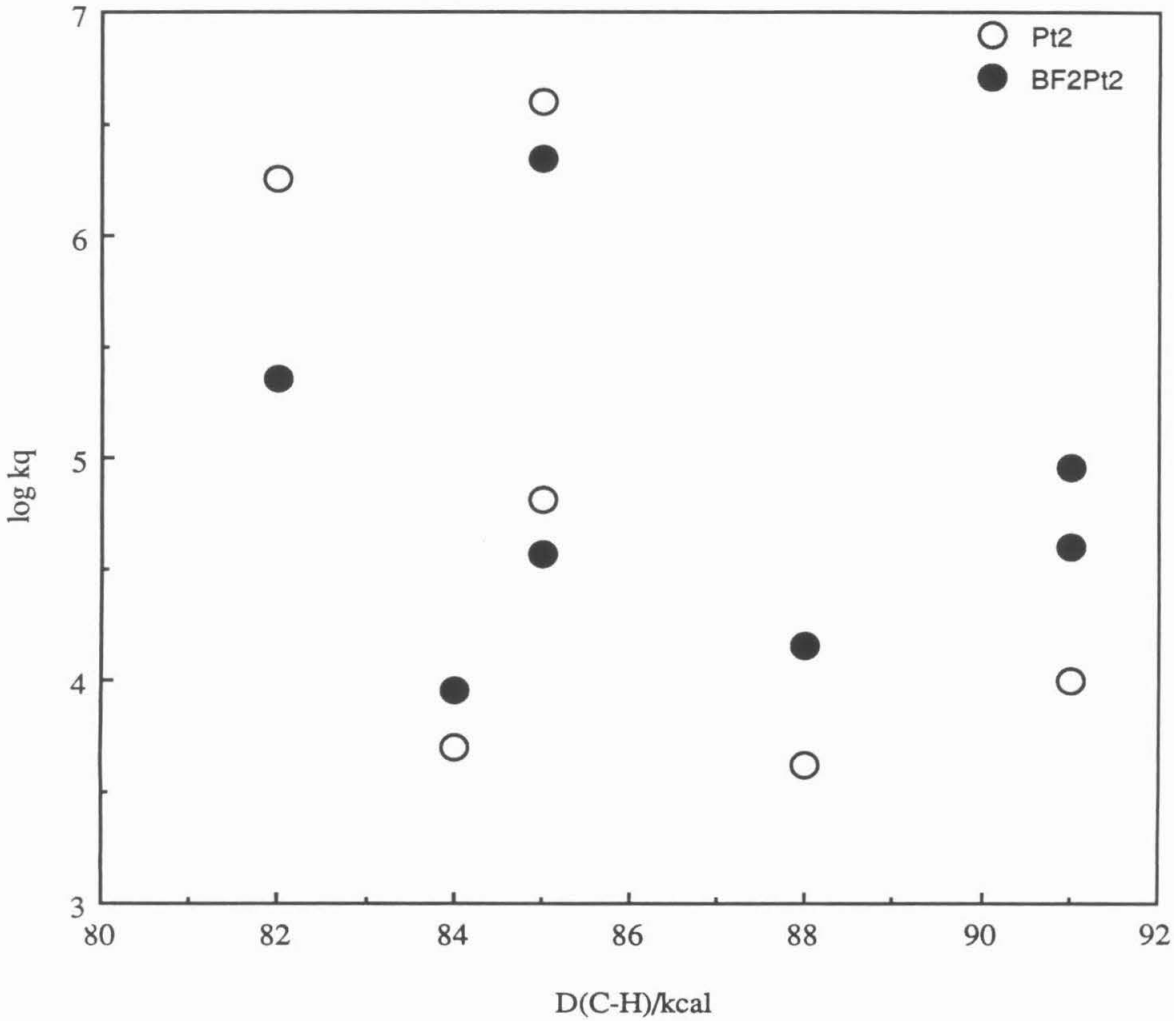
H-atom Transfer

In contrast to differences of several orders of magnitude observed in electron-transfer reactivity,[1, 12] quenching rates for $^3Pt_2^*$ and $^3BF_2Pt_2^*$ with a given H-atom donor are all within an order of magnitude[13] (Table 6 and Figure 5). Although differences in reactivities between $^3Pt_2^*$ and $^3BF_2Pt_2^*$ with alcohols are expected because of the loss of protons available for hydrogen bonding and the stronger Pt-H bond in $BF_2Pt_2H_2$, the steric bulk introduced by BF_2 groups can account for reactivity differences with alcohols. As demonstrated in Chapter 1, increasing steric bulk of the substrate increases k_q with small aliphatic alcohols but decreases k_q with the larger benzyl alcohols. This same trend is observed when steric bulk is increased at the axial site, as with the substitution of BF_2^+ groups for protons. The quenching of aliphatic alcohols is faster with BF_2Pt_2 than with Pt_2. The opposite is true for the benzyl alcohols.

The similarity in quenching rates of alcohols with Pt_2 and BF_2Pt_2 also implies that the ligands' oxygen atoms participate in the hydrogen-bonding of the alcohols to Pt_2, since the ligand protons have been removed. On the other hand, the large quenching rate for benzyl methyl ether[14] with $^3Pt_2^*$ indicates that the ligand protons, when present, also help in docking.

Reactivity differences with benzyl hydrocarbons are not easily rationalized, since the quenching is not well understood (see Chapter 1). However, an electron-transfer mechanism may be ruled out since the k_q change with BF_2 substitution is much smaller than the large

Figure 5 Quenching rates for $^3Pt_2^*$ and $^3BF_2Pt_2^*$ phosphorescence with H-atom donors in acetonitrile solutions at room temperature.



changes consistently observed for both reductive and oxidative electron transfer.

The efficiency of the dehydrogenation of isopropanol as measured by formation of $BF_2Pt_2H_2$ ($k_p=1x10^4\ M^{-1}s^{-1}$, F= 0.1) is identical to that for the reaction of Pt_2 with isopropanol, a counter-intuitive result since the axial dihydride is thought to result from disproportionation of the monohydride.[15] Changing the sterics and hydrophilicity of the axial site should affect the efficiency of dihydride formation if this mechanism reflects reality.

Table 6 Stern-Volmer quenching rate constants for the reaction of excited platinum dimers and organic H-atom donors

Substrate	$^3Pt_2{}^*$ Quenching Rate k_q ($M^{-1}s^{-1}$)	$^3BF_2Pt_2{}^*$ Quenching Rate k_q ($M^{-1}s^{-1}$)	C-H Bond Strength[16] (kcal/mol)
cumene	$5.0x10^3$	$9x10^3$	84
ethylbenzene	$6.4x10^4$	$3.7x10^4$	85
toluene	$4.2x10^3$	$1.4x10^4$	88
α-methylbenzyl alcohol	$1.8x10^6$	$2.3x10^5$	82
benzyl alcohol	$4x10^6$ $2.2x10^6$a	$2.2x10^6$	85
sec-butanol	$\sim10^4$	$4x10^4$	91
isopropanol	$\sim10^4$	$9x10^4$	91

a static quenching as measured by emission intensity quenching.

Conclusions

The emissive product of the reaction between BF_3 and Pt_2 is a species with a general structure identical to Pt_2 except for replacement of BF_2^+ groups for the eight ligand protons. The substantial changes in bond lengths that are due to this substitution are consistent with expectations and reflect an increase in the π-acidity of the pyrophosphito ligands. Evidence suggests ring strain in BF_2Pt_2's polycyclic ligand's structure.

Considering the changes in bond lengths, the photophysical properties of BF_2Pt_2 and Pt_2 are remarkably similar. The rates of emission quenching with H-atom donors also vary little between the two compounds, and those differences that exist are easily rationalized through previous results with the parent system.

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Appendix: Crystallographic Data for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

Table A1 Crystal and Intensity Collection Data for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

Formula: $Pt_2P_8O_{20}B_{7.46}F_{14.92}N_4C_{64}H_{144.54}$

Crystal color: Lime-green — Habit: Bladed

Crystal size: 0.07 × 0.21 × 0.56 mm

Space group: $P2_1/n$ (#14)

$a = 16.678(7)$Å

$b = 16.751(9)$Å — $\beta = 99.58(8)°$

$c = 18.131(24)$Å

$\rho_{calc} = 1.52$ g cm^{-3}

$\mu = 31.65$ cm^{-1} ($\mu r_{max} = 1.91$) — Transmission coeff. = 0.56 – 0.79

ω scan

$\lambda = 0.7107$Å — Graphite monochromator

2θ range: 2°–45° — Octants collected: $h, \pm k, \pm l$

T = 294°K

Number of reflections measured: 14269

Number of independent reflections: 6557

Number with $F_o^2 > 0$: 5401

Number with $F_o^2 > 3\sigma(F_o^2)$: 3299

Number of reflections used in refinement: 6557

Goodness of fit for merging data: 1.46

Final R-index: 0.1196 for 5401 reflections with $F_o^2 > 0$

Final R-index: 0.0774 for 3299 reflections with $F_o^2 > 3\sigma(F_o^2)$

Final goodness of fit: 2.00 for 373 parameters and 6557 reflections

Table A2 Final Anion Parameters for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

x, y, z and $U_{eq}{}^{a} \times 10^{4}$

Atom	x	y	z	U_{eq} or B
Pt	218(.5)	677(.5)	483(.4)	658(2)
P1	−806(3)	389(3)	1129(3)	801(17)
P2	−625(4)	1497(3)	−309(3)	808(17)
P3	1257(4)	999(3)	−138(3)	844(18)
P4	1074(4)	−112(3)	1309(3)	803(17)
O1a	−552(9)	211(8)	1981(7)	1141(51)
O1b	−1516(7)	985(9)	1057(7)	1032(43)
O13	1240(7)	408(7)	−858(6)	985(44)
O2a	−254(9)	2190(7)	−659(6)	899(43)
O2b	−1382(8)	1802(8)	−40(7)	1208(47)
O24	1009(8)	−1007(7)	1050(7)	1056(45)
O3a	1215(7)	1827(8)	−508(6)	908(40)
O3b	2138(8)	899(9)	299(9)	1219(54)
O4a	876(8)	−164(8)	2095(6)	1146(50)
O4b	1993(7)	80(8)	1377(6)	946(42)
B12	−1678(18)	1722(20)	628(15)	985(98)
F12a	−1320(9)	2315(7)	1140(8)	1616(56)
F12b	−2487(8)	1878(8)	569(7)	1546(50)
B23	599(20)	2417(19)	−447(13)	971(107)
F23a	738(7)	2731(7)	256(7)	1325(46)

Atom	x	y	z	U_{eq} or B
F23b	736(7)	3042(6)	−944(6)	1309(44)
B34	2377(27)	599(26)	913(24)	7.8(9) *
F34a	2360(12)	1323(12)	1420(9)	1689(80)
F34b	3191(9)	453(9)	1078(9)	1385(65)
B41	241(17)	166(17)	2443(18)	896(96)
F41a	439(8)	946(9)	2617(9)	1759(61)
F41b	165(7)	−232(9)	3061(6)	1570(53)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

* Isotropic displacement parameter, B

Table A3 Final Cation Parameters for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

	x, y, z and U_{eq}[a] $\times 10^4$				
Atom	x	y	z	U_{eq} or B	
N1	6514(10)	1775(9)	7595(9)	980(54)	
C1	6720(12)	2611(12)	7741(11)	7.9(5)	*
C2	7490(13)	2823(13)	8273(11)	9.2(6)	*
C3	7611(14)	3696(14)	8443(12)	10.5(6)	*
C4	8340(15)	3935(14)	8999(14)	12.9(8)	*
C5	7181(12)	1348(12)	7279(11)	8.4(5)	*
C6	7367(13)	1699(13)	6564(12)	10.5(6)	*
C7	7968(16)	1150(15)	6251(15)	13.5(8)	*
C8	8201(18)	1539(18)	5540(17)	18.0(11)	*
C9	6428(12)	1334(12)	8324(11)	8.5(5)	*
C10	5777(13)	1653(12)	8735(12)	10.0(6)	*
C11	5757(14)	1132(13)	9436(13)	11.6(7)	*
C12	5143(16)	1450(15)	9858(15)	15.5(9)	*
C13	5721(13)	1732(13)	7041(12)	8.8(6)	*
C14	5391(13)	921(13)	6788(11)	9.8(6)	*
C15	4604(14)	926(14)	6233(13)	11.7(7)	*
C16	4315(15)	109(17)	6025(14)	13.6(8)	*
N2	1829(10)	1850(11)	7285(9)	1127(58)	
C17	2408(13)	2555(13)	7435(12)	8.8(5)	*
C18	2511(15)	2919(16)	8255(14)	13.2(8)	*
C19	3149(18)	3623(17)	8395(14)	14.2(9)	*
C20	3903(19)	3265(18)	8419(16)	17.1(10)	*
C21	1829(12)	1661(12)	6451(11)	8.9(5)	*
C22	1248(13)	1013(13)	6134(12)	10.8(6)	*
C25	2109(15)	1158(15)	7761(13)	11.0(7)	*
C26	2923(15)	823(15)	7684(13)	13.4(8)	*
C29	971(15)	2086(14)	7409(12)	10.1(6)	*
C30	572(17)	2741(17)	7037(15)	14.3(9)	*
C31	−328(23)	2812(23)	7239(20)	19.1(13)	*
C32	−509(27)	3503(28)	7043(25)	26.7(19)	*
C23	1494	873	5361	16.0	*
C24	1000	1423	4809	20.0	*
C27	3209	197	8280	17.0	*
C28A	4059	−132	8173	19.1	*
C28B	3458	−564	7909	19.1	*
C28C	3333	593	9054	19.1	*

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

* Isotropic displacement parameter, B

Table A4 Assigned Hydrogen Parameters for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

	x, y and $z \times 10^4$			
Atom	x	y	z	B
HC1A	6281	2841	7934	9.0
HC1B	6764	2844	7272	9.0
HC2A	7942	2643	8062	11.0
HC2B	7480	2555	8733	11.0
HC3A	7147	3880	8628	13.0
HC3B	7655	3956	7988	13.0
HC4A	8344	4503	9054	15.0
HC4B	8314	3696	9469	15.0
HC4C	8822	3773	8829	15.0
HC5A	7025	807	7190	9.0
HC5B	7665	1368	7644	9.0
HC6A	7603	2211	6661	11.0
HC6B	6882	1739	6213	11.0
HC7A	7723	646	6136	13.0
HC7B	8443	1087	6620	13.0
HC8A	8573	1185	5355	15.0
HC8B	7726	1591	5181	15.0
HC8C	8446	2031	5665	15.0
HC9A	6934	1373	8655	9.0
HC9B	6308	793	8208	9.0
H10A	5264	1633	8418	11.0
H10B	5897	2189	8886	11.0
H11A	6272	1129	9743	13.0
H11B	5605	600	9285	13.0
H12A	5138	1132	10286	15.0
H12B	5300	1983	10008	15.0
H12C	4633	1453	9550	15.0
H13A	5805	2017	6608	9.0
H13B	5320	1992	7267	9.0
H14A	5300	639	7215	11.0
H14B	5787	663	6557	11.0
H15A	4680	1200	5793	13.0
H15B	4192	1186	6451	13.0
H16A	3821	140	5674	15.0
H16B	4714	−158	5795	15.0
H16C	4227	−172	6453	15.0
H17A	2984	2395	7387	9.0
H17B	2299	3001	7102	9.0
H18A	2675	2498	8607	11.0

Atom	x	y	z	B
H18B	1990	3104	8322	11.0
H19A	3114	3880	8858	13.0
H19B	3046	3998	8002	13.0
H20A	4305	3670	8505	15.0
H20B	3982	2892	8816	15.0
H20C	3915	3010	7960	15.0
H21A	2386	1461	6431	9.0
H21B	1749	2121	6168	9.0
H22A	697	1196	6076	11.0
H22B	1296	534	6417	11.0
H23A	1393	334	5209	13.0
H23B	2056	988	5389	13.0
H24A	1148	1350	4330	15.0
H24B	439	1307	4784	15.0
H24C	1101	1960	4964	15.0
H25A	1724	704	7612	9.0
H25B	2103	1258	8264	9.0
H26A	3298	1263	7745	11.0
H26B	2912	600	7202	11.0
H27A	2827	−228	8233	13.0
H27B	3249	430	8763	13.0
H28A	4233	−524	8544	15.0
H28B	4019	−365	7691	15.0
H28C	4441	293	8220	15.0
H28D	3633	−954	8282	15.0
H28E	3006	−764	7571	15.0
H28F	3890	−447	7645	15.0
H28G	3508	204	9427	15.0
H28H	3733	1000	9075	15.0
H28J	2835	820	9139	15.0
H29A	1030	2172	7941	9.0
H29B	649	1617	7291	9.0
H30A	543	2663	6520	11.0
H30B	874	3206	7195	11.0
H31A	−318	2752	7755	13.0
H31B	−677	2441	6962	13.0
H32A	−1048	3617	7127	15.0
H32B	−144	3876	7306	15.0
H32C	−502	3565	6514	15.0

Table A5 Anisotropic Parameters for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	851(5)	656(5)	525(4)	108(6)	288(3)	23(5)
P1	1007(45)	830(45)	647(37)	69(37)	372(32)	39(31)
P2	1202(50)	608(37)	713(38)	194(35)	450(36)	123(32)
P3	1070(51)	750(43)	781(38)	28(35)	356(36)	144(32)
P4	1039(50)	811(43)	610(35)	197(37)	283(32)	115(31)
O1a	1022(112)	1836(149)	685(93)	−30(101)	489(83)	66(92)
O1b	972(103)	1321(127)	937(97)	262(94)	551(81)	181(90)
O13	1403(116)	679(98)	947(98)	39(81)	414(82)	−293(75)
O2a	926(104)	828(97)	880(105)	124(90)	−32(86)	157(76)
O2b	1373(126)	1345(125)	1058(109)	810(101)	642(99)	401(94)
O24	1357(120)	763(97)	1048(105)	426(82)	202(87)	84(83)
O3a	959(102)	914(104)	956(98)	7(84)	467(79)	146(82)
O3b	809(106)	1513(145)	1307(126)	22(98)	91(92)	51(113)
O4a	1292(118)	1613(133)	561(81)	529(102)	236(81)	340(83)
O4b	810(101)	1206(108)	805(88)	26(83)	81(74)	271(80)
B12	941(233)	1272(274)	757(200)	30(208)	181(177)	280(190)
F12a	2174(161)	1185(113)	1536(129)	−370(103)	443(109)	−152(96)
F12b	1208(110)	1744(130)	1788(128)	627(99)	544(95)	313(99)
B23	1369(291)	1203(247)	368(145)	419(226)	225(170)	29(158)
F23a	1545(118)	1409(112)	1029(100)	110(84)	234(83)	−292(82)
F23b	1821(127)	932(89)	1233(102)	−93(84)	423(86)	283(79)
F34a	2068(208)	1778(194)	1140(156)	−237(159)	29(132)	137(139)
F34b	1039(135)	1207(151)	1888(168)	−30(108)	184(112)	205(120)
B41	716(222)	815(206)	1099(245)	−184(184)	−18(192)	−15(191)
F41a	1267(122)	1643(145)	2460(175)	−432(104)	584(108)	−779(124)
F41b	1283(110)	2465(170)	1053(96)	168(100)	461(81)	881(105)
N1	1203(146)	745(118)	1029(126)	157(104)	298(112)	32(98)
N2	1184(146)	1328(156)	920(128)	−255(128)	325(107)	−160(120)

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table A6 Complete Distances and Angles for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

	Distance(Å)		Distance(Å)
Pt –Pt	2.884(1)	C2 –C3	1.50(3)
Pt –P1	2.278(5)	C2 –HC2A	0.949
Pt –P2	2.291(6)	C2 –HC2B	0.951
Pt –P3	2.281(6)	C3 –C4	1.50(3)
Pt –P4	2.305(5)	C3 –HC3A	0.943
P1 –O1a	1.562(15)	C3 –HC3B	0.948
P1 –O1b	1.537(14)	C4 –HC4A	0.956
P1 –O13	1.558(13)	C4 –HC4B	0.948
P2 –O2a	1.505(14)	C4 –HC4C	0.947
P2 –O2b	1.515(14)	C5 –C6	1.50(3)
P2 –O24	1.613(14)	C5 –HC5A	0.949
P3 –O13	1.635(13)	C5 –HC5B	0.955
P3 –O3a	1.539(13)	C6 –C7	1.54(3)
P3 –O3b	1.558(16)	C6 –HC6A	0.948
P4 –O24	1.570(14)	C6 –HC6B	0.945
P4 –O4a	1.518(14)	C7 –C8	1.55(4)
P4 –O4b	1.549(13)	C7 –HC7A	0.946
O1a –B41	1.45(3)	C7 –HC7B	0.954
O1b –B12	1.46(3)	C8 –HC8A	0.958
O2a –B23	1.46(3)	C8 –HC8B	0.941
O2b –B12	1.39(3)	C8 –HC8C	0.931
O3a –B23	1.44(3)	C9 –C10	1.51(3)
O3b –B34	1.23(5)	C9 –HC9A	0.952
O4a –B41	1.43(3)	C9 –HC9B	0.943
O4b –B34	1.43(5)	C10 –C11	1.55(3)
B12 –F12a	1.42(3)	C10 –H10A	0.948
B12 –F12b	1.36(3)	C10 –H10B	0.950
B23 –F23a	1.36(3)	C11 –C12	1.48(4)
B23 –F23b	1.43(3)	C11 –H11A	0.943
B34 –F34a	1.53(5)	C11 –H11B	0.954
B34 –F34b	1.36(5)	C12 –H12A	0.942
B41 –F41a	1.37(3)	C12 –H12B	0.957
B41 –F41b	1.33(3)	C12 –H12C	0.936
N1 –C1	1.46(3)	C13 –C14	1.51(3)
N1 –C5	1.51(3)	C13 –H13A	0.949
N1 –C9	1.54(3)	C13 –H13B	0.947
N1 –C13	1.52(3)	C14 –C15	1.52(3)
C1 –C2	1.51(3)	C14 –H14A	0.940
C1 –HC1A	0.945	C14 –H14B	0.944
C1 –HC1B	0.948	C15 –C16	1.48(4)

	Distance(Å)		Distance(Å)
C15 –H15A	0.946	C27 –C28B	1.531
C15 –H15B	0.953	C27 –C28C	1.535
C16 –H16A	0.956	C27 –H27A	0.950
C16 –H16B	0.953	C27 –H27B	0.950
C16 –H16C	0.940	C28A –H28A	0.950
N2 –C17	1.52(3)	C28A –H28B	0.950
N2 –C21	1.55(3)	C28A –H28C	0.950
N2 –C25	1.47(3)	C28B –H28D	0.950
N2 –C29	1.54(3)	C28B –H28E	0.950
C17 –C18	1.59(3)	C28B –H28F	0.950
C17 –H17A	1.014	C28C –H28G	0.950
C17 –H17B	0.959	C28C –H28H	0.950
C18 –C19	1.58(4)	C28C –H28J	0.950
C18 –H18A	0.959	C29 –C30	1.40(4)
C18 –H18B	0.951	C29 –H29A	0.965
C19 –C20	1.39(4)	C29 –H29B	0.955
C19 –H19A	0.954	C30 –C31	1.61(5)
C19 –H19B	0.945	C30 –H30A	0.940
C20 –H20A	0.949	C30 –H30B	0.946
C20 –H20B	0.945	C31 –C32	1.23(6)
C20 –H20C	0.939	C31 –H31A	0.938
C21 –C22	1.50(3)	C31 –H31B	0.938
C21 –H21A	0.993	C32 –H32A	0.955
C21 –H21B	0.923	C32 –H32B	0.946
C22 –C23	1.543	C32 –H32C	0.967
C22 –H22A	0.958		
C22 –H22B	0.949		
C23 –C24	1.501		
C23 –H23A	0.950		
C23 –H23B	0.950		
C24 –H24A	0.950		
C24 –H24B	0.950		
C24 –H24C	0.950		
C25 –C26	1.50(3)		
C25 –H25A	1.001		
C25 –H25B	0.930		
C26 –C27	1.525		
C26 –H26A	0.961		
C26 –H26B	0.947		
C27 –C28A	1.563		

			Angle(°)				Angle(°)
P1	-Pt	-P2	90.8(2)	B23	-O3a	-P3	124.4(14)
P1	-Pt	-P3	178.2(2)	B34	-O3b	-P3	130.0(24)
P1	-Pt	-P4	88.9(2)	B41	-O4a	-P4	133.2(15)
P2	-Pt	-P3	89.3(2)	B34	-O4b	-P4	127.7(20)
P2	-Pt	-P4	178.0(2)	O2b	-B12	-O1b	119.1(22)
P3	-Pt	-P4	90.9(2)	F12a	-B12	-O1b	102.9(20)
P4	-O24	-P2	137.1(9)	F12b	-B12	-O1b	107.3(21)
P3	-O13	-P1	135.7(8)	F12a	-B12	-O2b	109.3(21)
Pt	-P1	-O1a	116.5(6)	F12b	-B12	-O2b	113.8(22)
Pt	-P1	-O1b	116.9(6)	F12b	-B12	-F12a	102.7(21)
Pt	-P1	-O13	111.6(5)	O3a	-B23	-O2a	118.4(21)
Pt	-P2	-O2a	118.3(6)	F23a	-B23	-O2a	110.8(21)
Pt	-P2	-O2b	117.3(6)	F23b	-B23	-O2a	106.1(20)
Pt	-P2	-O24	109.6(5)	F23a	-B23	-O3a	108.9(20)
Pt	-P3	-O3a	116.4(5)	F23b	-B23	-O3a	105.2(20)
Pt	-P3	-O3b	116.9(6)	F23b	-B23	-F23a	106.7(20)
Pt	-P3	-O13	109.7(5)	O4b	-B34	-O3b	132.2(36)
Pt	-P4	-O4a	115.8(6)	F34a	-B34	-O3b	100.7(31)
Pt	-P4	-O4b	115.5(5)	F34b	-B34	-O3b	115.8(35)
Pt	-P4	-O24	110.4(5)	F34a	-B34	-O4b	94.2(27)
Pt	-Pt	-P1	90.6(1)	F34b	-B34	-O4b	106.8(30)
Pt	-Pt	-P2	91.4(1)	F34b	-B34	-F34a	97.4(28)
Pt	-Pt	-P3	91.3(1)	O4a	-B41	-O1a	115.9(22)
Pt	-Pt	-P4	90.6(1)	F41a	-B41	-O1a	104.2(21)
O1b	-P1	-O1a	106.6(8)	F41b	-B41	-O1a	107.9(22)
O13	-P1	-O1a	100.5(7)	F41a	-B41	-O4a	107.6(21)
O13	-P1	-O1b	102.7(7)	F41b	-B41	-O4a	111.1(22)
O2b	-P2	-O2a	107.3(8)	F41b	-B41	-F41a	109.8(22)
O24	-P2	-O2a	100.0(7)	C5	-N1	-C1	110.9(14)
O24	-P2	-O2b	101.8(7)	C9	-N1	-C1	110.9(14)
O3a	-P3	-O13	101.8(7)	C13	-N1	-C1	108.5(15)
O3b	-P3	-O13	103.3(7)	C9	-N1	-C5	106.1(14)
O3b	-P3	-O3a	106.8(8)	C13	-N1	-C5	109.9(14)
O4a	-P4	-O24	102.1(7)	C13	-N1	-C9	110.4(14)
O4b	-P4	-O24	103.9(7)	C2	-C1	-N1	119.4(16)
O4b	-P4	-O4a	107.6(7)	HC1A	-C1	-N1	106.6
B41	-O1a	-P1	130.9(15)	HC1B	-C1	-N1	106.5
B12	-O1b	-P1	131.7(15)	HC1A	-C1	-C2	107.2
B23	-O2a	-P2	122.7(14)	HC1B	-C1	-C2	106.9
B12	-O2b	-P2	133.1(16)	HC1B	-C1	-HC1A	110.1

			Angle(°)				Angle(°)
C3	–C2	–C1	115.5(18)	HC8C	–C8	–HC8A	110.4
HC2A	–C2	–C1	108.3	HC8C	–C8	–HC8B	111.9
HC2B	–C2	–C1	108.1	C10	–C9	–N1	115.4(16)
HC2A	–C2	–C3	107.8	HC9A	–C9	–N1	107.9
HC2B	–C2	–C3	107.5	HC9B	–C9	–N1	108.3
HC2B	–C2	–HC2A	109.5	HC9A	–C9	–C10	107.4
C4	–C3	–C2	117.7(19)	HC9B	–C9	–C10	107.8
HC3A	–C3	–C2	107.6	HC9B	–C9	–HC9A	109.9
HC3B	–C3	–C2	107.2	C11	–C10	–C9	108.7(17)
HC3A	–C3	–C4	107.2	H10A	–C10	–C9	109.7
HC3B	–C3	–C4	106.9	H10B	–C10	–C9	109.9
HC3B	–C3	–HC3A	110.2	H10A	–C10	–C11	109.7
HC4A	–C4	–C3	109.0	H10B	–C10	–C11	109.2
HC4B	–C4	–C3	109.7	H10B	–C10	–H10A	109.6
HC4C	–C4	–C3	109.9	C12	–C11	–C10	109.5(19)
HC4B	–C4	–HC4A	109.1	H11A	–C11	–C10	110.3
HC4C	–C4	–HC4A	109.2	H11B	–C11	–C10	109.5
HC4C	–C4	–HC4B	109.9	H11A	–C11	–C12	109.7
C6	–C5	–N1	114.4(16)	H11B	–C11	–C12	108.1
HC5A	–C5	–N1	108.5	H11B	–C11	–H11A	109.8
HC5B	–C5	–N1	108.2	H12A	–C12	–C11	108.9
HC5A	–C5	–C6	108.5	H12B	–C12	–C11	107.6
HC5B	–C5	–C6	108.2	H12C	–C12	–C11	109.4
HC5B	–C5	–HC5A	109.1	H12B	–C12	–H12A	109.5
C7	–C6	–C5	109.0(18)	H12C	–C12	–H12A	111.4
HC6A	–C6	–C5	109.5	H12C	–C12	–H12B	110.0
HC6B	–C6	–C5	109.4	C14	–C13	–N1	118.4(17)
HC6A	–C6	–C7	109.5	H13A	–C13	–N1	106.8
HC6B	–C6	–C7	109.4	H13B	–C13	–N1	106.9
HC6B	–C6	–HC6A	110.1	H13A	–C13	–C14	107.4
C8	–C7	–C6	108.9(21)	H13B	–C13	–C14	107.4
HC7A	–C7	–C6	109.2	H13B	–C13	–H13A	109.8
HC7B	–C7	–C6	108.9	C15	–C14	–C13	115.4(18)
HC7A	–C7	–C8	110.6	H14A	–C14	–C13	107.7
HC7B	–C7	–C8	109.7	H14B	–C14	–C13	107.5
HC7B	–C7	–HC7A	109.5	H14A	–C14	–C15	108.0
HC8A	–C8	–C7	107.3	H14B	–C14	–C15	107.5
HC8B	–C8	–C7	108.3	H14B	–C14	–H14A	110.8
HC8C	–C8	–C7	109.3	C16	–C15	–C14	112.0(20)
HC8B	–C8	–HC8A	109.5	H15A	–C15	–C14	109.9

	Angle(°)		Angle(°)
H15B –C15 –C14	109.3	C22 –C21 –N2	114.7(16)
H15A –C15 –C16	108.5	H21A –C21 –N2	104.9
H15B –C15 –C16	107.5	H21B –C21 –N2	110.3
H15B –C15 –H15A	109.6	H21A –C21 –C22	106.9
H16A –C16 –C15	109.2	H21B –C21 –C22	111.5
H16B –C16 –C15	108.9	H21B –C21 –H21A	108.1
H16C –C16 –C15	110.0	C23 –C22 –C21	101.8
H16B –C16 –H16A	108.8	H22A –C22 –C21	110.9
H16C –C16 –H16A	109.8	H22B –C22 –C21	114.3
H16C –C16 –H16B	110.1	H22A –C22 –C23	110.1
C21 –N2 –C17	103.3(15)	H22B –C22 –C23	110.6
C25 –N2 –C17	112.1(16)	H22B –C22 –H22A	108.9
C29 –N2 –C17	110.8(16)	C24 –C23 –C22	108.2
C25 –N2 –C21	111.0(16)	H23A –C23 –C22	110.3
C29 –N2 –C21	110.3(15)	H23B –C23 –C22	109.2
C29 –N2 –C25	109.2(16)	H23A –C23 –C24	109.8
C18 –C17 –N2	115.6(17)	H23B –C23 –C24	109.8
H17A –C17 –N2	111.2	H23B –C23 –H23A	109.5
H17B –C17 –N2	116.3	H24A –C24 –C23	109.5
H17A –C17 –C18	103.0	H24B –C24 –C23	109.5
H17B –C17 –C18	105.6	H24C –C24 –C23	109.5
H17B –C17 –H17A	103.7	H24B –C24 –H24A	109.5
C19 –C18 –C17	113.7(20)	H24C –C24 –H24A	109.5
H18A –C18 –C17	108.4	H24C –C24 –H24B	109.5
H18B –C18 –C17	106.7	C26 –C25 –N2	116.3(20)
H18A –C18 –C19	109.4	H25A –C25 –N2	108.3
H18B –C18 –C19	110.0	H25B –C25 –N2	112.2
H18B –C18 –H18A	108.6	H25A –C25 –C26	104.0
C20 –C19 –C18	105.3(23)	H25B –C25 –C26	108.5
H19A –C19 –C18	109.9	H25B –C25 –H25A	106.8
H19B –C19 –C18	110.0	C27 –C26 –C25	111.9
H19A –C19 –C20	110.8	H26A –C26 –C25	106.6
H19B –C19 –C20	111.2	H26B –C26 –C25	110.8
H19B –C19 –H19A	109.6	H26A –C26 –C27	108.9
H20A –C20 –C19	108.0	H26B –C26 –C27	109.8
H20B –C20 –C19	108.7	H26B –C26 –H26A	108.8
H20C –C20 –C19	108.7	C28A –C27 –C26	109.7
H20B –C20 –H20A	110.0	C28B –C27 –C26	109.7
H20C –C20 –H20A	110.5	C28C –C27 –C26	109.3
H20C –C20 –H20B	110.8	H27A –C27 –C26	109.1

			Angle(°)
H27B	-C27	-C26	109.7
H27A	-C27	-C28A	109.4
H27B	-C27	-C28A	109.4
H27B	-C27	-H27A	109.5
H28A	-C28A	-C27	109.5
H28B	-C28A	-C27	109.5
H28C	-C28A	-C27	109.5
H28B	-C28A	-H28A	109.5
H28C	-C28A	-H28A	109.5
H28C	-C28A	-H28B	109.5
H28D	-C28A	-H28C	162.4
H28F	-C28A	-H28C	120.9
H28F	-C28A	-H28D	68.4
H28D	-C28B	-C27	109.5
H28E	-C28B	-C27	109.5
H28F	-C28B	-C27	109.5
H28E	-C28B	-H28D	109.5
H28F	-C28B	-H28D	109.5
H28F	-C28B	-H28E	109.5
H28G	-C28C	-C27	109.5
H28H	-C28C	-C27	109.5
H28J	-C28C	-C27	109.5
H28H	-C28C	-H28G	109.5
H28J	-C28C	-H28G	109.5
H28J	-C28C	-H28H	109.5
C30	-C29	-N2	120.7(20)
H29A	-C29	-N2	104.0
H29B	-C29	-N2	105.1
H29A	-C29	-C30	109.1
H29B	-C29	-C30	109.4
H29B	-C29	-H29A	107.9
C31	-C30	-C29	109.6(24)
H30A	-C30	-C29	108.3
H30B	-C30	-C29	108.3
H30A	-C30	-C31	110.0
H30B	-C30	-C31	109.9
H30B	-C30	-H30A	110.7
C32	-C31	-C30	101.4(33)
H31A	-C31	-C30	111.0
H31B	-C31	-C30	110.4

			Angle(°)
H31A	-C31	-C32	110.5
H31B	-C31	-C32	111.5
H31B	-C31	-H31A	111.6
H32A	-C32	-C31	109.6
H32B	-C32	-C31	111.6
H32C	-C32	-C31	110.1
H32B	-C32	-H32A	109.4
H32C	-C32	-H32A	107.6
H32C	-C32	-H32B	108.4

Table A7 Observed and Calculated Structure Factors for Tetrakis(tetra-*n*-butylammonium) tetrakis(bis(difluoroborato)-μ-pyrophosphito)diplatinate(II)

The columns contain, in order, l, $10F_{obs}$, $10F_{calc}$, and $10(F^2_{obs}-F^2_{calc})/\sigma F^2_{obs}$. A minus sign preceding F_{obs} indicates that F^2_{obs} is negative.

-17 0 l

1	227	144	9
3	275	69	21
5	374	311	7
7	572	450	19
9	318	214	9

-17 1 l

1	157	130	2
2	-177	56	-10
3	231	171	6
4	150	171	-1
5	360	145	29
6	492	378	22
7	117	54	2
8	333	297	6
9	-175	24	-9

-17 2 l

1	-55	109	-3
2	444	267	33
3	-164	11	-7
4	336	284	7
5	311	237	12
6	342	178	22
7	383	260	21
8	292	45	25

-17 3 l

1	422	292	22
2	100	45	1
3	544	366	36
4	-194	42	-10
5	485	262	42
6	307	159	23
7	151	83	4
8	139	96	2

-17 4 l

1	158	19	5
2	472	340	24
3	255	22	16
4	379	317	10
5	128	2	4
6	223	140	7
7	-145	13	-5

-17 5 l

1	349	216	19
2	125	27	3
3	384	257	20
4	-197	43	-10
5	110	168	-4
6	174	139	3

-16 0 l

2	105	10	3
4	404	317	12
6	806	706	21
8	510	450	9
10	290	239	6

-16 1 l

1	-104	96	-6
2	137	205	-6
3	78	106	-1
4	281	183	14
5	553	439	27
6	264	158	13
7	681	555	33
8	-174	10	-8
9	155	281	-17
10	112	102	0
11	249	127	15

-16 2 l

1	400	262	26
2	223	57	14
3	410	357	9
4	-107	118	-6
5	485	327	33
6	433	338	17
7	88	94	0
8	422	301	25
9	-95	124	-7
10	169	177	0
11	263	235	4

-16 3 l

1	167	37	7
2	525	386	31
3	147	113	2
4	506	427	16
5	57	123	-3
6	217	227	-1
7	252	167	11
8	-202	77	-12
9	172	51	7
10	359	306	9
11	-170	66	-9

-16 4 l

1	440	340	18
2	71	9	1
3	450	406	9
4	-68	52	-2
5	362	335	4
6	-110	26	-3
7	-38	12	0
8	192	89	9
9	356	266	13
10	158	96	4

-16 5 l

1	145	105	3
2	434	325	19
3	169	35	7
4	292	252	6
5	16	142	-5
6	-149	112	-9
7	177	231	-6
8	278	155	14
9	320	295	3

-16 6 l

1	-165	137	-11
2	-74	32	-1
3	209	142	6
4	-127	168	-11
5	296	100	24
6	363	275	14
7	-205	69	-11
8	521	400	25

-16 7 l

1	131	110	1
2	180	8	10
3	59	95	-1
4	-58	51	-1
5	133	256	-12
6	-50	61	-1
7	497	371	24

-16 8 l

2	-126	9	-3
3	-98	97	-4
4	-193	172	-18

-15 0 l

1	-215	13	-14
3	276	266	1
5	995	804	46
7	974	816	38
9	514	485	5
11	87	100	0
13	251	221	2

-15 1 l

1	230	166	8
2	-309	39	-33
3	214	215	0
4	559	388	42
5	211	251	-5
6	933	798	44
7	-147	32	-6
8	667	567	29
9	-60	97	-4
10	217	233	-2
11	385	223	30
12	80	47	1
13	224	154	7

-15 2 l

1	-56	112	-4
2	403	365	7
3	-269	30	-22
4	496	412	20
5	431	324	22
6	312	261	9
7	531	483	12
8	203	167	4
9	162	151	1
10	428	357	14
11	44	130	-4
12	413	358	12
13	-127	69	-5

-15 3 l

1	401	370	6
2	-104	103	-6
3	540	447	22
4	-44	4	0
5	487	384	24
6	272	189	13
7	-93	53	-4
8	-184	37	-10
9	373	376	0
10	122	65	3
11	534	525	2
12	-208	4	-11

-15 4 l

1	-69	12	-1
2	441	377	16
3	198	162	4
4	438	444	-1
5	-52	27	-1
6	-98	121	-7
7	-77	66	-3
8	345	281	11
9	309	184	17
10	625	567	14
11	-162	55	-7
12	490	461	6

-15 5 l

1	325	290	6
2	115	14	4
3	376	322	9
4	271	133	20
5	364	253	19
6	214	223	-1
7	194	75	9
8	431	375	11
9	526	415	25
10	284	257	3
11	528	439	19

-15 6 l

1	-119	159	-11
2	106	186	-6
3	251	181	9
4	333	210	18
5	410	300	22
6	-181	72	-10
7	507	455	11
8	297	183	15
9	470	438	6
10	456	325	24
11	276	159	16

-15 7 l

1	121	40	3
2	136	34	5
3	151	82	4
4	396	261	25
5	77	86	0
6	546	458	19
7	-199	49	-11
8	614	506	25
9	258	162	10
10	344	307	5

-15 8 l

1	95	38	2
2	288	85	21
3	298	152	20
4	-233	37	-15
5	276	328	-8
6	-186	16	-8
7	518	412	21
8	-66	38	-1

-15 9 l

1	209	235	-3
2	-81	53	-2
3	140	231	-9
4	212	206	0
5	68	58	0
6	377	218	27
7	126	5	4

-14 0 l

2	341	261	16
4	780	625	36
6	951	906	12
8	740	653	19
10	429	391	6
12	0	169	-5
14	474	482	-1

-14 1 l

1	98	38	2
2	187	160	3

3	319	264	9
4	366	271	19
5	828	728	33
6	65	108	-2
7	846	763	28
8	-168	30	-9
9	384	349	7
10	373	258	24
11	-75	143	-8
12	376	279	18
13	206	294	-12
14	236	172	7

-14 2 1

1	413	408	1
2	141	41	6
3	419	297	27
4	419	347	16
5	393	355	9
6	601	517	23
7	-168	13	-9
8	258	277	-3
9	456	358	21
10	155	170	-1
11	646	553	26
12	-144	45	-6
13	449	409	9
14	93	238	-14

-14 3 1

1	-93	5	-2
2	565	514	15
3	51	88	-1
4	359	351	1
5	209	211	0
6	86	140	-3
7	-102	118	-9
8	481	407	18
9	134	12	5
10	768	733	11
11	-173	71	-9
12	746	635	34
13	-176	88	-12
14	435	337	22

-14 4 1

1	439	426	2
2	-248	3	-19
3	388	388	0
4	-154	54	-8
5	289	276	2
6	105	5	3
7	373	293	16
8	192	190	0
9	768	648	37
10	276	65	22
11	857	714	45
12	117	2	3
13	544	490	13

-14 5 1

1	197	38	12
2	365	268	17
3	107	179	-7
4	361	298	12
5	97	184	-7
6	-137	11	-6
7	356	316	7
8	444	370	16
9	373	338	6
10	740	578	46
11	192	78	10
12	468	436	6
13	112	65	2

-14 6 1

1	278	161	16
2	193	154	4
3	315	220	16
4	386	303	17
5	307	182	21
6	521	472	11
7	-145	58	-7
8	630	528	27
9	382	283	17
10	249	261	-2
11	469	274	38
12	163	42	7

-14 7 1

1	-234	73	-17
2	-159	104	-12
3	188	250	-7
4	248	151	12
5	550	454	23
6	-173	75	-9
7	629	576	14
8	177	74	7
9	559	500	15
10	78	75	0
11	-211	80	-13
12	-74	23	-1

-14 8 1

1	-151	48	-7
2	-84	78	-3
3	122	29	4
4	376	337	7
5	209	69	12
6	549	468	19
7	11	10	0
8	626	528	25
9	264	25	19
10	145	198	-5
11	133	124	0

-14 9 1

1	147	55	5
2	311	275	5
3	-75	199	-12
4	195	108	8
5	241	268	-3
6	-110	5	-3
7	459	359	20
8	151	118	2
9	291	217	9

-14 10 1

1	322	353	-4
2	127	105	1
3	444	330	24
4	105	136	-2
5	113	121	0
6	258	121	14
7	167	76	6
8	152	107	3

-14 11 1

1	157	124	2
2	568	415	30
3	-313	33	-23
4	279	228	6
5	171	17	8

-13 0 1

1	278	211	12
3	532	470	19
5	661	597	16
7	748	628	31
9	465	458	1
11	141	156	-1
13	503	551	-8
15	725	720	1

-13 1 1

1	235	87	20
2	436	347	24
3	137	117	1
4	562	486	24
5	-109	78	-6
6	669	649	7
7	116	24	4
8	474	423	14
9	344	274	15
10	420	428	-2
11	316	279	6
12	183	268	-12
13	240	297	-9
14	605	628	-6
15	-199	107	-13

-13 2 1

1	-86	157	-12
2	377	222	32
3	372	315	13
4	269	220	9
5	527	469	17
6	-131	105	-10
7	466	411	15
8	273	282	-1
9	406	344	14
10	623	585	11
11	-226	120	-19
12	687	612	23
13	294	342	-8
14	375	367	1
15	446	421	5

-13 3 1

1	654	604	17
2	216	135	9
3	405	334	19
4	446	332	30
5	357	267	21
6	300	240	12
7	205	218	-1
8	381	212	34
9	765	695	23
10	-116	120	-9
11	937	885	18
12	30	42	0
13	717	647	21
14	240	230	1
15	170	211	-4

-13 4 1

1	151	144	0
2	536	500	10
3	91	84	0
4	212	285	-14
5	91	18	3
6	-123	36	-6
7	-196	42	-14
8	658	582	24
9	-55	87	-3
10	971	892	28
11	118	85	1
12	828	769	19
13	40	68	0
14	382	380	0

-13 5 1

1	479	463	4
2	153	50	7
3	197	159	5
4	60	193	-11
5	-80	141	-10
6	402	340	14
7	394	250	34
8	410	378	7
9	563	524	11
10	-166	81	-11
11	690	639	15
12	-81	60	-3
13	407	431	-4
14	184	129	4

-13 6 1

1	-119	36	-5
2	257	151	16
3	404	338	14
4	21	119	-4
5	513	474	10
6	151	25	7
7	670	601	21
8	204	142	6
9	379	423	-9
10	371	328	8
11	-118	2	-4
12	293	247	7
13	-150	207	-19
14	-234	52	-15

-13 7 1

1	169	27	9
2	-136	141	-11
3	-144	90	-9
4	461	426	8
5	248	130	13
6	753	673	25
7	-187	38	-11
8	639	625	4
9	84	83	0
10	260	185	11
11	-156	10	-8
12	193	117	7
13	-105	22	-3

-13 8 1

1	-60	23	-1
2	-220	62	-16
3	336	270	12
4	-115	14	-4
5	551	472	20
6	-96	108	-5
7	597	601	-1
8	205	92	10
9	460	370	18
10	89	113	-1
11	-215	35	-13
12	163	174	-1

-13 9 1

1	367	253	19
2	197	193	0
3	180	233	-6
4	308	273	5
5	100	9	3
6	466	383	20
7	276	114	17
8	467	380	19
9	335	219	21

10	113	21	3
11	371	312	11

-13 10 1

1	191	175	1
2	468	441	6
3	-98	153	-8
4	34	195	-10
5	184	210	-3
6	138	20	6
7	430	225	37
8	223	186	3
9	108	32	3
10	420	340	14

-13 11 1

1	440	452	-2
2	65	93	-1
3	466	380	16
4	-164	66	-10
5	49	124	-4
6	92	15	2
7	-82	85	-4
8	89	18	1

-13 12 1

1	9	118	-3
2	507	372	24
3	133	53	3
4	277	194	10
5	134	153	-1

-12 0 1

2	616	600	6
4	603	511	24
6	417	416	0
8	460	414	9
10	429	235	32
12	523	521	0
14	885	900	-3
16	695	688	1

-12 1 1

1	330	375	-11
2	358	366	-2
3	585	487	35
4	109	79	2
5	524	432	30
6	-133	145	-15
7	592	558	11
8	318	252	13
9	511	466	13
10	433	373	15
11	-194	55	-13
12	244	355	-21
13	767	732	11
14	206	210	0
15	788	770	5
16	92	53	1

-12 2 1

1	710	603	38
2	576	520	19
3	371	363	2
4	392	355	9
5	72	178	-10
6	550	475	24
7	283	287	0
8	580	498	26
9	591	548	13
10	390	407	-4
11	731	708	8
12	416	294	26
13	664	637	8
14	596	582	4
15	261	185	10
16	426	336	20

-12 3 1

1	446	351	26
2	720	717	1
3	348	286	14
4	457	446	3
5	338	309	6
6	192	39	15
7	352	366	-3
8	564	519	14
9	458	372	21
10	844	895	-18
11	-137	156	-14
12	854	848	2
13	267	275	-1
14	527	507	5
15	347	262	13
16	-178	8	-9

-12 4 1

1	626	602	8
2	-190	111	-16
3	449	395	15
4	257	185	14
5	305	280	5
6	-186	66	-15
7	357	285	18
8	101	135	-2
9	816	767	17
10	-122	211	-17
11	1001	976	9
12	-174	13	-9
13	606	638	-9
14	88	77	0
15	189	126	6

-12 5 1

1	215	19	16
2	371	293	21
3	-98	116	-8
4	147	90	5
5	362	414	-13
6	163	65	9
7	322	316	1
8	467	445	6
9	172	127	5
10	754	704	17
11	-90	64	-3
12	668	577	28
13	261	126	17
14	154	233	-9
15	276	270	0

-12 6 1

1	328	301	5
2	-172	184	-25
3	-93	16	-3
4	709	628	28
5	-113	2	-4
6	756	760	-1
7	-81	175	-12
8	592	526	20
9	433	385	12
10	114	42	3
11	282	299	-3
12	171	103	5
13	393	236	32
14	423	369	10
15	-92	122	-6

-12 7 1

1	83	68	0
2	-165	73	-10
3	530	508	6
4	-117	21	-4
5	813	765	17
6	-158	13	-8
7	828	795	11
8	127	77	3
9	376	350	6
10	97	136	-3
11	-46	42	-1
12	79	48	1
13	418	314	20
14	-105	76	-4

-12 8 1

1	-138	76	-8
2	172	192	-2
3	101	147	-3
4	481	516	-9
5	-80	1	-2
6	772	701	23
7	115	68	2
8	526	497	7
9	-120	108	-9
10	-202	101	-15
11	184	191	0
12	348	241	19
13	216	127	10

-12 9 1

1	-148	162	-14
2	240	315	-12
3	135	236	-11
4	-143	158	-17
5	473	468	1
6	-153	137	-13
7	505	461	10
8	232	267	-5
9	295	171	18
10	449	396	12
11	-124	152	-10
12	321	287	6

-12 10 1

1	524	515	2
2	-161	121	-11
3	309	317	-1
4	201	228	-3
5	292	30	26
6	356	280	13
7	257	218	5
8	181	242	-6
9	499	412	20
10	232	114	12
11	478	452	6

-12 11 1

1	161	138	1
2	556	459	23
3	-185	90	-11
4	107	204	-8
5	-105	66	-5
6	-161	19	-7
7	260	85	17
8	350	298	8
9	174	38	7
10	539	416	28

-12 12 1

1	449	365	15
2	141	11	5
3	414	333	13
4	73	129	-3
5	-180	54	-10
6	97	98	0
7	-121	127	-7
8	-176	83	-10

-12 13 1

1	-166	18	-7
2	184	193	0
3	-42	213	-12
4	66	61	0
5	389	290	15

-11 0 1

1	307	287	4
3	983	947	16
5	676	608	20
7	532	528	1
9	284	235	6
11	247	277	-4
13	1026	984	11
15	973	958	3
17	389	469	-11

-11 1 1

1	809	763	19
2	659	631	11
3	359	233	30
4	692	669	9
5	40	28	0
6	556	543	4
7	565	513	18
8	561	567	-2
9	440	474	-10
10	-184	84	-14
11	690	586	37
12	645	631	4
13	416	315	22
14	890	908	-6
15	217	135	8
16	628	630	0
17	-89	101	-5

-11 2 1

1	671	704	-13
2	948	871	34
3	630	582	18
4	505	442	21
5	422	358	18
6	458	443	5
7	655	637	7
8	603	624	-7
9	632	585	16
10	900	892	3
11	79	141	-4
12	644	688	-15
13	604	546	17
14	440	436	1
15	641	618	7
16	112	22	3
17	297	226	11

-11 3 1

1	1477	1424	23
2	680	676	1
3	655	595	23
4	345	333	3
5	209	154	8
6	387	217	42
7	556	576	-7

8	518	473	14
9	851	826	9
10	508	445	17
11	900	862	14
12	144	264	-15
13	706	693	4
14	410	319	19
15	225	164	8
16	364	145	34

-11 4 1

1	568	505	21
2	844	833	4
3	-147	79	-11
4	256	252	0
5	-73	129	-10
6	218	192	4
7	358	155	43
8	628	610	6
9	320	273	9
10	783	761	8
11	65	55	0
12	729	740	-3
13	-119	9	-4
14	332	316	3
15	-144	58	-7
16	-98	165	-11

-11 5 1

1	551	525	9
2	215	188	4
3	266	243	4
4	472	462	3
5	-204	54	-17
6	461	519	-19
7	452	422	9
8	125	10	6
9	596	595	0
10	143	79	5
11	501	509	-2
12	200	70	11
13	439	440	0
14	367	316	10
15	-73	57	-2
16	442	442	0

-11 6 1

1	92	99	0
2	-78	124	-7
3	533	585	-18
4	-86	56	-3
5	1010	997	5
6	265	248	3
7	695	708	-4
8	350	369	-4
9	-175	208	-24
10	461	417	11
11	177	144	3
12	297	349	-10
13	387	349	7
14	243	115	13
15	597	573	6

-11 7 1

1	138	164	-3
2	403	424	-5
3	-55	184	-14
4	1093	1003	36
5	-148	172	-18
6	1045	991	21
7	234	187	7
8	593	536	18
9	307	190	19
10	115	56	3
11	-125	194	-17
12	337	268	15
13	100	166	-5
14	586	528	14
15	195	123	6

-11 8 1

1	-144	92	-9
2	370	267	20
3	750	694	18
4	275	302	-5
5	872	851	7
6	-239	30	-18
7	717	654	20
8	-120	55	-5
9	233	162	12
10	162	121	4
11	157	129	2
12	123	98	1
13	458	405	12
14	97	57	1

-11 9 1

1	484	434	14
2	284	285	0
3	427	383	11
4	587	518	20
5	-72	113	-5
6	539	517	5
7	260	256	0
8	204	274	-10
9	464	437	6
10	-124	84	-6
11	431	452	-4
12	318	225	15
13	98	186	-6

-11 10 1

1	27	109	-3
2	402	420	-3
3	291	241	8
4	-123	205	-17
5	411	352	13
6	258	161	12
7	265	203	9
8	571	500	17
9	95	5	2
10	615	607	2
11	-292	102	-28
12	436	426	2

-11 11 1

1	519	471	11
2	-214	55	-13
3	380	347	7
4	217	120	10
5	-44	48	-1
6	-170	69	-10
7	187	283	-12
8	76	8	2
9	509	518	-1
10	-226	61	-13
11	497	563	-14

-11 12 1

1	-30	50	0
2	444	338	24
3	282	116	18
4	-155	67	-8
5	-6	138	-5
6	140	88	3
7	230	128	10
8	491	338	29
9	149	106	2
10	501	459	8

-11 13 1

1	226	178	5
2	-121	166	-11
3	-123	60	-4
4	386	280	18
5	-163	44	-7
6	354	314	7
7	-67	152	-7
8	281	181	11

-11 14 1

1	81	124	-2
2	227	16	12
3	271	289	-2
4	-200	109	-12

-10 0 1

2	1090	1078	6
4	1116	1089	10
6	589	580	2
8	726	613	34
10	-83	172	-9
12	943	972	-8
14	940	905	9
16	933	801	32

-10 1 1

1	921	932	-5
2	699	674	11
3	938	945	-3
4	281	291	-2
5	689	755	-31
6	224	229	-1
7	744	728	7
8	626	607	7
9	364	327	10
10	643	638	1
11	462	509	-14
12	376	386	-2
13	882	868	5
14	355	312	9
15	956	900	21
16	133	88	3
17	527	450	19

-10 2 1

1	1548	1529	8
2	893	841	24
3	615	626	-4
4	693	754	-29
5	140	77	6
6	634	598	15
7	877	869	3
8	610	609	0
9	873	917	-20
10	188	70	12
11	784	801	-6
12	491	498	-2
13	552	605	-17
14	687	668	6
15	191	93	9
16	537	518	4
17	95	234	-13

-10 3 1

1	817	779	16
2	1222	1195	12
3	569	503	25
4	153	253	-17
5	283	243	10
6	681	632	20
7	431	456	-7
8	846	830	7
9	430	343	23
10	864	864	0
11	134	191	-6
12	681	697	-5
13	258	178	11
14	354	334	4
15	390	358	6
16	-176	169	-16
17	240	136	10

-10 4 1

1	1264	1215	22
2	181	107	9
3	324	371	-13
4	-97	230	-28
5	339	265	18
6	-136	143	-16
7	746	739	2
8	271	161	22
9	787	773	5
10	227	160	9
11	655	615	13
12	-60	52	-2
13	518	468	14
14	159	119	4
15	-21	125	-4
16	142	108	2
17	507	457	12

-10 5 1

1	-27	73	-2
2	563	506	20
3	778	804	-11
4	241	229	2
5	860	899	-17
6	529	506	7
7	-47	176	-13
8	586	588	0
9	-129	43	-7
10	478	498	-6
11	320	228	17
12	460	452	2
13	359	383	-5
14	246	121	15
15	451	465	-3
16	318	321	0

-10 6 1

1	537	550	-4
2	753	776	-10
3	-82	160	-11
4	1156	1133	10
5	383	354	7
6	1106	1079	12
7	430	428	0
8	291	301	-2
9	394	410	-4
10	208	72	13
11	517	419	27
12	441	391	12
13	374	352	5
14	705	673	9
15	61	37	0
16	658	655	0

-10 7 1

1	467	439	8
2	138	17	7
3	1024	1024	0
4	263	335	-13

5	1311	1318	-3
6	411	322	21
7	774	740	13
8	53	202	-13
9	228	154	10
10	290	292	0
11	230	181	6
12	330	300	5
13	646	608	11
14	-120	184	-12
15	769	714	16
16	197	117	6

-10 8 1

1	277	201	14
2	665	646	6
3	424	381	10
4	1125	1005	47
5	424	322	24
6	730	714	5
7	47	19	0
8	395	330	16
9	-38	98	-4
10	65	93	-1
11	36	131	-4
12	298	279	3
13	236	139	12
14	674	629	12
15	-230	13	-13

-10 9 1

1	280	229	9
2	554	509	12
3	600	600	0
4	406	317	19
5	524	492	9
6	-110	2	-4
7	341	235	20
8	407	425	-3
9	-81	24	-2
10	558	542	4
11	-255	54	-20
12	180	289	-15
13	438	407	6
14	155	49	5

-10 10 1

1	472	470	0
2	254	239	2
3	469	420	12
4	371	292	15
5	195	41	13
6	-148	185	-18
7	499	479	5
8	132	19	5
9	708	734	-8
10	-216	30	-13
11	672	631	11
12	-118	105	-7
13	-244	247	-29

-10 11 1

1	291	1	25
2	449	440	2
3	175	198	-3
4	-168	54	-10
5	-164	9	-8
6	368	312	12
7	139	77	3
8	735	641	25
9	248	79	16
10	823	734	25
11	-118	57	-4
12	438	446	-1

-10 12 1

1	375	339	6
2	157	56	6
3	-140	101	-8
4	165	89	6
5	165	148	1
6	461	298	32
7	443	358	19
8	-198	157	-18
9	619	563	13
10	158	16	6
11	538	524	3

-10 13 1

1	-195	73	-12
2	-221	37	-13
3	262	250	1
4	149	67	4
5	503	347	32
6	-136	166	-12
7	274	316	-5
8	433	311	20
9	141	93	2

-10 14 1

1	-203	33	-10
2	280	232	6
3	-195	89	-11
4	445	389	10
5	129	144	-1
6	372	372	0
7	65	85	0

-9 0 1

1	1353	1396	-23
3	579	573	2
5	1130	1123	2
7	731	848	-41
9	225	25	18
11	1150	1127	7
13	560	545	3
15	918	902	4
17	564	502	11

-9 1 1

1	282	344	-17
2	989	1006	-9
3	115	55	5
4	961	938	12
5	-116	26	-8
6	882	930	-25
7	572	577	-2
8	648	593	24
9	583	619	-14
10	182	246	-11
11	578	602	-8
12	797	772	10
13	-100	276	-29
14	849	812	13
15	-6	2	0
16	798	725	24
17	121	242	-11
18	319	285	6

-9 2 1

1	738	830	-46
2	1050	1048	0
3	1105	1096	4
4	-166	8	-14
5	748	771	-11
6	746	686	28
7	852	859	-3
8	1059	1071	-5
9	280	56	33
10	944	930	6
11	308	412	-27
12	835	778	22
13	497	538	-12
14	145	165	-2
15	828	756	24
16	285	240	7
17	399	435	-8
18	528	479	11

-9 3 1

1	1708	1675	15
2	522	604	-33
3	845	838	3
4	555	566	-4
5	628	629	0
6	286	256	8
7	1120	1131	-5
8	393	342	14
9	1200	1226	-12
10	-237	194	-36
11	672	691	-7
12	338	302	7
13	495	473	6
14	327	248	15
15	-32	157	-8
16	403	417	-3
17	581	527	14
18	-188	180	-18

-9 4 1

1	-198	2	-16
2	841	851	-5
3	124	140	-2
4	-205	144	-32
5	335	298	11
6	932	927	2
7	-210	61	-20
8	881	831	22
9	173	55	11
10	909	931	-9
11	-128	94	-9
12	387	382	1
13	179	164	2
14	-173	50	-11
15	56	16	0
16	533	500	8
17	-246	18	-18

-9 5 1

1	1002	1006	-1
2	873	859	6
3	129	146	-2
4	699	707	-3
5	348	336	3
6	666	659	3
7	854	857	-1
8	134	127	0
9	591	635	-16
10	135	5	7
11	480	406	21
12	524	474	14
13	359	274	19
14	543	565	-6
15	171	237	-8
16	418	403	2
17	471	507	-7

-9 6 1

1	615	573	16
2	374	356	4
3	1290	1289	0
4	297	272	6
5	1251	1328	-37
6	571	550	8
7	659	655	1
8	477	454	7
9	-122	50	-6
10	329	383	-14
11	233	261	-5
12	331	383	-10
13	882	896	-5
14	88	214	-10
15	698	721	-6
16	137	199	-5
17	536	482	13

-9 7 1

1	224	127	16
2	1292	1266	11
3	370	355	3
4	1406	1391	6
5	471	418	15
6	991	981	4
7	159	231	-10
8	306	382	-18
9	156	176	-2
10	177	110	7
11	346	283	12
12	576	620	-13
13	467	390	18
14	918	913	1
15	244	112	14
16	703	643	16

-9 8 1

1	685	683	0
2	210	208	0
3	1196	1181	6
4	493	430	19
5	983	988	-2
6	329	241	17
7	387	296	21
8	-24	78	-2
9	101	22	3
10	198	160	4
11	281	256	4
12	-79	138	-7
13	693	703	-3
14	117	150	-2
15	729	683	13
16	-144	49	-3

-9 9 1

1	366	318	12
2	462	522	-16
3	328	322	1
4	746	689	20
5	357	219	28
6	351	286	14
7	299	233	15
8	206	16	16
9	557	545	3
10	135	86	3
11	369	398	-6
12	211	238	-3
13	-166	18	-8
14	546	503	10
15	-272	37	-17

-9 10 1

1	-57	42	-1
2	508	460	14
3	224	324	-17
4	80	105	-1

5	-187	55	-12
6	318	341	-4
7	-201	11	-12
8	714	743	-9
9	-158	29	-7
10	720	697	7
11	159	48	7
12	464	421	9
13	157	195	-4
14	-208	32	-11

-9 11 1

1	448	443	1
2	177	123	5
3	-147	131	-13
4	-242	41	-19
5	264	243	3
6	-178	145	-15
7	725	645	24
8	153	172	-1
9	965	877	28
10	142	21	5
11	700	642	15
12	234	83	12
13	306	227	12

-9 12 1

1	132	14	4
2	206	156	6
3	-202	57	-12
4	193	93	8
5	342	274	11
6	423	384	8
7	314	330	-2
8	774	673	27
9	258	111	14
10	874	682	54
11	-101	190	-10
12	416	361	11

-9 13 1

1	232	104	12
2	143	162	-1
3	-63	21	-1
4	393	312	15
5	264	224	5
6	529	446	18
7	482	340	28
8	141	197	-4
9	579	401	40
10	113	103	0

-9 14 1

1	-111	190	-12
2	-145	9	-5
3	277	327	-6
4	-108	125	-8
5	436	385	9
6	177	90	5
7	393	318	13
8	303	169	19
9	178	8	8

-9 15 1

1	100	76	1
2	333	298	5
3	-87	102	-4
4	349	356	-1
5	-143	17	-4
6	314	345	-4

-8 0 1

2	1386	1454	-37
4	2127	2242	-41
6	1283	1395	-47
8	534	445	27
10	708	806	-33
12	483	511	-6
14	876	802	20
16	573	627	-11
18	204	192	1

-8 1 1

1	1076	1050	14
2	110	59	4
3	1480	1518	-20
4	379	395	-5
5	1439	1435	2
6	117	183	-10
7	829	872	-22
8	520	475	18
9	76	78	0
10	583	658	-33
11	706	765	-25
12	282	290	-2
13	541	568	-9
14	160	28	9
15	818	842	-8
16	350	263	16
17	438	448	-2
18	411	371	8

-8 2 1

1	769	654	56
2	816	830	-7
3	191	211	-4
4	1332	1401	-37
5	509	590	-37
6	690	760	-35
7	1160	1205	-24
8	209	253	-11
9	1057	1106	-24
10	308	373	-17
11	625	720	-39
12	622	626	-1
13	-139	205	-23
14	433	495	-18
15	289	192	18
16	762	739	8
17	568	549	5
18	189	263	-8

-8 3 1

1	-82	158	-15
2	917	801	58
3	552	651	-47
4	-77	35	-4
5	315	320	-1
6	1387	1340	24
7	164	238	-15
8	1293	1326	-16
9	405	402	0
10	1060	1122	-30
11	251	400	-38
12	438	481	-13
13	-168	95	-15
14	-72	12	-2
15	494	496	0
16	568	547	5
17	282	341	-10
18	716	695	6

-8 4 1

1	1554	1564	-5
2	258	223	8
3	454	426	10
4	-189	52	-23
5	739	802	-32
6	474	471	1
7	1068	1152	-45
8	238	283	-10
9	965	1006	-19
10	332	343	-3
11	612	627	-5
12	86	110	-1
13	114	274	-25
14	239	187	8
15	405	421	-4
16	-42	82	-2
17	761	694	20
18	146	107	2

-8 5 1

1	443	415	9
2	786	846	-30
3	215	176	7
4	101	40	4
5	938	958	-10
6	965	1005	-20
7	481	537	-21
8	822	794	13
9	-86	171	-15
10	708	714	-2
11	60	152	-8
12	306	354	-10
13	729	764	-12
14	-110	49	-4
15	326	367	-9
16	440	453	-3
17	-53	178	-9

-8 6 1

1	775	734	18
2	1155	1187	-15
3	265	246	4
4	865	852	6
5	512	460	18
6	930	992	-31
7	677	693	-6
8	405	520	-38
9	618	516	38
10	155	167	-1
11	385	347	9
12	807	796	3
13	417	347	17
14	866	910	-15
15	-216	82	-15
16	550	532	4
17	417	303	21

-8 7 1

1	1179	1197	-8
2	143	248	-15
3	1631	1638	-3
4	308	281	6
5	1222	1187	16
6	591	553	14
7	530	583	-19
8	281	243	7
9	-166	71	-12
10	-132	103	-11
11	623	565	19
12	308	299	1
13	1019	1053	-13
14	307	216	13
15	806	806	0
16	-89	17	-2
17	433	408	4

-8 8 1

1	111	90	1
2	1426	1442	-7
3	170	264	-13
4	1186	1250	-28
5	315	267	12
6	646	673	-10
7	-117	79	-8
8	-78	2	-2
9	-56	157	-11
10	351	317	7
11	-108	51	-5
12	803	697	36
13	-80	120	-6
14	806	818	-3
15	104	152	-3
16	568	548	4

-8 9 1

1	434	419	4
2	204	182	3
3	887	896	-3
4	203	202	0
5	467	454	3
6	-205	31	-15
7	-131	3	-6
8	438	460	-6
9	278	250	5
10	411	448	-9
11	185	191	0
12	120	186	-6
13	476	504	-6
14	-52	74	-2
15	471	464	1

-8 10 1

1	368	366	0
2	-147	210	-23
3	259	206	8
4	338	276	14
5	-38	183	-11
6	125	148	-2
7	706	666	13
8	-66	145	-7
9	731	779	-15
10	-189	41	-10
11	624	557	17
12	-220	66	-16
13	186	59	8
14	327	239	13
15	200	117	7

-8 11 1

1	-58	20	-1
2	286	242	7
3	-142	82	-9
4	-202	62	-14
5	235	96	18
6	646	609	11
7	279	282	0
8	1022	975	16
9	129	153	-1
10	836	783	16
11	-180	77	-10
12	424	356	13
13	-53	31	0
14	211	20	11

-8 12 1

1	297	314	-3
2	131	64	4
3	127	9	5
4	125	158	-3
5	305	294	1
6	401	315	18

7	735	701	9
8	389	327	10
9	918	814	31
10	-207	50	-11
11	517	514	0
12	335	185	22
13	-160	170	-12

-8 13 1

1	-157	132	-13
2	-33	183	-9
3	274	209	10
4	-163	159	-15
5	489	369	26
6	347	286	11
7	459	317	26
8	646	538	26
9	161	47	6
10	430	392	6
11	221	263	-4

-8 14 1

1	115	83	1
2	377	241	23
3	-119	33	-3
4	488	346	31
5	146	89	3
6	502	369	27
7	286	195	12
8	219	103	9
9	-41	161	-7
10	295	186	13

-8 15 1

1	257	258	0
2	-126	71	-5
3	379	330	8
4	-176	0	-8
5	410	355	10
6	104	21	2
7	208	218	0

-8 16 1

1	205	200	0
2	292	278	1
3	-252	64	-15

-7 0 1

1	1303	1274	16
3	2486	2493	-2
5	2217	2226	-2
7	850	897	-18
9	370	307	14
11	735	817	-28
13	391	451	-13
15	727	727	0
17	363	265	13
19	-52	137	-4

-7 1 1

1	90	101	-1
2	1612	1651	-21
3	49	73	-1
4	2236	2368	-59
5	573	561	5
6	918	1077	-97
7	327	366	-13
8	238	312	-24
9	547	607	-28
10	506	573	-27
11	348	302	12
12	687	705	-7
13	338	280	14
14	457	577	-38
15	313	246	13
16	555	619	-19
17	427	421	1
18	200	132	6
19	408	370	8

-7 2 1

1	507	412	39
2	114	136	-3
3	1812	1808	2
4	71	222	-23
5	699	790	-50
6	1596	1719	-65
7	398	438	-14
8	909	997	-49
9	558	583	-11
10	1044	1120	-39
11	654	693	-17
12	448	530	-26
13	310	340	-7
14	37	71	-1
15	616	733	-42
16	543	543	0
17	481	439	11
18	621	657	-9

-7 3 1

1	1508	1552	-24
2	45	22	0
3	319	341	-7
4	1027	1086	-34
5	844	860	-8
6	261	147	25
7	1764	1785	-10
8	395	398	0
9	1371	1472	-52
10	769	795	-12
11	776	840	-29
12	96	149	-5
13	-29	208	-16
14	358	356	0
15	414	404	2
16	544	437	29
17	741	729	3
18	189	223	-3

-7 4 1

1	186	148	6
2	802	787	8
3	216	108	21
4	493	480	5
5	114	46	6
6	1329	1311	9
7	467	534	-27
8	1171	1221	-25
9	473	454	6
10	1087	1113	-12
11	210	285	-16
12	467	453	4
13	409	321	22
14	145	126	2
15	217	89	13
16	665	621	13
17	103	136	-2
18	682	716	-9

-7 5 1

1	1279	1279	0
2	335	369	-10
3	248	219	6
4	572	540	14
5	543	517	11
6	592	544	21
7	857	859	0
8	508	550	-16
9	947	928	9
10	139	96	4
11	605	610	-1
12	409	493	-24
13	-40	62	-2
14	581	573	2
15	339	309	6
16	-162	119	-13
17	535	551	-3
18	-195	17	-9

-7 6 1

1	1516	1439	36
2	731	744	-6
3	601	687	-39
4	239	216	4
5	970	936	17
6	487	498	-4
7	335	359	-7
8	619	585	13
9	126	166	-4
10	518	509	2
11	539	548	-3
12	-235	205	-34
13	967	984	-6
14	-183	79	-11
15	480	596	-30
16	269	155	14
17	-111	251	-18

-7 7 1

1	320	353	-8
2	1692	1700	-3
3	223	191	7
4	1461	1460	0
5	514	547	-12
6	871	933	-30
7	356	284	20
8	102	204	-12
9	181	149	4
10	436	453	-5
11	214	49	16
12	1001	994	2
13	-94	125	-6
14	1015	1025	-3
15	-43	3	0
16	504	556	-12
17	110	43	2

-7 8 1

1	1211	1198	6
2	-97	97	-7
3	1510	1545	-16
4	143	245	-17
5	1166	1152	6
6	182	149	5
7	462	454	2
8	185	178	0
9	422	314	27
10	243	200	6
11	736	736	0
12	-104	155	-10
13	960	942	6
14	-88	64	-3
15	656	680	-6
16	246	123	13

-7 9 1

1	263	350	-20
2	980	965	6
3	119	225	-13
4	749	733	6
5	-95	24	-3
6	437	387	14
7	335	329	1
8	206	185	3
9	498	470	8
10	374	312	13
11	354	297	11
12	542	563	-5
13	-118	45	-4
14	505	472	7
15	344	174	21
16	496	345	29

-7 10 1

1	267	241	4
2	357	330	6
3	336	380	-10
4	133	137	0
5	108	63	3
6	489	460	8
7	143	184	-4
8	966	884	31
9	220	211	1
10	600	605	-1
11	145	103	3
12	-105	199	-14
13	268	248	2
14	203	139	6
15	157	161	0

-7 11 1

1	311	405	-20
2	-233	58	-22
3	-188	79	-13
4	-198	37	-13
5	570	535	11
6	386	354	7
7	1077	993	31
8	147	236	-9
9	962	912	17
10	-217	159	-20
11	468	455	3
12	183	49	8
13	281	76	20
14	-40	28	0

-7 12 1

1	215	187	4
2	148	179	-3
3	-159	61	-10
4	324	223	18
5	357	313	9
6	718	674	13
7	430	384	9
8	931	907	7
9	111	170	-4
10	587	586	0
11	98	134	-2
12	216	248	-3
13	266	176	10

-7 13 1

1	207	242	-5
2	301	226	11
3	181	9	10
4	428	339	19
5	168	161	0
6	258	322	-9
7	632	559	18
8	376	223	25
9	488	456	6
10	257	150	12
11	370	260	18

12	288	310	-3

-7 14 1

1	212	238	-3
2	136	177	-3
3	403	354	9
4	163	62	6
5	429	369	12
6	346	135	34
7	226	200	3
8	416	270	25
9	-88	68	-3
10	-217	45	-14

-7 15 1

1	-121	82	-5
2	398	340	10
3	-8	70	-1
4	374	368	0
5	123	22	3
6	303	256	6
7	154	41	5
8	-145	28	-5

-7 16 1

1	327	293	5
2	-106	116	-5
3	400	322	13
4	-188	38	-8
5	254	260	0
6	-54	129	-4

-6 0 1

2	2061	2222	-79
4	2746	2964	-71
6	1524	1648	-54
8	514	447	21
10	799	905	-42
12	740	795	-19
14	390	473	-17
16	423	502	-15
18	-141	8	-4

-6 1 1

1	1454	1454	0
2	524	598	-36
3	2669	2752	-33
4	762	772	-6
5	2075	2089	-6
6	364	417	-21
7	650	730	-42
8	445	514	-30
9	385	475	-36
10	265	391	-36
11	690	855	-81
12	301	283	4
13	349	433	-24
14	287	198	17
15	725	753	-10
16	308	331	-5
17	309	277	6
18	490	422	17
19	-67	159	-8

-6 2 1

1	824	858	-20
2	711	820	-67
3	409	455	-19
4	1616	1718	-56
5	1727	1776	-25
6	871	972	-60
7	974	1009	-20
8	252	284	-8
9	1023	1124	-56
10	1038	1082	-23
11	769	826	-26
12	537	631	-37
13	118	132	-1
14	516	578	-20
15	497	504	-2
16	461	510	-13
17	570	636	-19
18	64	166	-7
19	541	567	-6

-6 3 1

1	86	278	-42
2	-127	16	-10
3	552	616	-33
4	829	816	7
5	-106	119	-13
6	2246	2427	-81
7	-105	51	-7
8	1830	1927	-47
9	798	790	3
10	1551	1628	-38
11	826	840	-6
12	324	335	-3
13	169	228	-8
14	307	251	11
15	176	310	-23
16	597	597	0
17	178	249	-8
18	700	704	-1
19	-182	7	-8

-6 4 1

1	987	990	-2
2	387	365	7
3	417	482	-26
4	129	124	0
5	1406	1521	-64
6	584	583	0
7	1637	1636	0
8	665	625	18
9	1454	1557	-52
10	339	374	-10
11	821	851	-13
12	-81	38	-3
13	66	140	-6
14	97	155	-5
15	343	380	-8
16	-129	85	-7
17	601	660	-16
18	-286	95	-22

-6 5 1

1	600	621	-9
2	727	794	-36
3	775	715	30
4	-36	16	0
5	810	804	3
6	1050	1036	7
7	299	252	11
8	1185	1218	-17
9	335	312	6
10	903	978	-36
11	279	335	-12
12	281	287	-1
13	715	686	11
14	85	130	-3
15	268	212	9
16	455	391	14
17	-50	17	0
18	529	538	-1

-6 6 1

1	539	554	-6
2	1462	1459	1
3	466	462	1
4	834	876	-23
5	-32	28	-1
6	633	634	0
7	616	615	0
8	-74	20	-3
9	836	803	15
10	501	480	6
11	8	176	-12
12	856	892	-14
13	-201	132	-19
14	748	742	2
15	74	161	-6
16	317	331	-2
17	329	265	11
18	-220	21	-12

-6 7 1

1	1884	1876	3
2	202	208	-1
3	1416	1425	-4
4	-167	53	-13
5	1127	1161	-17
6	109	35	5
7	218	236	-4
8	138	27	8
9	466	431	11
10	-270	73	-28
11	918	899	7
12	214	279	-9
13	1178	1163	6
14	-144	192	-16
15	615	629	-4
16	248	18	17
17	397	237	26

-6 8 1

1	442	367	23
2	1317	1353	-17
3	255	130	22
4	1492	1419	33
5	240	318	-21
6	822	761	26
7	181	218	-6
8	68	9	1
9	186	226	-6
10	752	777	-8
11	329	356	-5
12	1037	1039	0
13	82	256	-17
14	771	787	-5
15	-110	18	-3
16	432	405	5
17	-119	123	-7

-6 9 1

1	658	689	-12
2	-127	152	-15
3	907	899	3
4	259	180	13
5	862	850	4
6	369	363	1
7	-93	221	-20
8	642	630	4
9	393	335	13
10	378	331	10
11	638	627	3
12	-138	216	-18
13	695	603	26
14	-325	3	-27
15	349	331	3
16	343	305	6

-6 10 1

1	452	530	-25
2	638	617	7
3	79	98	-1
4	470	343	37
5	366	368	0
6	-61	72	-3
7	1030	980	19
8	227	199	4
9	687	674	4
10	280	232	8
11	244	318	-12
12	287	293	0
13	-213	5	-12
14	195	150	4
15	392	342	10

-6 11 1

1	-147	53	-8
2	295	308	-2
3	69	74	0
4	575	468	32
5	-77	133	-9
6	745	798	-19
7	156	81	6
8	1098	1060	13
9	233	278	-7
10	543	571	-7
11	300	95	27
12	260	173	11
13	134	9	5
14	301	214	12

-6 12 1

1	295	349	-11
2	349	261	17
3	-77	4	-2
4	208	273	-10
5	549	576	-8
6	249	280	-4
7	929	864	21
8	187	208	-2
9	708	704	1
10	64	17	1
11	398	298	20
12	284	126	19
13	-63	11	0
14	376	225	18

-6 13 1

1	447	448	0
2	-15	224	-14
3	526	452	18
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5	469	416	12
6	552	476	20
7	105	215	-11
8	540	489	12
9	53	12	0
10	249	229	2
11	306	231	10
12	88	73	0

-6 14 1

1	208	145	6
2	578	558	5
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5	144	14	5
6	383	288	19
7	247	234	1
8	193	0	10

9	140	127	0
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11	-73	27	-1

-6 15 1

1	443	435	1
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3	505	423	17
4	259	65	17
5	358	276	14
6	-144	39	-6
7	-32	124	-4
8	183	34	8
9	-196	144	-14

-6 16 1

1	151	166	-1
2	244	338	-12
3	-68	1	-1
4	342	292	8
5	-242	129	-20
6	154	139	1
7	185	131	4

-5 0 1

1	1615	1562	29
3	2943	2971	-8
5	1812	1978	-71
7	772	860	-39
9	1028	1171	-62
11	1152	1276	-49
13	671	754	-25
15	536	582	-10
17	48	171	-6
19	-179	261	-24

-5 1 1

1	309	373	-23
2	1850	1825	13
3	859	815	26
4	3115	3318	-73
5	1040	1066	-16
6	875	952	-48
7	770	798	-15
8	779	800	-12
9	329	372	-14
10	1340	1392	-27
11	185	222	-7
12	894	988	-46
13	63	48	0
14	616	688	-28
15	-206	219	-32
16	441	425	4
17	358	397	-8
18	-83	31	-2
19	284	328	-6

-5 2 1

1	1191	1104	52
2	1212	1220	-5
3	1700	1681	10
4	1424	1494	-41
5	1903	1965	-31
6	1931	2031	-50
7	260	210	12
8	1548	1624	-40
9	923	962	-21
10	1223	1284	-32
11	1169	1249	-41
12	72	88	-1
13	452	534	-30
14	156	327	-28
15	559	620	-19
16	493	538	-13
17	-123	219	-20
18	586	621	-9
19	110	126	-1

-5 3 1

1	-90	123	-12
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5	1836	1860	-11
6	580	631	-26
7	2202	2261	-26
8	364	343	7
9	1976	2074	-45
10	634	733	-44
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12	361	463	-31
13	-175	48	-13
14	127	217	-10
15	426	492	-18
16	101	212	-12
17	614	663	-14
18	-119	23	-4
19	537	545	-1

-5 4 1

1	1317	1291	14
2	137	210	-14
3	391	283	36
4	982	1013	-18
5	314	270	12
6	1739	1867	-66
7	114	38	6
8	1692	1746	-26
9	589	562	11
10	1276	1292	-8
11	39	26	0
12	427	386	11
13	291	291	0
14	268	292	-4
15	-174	52	-11
16	476	438	9
17	-58	7	-1
18	657	600	16

-5 5 1

1	670	632	19
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3	610	621	-6
4	773	794	-11
5	962	963	0
6	510	570	-26
7	1270	1329	-31
8	141	59	8
9	1389	1400	-5
10	425	434	-2
11	581	516	22
12	697	674	8
13	103	44	3
14	453	457	-1
15	218	280	-10
16	-129	114	-9
17	429	432	0
18	-159	56	-7

-5 6 1

1	1651	1740	-45
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3	1602	1615	-6
4	403	392	3
5	1077	1102	-13
6	963	1013	-26
7	-135	200	-25
8	672	669	0
9	629	728	-43
10	513	487	8
11	905	913	-3
12	257	203	10
13	834	860	-9
14	305	265	7
15	526	437	22
16	312	248	10
17	190	80	7
18	418	306	17

-5 7 1

1	206	142	11
2	1916	2035	-56
3	184	23	16
4	1377	1397	-10
5	77	108	-2
6	349	378	-8
7	-56	195	-18
8	474	506	-10
9	-183	110	-17
10	1055	1079	-10
11	404	341	14
12	1183	1201	-7
13	400	487	-19
14	811	747	21
15	209	182	2
16	400	360	7
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-5 8 1

1	1282	1360	-38
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3	1208	1234	-13
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5	900	932	-15
6	267	312	-9
7	351	418	-21
8	363	341	5
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10	305	286	3
11	1048	1021	10
12	587	534	14
13	1182	1005	62
14	79	184	-7
15	440	440	0
16	-60	125	-5
17	246	149	9

-5 9 1

1	595	605	-3
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3	401	438	-10
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5	740	744	-1
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7	673	713	-15
8	-168	156	-18
9	404	420	-4
10	558	600	-12
11	404	340	14
12	793	692	30
13	382	179	35
14	497	405	20
15	326	254	10
16	190	178	1

-5 10 1

1	453	492	-12
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3	694	685	3
4	413	417	-1
5	421	398	6
6	1185	1135	20
7	311	229	15
8	742	783	-15
9	347	158	31
10	471	459	2
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12	192	135	5
13	334	254	14
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15	-162	51	-6
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-5 11 1

1	570	572	0
2	169	91	7
3	273	238	7
4	-195	49	-13
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7	1106	1088	6
8	134	74	4
9	707	695	3
10	172	114	5
11	346	315	5
12	125	112	0
13	199	106	7
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15	496	451	8

-5 12 1

1	370	369	0
2	101	219	-11
3	437	419	4
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6	713	710	0
7	-83	166	-9
8	830	818	3
9	-161	9	-8
10	249	281	-5
11	-259	5	-18
12	168	88	5
13	309	228	11
14	216	236	-2

-5 13 1

1	-236	196	-26
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3	225	10	16
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7	400	448	-9
8	154	23	6
9	229	267	-5
10	-163	103	-9
11	-51	81	-2
12	406	292	20
13	101	60	1

-5 14 1

1	706	723	-4
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3	640	625	4
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5	527	472	13
6	-179	87	-10
7	-117	53	-4
8	124	164	-3
9	-145	79	-8
10	-187	11	-8
11	327	314	1

-5 15 1

1	131	79	2
2	651	630	5
3	-169	39	-7
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5	-178	60	-9
6	-64	172	-8
7	-251	0	-18
8	323	81	28
9	-201	136	-16
10	296	221	9

-5 16 1

1	426	388	7
2	-167	18	-7
3	387	371	3
4	177	130	4
5	107	169	-4
6	75	136	-3
7	-114	25	-3
8	181	205	-1

-5 17 1

1	165	170	0
2	114	236	-9
3	-172	58	-7
4	234	170	5

-4 0 1

2	337	72	60
4	3030	2914	34
6	1590	1586	1
8	1266	1307	-17
10	1861	1917	-20
12	1177	1288	-42
14	875	876	0
16	332	349	-3
18	-70	101	-3

-4 1 1

1	1546	1646	-62
2	290	273	5
3	2986	3113	-47
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6	1355	1404	-30
7	524	491	15
8	1047	1117	-42
9	1222	1356	-77
10	400	393	2
11	1518	1538	-9
12	187	129	9
13	915	1004	-42
14	32	188	-12
15	563	620	-18
16	452	381	18
17	220	159	7
18	217	324	-17
19	201	259	-7

-4 2 1

1	939	895	28
2	676	724	-29
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4	1866	1907	-21
5	2244	2282	-17
6	90	4	4
7	1841	1987	-75
8	594	579	7
9	1466	1574	-58
10	914	976	-33
11	424	435	-3
12	1075	1088	-6
13	336	347	-2
14	676	690	-5
15	664	652	4
16	-106	267	-26
17	624	625	0
18	197	54	11
19	372	442	-12

-4 3 1

1	118	98	2
2	1456	1550	-57
3	601	525	38
4	1387	1522	-83
5	656	581	38
6	2288	2401	-50
7	304	271	9
8	1934	2030	-46
9	660	626	15
10	1094	1147	-27
11	312	340	-7
12	141	45	7
13	374	369	1
14	545	603	-19
15	323	295	5
16	678	654	7
17	-207	108	-15
18	613	604	2
19	168	172	0

-4 4 1

1	844	897	-33
2	299	156	35
3	680	692	-6
4	187	159	5
5	1610	1643	-17
6	194	208	-2
7	2013	2026	-5
8	327	304	6
9	1529	1602	-36
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11	557	469	30
12	23	131	-6
13	-95	235	-21
14	184	86	8
15	425	432	-1
16	292	186	14
17	535	535	0
18	-194	95	-12
19	544	434	21

-4 5 1

1	1242	1218	13
2	351	283	20
3	394	426	-13
4	455	554	-44
5	472	428	17
6	1485	1515	-15
7	101	110	0
8	1126	1140	-7
9	292	440	-42
10	1046	1066	-9
11	691	722	-12
12	-112	14	-4
13	708	646	21
14	111	314	-23
15	333	260	12
16	358	309	10
17	-84	72	-3
18	469	432	6

-4 6 1

1	126	59	7
2	1579	1626	-24
3	79	184	-13
4	997	1033	-20
5	954	913	21
6	253	227	6
7	804	826	-10
8	579	596	-7
9	863	880	-7
10	1373	1372	0
11	-44	128	-6
12	1152	1078	28
13	325	274	9
14	657	532	35
15	313	297	2
16	120	176	-3
17	396	295	18
18	291	106	18

-4 7 1

1	1614	1618	-2
2	247	299	-14
3	1668	1643	12
4	73	150	-9
5	642	607	15
6	295	350	-16
7	420	438	-5
8	206	245	-8
9	1186	1236	-22
10	-99	11	-3
11	1503	1404	39
12	432	397	7
13	1144	1014	45
14	439	363	17
15	543	436	23
16	-84	105	-5
17	185	27	8
18	-18	141	-4

-4 8 1

1	318	329	-3
2	1485	1566	-40
3	-120	22	-7
4	703	770	-31
5	363	345	5
6	544	587	-16
7	708	604	39
8	186	275	-16
9	247	329	-17
10	1124	1040	33
11	462	439	5
12	1277	1127	54
13	432	368	12
14	760	625	37
15	-32	47	-1
16	211	212	0
17	-84	103	-4

-4 9 1

1	1030	1113	-40
2	147	96	5
3	688	780	-39
4	906	907	0
5	817	846	-12
6	905	892	5
7	602	608	-2
8	816	786	11
9	250	224	4
10	301	346	-9
11	834	714	38
12	372	311	12
13	693	583	28
14	336	113	27
15	124	199	-5
16	371	362	1

-4 10 1

1	621	656	-13
2	660	729	-28
3	639	619	7
4	657	688	-11
5	1263	1269	-2
6	597	536	19
7	862	806	21
8	280	271	1
9	649	645	1
10	318	225	15
11	553	431	30
12	403	327	14
13	63	84	0
14	-78	84	-3
15	606	485	25
16	48	30	0

-4 11 1

1	212	101	13
2	-99	95	-6
3	-69	144	-10
4	780	796	-6
5	127	137	0
6	1008	986	8
7	535	417	29
8	830	867	-11
9	-38	13	0
10	404	360	9
11	77	120	-2
12	-114	96	-6
13	107	8	3
14	422	338	14
15	-186	102	-10

-4 12 1

1	-104	266	-25
2	490	447	11
3	543	476	18
4	317	332	-3
5	690	686	1
6	81	29	1
7	813	823	-3
8	199	162	4
9	331	297	6
10	148	69	4
11	-170	112	-12
12	110	98	0
13	174	138	2
14	189	247	-5

-4 13 1

1	666	694	-8
2	-155	0	-7
3	826	833	-2
4	507	433	18
5	299	386	-17
6	435	435	0
7	61	55	0
8	357	248	18
9	299	124	24
10	153	118	2
11	325	222	15
12	-192	3	-9
13	419	322	15

-4 14 1

1	-148	83	-7
2	869	900	-9
3	125	69	3
4	702	692	3
5	121	100	1
6	290	211	11
7	286	208	12
8	229	51	16

9	169	53	6
10	290	230	8
11	-158	16	-6
12	408	322	13

-4 15 1

1	754	746	2
2	130	118	0
3	601	653	-13
4	-99	46	-3
5	331	296	6
6	-183	25	-10
7	-211	7	-11
8	-15	42	0
9	-171	192	-16
10	45	74	0

-4 16 1

1	89	14	1
2	465	468	0
3	153	95	3
4	251	261	-1
5	254	138	12
6	-90	1	-2
7	222	239	-1
8	-46	137	-6

-4 17 1

1	153	250	-10
2	209	6	12
3	422	188	35
4	273	190	9
5	-215	54	-11

-3 0 1

1	2375	2355	12
3	477	25	86
5	2206	2384	-71
7	92	81	0
9	1466	1456	4
11	1927	1928	0
13	1390	1456	-23
15	668	713	-11
17	173	127	3
19	269	303	-4

-3 1 1

1	154	38	15
2	1372	1375	-1
3	399	414	-7
4	2053	2179	-64
5	494	539	-22
6	-188	97	-25
7	1366	1432	-38
8	1286	1323	-21
9	1121	1126	-2
10	1130	1188	-32
11	-156	125	-18
12	1604	1643	-17
13	301	279	4
14	1023	1026	-1
15	357	355	0
16	243	214	5
17	297	289	1
18	-48	181	-10
19	106	226	-9

-3 2 1

1	1546	1464	48
2	744	751	-3
3	763	794	-19
4	364	422	-22
5	214	254	-11
6	1946	2070	-62
7	228	111	22
8	1356	1424	-38
9	881	928	-25
10	665	731	-31
11	1057	1053	2
12	224	249	-4
13	1072	1164	-42
14	622	720	-34
15	421	388	7
16	663	648	4
17	-172	63	-9
18	532	513	4
19	397	268	20

-3 3 1

1	2139	2167	-13
2	411	319	32
3	1474	1381	53
4	421	557	-65
5	1813	1858	-23
6	348	333	5
7	1425	1416	4
8	287	293	-1
9	1591	1638	-23
10	100	17	4
11	-107	73	-7
12	694	634	22
13	818	765	20
14	418	375	10
15	953	934	6
16	203	152	5
17	708	656	14
18	190	197	0
19	296	373	-10

-3 4 1

1	329	466	-55
2	195	280	-23
3	196	222	-6
4	1291	1377	-51
5	-90	176	-19
6	1881	2066	-93
7	276	298	-6
8	1184	1184	0
9	832	738	42
10	876	790	38
11	117	194	-9
12	446	405	11
13	-38	89	-3
14	780	725	18
15	236	173	7
16	711	602	30
17	190	228	-3
18	569	452	23
19	-123	99	-5

-3 5 1

1	277	335	-20
2	685	685	0
3	231	106	20
4	602	529	34
5	980	931	26
6	-75	30	-3
7	1331	1327	1
8	406	385	6
9	1448	1385	29
10	1111	1027	37
11	397	336	14
12	786	705	29
13	344	318	5
14	447	345	20
15	475	463	2
16	311	273	5
17	365	438	-12
18	-82	26	-1

-3 6 1

1	1592	1609	-9
2	398	509	-42
3	1045	1044	0
4	558	577	-8
5	801	704	47
6	823	840	-8
7	436	372	20
8	1213	1186	12
9	1449	1495	-21
10	891	881	4
11	1742	1583	61
12	141	36	5
13	925	792	45
14	431	410	4
15	355	270	13
16	387	292	16
17	-175	10	-7
18	371	284	14

-3 7 1

1	132	203	-12
2	1376	1447	-38
3	315	399	-25
4	813	845	-15
5	645	664	-9
6	220	16	21
7	681	629	20
8	898	902	-1
9	319	346	-5
10	1838	1752	33
11	137	2	5
12	1389	1252	49
13	381	313	12
14	611	532	19
15	-123	143	-9
16	247	138	10
17	191	132	4
18	-209	183	-15

-3 8 1

1	1470	1507	-19
2	379	338	13
3	773	799	-12
4	147	84	7
5	389	429	-12
6	171	244	-12
7	192	65	13
8	220	277	-10
9	707	711	-1
10	-89	186	-12
11	1356	1172	66
12	410	238	31
13	911	811	29
14	116	63	2
15	344	290	8
16	258	158	10
17	-256	44	-14

-3 9 1

1	463	515	-17
2	711	744	-14
3	459	428	9
4	718	704	5
5	762	818	-23
6	548	593	-15
7	1001	954	18
8	406	381	6
9	536	532	1
10	725	572	47
11	368	315	12
12	762	681	23
13	-116	17	-4
14	383	312	10
15	438	314	22
16	-270	58	-19

-3 10 1

1	747	742	2
2	187	133	6
3	577	575	0
4	1331	1277	23
5	533	593	-19
6	826	866	-15
7	614	517	31
8	1127	1018	39
9	124	50	4
10	351	386	-6
11	423	343	15
12	132	176	-4
13	252	180	9
14	440	343	17
15	-208	47	-10
16	582	506	14

-3 11 1

1	251	217	6
2	70	0	1
3	893	894	0
4	-225	143	-23
5	1004	1022	-7
6	621	560	18
7	1203	1077	47
8	362	275	16
9	462	480	-4
10	34	70	-1
11	376	209	28
12	-78	111	-5
13	196	210	-1
14	218	93	11
15	624	523	20

-3 12 1

1	551	557	-1
2	465	423	11
3	373	457	-20
4	781	792	-3
5	-158	182	-18
6	965	876	30
7	391	367	4
8	578	510	17
9	-132	132	-10
10	102	194	-8
11	223	145	7
12	170	92	5
13	-53	164	-6
14	508	340	28

-3 13 1

1	-301	65	-27
2	862	905	-15
3	511	467	10
4	631	661	-9
5	638	653	-4
6	-155	85	-9
7	392	367	5
8	386	210	32
9	95	170	-5
10	344	237	18
11	-286	46	-24
12	417	290	20
13	129	120	0

-3 14 1

1	880	880	0
2	-87	146	-7
3	992	1010	-6
4	70	272	-19
5	352	393	-7
6	25	175	-9
7	-37	15	0
8	245	152	10
9	379	297	17
10	-65	88	-3
11	277	290	-1
12	234	63	12

-3 15 1

1	194	107	7
2	852	801	15
3	-104	28	-3
4	489	502	-3
5	-255	40	-20
6	192	129	5
7	81	1	1
8	162	222	-5
9	-237	41	-14
10	302	293	1

-3 16 1

1	462	458	0
2	191	112	6
3	479	378	20
4	133	165	-2
5	-191	138	-14
6	315	269	7
7	181	138	3
8	386	198	27

-3 17 1

1	-138	74	-6
2	438	229	36
3	-117	152	-9
4	-194	114	-13
5	480	377	23
6	218	53	10

-2 0 1

2	3119	3081	13
4	962	965	-1
6	-107	3	-4
8	752	805	-23
10	594	618	-8
12	1994	2123	-44
14	1037	1028	2
16	-307	107	-18
18	-321	228	-22

-2 1 1

1	2239	2295	-27
2	465	400	33
3	1546	1614	-43
4	2407	2539	-60
5	415	589	-89
6	997	984	8
7	433	360	28
8	387	469	-33
9	1026	979	26
10	317	402	-27
11	1635	1642	-3
12	-75	79	-4
13	1494	1495	0
14	384	411	-6
15	433	372	12
16	389	333	9
17	260	205	6
18	316	222	12
19	441	298	24

-2 2 1

1	414	495	-41
2	857	794	40
3	708	630	46
4	740	696	25
5	1674	1664	5
6	258	183	20
7	609	555	25
8	813	698	57
9	1552	1402	71
10	813	781	14
11	-101	105	-8
12	1365	1312	22
13	897	773	44
14	894	766	43
15	881	818	19
16	-129	79	-5
17	753	612	34
18	-32	239	-12
19	353	270	13

-2 3 1

1	1824	1850	-14
2	84	258	-30
3	656	605	26
4	1060	1021	23
5	691	675	8
6	1404	1365	20
7	610	543	28
8	1400	1353	23
9	332	342	-2
10	459	481	-7
11	649	577	26
12	815	743	26
13	642	711	-21
14	1255	1127	46
15	250	1	16
16	1068	908	47
17	382	213	24
18	596	514	16
19	165	202	-3

-2 4 1

1	136	293	-37
2	665	774	-63
3	544	449	40
4	833	794	21
5	2106	1936	74
6	142	55	7
7	2304	2170	53
8	495	459	13
9	1248	1186	30
10	559	460	33
11	159	109	4
12	349	198	34
13	1057	897	56
14	144	107	2
15	1074	909	49
16	341	275	9
17	631	577	12
18	-148	128	-8
19	414	280	23

-2 5 1

1	1016	1078	-37
2	538	654	-59
3	934	925	4
4	669	625	21
5	483	456	9
6	1643	1646	-1
7	345	343	0
8	1985	1810	71
9	819	803	6
10	1072	1003	29
11	966	833	50
12	264	219	6
13	644	505	37
14	702	605	26
15	381	344	6
16	543	486	11
17	170	87	4
18	457	345	20

-2 6 1

1	667	635	14
2	1283	1373	-51
3	626	618	3
4	1173	1198	-13
5	771	753	8
6	273	284	-2
7	1248	1174	34
8	1099	1065	15
9	1161	1101	25
10	2085	1918	61
11	212	292	-14
12	1067	902	60
13	247	213	4
14	573	463	26
15	371	349	3
16	170	188	-1
17	304	288	1
18	206	240	-3

-2 7 1

1	1168	1259	-50
2	236	311	-18
3	622	681	-27
4	787	760	12
5	367	306	16
6	952	951	0
7	561	518	15
8	256	255	0
9	1823	1742	32
10	335	308	5
11	1510	1376	50
12	-70	70	-2
13	860	772	28
14	47	208	-10
15	248	247	0
16	150	78	4
17	-217	114	-13
18	-102	56	-3

-2 8 1

1	390	449	-19
2	722	822	-48
3	333	251	21
4	365	386	-6
5	127	0	6
6	256	299	-10
7	153	103	4
8	516	490	7
9	185	143	5
10	1273	1155	46
11	-135	211	-17
12	987	851	46
13	-109	1	-3
14	376	357	3
15	261	146	12
16	-271	96	-22
17	193	114	5

-2 9 1

1	657	746	-39
2	-139	73	-10
3	934	896	17
4	701	673	11
5	611	652	-15
6	901	874	11
7	376	432	-14
8	769	704	23
9	591	566	7
10	160	283	-17
11	803	662	43
12	-158	56	-7
13	465	376	23
14	244	209	3
15	195	179	1
16	533	363	31

-2 10 1

1	-90	19	-4
2	498	531	-10
3	859	880	-9
4	632	589	14
5	1182	1209	-11
6	587	615	-8
7	1108	1036	27
8	-72	15	-1
9	548	483	17
10	514	396	29
11	115	129	-1
12	446	362	16
13	320	176	20
14	-197	114	-13
15	566	435	26
16	152	25	4

-2 11 1

1	77	143	-5
2	522	563	-13
3	324	263	12
4	1387	1345	17
5	426	386	10
6	1148	1043	40
7	215	270	-9
8	695	646	15
9	95	13	2
10	185	227	-4
11	-120	89	-6
12	153	103	4
13	136	25	4
14	530	445	17
15	162	5	5

-2 12 1

1	-60	114	-6
2	536	637	-32
3	918	950	-11
4	201	269	-12
5	986	930	20
6	79	84	0
7	842	774	22
8	253	274	-3
9	201	276	-11
10	191	196	0
11	-155	2	-8
12	198	172	2
13	370	302	10
14	202	158	3

-2 13 1

1	909	951	-15
2	409	362	9
3	761	776	-5
4	785	724	20
5	287	365	-15
6	628	541	23
7	339	211	21
8	401	436	-7

9	376	329	9
10	-99	84	-4
11	384	367	2
12	-86	72	-3
13	364	305	9

-2 14 1

1	116	8	4
2	992	984	2
3	439	346	18
4	767	709	18
5	320	296	4
6	-255	66	-19
7	284	225	8
8	293	278	2
9	161	154	0
10	414	406	1
11	358	145	28
12	537	403	26

-2 15 1

1	738	705	9
2	138	9	5
3	782	726	16
4	-105	5	-3
5	138	264	-13
6	-125	2	-4
7	357	211	21
8	-216	7	-12
9	414	355	10
10	300	100	20

-2 16 1

1	249	63	15
2	466	443	4
3	-40	169	-8
4	161	204	-4
5	309	315	-1
6	-16	55	0
7	-176	217	-22
8	248	267	-2
9	198	103	5

-2 17 1

1	-79	194	-10
2	207	121	7
3	-113	151	-8
4	396	334	10
5	-240	5	-13
6	443	427	2

-1 0 1

3	2681	2841	-57
5	1519	1592	-35
7	562	416	45
9	671	522	37
11	1711	1523	62
13	1795	1578	66
15	259	176	8
17	174	233	-5
19	360	378	-3

-1 1 1

1	512	575	-46
2	2903	2919	-6
3	360	428	-30
4	1586	1369	118
5	372	262	32
6	908	895	7
7	554	414	51
8	455	318	40
9	934	789	64
10	1013	929	38
11	293	164	25
12	1978	1794	71
13	388	352	8
14	939	731	73
15	529	486	11
16	-130	164	-14
17	159	209	-5
18	279	277	0
19	150	107	3

-1 2 1

1	2131	2340	-110
2	1009	838	107
3	100	205	-16
4	1605	1459	77
5	-113	111	-11
6	870	793	38
7	734	717	7
8	527	432	31
9	252	90	24
10	169	160	1
11	1458	1253	85
12	649	602	15
13	988	953	13
14	996	955	14
15	185	115	7
16	866	725	41
17	352	242	16
18	427	379	8
19	343	222	24

-1 3 1

1	1080	1019	38
2	490	574	-39
3	1555	1400	83
4	513	296	71
5	1916	1734	83
6	148	31	8
7	2005	1789	90
8	312	212	20
9	502	472	9
10	114	100	1
11	364	354	2
12	883	779	39
13	1277	1134	53
14	176	271	-11
15	1182	1098	28
16	402	225	29
17	775	754	5
18	-97	106	-4
19	287	267	2

-1 4 1

1	210	48	19
2	278	338	-16
3	969	951	9
4	1778	1825	-23
5	824	855	-16
6	2937	2722	72
7	-58	113	-6
8	1683	1621	27
9	320	352	-8
10	452	476	-7
11	-63	16	-1
12	547	537	2
13	271	106	22
14	1129	1004	43
15	223	275	-6
16	879	796	22
17	-221	119	-14
18	570	479	18
19	145	5	3

-1 5 1

1	-102	107	-10
2	1437	1367	37
3	1034	966	35
4	1405	1409	-2
5	2170	1948	90
6	-85	195	-18
7	1405	1321	39
8	257	8	26
9	1269	1244	10
10	1025	907	47
11	-191	171	-20
12	366	289	14
13	543	403	33
14	678	499	46
15	760	646	30
16	268	248	2
17	630	500	28
18	163	128	2

-1 6 1

1	1521	1465	28
2	809	837	-14
3	1431	1467	-18
4	875	851	12
5	370	421	-15
6	1100	1111	-5
7	-22	73	-2
8	791	794	-1
9	1730	1585	58
10	700	582	39
11	1089	987	39
12	-108	7	-3
13	748	647	30
14	380	298	13
15	405	328	15
16	480	349	23
17	234	144	7
18	-59	236	-14

-1 7 1

1	-110	27	-5
2	1306	1277	14
3	615	663	-20
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5	733	712	8
6	322	337	-3
7	232	345	-27
8	1360	1265	41
9	451	390	15
10	1547	1419	50
11	-212	33	-13
12	864	771	30
13	-127	25	-4
14	455	404	10
15	-226	105	-15
16	-265	35	-16
17	-139	72	-5

-1 8 1

1	1119	1187	-35
2	169	49	12
3	831	960	-65
4	-54	15	-1
5	336	272	18
6	71	98	-1
7	790	723	26
8	240	170	10
9	1390	1310	32
10	-124	75	-6
11	710	726	-5
12	126	12	5
13	491	464	6
14	104	114	0
15	107	236	-10
16	95	157	-3
17	-85	186	-8

-1 9 1

1	-82	15	-2
2	1330	1275	25
3	426	447	-6
4	421	494	-24
5	855	807	21
6	-36	153	-10
7	903	845	22
8	864	743	44
9	371	361	2
10	617	696	-23
11	-171	22	-9
12	624	519	28
13	430	280	26
14	191	268	-8
15	415	351	11
16	-274	95	-18

-1 10 1

1	430	413	5
2	539	514	9
3	567	593	-9
4	1315	1295	8
5	445	412	9
6	1176	1182	-2
7	169	113	5
8	669	675	-1
9	503	495	2
10	180	158	2
11	336	384	-9
12	256	225	4
13	296	285	1
14	468	398	13
15	101	152	-2
16	497	412	14

-1 11 1

1	371	378	-1
2	258	167	16
3	1078	1044	14
4	-87	69	-4
5	1168	1180	-5
6	-157	14	-9
7	824	816	2
8	143	21	6
9	356	333	4
10	37	101	-2
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13	183	191	0

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12	260	54	17

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6	598	569	19
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8	54	56	0
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10	382	322	24
11	1665	1561	57
12	458	392	25
13	1008	988	11
14	595	518	32
15	53	31	0
16	351	328	6
17	285	273	2
18	78	174	-9
19	455	383	25

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3	1644	1527	75
4	1215	1263	-36
5	863	801	44
6	286	306	-7
7	906	842	44
8	630	566	36
9	115	58	6
10	389	396	-3
11	539	479	28
12	1162	1089	41
13	729	735	-2
14	398	264	37
15	826	811	6
16	318	199	23
17	606	551	20
18	219	204	2
19	237	208	5

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3	2622	2307	135
4	2367	2196	81
5	639	560	46
6	1521	1502	12
7	99	24	5
8	1098	1024	47
9	78	28	3
10	-2	22	0
11	551	503	22
12	602	631	-13
13	287	219	15
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15	111	60	3
16	945	908	16
17	-124	67	-6
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19	104	111	0

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6	506	487	9
7	1628	1475	86
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16	199	151	5
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3	1439	1385	34
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7	533	488	45
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9	761	684	42
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12	203	8	19
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16	723	660	22
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18	363	349	3

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3	1303	1331	-18
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5	939	948	-6
6	835	854	-11
7	737	670	36
8	851	862	-6
9	387	373	4
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11	311	197	26
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13	254	148	17
14	529	476	17
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18	410	389	4

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3	1531	1535	-2
4	156	10	15
5	385	385	0
6	580	510	35
7	1159	1119	24
8	153	17	11
9	1289	1260	15
10	145	105	4
11	806	779	13
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14	-165	92	-13
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16	238	145	12
17	346	305	8

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10	948	890	28
11	83	58	1
12	664	588	29
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14	395	342	13
15	103	124	-1
16	-158	47	-8
17	198	101	9

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1	1195	1231	-23
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3	984	980	2
4	923	949	-15
5	-103	45	-7
6	1103	1052	29
7	596	596	0
8	872	783	43
9	865	824	20
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13	541	534	2
14	396	410	-3
15	210	269	-9
16	433	300	27

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6	-181	148	-25
7	1054	1012	22
8	478	500	-8
9	164	200	-5
10	523	484	13
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12	407	395	3
13	485	531	-13
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16	139	99	2

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2	849	850	0
3	117	218	-17
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5	216	296	-19
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7	-111	199	-22
8	506	528	-8
9	-146	55	-10
10	61	38	1
11	-26	55	-1
12	347	388	-10
13	52	143	-5
14	547	492	15
15	186	124	6

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0	540	519	6
1	470	456	5
2	365	330	11
3	680	680	0
4	395	354	14

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Page 15

5	641	664	-10
6	-58	60	-3
7	546	541	1
8	280	154	25
9	281	271	2
10	352	426	-20
11	104	59	2
12	257	251	1
13	362	395	-7
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8	345	299	9

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9	1672	1636	17
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13	790	849	-23
15	-86	93	-5
17	312	270	6
19	400	493	-18

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16	165	173	0
17	295	279	2
18	362	369	-1
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2	1482	1391	54
3	1156	1071	52
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5	299	229	17
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15	62	106	-2
16	589	670	-22
17	-161	215	-21
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4	827	933	-63
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6	278	402	-36
7	1302	1207	48
8	437	387	16
9	418	439	-6
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11	850	768	33
12	275	308	-6
13	611	665	-16
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15	847	946	-33
16	146	86	3
17	493	578	-18
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0	2206	2171	15
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3	69	215	-18
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5	347	331	4
6	2562	2488	28
7	143	196	-7
8	1282	1211	32
9	130	190	-8
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11	-99	203	-17
12	391	379	2
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14	834	922	-28
15	156	41	5
16	645	749	-28
17	316	108	20
18	318	417	-13

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2	1387	1424	-21
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5	1921	1847	33
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8	649	697	-19
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13	374	416	-8
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16	-299	75	-21
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12	571	638	-15
13	332	428	-16
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15	164	222	-4

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13	251	237	1

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9	604	642	-8
10	69	155	-4
11	500	544	-9

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7	104	39	2
8	412	465	-10
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16	181	283	-15
17	179	307	-18
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5	2129	2114	6
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7	406	488	-32
8	1165	1167	-1
9	413	334	23
10	938	960	-10
11	509	515	-1
12	220	225	0
13	454	488	-9
14	-123	19	-5
15	425	516	-22

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16	145	220	-8
17	244	335	-14
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7	581	630	-22
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9	580	590	-4
10	509	496	4
11	121	141	-2
12	526	530	-1
13	-109	98	-6
14	573	726	-45
15	-133	75	-6
16	465	587	-28
17	131	48	4
18	160	255	-10

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7	1509	1476	15
8	238	281	-10
9	359	346	3
10	261	78	28
11	418	413	1
12	132	188	-5
13	510	576	-17
14	-150	91	-8
15	733	791	-17
16	308	179	15
17	455	490	-7
18	71	129	-2

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0	268	170	22
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3	1196	1249	-30
4	2592	2497	36
5	1149	1053	48
6	1790	1749	18
7	569	516	18
8	463	480	-5
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10	118	108	1
11	359	285	15
12	362	367	-1
13	-136	237	-22
14	642	662	-6
15	-256	181	-23
16	576	617	-9
17	316	278	4
18	308	265	4

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5	607	651	-18
6	767	770	-1
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12	451	515	-15
13	284	299	-2
14	250	27	17
15	389	487	-21
16	309	347	-5
17	321	342	-2

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13	250	329	-12
14	-169	186	-17
15	79	183	-6
16	168	212	-3
17	354	417	-10

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3	477	458	6
4	-89	161	-15
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6	787	847	-26
7	532	516	4
8	904	879	9
9	247	190	8
10	731	768	-12
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12	508	581	-18
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14	-258	155	-24
15	-125	29	-3
16	-192	198	-16

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5	374	434	-20
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7	770	727	15
8	611	608	0
9	726	704	7
10	-179	10	-8
11	666	691	-7
12	493	565	-17
13	362	509	-27
14	414	448	-6
15	53	101	-1
16	353	226	16

2 10 1

0	448	589	-46
1	967	970	-1

2	995	1034	-17
3	987	1084	-42
4	146	50	6
5	788	804	-6
6	565	441	35
7	719	726	-2
8	582	657	-21
9	198	244	-5
10	92	346	-28
11	540	513	6
12	431	474	-9
13	582	653	-16
14	297	250	6
15	399	390	1

2 11 1

0	374	358	3
1	500	549	-14
2	541	585	-14
3	341	294	11
4	774	782	-3
5	121	263	-18
6	633	624	2
7	426	385	11
8	281	291	-1
9	-183	84	-11
10	107	147	-3
11	-177	30	-9
12	454	586	-29
13	120	137	-1
14	429	478	-7

2 12 1

0	368	329	8
1	237	276	-6
2	-153	147	-14
3	360	438	-16
4	75	5	1
5	390	383	1
6	-87	124	-7
7	457	426	7
8	377	289	18
9	-74	87	-3
10	404	317	15
11	119	182	-4
12	146	147	0
13	369	439	-10

2 13 1

0	134	77	3
1	421	411	2
2	327	355	-6
3	151	168	-1
4	309	234	13
5	221	142	9
6	392	326	13
7	396	390	1
8	272	310	-5
9	548	593	-10
10	373	66	32
11	381	408	-4
12	86	230	-9

2 14 1

0	745	745	0
1	174	236	-8
2	350	309	8
3	-157	184	-17
4	252	2	20
5	313	210	15
6	259	355	-14
7	26	201	-10
8	584	534	11
9	146	113	2
10	563	591	-5
11	-253	11	-13

2 15 1

0	-158	129	-10
1	323	358	-6
2	120	18	4
3	108	86	1
4	161	16	7
5	-209	53	-12
6	84	10	1
7	298	338	-6
8	207	62	8
9	364	496	-21
10	-178	74	-7

2 16 1

0	302	306	0
1	-76	69	-2
2	274	244	3
3	47	144	-4
4	-46	41	-1
5	144	213	-6
6	-174	86	-8
7	-190	76	-9
8	138	306	-18

2 17 1

0	-123	90	-6
1	157	173	-1
2	309	232	10
3	-171	82	-9
4	259	313	-7
5	-226	20	-13

3 0 1

1	1745	1670	42
3	1402	1306	57
5	1687	1676	5
7	2366	2377	-4
9	1962	2040	-35
11	1015	1096	-36
13	206	164	5
15	-177	8	-9
17	198	332	-17

3 1 1

0	1134	942	124
1	257	309	-17
2	597	639	-24
3	1663	1533	70
4	337	377	-15
5	1096	1052	26
6	1293	1268	13
7	143	169	-4
8	1858	1886	-12
9	271	184	19
10	1249	1276	-13
11	123	77	4
12	231	289	-10
13	183	251	-10
14	167	114	5
15	199	232	-5
16	232	251	-2
17	-175	111	-10
18	213	386	-23

3 2 1

0	400	476	-35
1	1094	1050	29
2	698	578	64
3	1250	1183	40
4	2448	2179	107
5	204	73	24
6	1045	1014	17
7	810	812	0
8	359	281	22
9	937	954	-8
10	447	419	9
11	277	306	-6
12	215	363	-28
13	98	77	1
14	361	462	-26
15	-74	87	-3
16	167	253	-9
17	115	282	-19
18	82	80	0

3 3 1

0	2334	2291	19
1	914	962	-30
2	1416	1308	61
3	3071	2937	46
4	849	719	69
5	2459	2457	0
6	-149	4	-12
7	780	837	-29
8	480	619	-57
9	243	215	6
10	246	245	0
11	333	320	3
12	168	10	10
13	464	529	-18
14	-184	70	-11
15	358	519	-33
16	-94	1	-2
17	268	277	-1
18	-149	138	-10

3 4 1

0	1003	807	109
1	248	110	26
2	2690	2470	82
3	1083	1053	17
4	2420	2236	73
5	525	591	-29
6	1897	1847	22
7	84	108	-2
8	397	424	-8
9	-96	84	-6
10	331	233	24
11	212	273	-11
12	612	632	-6
13	282	232	8
14	554	670	-31
15	96	203	-9
16	445	505	-12
17	-67	139	-5
18	162	190	-2

3 5 1

0	839	914	-45
1	1251	1307	-33
2	209	245	-7
3	2412	2451	-16
4	175	27	16
5	1729	1765	-17
6	877	785	43
7	840	840	0
8	528	484	15
9	158	160	0
10	666	657	3
11	497	571	-21
12	286	419	-24
13	441	475	-7
14	-35	179	-8
15	483	671	-44
16	270	261	1
17	-37	334	-26

3 6 1

0	203	245	-8
1	1198	1301	-59
2	1343	1311	17
3	511	546	-14
4	1205	1265	-31
5	613	601	5
6	427	506	-26
7	727	714	5
8	156	135	2
9	814	883	-28
10	461	530	-18
11	466	476	-2
12	159	169	-1
13	314	253	8
14	412	461	-11
15	230	304	-9
16	293	363	-9
17	327	375	-6

3 7 1

0	1313	1441	-70
1	280	187	19
2	1248	1400	-84
3	380	402	-6
4	292	328	-9
5	52	41	0
6	778	686	39
7	381	408	-7
8	880	887	-2
9	181	197	-2
10	628	698	-21
11	-77	67	-3
12	305	446	-30
13	-260	65	-18
14	-57	133	-6
15	-264	158	-21
16	156	335	-18

3 8 1

0	626	688	-27
1	1335	1430	-47
2	199	196	0
3	313	358	-12
4	322	310	3
5	417	410	1
6	482	468	4
7	963	942	8
8	542	554	-3
9	713	723	-3
10	-98	13	-3
11	640	658	-5
12	347	371	-4
13	292	205	11
14	-169	103	-9
15	142	120	1
16	-223	34	-10

3 9 1

0	1320	1424	-51
1	1308	1351	-19
2	913	925	-5
3	627	686	-24
4	150	121	3
5	577	651	-26
6	600	693	-32
7	604	622	-6
8	659	759	-33
9	203	147	6
10	531	550	-5
11	299	300	0

12	478	534	-12
13	409	487	-14
14	278	140	13
15	158	253	-8

3 10 1

0	872	911	-16
1	974	982	-3
2	1043	1115	-33
3	321	317	0
4	837	906	-28
5	296	255	8
6	673	721	-16
7	500	421	19
8	313	344	-5
9	422	442	-4
10	327	294	5
11	239	379	-20
12	489	568	-17
13	402	265	19
14	454	455	0
15	167	38	5

3 11 1

0	445	452	-2
1	528	607	-24
2	609	656	-16
3	791	751	14
4	-243	77	-21
5	588	618	-9
6	102	241	-13
7	541	479	17
8	255	166	11
9	-174	20	-8
10	-131	10	-4
11	277	458	-31
12	-221	106	-13
13	378	515	-22
14	-285	63	-17

3 12 1

0	142	254	-14
1	107	166	-5
2	464	380	20
3	-78	2	-2
4	464	453	2
5	139	4	6
6	376	388	-2
7	-158	117	-10
8	-33	145	-6
9	272	300	-4
10	-50	88	-2
11	-102	202	-11
12	371	402	-4
13	-166	12	-6

3 13 1

0	611	582	8
1	171	238	-7
2	287	275	2
3	339	257	15
4	106	0	3
5	219	295	-10
6	270	312	-6
7	150	309	-20
8	549	533	3
9	-253	65	-16
10	353	434	-13
11	163	165	0
12	-277	157	-20

3 14 1

0	-108	161	-10
1	634	588	11
2	156	225	-7
3	-73	81	-3
4	300	235	9
5	190	229	-4
6	198	221	-2
7	462	504	-8
8	100	114	0
9	558	542	3
10	-269	25	-16
11	327	301	3

3 15 1

0	619	651	-7
1	-47	73	-2
2	313	260	7
3	89	44	1
4	-208	51	-12
5	-182	29	-9
6	-198	279	-26
7	-175	56	-7
8	335	403	-12
9	-322	18	-22

3 16 1

0	63	60	0
1	306	303	0
2	238	148	9
3	-132	150	-10
4	141	198	-4
5	81	45	1
6	189	52	8
7	153	225	-6

3 17 1

0	228	204	2
1	329	239	12
2	182	147	2
3	413	309	18
4	149	65	4
5	-183	227	-13

4 0 1

0	1036	1012	15
2	384	275	37
4	48	86	-2
6	1680	1643	18
8	2255	2287	-13
10	1473	1536	-29
12	316	364	-11
14	120	11	5
16	261	243	2
18	295	337	-5

4 1 1

0	902	892	6
1	313	260	17
2	1842	1791	26
3	1122	1001	72
4	794	743	28
5	1179	1202	-13
6	758	755	1
7	1266	1283	-9
	-117	67	-7
9	1527	1566	-18
10	-146	39	-9
11	689	771	-33
12	190	311	-20
13	153	122	2
14	-198	240	-28
15	-146	78	-9
16	50	96	-1
17	182	323	-15
18	-122	22	-3

4 2 1

0	710	705	2
1	993	995	-1
2	1061	1046	9
3	2059	2034	11
4	539	475	27
5	1279	1232	25
6	469	448	8
7	860	873	-6
8	909	917	-3
9	75	100	-1
10	559	616	-21
11	518	564	-15
12	-184	141	-17
13	170	352	-33
14	-77	29	-2
15	228	294	-9
16	276	183	11
17	-22	81	-1
18	154	278	-8

4 3 1

0	890	824	40
1	576	552	12
2	2263	2081	78
3	795	747	26
4	2151	2045	46
5	207	93	17
6	959	935	12
7	130	203	-12
8	364	335	8
9	372	384	-3
10	466	540	-24
11	36	110	-4
12	361	435	-18
13	120	124	0
14	469	512	-10
15	-109	53	-4
16	127	264	-15
17	112	97	0

4 4 1

0	343	239	30
1	1454	1503	-28
2	555	511	20
3	2898	3015	-58
4	653	549	47
5	1370	1446	-40
6	172	107	9
7	512	513	0
8	-200	18	-19
9	201	250	-9
10	185	179	0
11	541	547	-1
12	468	451	4
13	565	667	-29
14	-206	163	-20
15	389	498	-22
16	126	101	1
17	-244	247	-26

4 5 1

0	957	957	0
1	407	463	-23
2	1287	1245	23
3	121	218	-18
4	1739	1673	31
5	292	360	-19
6	1165	1158	3
7	455	514	-20
8	-57	28	-2
9	652	724	-28
10	579	599	-6
11	573	593	-6
12	472	533	-15
13	158	180	-1
14	550	634	-21
15	177	225	-5
16	352	369	-2
17	251	225	2

4 6 1

0	1514	1533	-9
1	805	885	-44
2	167	159	1
3	814	809	2
4	131	76	5
5	1084	1166	-42
6	618	591	10
7	367	387	-5
8	789	890	-42
9	309	233	13
10	696	795	-34
11	259	410	-26
12	251	387	-25
13	318	348	-5
14	127	113	0
15	181	359	-22
16	49	308	-19
17	238	169	4

4 7 1

0	429	434	-1
1	1319	1332	-7
2	714	744	-14
3	188	35	16
4	320	397	-21
5	482	480	0
6	-137	143	-14
7	927	959	-13
8	154	113	3
9	753	783	-11
10	-178	98	-11
11	624	622	0
12	-171	60	-10
13	-65	40	-1
14	-146	108	-8
15	281	250	3
16	-158	73	-7

4 8 1

0	1187	1220	-17
1	439	475	-12
2	850	923	-36
3	61	161	-9
4	363	390	-7
5	364	368	-1
6	747	729	7
7	255	270	-2
8	926	1029	-41
9	-56	65	-2
10	323	511	-38
11	242	122	11
12	332	380	-9
13	-262	173	-23
14	-200	102	-12
15	114	88	1
16	245	209	3

4 9 1

0	1007	1044	-17
1	985	1001	-7
2	671	696	-9
3	145	117	3
4	886	927	-17
5	424	421	0

6	404	430	-6
7	655	643	3
8	113	188	-7
9	564	712	-44
10	-201	120	-14
11	271	329	-9
12	244	344	-15
13	-181	165	-13
14	207	288	-9
15	-242	87	-13

4 10 1

0	782	811	-12
1	1069	1052	7
2	468	446	6
3	975	982	-2
4	184	64	13
5	832	896	-25
6	266	356	-17
7	410	438	-7
8	207	234	-3
9	-221	120	-18
10	335	289	7
11	379	381	0
12	291	216	9
13	466	446	4
14	156	10	5

4 11 1

0	562	611	-15
1	434	399	9
2	751	780	-10
3	-48	242	-19
4	727	730	0
5	-97	170	-11
6	540	571	-9
7	95	141	-3
8	-121	77	-6
9	198	16	11
10	123	249	-12
11	-124	78	-5
12	317	487	-26
13	160	5	5

4 12 1

0	-127	183	-15
1	391	410	-4
2	51	31	0
3	471	456	3
4	208	138	7
5	352	410	-12
6	135	266	-15
7	241	302	-9
8	212	202	1
9	98	68	1
10	184	170	1
11	292	302	-1
12	-113	53	-3
13	-25	288	-18

4 13 1

0	267	259	1
1	475	451	5
2	343	257	15
3	47	45	0
4	393	393	0
5	310	254	10
6	287	331	-6
7	560	491	16
8	166	112	3
9	394	401	-1
10	204	143	5
11	274	200	7

4 14 1

0	824	762	18
1	275	124	18
2	182	302	-15
3	219	264	-5
4	212	209	0
5	137	271	-16
6	431	453	-4
7	84	180	-7
8	503	500	0
9	94	49	1
10	162	301	-13

4 15 1

0	-256	32	-15
1	482	452	7
2	160	48	6
3	90	87	0
4	181	13	9
5	173	267	-10
6	-119	123	-8
7	448	373	14
8	208	5	9
9	349	293	7

4 16 1

0	451	413	7
1	304	184	13
2	129	244	-11
3	245	237	1
4	-195	9	-8
5	-194	78	-10
6	-168	166	-14
7	-55	15	0

4 17 1

0	-213	223	-23
1	424	194	35
2	455	404	8
3	-78	110	-3
4	153	262	-6

5 0 1

1	867	872	-3
3	48	119	-6
5	1276	1247	15
7	2032	2104	-32
9	1843	1945	-44
11	578	705	-46
13	-86	47	-3
15	71	137	-3
17	241	343	-15

5 1 1

0	706	720	-8
1	805	776	17
2	193	184	2
3	269	208	14
4	1204	1178	14
5	938	881	31
6	1029	1068	-21
7	306	242	15
8	1608	1627	-9
9	-55	142	-9
10	1021	1133	-51
11	37	270	-27
12	192	200	-1
13	180	190	-1
14	-152	54	-8
15	152	211	-6
16	-134	244	-21
17	116	62	2

5 2 1

0	495	416	35
1	498	447	22
2	1141	1071	41
3	1242	1243	0
4	1355	1375	-11
5	756	811	-29
6	920	982	-34
7	788	793	-2
8	497	456	14
9	833	884	-22
10	427	419	2
11	233	310	-17
12	330	395	-18
13	-239	32	-18
14	189	383	-32
15	-144	43	-6
16	-59	130	-5
17	41	218	-11

5 3 1

0	148	41	11
1	1567	1595	-15
2	781	802	-11
3	1848	1804	21
4	982	997	-8
5	1291	1280	5
6	95	140	-5
7	478	433	16
8	364	379	-4
9	376	368	2
10	170	195	-3
11	502	578	-24
12	266	170	13
13	508	563	-14
14	154	155	0
15	310	351	-6
16	-142	68	-6
17	253	92	13

5 4 1

0	1510	1498	6
1	241	252	-2
2	1983	1943	18
3	739	711	14
4	1826	1752	34
5	334	319	3
6	680	664	7
7	368	332	10
8	246	162	15
9	272	216	12
10	628	703	-27
11	300	304	0
12	675	751	-24
13	-191	76	-11
14	508	540	-7
15	-107	85	-4
16	155	291	-15
17	131	75	2

5 5 1

0	590	661	-36
1	1529	1574	-24
2	257	184	15
3	1647	1767	-61
4	364	388	-7
5	1019	1077	-30
6	619	601	7
7	489	474	4
8	724	706	7
9	344	307	8
10	664	675	-3
11	691	723	-10
12	285	364	-13
13	563	675	-29
14	-131	107	-8
15	374	387	-2
16	326	169	18

5 6 1

0	124	246	-24
1	960	928	16
2	1051	1001	25
3	444	423	7
4	856	836	9
5	697	715	-7
6	833	849	-7
7	982	969	5
8	262	193	12
9	690	766	-27
10	272	324	-10
11	478	525	-12
12	380	416	-6
13	-108	142	-8
14	-157	337	-33
15	176	240	-6
16	-165	125	-9

5 7 1

0	1174	1273	-53
1	374	317	18
2	629	616	5
3	412	413	0
4	187	263	-17
5	589	623	-13
6	741	758	-6
7	361	339	6
8	916	943	-11
9	-150	6	-6
10	556	570	-3
11	214	185	3
12	352	293	12
13	155	12	6
14	282	158	15
15	-158	13	-6
16	-130	222	-15

5 8 1

0	532	591	-25
1	745	798	-25
2	-114	127	-13
3	85	82	0
4	173	192	-2
5	498	558	-19
6	117	74	3
7	824	829	-2
8	135	38	5
9	661	707	-14
10	-205	43	-12
11	291	406	-20
12	-62	145	-7
13	-87	31	-2
14	-225	117	-16
15	-135	199	-13

5 9 1

0	783	803	-8
1	866	933	-31
2	266	283	-4
3	810	881	-31
4	-92	195	-16
5	470	512	-11
6	601	603	0
7	247	60	18
8	545	619	-21
9	202	159	4
10	381	365	3

11	362	203	25
12	250	209	5
13	203	257	-5
14	253	111	12

5 10 1

0	782	816	-13
1	423	389	9
2	1015	997	7
3	-201	74	-16
4	961	1059	-39
5	-258	44	-22
6	398	393	1
7	267	275	-1
8	-179	71	-10
9	85	235	-14
10	-92	244	-17
11	311	182	16
12	342	409	-10
13	99	19	2
14	-52	274	-15

5 11 1

0	-85	72	-4
1	756	765	-3
2	188	149	4
3	866	876	-3
4	-101	174	-14
5	707	727	-6
6	-102	79	-4
7	-103	260	-20
8	-144	8	-5
9	205	244	-5
10	-59	71	-2
11	362	335	4
12	-273	4	-15
13	163	316	-16

5 12 1

0	458	505	-12
1	193	155	4
2	517	581	-17
3	187	168	2
4	551	590	-11
5	238	315	-11
6	525	477	11
7	168	260	-10
8	-178	1	-8
9	188	142	3
10	100	205	-7
11	-78	62	-2
12	119	254	-11

5 13 1

0	531	503	7
1	174	259	-10
2	130	164	-2
3	439	400	10
4	258	305	-7
5	447	451	0
6	410	438	-6
7	189	224	-3
8	209	365	-22
9	61	67	0
10	166	243	-8
11	-106	173	-8

5 14 1

0	-30	104	-3
1	384	382	0
2	124	97	1
3	39	42	0
4	274	288	-1
5	439	441	0
6	159	298	-14
7	418	463	-8
8	-120	16	-3
9	404	324	13
10	227	100	6

5 15 1

0	488	500	-2
1	-185	112	-12
2	96	229	-10
3	-134	5	-5
4	143	212	-6
5	177	113	4
6	455	339	20
7	97	46	2
8	241	302	-7

5 16 1

0	207	220	-1
1	313	337	-4
2	242	279	-4
3	267	68	17
4	219	132	7
5	-179	113	-10
6	-211	41	-11

5 17 1

0	222	261	-4
1	397	425	-4
2	193	143	3

6 0 1

0	176	81	14
2	126	145	-3
4	808	745	33
6	2047	1991	24
8	1592	1675	-39
10	735	814	-31
12	108	33	3
14	-47	100	-3
16	194	343	-22

6 1 1

0	715	699	9
1	195	57	21
2	656	657	0
3	384	471	-35
4	588	643	-26
5	1328	1307	11
6	-27	93	-4
7	1178	1187	-4
8	157	134	3
9	1177	1248	-33
10	200	235	-6
11	329	306	5
12	237	265	-4
13	194	50	11
14	288	250	5
15	-46	186	-10
16	-226	127	-15
17	303	303	0

6 2 1

0	1122	1215	-57
1	1045	1065	-12
2	800	821	-11
3	1402	1337	34
4	449	347	36
5	457	464	-2
6	552	536	6
7	273	269	0
8	943	1033	-43
9	181	266	-16
10	412	488	-21
11	450	462	-3
12	90	18	2
13	428	542	-30
14	83	73	0
15	185	251	-7
16	110	193	-6
17	-9	67	-1

6 3 1

0	1005	980	14
1	336	102	56
2	1399	1374	13
3	884	815	36
4	1579	1602	-11
5	310	342	-9
6	670	694	-11
7	173	226	-9
8	255	287	-7
9	220	309	-20
10	579	657	-26
11	-186	132	-16
12	600	707	-32
13	151	16	5
14	442	466	-5
15	20	28	0
16	186	164	2

6 4 1

0	496	508	-5
1	2059	2052	3
2	333	225	28
3	1695	1662	16
4	-56	101	-6
5	845	826	9
6	497	465	11
7	98	39	3
8	210	242	-5
9	518	551	-11
10	-77	106	-5
11	850	937	-31
12	214	114	8
13	497	633	-33
14	306	19	24
15	337	352	-2
16	-235	64	-13

6 5 1

0	1017	1035	-9
1	44	53	0
2	1548	1489	29
3	348	402	-17
4	871	810	29
5	435	435	0
6	621	633	-5
7	660	625	13
8	-132	34	-7
9	526	525	0
10	598	646	-14
11	352	460	-24
12	648	619	8
13	-105	9	-2
14	328	494	-30
15	283	156	15
16	-133	157	-9

6 6 1

0	1139	1178	-20
1	251	295	-10
2	213	138	14
3	626	645	-8
4	691	718	-11
5	643	724	-34
6	843	882	-17
7	463	520	-17
8	754	803	-18
9	177	37	9
10	339	381	-9
11	304	381	-13
12	349	322	4
13	328	342	-2
14	303	197	13
15	143	135	0

6 7 1

0	137	58	7
1	573	614	-17
2	286	230	14
3	240	315	-18
4	161	58	9
5	749	803	-23
6	594	586	2
7	764	797	-12
8	285	294	-1
9	716	739	-7
10	-72	8	-1
11	287	387	-20
12	-69	111	-4
13	-94	44	-3
14	-106	7	-2
15	-77	211	-11

6 8 1

0	945	989	-21
1	432	480	-17
2	-60	114	-7
3	198	192	1
4	397	354	11
5	-82	73	-4
6	776	842	-25
7	337	303	6
8	577	668	-28
9	168	152	1
10	579	581	0
11	118	134	-1
12	-189	162	-17
13	-124	130	-7
14	135	192	-4
15	137	139	0

6 9 1

0	574	683	-44
1	338	409	-19
2	759	809	-21
3	155	123	3
4	448	482	-9
5	459	456	0
6	-105	105	-8
7	679	711	-10
8	296	354	-12
9	377	443	-15
10	307	237	11
11	168	272	-12
12	160	251	-9
13	-46	52	-1
14	81	196	-6

6 10 1

0	309	351	-11
1	730	762	-13
2	177	80	9
3	988	1089	-41
4	226	142	11
5	301	356	-9
6	-203	168	-19
7	-57	98	-3

8	248	281	-4
9	301	363	-10
10	122	225	-8
11	269	302	-4
12	-131	48	-4
13	368	297	10

6 11 1

0	640	680	-13
1	137	27	7
2	882	855	10
3	-135	15	-6
4	804	832	-9
5	207	210	-10
6	466	373	21
7	35	47	0
8	-100	63	-3
9	-105	41	-3
10	240	265	-3
11	-121	47	-4
12	306	300	0

6 12 1

0	229	286	-9
1	638	562	22
2	-178	30	-10
3	629	697	-21
4	199	267	-8
5	621	643	-6
6	249	350	-16
7	199	191	0
8	184	193	0
9	-312	118	-26
10	-136	86	-6
11	165	200	-3

6 13 1

0	263	207	7
1	93	199	-8
2	358	414	-12
3	-111	143	-9
4	434	492	-14
5	404	465	-11
6	328	355	-4
7	285	410	-19
8	293	39	21
9	234	250	-1
10	223	97	8

6 14 1

0	450	332	24
1	109	30	3
2	-160	55	-8
3	203	228	-2
4	390	361	5
5	291	310	-2
6	410	442	-6
7	-278	128	-20
8	456	366	15
9	173	47	7

6 15 1

0	164	94	4
1	116	276	-15
2	-226	67	-14
3	172	112	4
4	53	92	-1
5	361	296	10
6	-222	57	-11
7	327	330	0

6 16 1

0	442	324	21
1	284	285	0
2	74	126	-2
3	-241	182	-21
4	-184	67	-8
5	126	94	1

7 0 1

1	291	159	31
3	-78	70	-5
5	2116	2181	-27
7	1097	1105	-3
9	847	859	-4
11	-84	149	-10
13	142	120	1
15	347	394	-10

7 1 1

0	834	894	-35
1	662	647	8
2	275	333	-18
3	390	297	30
4	995	1008	-6
5	302	192	28
6	1168	1159	4
7	-113	80	-8
8	1068	1138	-31
9	153	204	-6
10	452	467	-4
11	260	267	-1
12	73	47	0
13	56	265	-18
14	93	148	-3
15	-74	166	-8
16	236	329	-12

7 2 1

0	1133	1084	27
1	422	416	2
2	936	874	33
3	237	202	9
4	388	415	-9
5	420	389	10
6	167	241	-14
7	776	789	-6
8	-129	124	-12
9	482	595	-35
10	419	450	-8
11	-281	186	-34
12	451	522	-19
13	-98	6	-3
14	375	320	10
15	-136	119	-8
16	-227	141	-18

7 3 1

0	253	102	31
1	1153	1125	15
2	326	353	-8
3	949	904	23
4	162	132	4
5	595	523	27
6	-190	35	-18
7	-54	60	-2
8	-123	178	-17
9	521	530	-2
10	235	235	0
11	691	757	-21
12	-223	10	-13
13	470	557	-19
14	20	58	0
15	-177	242	-24
16	169	91	4

7 4 1

0	1401	1444	-23
1	371	425	-19
2	1483	1506	-11
3	193	136	10
4	883	931	-24
5	243	187	10
6	153	118	4
7	347	278	16
8	241	291	-11
9	166	8	9
10	662	757	-31
11	208	107	10
12	574	716	-37
13	180	26	8
14	277	454	-31
15	-193	86	-11
16	204	104	5

7 5 1

0	-56	197	-22
1	1094	1169	-40
2	123	21	7
3	726	688	17
4	201	141	10
5	426	466	-14
6	537	532	1
7	100	190	-9
8	412	439	-7
9	416	336	20
10	266	293	-4
11	568	638	-19
12	90	44	1
13	326	536	-42
14	-183	182	-15
15	-171	217	-18

7 6 1

0	1010	1019	-4
1	282	207	16
2	528	480	17
3	395	390	1
4	289	249	9
5	561	599	-14
6	499	573	-24
7	767	723	16
8	208	284	-14
9	398	492	-25
10	153	252	-12
11	-57	153	-7
12	261	374	-17
13	-103	164	-10
14	121	224	-8
15	84	175	-6

7 7 1

0	1162	1204	-21
1	133	82	4
2	-12	12	0
3	202	98	14
4	645	631	5
5	387	423	-10
6	715	741	-9
7	284	346	-11
8	679	717	-12
9	287	252	6
10	459	416	9
11	277	117	18
12	-156	48	-7
13	-164	68	-7
14	91	234	-12

7 8 1

0	248	233	3
1	341	328	4
2	336	427	-26
3	372	445	-20
4	86	265	-26
5	427	464	-10
6	346	422	-17
7	703	791	-28
8	352	335	3
9	554	609	-14
10	99	176	-5
11	220	315	-13
12	263	123	14
13	201	120	7
14	-79	109	-4

7 9 1

0	347	337	2
1	499	502	-1
2	382	290	22
3	653	694	-14
4	297	362	-12
5	227	161	8
6	471	455	4
7	310	309	0
8	475	567	-24
9	376	415	-7
10	317	422	-20
11	237	273	-5
12	-16	80	-1
13	159	216	-4

7 10 1

0	535	633	-33
1	75	63	0
2	775	760	5
3	349	264	18
4	536	582	-13
5	296	239	9
6	241	178	8
7	269	241	4
8	227	286	-8
9	225	275	-6
10	277	381	-18
11	-88	170	-8
12	317	299	2

7 11 1

0	-117	138	-10
1	649	631	5
2	311	277	6
3	807	918	-39
4	260	113	18
5	522	520	0
6	-221	59	-15
7	169	68	8
8	226	11	14
9	236	230	0
10	-78	88	-3
11	-129	270	-18
12	-75	34	-1

7 12 1

0	397	395	0
1	44	161	-7
2	713	706	2
3	-115	84	-5
4	719	696	6
5	204	348	-23
6	253	345	-14
7	341	263	12
8	-133	6	-4
9	29	63	0
10	210	160	4

11	-307	2	-15

7 13 1

0	205	204	0
1	373	371	0
2	-160	100	-9
3	474	523	-11
4	398	402	0
5	319	354	-6
6	395	422	-5
7	-91	178	-9
8	301	277	3
9	-183	68	-8

7 14 1

0	-138	54	-5
1	163	83	5
2	-80	208	-14
3	222	282	-7
4	-192	226	-21
5	428	436	-1
6	256	167	9
7	484	402	14
8	129	5	3

7 15 1

0	299	228	9
1	51	67	0
2	-263	9	-17
3	-116	15	-3
4	-51	250	-14
5	-190	36	-8
6	382	359	3

7 16 1

0	409	237	26
1	257	182	7
2	-180	232	-19
3	201	7	9

8 0 1

0	508	522	-6
2	560	602	-19
4	1254	1243	5
6	812	809	1
8	654	761	-41
10	208	222	-2
12	84	149	-5
14	343	295	7

8 1 1

0	144	148	0
1	607	573	16
2	105	166	-8
3	110	4	6
4	531	559	-15
5	1117	1116	0
6	126	87	3
7	740	776	-15
8	162	132	3
9	369	450	-20
10	138	188	-5
11	77	74	0
12	211	230	-2
13	218	173	5
14	242	178	7
15	68	309	-23

8 2 1

0	336	307	8
1	1083	1047	19
2	166	289	-29
3	708	713	-2
4	417	358	19
5	367	370	-1
6	710	678	13
7	-128	15	-7
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9	244	207	6
10	396	264	28
11	376	457	-18
12	-236	75	-17
13	298	389	-14
14	152	98	3
15	-177	171	-13

8 3 1

0	1506	1516	-5
1	74	65	0
2	1104	1097	3
3	-165	21	-12
4	697	659	16
5	440	422	5
6	292	310	-4
7	-29	150	-9
8	233	265	-5
9	174	232	-9
10	594	618	-7
11	37	89	-1
12	540	540	0
13	-199	108	-15
14	217	338	-17
15	-182	93	-10

8 4 1

0	-171	50	-14
1	1088	1047	20
2	-73	47	-3
3	842	799	20
4	-131	101	-11
5	400	393	2
6	35	16	0
7	86	74	0
8	31	50	0
9	431	502	-18
10	70	25	1
11	587	723	-39
12	126	81	2
13	404	473	-15
14	278	108	16
15	-227	153	-16

8 5 1

0	1277	1247	14
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2	739	764	-10
3	216	222	-1
4	422	452	-10
5	284	201	16
6	104	276	-25
7	256	236	3
8	242	207	5
9	318	292	4
10	399	449	-11
11	154	71	5
12	493	568	-17
13	219	201	1
14	-135	254	-18
15	134	113	0

8 6 1

0	659	628	12
1	558	592	-14
2	49	179	-14
3	207	225	-3
4	450	427	7
5	208	299	-16
6	660	698	-14
7	71	208	-12
8	493	525	-8
9	-27	87	-2
10	-112	116	-7
11	230	335	-16
12	140	130	0
13	180	245	-6
14	-117	230	-15

8 7 1

0	156	210	-9
1	381	350	8
2	-105	36	-5
3	305	329	-6
4	-251	77	-25
5	579	595	-5
6	33	127	-5
7	683	775	-29
8	268	296	-4
9	512	476	9
10	-51	63	-1
11	111	108	0
12	-268	63	-18
13	102	188	-6
14	-178	43	-8

8 8 1

0	427	494	-20
1	154	256	-19
2	257	142	20
3	410	370	10
4	277	380	-21
5	175	142	3
6	612	603	2
7	-122	130	-8
8	623	696	-20
9	256	291	-4
10	375	385	-2
11	-68	142	-6
12	219	19	12
13	-179	77	-9

8 9 1

0	393	421	-8
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2	434	503	-19
3	484	469	4
4	423	439	-4
5	75	219	-12
6	220	152	8
7	546	577	-8
8	307	347	-7
9	405	465	-11
10	278	356	-11
11	118	216	-8
12	374	213	21

8 10 1

0	128	98	2
1	542	602	-19
2	336	327	1
3	553	572	-5
4	226	221	0
5	226	198	4
6	404	262	27
7	222	173	5
8	161	306	-18
9	416	372	8
10	-90	231	-16
11	119	291	-17
12	-141	10	-4

8 11 1

0	534	530	1
1	292	295	0
2	719	731	-3
3	-119	62	-5
4	482	544	-15
5	51	41	0
6	-118	144	-10
7	-52	5	0
8	341	176	25
9	-29	118	-4
10	164	254	-8
11	-64	55	-1

8 12 1

0	-136	54	-6
1	519	570	-12
2	-84	42	-2
3	663	717	-16
4	160	235	-10
5	337	389	-10
6	139	260	-13
7	226	65	13
8	-130	106	-7
9	195	153	3
10	142	26	4

8 13 1

0	241	256	-2
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2	451	510	-13
3	244	326	-11
4	265	347	-13
5	360	427	-11
6	124	207	-6
7	326	292	4
8	344	48	29

8 14 1

0	192	132	6
1	-172	168	-15
2	-82	182	-12
3	-152	190	-15
4	393	420	-5
5	296	137	19
6	467	386	13
7	-12	33	0

8 15 1

0	-65	87	-3
1	154	75	4
2	-377	15	-32
3	185	185	0
4	152	1	5

8 16 1

0	284	206	8

9 0 1

1	65	7	2
3	410	373	11
5	909	865	19
7	514	587	-24
9	101	240	-16
11	-169	10	-8
13	221	225	0
15	355	341	2

9 1 1

0	937	954	-8
1	257	164	18
2	118	126	-1
3	540	479	23
4	1111	1066	21
5	-78	115	-7
6	728	698	12
7	124	87	3
8	266	351	-17
9	-121	108	-10
10	-62	174	-10
11	163	210	-6
12	36	28	0
13	304	151	20
14	269	242	3
15	-192	47	-9

9 2 1

0	1255	1230	12
1	344	335	2
2	993	949	21
3	285	218	13
4	320	309	2
5	743	762	-7
6	-53	92	-4
7	326	335	-2
8	72	72	0
9	204	284	-13
10	296	309	-2
11	246	183	8
12	370	348	4
13	-222	20	-12
14	316	194	15

9 3 1

0	354	434	-23
1	1410	1372	18
2	195	60	15
3	949	927	10
4	471	533	-20
5	418	475	-17
6	160	161	0
7	44	137	-6
8	-102	142	-11
9	257	367	-20
10	46	202	-11
11	502	481	5
12	217	103	10
13	311	344	-5
14	177	48	8

9 4 1

0	1559	1572	-6
1	54	254	-25
2	1140	1185	-21
3	196	193	0
4	625	618	2
5	270	214	12
6	-173	11	-11
7	-96	150	-11
8	263	240	4
9	155	90	5
10	441	528	-20
11	137	156	-1
12	418	462	-9
13	-173	114	-10
14	350	221	18

9 5 1

0	155	16	10
1	856	808	20
2	181	169	2
3	587	580	2
4	121	166	-6
5	275	282	-1
6	274	250	5
7	251	152	12
8	349	299	10
9	352	306	9
10	241	29	18
11	390	391	0
12	216	172	4
13	253	311	-7
14	149	138	0

9 6 1

0	428	460	-9
1	-96	168	-14
2	365	413	-13
3	210	174	5
4	116	177	-7
5	420	420	0
6	158	123	3
7	625	691	-20
8	264	165	14
9	230	219	1
10	-235	159	-21
11	-23	68	-1
12	-147	241	-19
13	128	222	-7

9 7 1

0	485	496	-3
1	173	271	-17
2	-140	103	-11
3	-159	125	-15
4	500	483	5
5	-157	38	-8
6	605	620	-4
7	-197	25	-10
8	517	560	-10
9	-88	77	-3
10	-213	182	-20
11	-286	103	-24
12	53	117	-2
13	-251	55	-15

9 8 1

0	114	161	-4
1	81	36	2
2	334	300	8
3	346	286	14
4	105	109	0
5	533	610	-23
6	141	43	6
7	521	494	6
8	185	133	5
9	289	410	-19
10	16	142	-5
11	-29	79	-1
12	-174	91	-9

9 9 1

0	-164	35	-11
1	364	375	-2
2	346	322	5
3	223	340	-20
4	239	312	-11
5	85	66	0
6	457	484	-7
7	-89	129	-6
8	287	403	-20
9	312	350	-6
10	-145	204	-14
11	119	223	-9
12	-173	9	-6

9 10 1

0	459	454	1
1	261	135	16
2	519	565	-12
3	279	365	-17
4	-76	239	-18
5	213	224	-1
6	-93	31	-2
7	325	308	3
8	283	326	-6
9	289	213	10
10	337	278	9
11	-156	64	-6

9 11 1

0	-96	97	-5
1	713	666	14
2	68	93	-1
3	552	546	1
4	127	20	4
5	-131	149	-11
6	-71	48	-2
7	-194	54	-11
8	119	103	0
9	252	252	0
10	73	65	0

9 12 1

0	473	425	11
1	178	34	8
2	588	628	-10
3	72	182	-9
4	332	391	-10
5	162	230	-6
6	-62	132	-5
7	-152	114	-10
8	105	128	-1
9	-237	12	-13

9 13 1

0	-151	34	-8
1	429	395	7
2	291	207	12
3	403	376	6
4	338	402	-11
5	-189	167	-16
6	341	299	6
7	-383	30	-31

9 14 1

0	89	99	0
1	198	62	10
2	158	180	-2
3	328	319	1
4	247	79	13
5	360	339	3

9 15 1

0	191	128	5
1	-165	35	-7
2	-239	96	-16

10 0 1

0	-167	67	-14
2	771	718	23
4	1104	1132	-12
6	520	531	-3
8	180	191	-1
10	-136	128	-12
12	-248	95	-19
14	316	320	0

10 1 1

0	551	529	8
1	297	181	28
2	506	476	10
3	946	889	24
4	209	209	0
5	753	806	-21
6	-35	131	-7
7	299	288	2
8	34	60	0
9	131	244	-15
10	26	158	-7
11	193	91	8
12	-82	131	-6
13	-262	179	-24
14	84	74	0

10 2 1

0	696	703	-3
1	1151	1066	39
2	404	403	0
3	705	693	4
4	678	674	1
5	299	277	5
6	263	301	-7
7	-116	25	-5
8	322	248	14
9	185	229	-5
10	71	275	-22
11	201	309	-14
12	-32	60	-1
13	-35	183	-8
14	41	161	-5

10 3 1

0	1934	1928	2
1	281	244	7
2	1092	1046	20
3	341	287	11
4	561	544	5
5	311	272	8
6	27	1	0
7	-171	46	-12
8	-253	230	-41
9	22	126	-4
10	419	357	13
11	155	204	-5
12	324	342	-2
13	34	11	0

10 4 1

0	250	312	-12
1	1184	1146	17
2	-129	12	-7
3	695	734	-14
4	-45	129	-6
5	-94	123	-9
6	-60	197	-15
7	-156	130	-16
8	-123	129	-10
9	227	321	-16
10	52	121	-3
11	331	383	-8
12	137	98	2
13	108	258	-14

10 5 1

0	782	815	-13
1	92	7	4
2	629	596	12
3	144	182	-4
4	207	182	4
5	330	272	12

6	43	83	-1
7	343	409	-14
8	240	185	6
9	-216	82	-15
10	157	288	-16
11	115	87	1
12	174	275	-10
13	-177	122	-10

10 6 1

0	-97	23	-3
1	519	487	10
2	118	146	-3
3	161	203	-5
4	363	334	7
5	-134	1	-5
6	603	649	-13
7	213	264	-6
8	463	379	18
9	193	87	8
10	-79	34	-2
11	-22	204	-10
12	84	144	-3

10 7 1

0	257	179	12
1	-101	66	-5
2	112	224	-15
3	438	446	-2
4	78	37	1
5	550	592	-12
6	-207	116	-15
7	516	548	-7
8	-167	105	-10
9	281	262	2
10	-191	48	-10
11	125	45	3
12	-286	70	-19

10 8 1

0	140	56	6
1	178	62	11
2	276	304	-5
3	78	206	-11
4	586	513	21
5	-97	30	-3
6	461	489	-6
7	-178	45	-9
8	405	380	4
9	-272	116	-20
10	200	96	8
11	-102	69	-4

10 9 1

0	272	277	0
1	176	188	-1
2	274	359	-17
3	-102	247	-22
4	46	105	-2
5	311	362	-8
6	75	12	1
7	410	333	14
8	188	256	-7
9	55	199	-8
10	212	207	0
11	78	48	0

10 10 1

0	-62	24	-1
1	579	631	-15
2	-183	66	-12
3	383	355	5
4	-103	140	-8
5	-150	17	-6
6	171	230	-6
7	152	195	-3
8	-127	178	-13
9	305	281	3
10	-192	85	-11

10 11 1

0	510	529	-4
1	304	98	28
2	549	592	-11
3	-91	38	-2
4	306	257	8
5	152	12	6
6	-129	7	-5
7	151	57	6
8	329	224	13
9	-102	35	-2

10 12 1

0	-205	95	-14
1	483	475	1
2	181	167	1
3	328	404	-15
4	238	236	0
5	159	112	3
6	-172	105	-10
7	-115	39	-3

10 13 1

0	280	244	5
1	-178	116	-12
2	393	319	12
3	201	291	-11
4	194	115	6
5	278	235	5
6	193	12	8

10 14 1

0	140	53	4
1	-79	143	-7
2	162	171	0
3	-196	64	-10

11 0 1

1	687	703	-6
3	936	927	3
5	772	779	-2
7	364	362	0
9	281	192	13
11	130	55	4
13	283	208	9

11 1 1

0	-183	42	-14
1	506	465	13
2	919	867	21
3	376	304	16
4	758	799	-14
5	187	196	-1
6	447	374	18
7	230	38	17
8	204	303	-18
9	-166	130	-13
10	67	147	-4
11	142	147	0
12	-167	106	-9
13	-40	82	-1

11 2 1

0	1290	1237	23
1	423	308	28
2	883	785	39
3	569	474	29
4	532	422	30
5	439	342	24
6	-113	6	-5
7	85	245	-16
8	228	242	-2
9	121	217	-9
10	326	261	12
11	139	124	1
12	-116	233	-16
13	-142	110	-7

11 3 1

0	174	164	1
1	1064	1027	15
2	137	42	6
3	723	665	21
4	141	200	-7
5	98	111	0
6	84	22	2
7	258	258	0
8	104	115	0
9	381	344	8
10	-135	144	-10
11	290	313	-3
12	190	35	8

11 4 1

0	851	835	7
1	-69	19	-2
2	670	615	18
3	150	1	8
4	289	208	14
5	-103	178	-16
6	94	129	-2
7	194	153	4
8	220	304	-11
9	-207	51	-12
10	185	346	-22
11	196	78	9
12	296	212	10

11 5 1

0	305	204	21
1	629	587	14
2	-28	65	-1
3	256	223	6
4	344	442	-24
5	-190	75	-12
6	278	249	4
7	381	262	23
8	-196	179	-18
9	170	206	-3
10	118	42	3
11	-120	249	-17
12	-79	50	-2

11 6 1

0	502	472	9
1	83	167	-7
2	286	354	-15
3	395	445	-12
4	-139	138	-13
5	659	556	31
6	-12	111	-3
7	372	399	-5
8	-181	129	-14
9	192	116	6
10	-23	189	-9
11	-306	56	-23

11 7 1

0	78	125	-3
1	116	180	-7
2	358	420	-14
3	290	252	8
4	590	583	2
5	-120	11	-4
6	576	605	-7
7	97	60	1
8	426	277	26
9	137	76	3
10	78	11	1
11	-202	61	-11

11 8 1

0	-118	56	-7
1	-138	65	-7
2	-106	37	-4
3	477	448	7
4	66	71	0
5	476	497	-4
6	-60	5	-1
7	453	422	5
8	-193	61	-11
9	79	108	-1
10	192	68	8

11 9 1

0	-45	119	-5
1	283	283	0
2	98	53	2
3	92	245	-16
4	336	257	13
5	159	54	6
6	428	339	18
7	-161	92	-8
8	238	181	6
9	135	220	-7

11 10 1

0	566	586	-5
1	15	136	-6
2	456	478	-5
3	80	29	1
4	258	92	17
5	-69	143	-7
6	-162	89	-9
7	53	137	-4
8	333	202	17

11 11 1

0	80	157	-5
1	555	537	4
2	100	156	-3
3	317	308	1
4	-234	74	-16
5	-238	41	-16
6	135	27	4
7	-238	120	-17

11 12 1

0	377	347	5
1	-106	184	-12
2	280	363	-14
3	123	185	-5
4	155	117	2
5	-112	100	-6
6	172	0	7

11 13 1

0	-234	56	-15
1	144	254	-13

2	204	206	0
3	-93	132	-7
4	-232	179	-23

11 14 l

0	-228	87	-14

12 0 l

0	-179	60	-15
2	804	770	12
4	716	731	-5
6	411	452	-9
8	210	235	-3
10	-167	3	-7
12	150	176	-2

12 1 l

0	355	281	16
1	530	545	-4
2	405	295	27
3	666	617	15
4	189	212	-2
5	590	564	7
6	82	27	1
7	321	354	-6
8	82	81	0
9	-106	105	-7
10	267	123	15
11	-74	68	-2
12	-127	93	-5

12 2 l

0	265	179	14
1	804	682	44
2	402	320	19
3	487	497	-2
4	445	383	14
5	-239	49	-19
6	353	304	10
7	391	237	29
8	155	219	-6
9	207	256	-6
10	16	43	0
11	239	191	5
12	-153	60	-6

12 3 l

0	793	753	15
1	164	118	4
2	646	588	18
3	287	140	25
4	268	169	14
5	135	77	4
6	289	223	11
7	122	139	-1
8	423	389	7
9	122	119	0
10	234	301	-9
11	-137	0	-4

12 4 l

0	309	237	12
1	694	637	19
2	-130	64	-8
3	410	316	20
4	217	171	6
5	-115	88	-6
6	-124	39	-5
7	474	407	15
8	-259	9	-19
9	399	310	17
10	-89	39	-2
11	-174	216	-18

12 5 l

0	547	496	16
1	-165	69	-10
2	413	347	15
3	421	435	-3
4	-144	189	-17
5	292	339	-9
6	72	200	-10
7	-112	139	-9
8	224	290	-9
9	-131	14	-4
10	208	209	0
11	70	28	1

12 6 l

0	230	204	4
1	366	327	8
2	417	356	13
3	252	342	-15
4	528	580	-13
5	122	116	0
6	478	442	7
7	-57	119	-4
8	284	156	15
9	107	183	-6
10	-145	22	-5

12 7 l

0	-133	167	-15
1	166	161	0
2	380	318	13
3	601	628	-7
4	122	263	-15
5	564	591	-6
6	141	18	5
7	392	316	12
8	-12	47	0
9	115	69	2
10	-267	65	-18

12 8 l

0	195	62	11
1	-188	64	-12
2	278	256	3
3	-194	96	-13
4	449	471	-5
5	211	170	5
6	472	397	14
7	-169	2	-7
8	-105	132	-7
9	152	68	5

12 9 l

0	340	314	5
1	176	122	5
2	278	166	18
3	238	152	9
4	223	28	15
5	258	274	-2
6	-40	33	0
7	142	167	-1
8	153	147	0

12 10 l

0	79	240	-14
1	364	394	-5
2	-121	94	-7
3	79	192	-8
4	-152	91	-9
5	-134	20	-5
6	104	108	0
7	122	115	0

12 11 l

0	488	466	5
1	270	194	10
2	403	377	5
3	218	74	13
4	42	40	0
5	88	30	2
6	375	55	25

12 12 l

0	127	176	-4
1	465	377	16
2	239	178	6
3	59	133	-3
4	162	64	6

12 13 l

0	187	250	-7
1	-259	172	-23

13 0 l

1	419	412	1
3	614	565	14
5	462	473	-2
7	251	271	-2
9	210	22	12

13 1 l

0	383	245	33
1	232	204	4
2	428	400	6
3	-212	150	-21
4	478	439	9
5	-253	15	-18
6	352	373	-4
7	183	61	8
8	-128	132	-9
9	-207	110	-13
10	-190	51	-10

13 2 l

0	453	443	2
1	401	333	14
2	396	342	12
3	311	249	10
4	-291	97	-29
5	392	364	5
6	173	178	0
7	209	221	-1
8	141	224	-8
9	-222	46	-14
10	179	202	-2

13 3 l

0	-9	125	-5
1	394	492	-22
2	99	158	-4
3	281	269	2
4	-131	133	-10
5	-47	120	-5
6	-103	182	-11
7	436	388	9
8	-223	113	-16
9	424	301	22
10	121	10	3

13 4 l

0	483	475	2
1	-125	64	-6
2	509	486	6
3	29	174	-8
4	101	17	3
5	159	22	7
6	322	266	8
7	-105	60	-4
8	367	354	2
9	-48	19	0
10	187	221	-3

13 5 l

0	-127	23	-5
1	426	352	17
2	299	246	8
3	332	294	7
4	317	325	-1
5	-65	39	-1
6	-192	154	-19
7	-22	245	-15
8	-163	32	-7
9	-152	204	-17

13 6 l

0	333	279	10
1	327	254	13
2	329	268	11
3	557	484	18
4	313	235	11
5	474	422	11
6	-195	72	-10
7	68	173	-6
8	297	124	21
9	-68	27	-1

13 7 l

0	122	53	4
1	288	246	7
2	478	444	9
3	58	186	-8
4	601	540	14
5	100	127	-1
6	345	306	6
7	-202	50	-10
8	-84	107	-5

13 8 l

0	187	17	12
1	274	100	21
2	257	50	18
3	323	412	-14
4	-133	142	-9
5	383	322	10
6	144	16	5
7	113	170	-4

13 9 l

0	210	88	12
1	179	162	1
2	152	106	3
3	-141	11	-5
4	316	229	11
5	171	50	6
6	-135	161	-11

13 10 l

0	366	351	2
1	99	118	-1
2	294	206	12
3	132	90	3
4	28	18	0

5 260 116 14
13 11 1
0 231 209 2
1 330 366 -6
2 -234 47 -14
3 -239 93 -17
13 12 1
0 487 384 21
1 274 159 12
14 0 1
0 217 216 0
2 336 289 8
4 322 361 -7
6 412 320 19
8 -167 92 -10
14 1 1
0 -118 158 -12
1 368 261 21
2 117 44 3
3 271 306 -6
4 -139 10 -6
5 316 335 -3
6 57 76 0
7 212 197 1
8 7 89 -1
9 151 4 6
14 2 1
0 144 88 4
1 143 184 -4
2 299 205 16
3 248 113 15
4 183 215 -4
5 46 122 -3
6 94 265 -15
7 130 217 -7
8 -104 86 -4
9 -96 185 -9
14 3 1
0 411 353 12
1 151 165 -1
2 349 273 15
3 -153 18 -7
4 -201 17 -12
5 268 173 12
6 308 237 10
7 157 153 0
8 369 301 10
9 -309 15 -20
14 4 1
0 36 80 -1
1 454 382 17
2 125 118 0
3 -167 165 -16
4 88 7 2
5 141 109 2
6 -144 31 -5
7 248 261 -1
8 122 18 3
14 5 1
0 237 316 -12
1 -144 59 -7
2 252 271 -2
3 404 247 29
4 173 90 6
5 -143 133 -10
6 153 148 0
7 -261 65 -16
8 -92 153 -7
14 6 1
0 175 135 4
1 346 223 22
2 336 299 6
3 160 154 0
4 466 355 22
5 114 42 2
6 -92 171 -9
7 -246 91 -15
14 7 1
0 171 119 4
1 216 268 -6
2 -106 119 -6
3 538 458 16
4 -69 92 -3
5 332 266 9
6 -304 7 -24
14 8 1
0 185 110 7
1 132 8 5
2 341 314 4
3 -173 82 -9
4 380 299 12
5 -144 65 -6
6 361 181 16
14 9 1
0 -158 179 -16
1 -230 75 -15
2 169 39 6
3 -131 207 -14
4 -108 75 -4
14 10 1
0 -61 105 -3
1 289 245 6
2 -315 76 -26
3 -218 3 -8
14 11 1
0 419 346 12
15 0 1
1 292 293 0
3 197 224 -3
5 260 295 -5
7 -33 167 -7
15 1 1
0 243 151 14
1 -136 93 -8
2 255 190 10
3 77 9 1
4 382 289 17
5 250 43 16
6 364 226 21
7 -173 114 -10
15 2 1
0 23 154 -6
1 114 141 -2
2 275 155 18
3 -159 131 -12
4 -203 44 -12
5 94 218 -9
6 254 169 9
7 148 125 1
15 3 1
0 302 63 26
1 278 213 10
2 -148 34 -7
3 -86 76 -4
4 -281 78 -23
5 -89 136 -6
6 -86 126 -5
7 235 221 1
15 4 1
0 327 345 -3
1 -44 58 -1
2 172 169 0
3 -71 37 -1
4 207 6 12
5 -137 45 -5
6 -158 156 -12
15 5 1
0 -202 50 -12
1 372 221 25
2 -87 170 -10
3 29 106 -3
4 152 119 2
5 154 27 6
6 -103 65 -4
15 6 1
0 -120 163 -12
1 309 184 17
2 311 135 20
3 415 302 19
4 -202 52 -10
5 151 155 0
15 7 1
0 187 190 0
1 -88 95 -4
2 413 326 16
3 199 73 10
4 298 266 4
15 8 1
0 -203 56 -13
1 212 202 1
2 34 33 0
3 -81 275 -18
15 9 1
0 -66 28 -1
1 -76 94 -4
16 0 1
0 -71 151 -8
2 95 162 -4
4 -121 263 -20
16 1 1
0 228 105 13
1 93 204 -9
2 131 50 4
3 -226 183 -21
4 -185 56 -9
5 -61 185 -9
16 2 1
0 109 173 -5
1 191 147 4
2 -65 128 -6
3 -50 46 -1
4 205 153 5
5 -177 112 -11
16 3 1
0 402 280 21
1 179 88 7
2 121 66 2
3 -206 66 -12
4 116 78 2
5 146 93 3
16 4 1
0 101 39 2
1 207 184 2
2 35 9 0
3 -232 20 -16
4 -249 10 -16
16 5 1
0 214 185 2
1 330 120 27
2 -64 126 -5
3 -48 142 -6
4 -229 20 -9
16 6 1
0 296 189 14
1 171 119 3
2 295 254 5
3 -270 50 -12
16 7 1
0 100 68 1
1 234 228 0
17 0 1
1 70 204 -9
3 119 165 -3
17 1 1
0 290 181 16
1 -150 20 -5
2 128 180 -3
3 -75 16 -1
17 2 1
0 127 139 0
1 40 153 -5
2 -174 3 -7
17 3 1
0 268 99 15
1 -196 93 -13
2 -134 34 -5
17 4 1
0 93 211 -10

Fluoroborated Pt2 POP4. Page 27

1 179 15 8 17 5 1 0 170 109 3

Chapter 3

Design of the Positron Annihilation Mass Spectrometer

Robert J. Sweeney, Jesse L. Beauchamp

Introduction

The positron,[1-3] or antielectron e^+, is a particle with mass identical to an electron but charge opposite in polarity and equal in magnitude. A positron and an electron annihilate, or convert to photons, each other at a rate proportional to the square of the overlap between their wave functions. Nevertheless, positronium (Ps), an "atom" composed of an electron and a positron, exists. The two low-energy forms of Ps are para-Ps, with particle spins antiparallel, and ortho-Ps, with parallel spins. Ps is formed in a 3:1 ratio of triplet o-Ps and singlet p-Ps. The lifetime of each species in vacuum because of annihilation is 125 psec for p-Ps and 140 nsec for o-Ps. The difference in these lifetimes reflects the influence of conservation of total spin angular momentum on the annihilation products. p-Ps annihilates into two 512 keV photons at 180^o to one another while o-Ps produces three photons with a combined energy of 1.02 MeV.

p-Ps must produce at least two photons in annihilation to obey the conservation of linear momentum. The energy of each of the two photons equals the rest mass of the electron (or positron). o-Ps has nonzero spin angular momentum, so a minimum of three photons are produced in its annihilation. If only two photons were emitted, the vector sum of their intrinsic angular momenta could be either two or zero units, but not one. The energies and relative directions of the photons must ensure conservation of linear momentum.

The creation of the third photon in o-Ps's annihilation effectively involves an extra step and increases the lifetime. Similarly, annihilation of p-Ps into four photons, which is allowed, is even slower; a negligible fraction of Ps atoms experience this process.

In general, the annihilation of an electron and a positron of opposite spin into two photons proceeds at a rate λ_p

$\lambda_p = (\tau_p^o)^{-1} = 4\pi r_o^2 c\Psi(0)$

r^o = the classical radius of the electron

$\Psi(0)$ = the wave function of the electron at the positron

Positronium may be thought of as a very light isotope of the hydrogen atom in which the replacement of a positron for a proton in the nucleus makes the reduced mass one-half that of the hydrogen atom, or $m_e/2$. Consequently, the atomic radius increases from 0.53 Å to 1.06 Å and the ionization potential (IP) is halved from 13.6 eV to 6.8 eV, which limits the chemical options open to positrons. For example, the low IP of Ps prevents thermal (near zero kinetic energy) positrons from being able to oxidize most common organic species, since organics usually have IPs above 7 eV.

$e^+ + R \text{ ----> } Ps + R\cdot \qquad \Delta H = IP(R) - IP(Ps)$

Energetic positrons are able to oxidize molecules if their kinetic energy falls within the Ore gap, i.e., if the positron kinetic energy E_+ is between IP(R) and IP(R) - IP(Ps).

Above IP(R), the positron creates a "spur" or trail of free electrons and ionized molecules in its path until E_+ falls below IP(R).

$$e^+ + R \text{ ----> } e^+ + e^- + R^+$$

Below IP(R) - IP(Ps), Ps formation is thermodynamically unfavorable and annihilation must result from some long-term association between the positron and a substrate. This may result in either a 1:1 positron attachment complex (PAC) in which the positron occupies a wave function within a molecule or a cluster of molecules about one positron.

In the gas phase at relatively low pressures, clustering is unlikely.[4] With low-kinetic-energy positrons, oxidation reactions are not possible. The only feasible reaction path involves PAC formation. Because of the limited expected lifetimes of such species (ca. 1 nsec), they are not available for direct study. Data collected from positron experiments are generally refer to only properties of the annihilation photons, e.g., their angular and temporal distributions.[5, 6]

The positron affinities A_+ and the corresponding positronic wave functions for various atoms and molecules have been calculated. Schraeder's[7] calculations help in qualitatively describing tendencies in positron-molecule bonding. The positron affinities for the hydrogen atom and the second row elements Li through F, (Table 1) show that none of the free atoms should bind positrons.

Table 1. Critical charges for the attachment of positrons to free atoms.

ATOM	A_+ (eV)	CRITICAL CHARGE
H	-1.20	0.145
Li	-1.51	0.280
Be	-1.83	0.269
B	-3.22	0.359
C	-4.54	0.415
N	-6.46	0.494
O	-8.48	0.561
F	-11.05	0.640

In fact, the interaction becomes more repulsive as one goes right in a periodic series. This trend is expected; as nuclear shielding and polarizability decrease, the positron "feels" more of the repulsive nuclear potential.

Anions have favorable interactions with a positron because the long-distance potential is attractive. The amount of anionic charge an atom must possess in order to bind a positron is therefore greater than one electronic charge.[7] (Table 1)

In a molecule, the critical charge may be acquired through polarization of electronic molecular orbitals toward the atom on which the positron is localized. Larger, delocalized molecules therefore provide the polarizability required for a stable positronic complex. Since F, O, N and C have high critical charges, positrons in

organic structures are expected to localize about hydrogen atoms. Positron attachment, not surprisingly, behaves oppositely to electron attachment, which is favored by electronegative elements.

Positronic wave functions calculated for monosubstituted benzenes display trends that can be extrapolated to other organic systems.[7] In eight substituted benzenes investigated, the positron consistently localizes on a hydrogen atom. The positron also stays within the molecular plane, not in the π system. By localizing in the σ framework, the positron can interact with both lobes of the π system, polarizing them toward itself and gaining stabilization.

Calculations predict that benzene itself will not bind a positron. Possibly such a highly symmetric molecule cannot provide a unique site for positron binding that is available in the monosubstituted cases. With the positron delocalized over six protons, the electron density that each could polarize toward itself would be one-sixth that in a monosubstituted benzene. A highly delocalized positron cannot create an attractive center for binding. Thus we have another interesting contrast between positron and electron binding: While the most stable electron wave functions are nodeless and delocalized, positrons prefer wave functions that are localized and therefore have nodes. Calculations of the positronic wave functions for fluorobenzene[7] demonstrate that the most stable orbital has four nodes. The nodeless wave function lies much higher in energy.

Positrons in molecular complexes annihilate those electrons with which they have the greatest overlap. In the case of monosubstituted benzenes, electrons in σ-type MOs localized near the para-hydrogen atom are the most likely candidates for annihilation. The annihilation of a C-H σ-bonding electron leaves a cation with a very low-lying hole. This electronically excited cation undergoes rapid internal conversion to produce a vibrationally excited molecular cation in its ground electronic state which may fragment, as in electron impact mass spectrometry. This presents the possibility of using positron attachment as an ionization technique in mass spectrometry.

An important difference between positron attachment mass spectrometry (PAMS) and more conventional ionization methods is the potential selectivity; theory hints that positron attachment may depend strongly on molecular symmetry properties. For example, attachment may require the presence of a symmetry-unique proton. This criterion excludes PAC formation with such common atmospheric constituents as dioxygen, dinitrogen, carbon dioxide, water and argon. PAMS of atmospheric gas would therefore show only trace components.

Within molecules that do attach positrons, further selectivity may exist in the annihilation of specific electrons. In the case of the monosubstituted benzenes, electrons occupying C-H σ-type molecular orbitals should be annihilated at a much faster rate than other types.

Before such theories are evaluated, positron attachment must be demonstrated and relative rates of PAC annihilation determined for a series of molecules. The first report of low-energy positron attachment[8] concentrated on a series of alkanes, but there was no means of determining the reaction products or identifying the kinetic energy of the attaching positrons. Nevertheless, this study established the existence of the bound positron. Trapped positrons within a vacuum system were exposed to controlled amounts of alkanes and the positrons' lifetimes to annihilation measured by detection of the gamma photons emitted. Annihilation rates per unit pressure remained nearly constant from 10^{-8} to 10^{-6} torr of alkane, discounting clustering as a mechanism for the observed annihilation. Annihilation rates increased with carbon number from butane up, but began to level off at nonane. This effect is rationalized by assuming that the lifetime of the PAC to dissociation increases with the carbon number of the alkane. Dissociation of the PAC occurs faster than annihilation for smaller alkanes, but around C_9 the two rates are approximately equal. Once dissociation lifetimes are significantly longer than annihilation lifetimes, the quenching rate has reached its upper limit. Certainly, similar studies with other chemical species are of great interest.

Mass Spectrometer Design

The design of a positron annihilation mass spectrometer (see Figure 1) may be subdivided into three divisions:

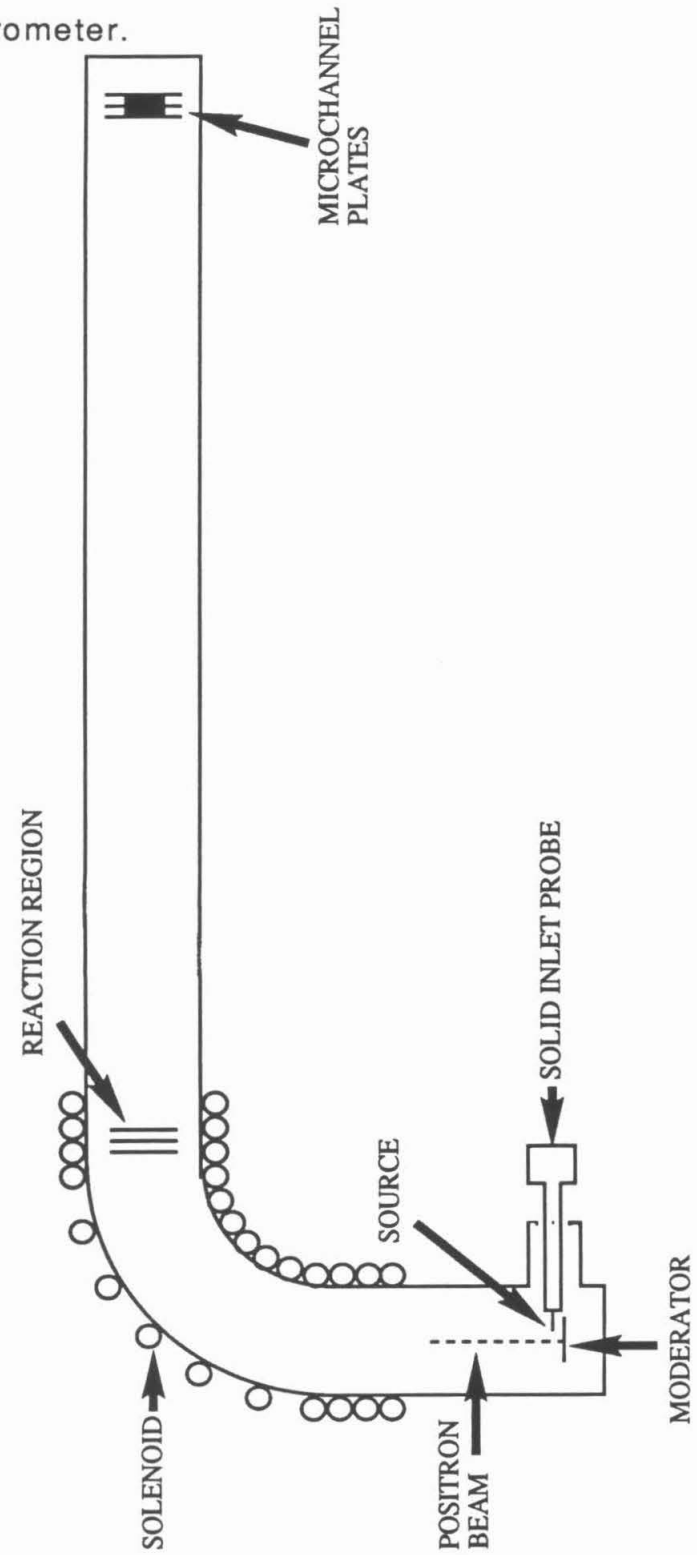
1. The production of a slow positron beam;
2. The promotion of positron attachment reactions;
3. The determination of reaction product distributions.

The slow positron beam

When first created through nuclear decay, positrons possess very high kinetic energies (0.5 to 1.9 MeV[9]), but positrons must be slowed down to lower energies for this experiment. The deceleration of energetic positrons by moderator foils has been studied extensively, as has the production of slow positron beams.[9, 10] Moderators are customarily metals, metal oxides or sulfides that have a negative positron work function. In analogy to electrons, the positron work function is the energy required to remove a positron from a material. Substances with negative positron work functions spontaneously emit low-energy positrons normal to their surface. Energetic positrons penetrate the surface and emerge with efficiencies up to 10^{-3} and kinetic energies below 6 eV.

Many moderator geometries have been investigated, the simplest being the backscattering and transmission geometries. Tungsten foil moderators in the backscattering geometry have been

Figure 1. A schematic diagram of the Positron Annihilation Mass Spectrometer.



used in the creation of slow positron beams.[10] This moderator provided beams of 1200 $e^+ s^{-1}$ from a 700μCi ^{22}Na source, with an overall efficiency of 4.7×10^{-5}. Positron kinetic-energy distributions from tungsten moderators maximize at 4 eV, with a spread of 1.5 eV.

The PAMS instrument will use a 100 mCi ^{58}Co positron source. ^{58}Co produces 0.15 e^+ per annihilation event and has a lifetime of 70 days, and emitted positrons initially have 470 keV kinetic energy. The positron source, electroplated onto a copper needle, is introduced into the vacuum chamber on a solid inlet probe. The probe is sealed to vacuum with teflon V-rings.

Tungsten foil is held between stainless steel plates attached to a flange at the end of the vacuum chamber. Electrical feedthroughs in the flange allow biasing of the moderator to vary the kinetic energy of the emitted positron beam. A rough estimate of the positron current delivered by a 100mCi source (3.7×10^{10} disintegrations s^{-1} Ci^{-1}) with moderator efficiency of 10^{-4} (reasonable for tungsten) is 3.7×10^5 $e^+ s^{-1}$.

Moderated positrons are guided around a 90° bend by a solenoidal field in an effort to prevent nonmoderated positrons and gamma rays from reaching the detector. The curvature of the small (200 Gauss) magnetic field will not cause moderated positrons to move off-center more than a few millimeters, while energetic particles and photons should pass through the field into the vacuum chamber walls. The slow positron beam is then guided into the reaction region where attachment takes place.

The attachment process

The forces involved in electron attachment reactions with neutral molecules at long distances should also apply to positron attachment, and extensive analogies between the two will serve as a basis for the following treatment of positron attachment.

Initial electron-neutral interactions are dominated by the charge-dipole coulombic attraction. At short distances, detailed molecular potentials become more important since the charged particle no longer feels the average charge distribution. Instead, a vibrationally excited attachment complex forms, and the analogy between positronic and electronic processes is no longer valid. Upon formation of an electron attachment product, both the electron's kinetic energy and the electron attachment energy are randomly channeled into the ion's vibrational modes. If this energy is sufficiently large, anion formation may be accompanied by rapid dissociation of the molecular anion into charged and neutral fragments. Dissociation may also take the form of electron ejection with regeneration of the starting materials. Alternatively, the excited anion may be stabilized by transferring some of its energy to other molecules through collisions. If the anion possesses many vibrational degrees of freedom, the energy may be distributed among many modes that do not promote dissociation. As expected, the cross section for nondissociative electron attachment reaches a maximum at zero electron kinetic energy.[11] This condition channels the least energy into modes that promote dissociation. Clearly, efficient PAC formation requires very low (effectively zero) energy positrons.

A reliable calculation of the ion current produced by annihilation requires some knowledge of the cross section for positron attachment. As this is not known, the cross section for dissociative electron attachment to CCl_4, which peaks strongly at zero energy, will be used as an example. Chutjian and Alajajian[12] approximate the cross section for low-energy, dissociative electron attachment to CCl_4 by

$$\sigma(E) = NaE^{-1/2}\exp(-E^2/b^2)$$

$$N = 5.45\times10^{-14}\ cm^2,\quad a = 0.117\ eV^{1/2},\quad b = 0.005\ eV,$$

where E is the kinetic energy of the attaching electron. This equation gives a cross section of $300A^2$ at thermal energies.

From the attachment rate of a positron with velocity v

$$R = N_o\sigma(v)v,$$

one may define a differential rate of attachment

$$dR = N_o\sigma(v)dv,$$

with N_o being the density of the attaching gas. The differential number of attachments (dN_a) is this differential rate multiplied by the time spent at that velocity.

$$dN_a = N_o\sigma(v)dv\ [dx/dv] = N_o\sigma(v)dx$$

x = position of positron

This expression, when integrated, produces the theoretical number of attachments that each positron can experience as it changes

velocity over some distance, for example, a positron slowing from 5 to 0 eV over 0.25 cm. By reducing the integration limits to 0.07 and 0 eV to simplify the integral, one obtains

$$N_a = 12.3 \text{ torr}^{-1} \text{ positron}^{-1}.$$

With the estimated positron current of 3.7×10^5 e^+ s^{-1}, this allows 4.6×10^6 attachments s^{-1} $torr^{-1}$, or one annihilation per 200 μsec at one millitorr pressure. A similar calculation with the cross section expression for SF_6 gives one annihilation per 550 μsec.

These estimates demonstrate the feasibility of collecting a full positron annihilation mass spectrum in a reasonable amount of time with the proposed source intensity.

A variation of Shmikk's reflectron device[13] creates the zero energy positrons necessary for attachment. Our version consists of two grids held parallel to each other and perpendicular to the positron's axis of motion. For a 5 eV positron beam, the first grid that the particles encounter is held at ground and the second at 10V. The electric field between the grids slows the positrons and effectively stops and turns them around in the middle. While turning around, the positrons have zero kinetic energy in the axis of motion, and it is during this time that attachment is most probable. The lifetime of a PAC because of annihilation being ca. 1 nsec, the ion will not have time to exit the reflectron before annihilation. This situation corresponds to the calculation above.

A reagent gas for attachment enters the reaction region through a hypodermic needle aimed toward the center of the two grids. The needle creates a high-pressure region where annihilation is most likely, without overwhelming the pumping capacity of the vacuum system. Pressures of one millitorr can be maintained in the reaction region while keeping the main chamber below 10^{-5} torr.

Product distributions

Following annihilation, the energetic molecular cation remaining may fragment into a number of neutral species and one smaller cation. Circuits triggered by the gamma rays produced in annihilation change voltages on the grids before the cation exits from the reaction region. The grids rapidly switch from 10V and ground to 100V and 105V, now pushing the cation away from the source region to an ion detector. The time that passes between detection of the annihilation photon and detection of the ion serves as the time-of-flight (TOF). From a TOF spectrum, a mass spectrum can be obtained using

$$TOF = d(2V)^{-1/2}(m/z)^{1/2}$$

d = distance traveled, V = accelerating voltage, (m/z) = ion mass.

A standard method for the detection of gamma rays is the use of plastic scintillators. Certain plastics, such as poly(methylmethacrylate) or PMMA, are able to convert high-energy photons which pass through them into many lower-energy photons

(λ=420 nm). With the proper construction, PMMA sheets contain the low energy photons through internal reflectance, allowing their detection by a photomultiplier tube (PMT) connected to one end of the sheet.

In our case, a 5 mm thick Bicron PMMA cylinder wrapped around the vacuum chamber captures the photons. A lucite light pipe attached to the scintillator guides the 420 nm photons to the face of an EMI photomultiplier tube. The PMT signal passes through an Amptek A101 amplifier, which discriminates against false signals caused by thermal emission of electrons in the PMT. The A101 outputs a rectangular 5V, 220 nsec pulse, which triggers the switching of grid voltages and begins timing the TOF.

The Bicron scintillator converts each 300 eV of a gamma ray photon into one 420 nm photon with an efficiency of 5%. This produces approximately 170 detectable photons per annihilation event (two photons at 512 keV each). A PMT quantum efficiency of 18% and gain of 10^7 create a pulse of 19 picocoulombs to the discriminator.

A chevron multichannel plate (MCP) detector records the arrival of the cation at the end of the flight tube. Microchannel plates act as electron multipliers, providing a gain of up to 10^8. The MCP pulse triggers a second Amptek A101 amplifier/discriminator whose output stops the timing circuitry. This pulse also causes the computer to collect the TOF datum from the external electronics and to reset all devices for the next annihilation event.

The start (PMT) and stop (MCP) pulses open and close a gate through which passes the output from a 20 MHz clock. The clock pulses during the ion flight enter a Metrabyte MCN8 counting board, which talks directly to a computer. The number of clock pulses allowed to reach the counter provides the TOF, when multiplied by 50 nsec.

Data Analysis

Two forms of data are extracted from the positron annihilation mass spectra: the internal energy of the molecular cation when formed and the relative positron annihilation rates for gaseous reagents.

Cation internal energy

An expression for the total internal energy of the cation first formed by the annihilation event ($E_{int}[R^+]$) is the sum of terms that require detailed knowledge of both the positron affinity of the attaching molecule and the identities of annihilated electrons.

$$R + e^+ \xrightarrow{A_+} Re^+ \xrightarrow{-2\gamma} R^{+*} \xrightarrow{IP-IP'} R^+ \longrightarrow B^+ + C + \ldots$$

$E_{int}[R^+] = A_+ + IP' - IP$

IP = first ionization energy of the molecule R

IP' = ionization energy of the molecular orbital occupied by the annihilated electron

Since IP is known through photoelectron spectroscopy (PES), three unknown energy terms remain in the energy expression.

The internal energy of molecular cations may be extracted from its fragmentation pattern with the use of photoelectron-photoion coincidence (PEPICO) breakdown curves. In PEPICO experiments, high-energy photons (of energy hν) ionize a molecule and the resulting free electron and cation are analyzed. The cation detector is triggered only if the ejected electron possesses nearly zero kinetic energy. This indicates that the molecular cation, when

initially formed, had hν - IP internal energy. The energy disperses among the various vibrational and rotational modes of the cation and leads to fragmentation. The ionic product distributions from PEPICO experiments should match with the PAMS spectra of molecules when

$$E_{int}[R^+] = A_+ + IP' - IP = h\nu - IP, \text{ or}$$

$$h\nu = IP' + A_+.$$

Thus, comparison of the spectra from PAMS and PEPICO to determine hν reveals the value of IP' - A_+. This analysis assumes that the PAMS fragmentation pattern results from the selective annihilation of electrons from a single MO of the PAC, which may or may not apply.

The positron affinity must be positive if binding takes place, so an upper limit can be placed on IP'. If one assumes that the positron affinity takes on values similar to those for electron affinities, usually less than about 5 eV, one can also give IP' a lower bound of hν - 5 eV. IP' should not be expected to correspond to a vertical or adiabatic transition in the PES spectrum, since the electronically excited molecular cation is formed from the PAC's distorted geometry. IP' therefore correlates with a high ν vibronic peak in the PES ionization band.

All considered, the IP of the annihilated electron can be known within a range of perhaps 5 eV through this analysis, which allows one to distinguish between the HOMO, weakly and strongly bonding orbitals and core atomic orbitals. For example, if PAMS of ethylene yields an ion distribution of 80% $C_2H_2^+$ and 20% $C_2H_4^+$, hν

Figure 2. The PEPICO diagram for ethylene.[14]

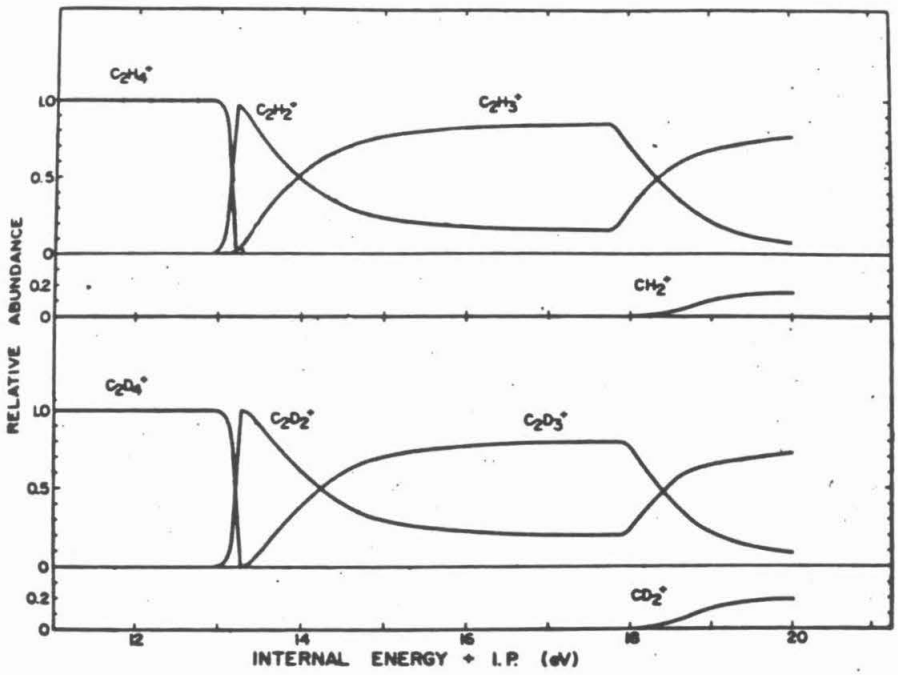
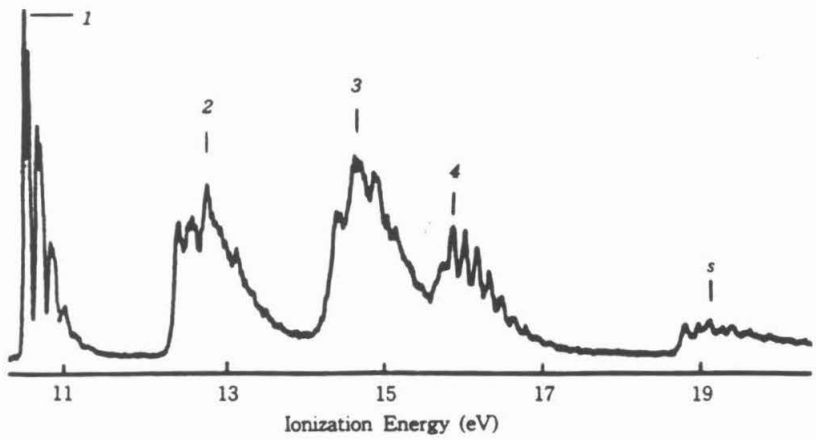
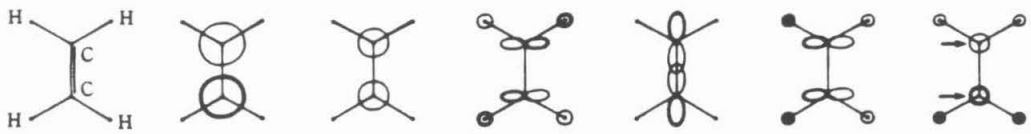


Figure 3. The photoelectron spectrum for ethylene.[15]



	Exptl.	SCF MO [6-31 G]		
	I_v(eV)	$-\varepsilon$(eV)	MO	Character
1	10.51	12.12	$1b_{2u}$ (8)	$\pi_{C=C}$
2	12.85	13.50	$1b_{2g}$ (7)	π_{CH_2}-(pseudo)
3	14.66	15.68	$3a_g$ (6)	σ_{CC}
4	15.87	17.35	$1b_{3u}$ (5)	π_{CH_2}+(pseudo)
	19.1	21.20	$2b_{1u}$ (4)	C_{2s}-



9 (vacant) 8 7 6 5 4

can be estimated from the PEPICO spectrum[14] (Figure 2) as 13.2 eV. IP' must then lie between 13.2 and 8.2 eV, which implicates π^{-}(C=C) or $\pi(CH_2)$ electrons in the annihilation[15] (Figure 3).

Relative annihilation rates

Competition experiments, in which two compounds of known relative concentration are exposed to the same positron beam, produce relative annihilation rates. The mass spectrum collected from the experiment is a weighted sum of the spectra from the individual PAMS experiments. A comparison of relative concentrations in the reaction region and peak heights from the TOF spectrum provide a quantitative evaluation of the relative affinity of each reagent for positrons. Many such experiments will develop a "positron reactivity ladder" from which theoretical predictions can be evaluated.

The annihilation rate is dependent on both the attachment cross section and the lifetime of the PAC with respect to dissociation back to the positron and neutral molecule. The lifetime of PACs with respect to annihilation is assumed relatively invariant, about 1 nsec. Dissociation is discouraged by the presence of many vibrational modes, which randomize the attachment energy. The lifetimes of larger, less rigid molecules should therefore be longer than those of smaller species. For very small molecules, the very short PAC dissociative lifetimes ($<<1$ nsec) may prevent observation of annihilation and its products.

Instrumental Details

The following section contains a detailed description of the positron annihilation mass spectrometer, which was designed but only partially constructed. Drawings of all parts are held by the Beauchamp group at Caltech.

The Source Region

A 100 millicurie Co-58 radioactive source attached to a copper needle is introduced into the vacuum chamber via a solid inlet system. This inlet allows some motion of the source within the chamber, but most importantly makes it possible to rapidly position the radioactive source. Immediately after the seals are made about the inlet probe, lead shielding must be built around the source region. The source is ordered from New England Nuclear-Dupont in Massachusetts.

The Co-58 source emits positrons spontaneously, but they have an initial kinetic energy of around 500 keV, which is too high for attachment. A tungsten foil directly behind the source is used as a moderator. High-energy positrons entering the foil have a probability of about one in 10^4 of being spontaneously reemitted normal to the foil surface with low kinetic energy, about 5 eV. The moderator is attached to an aluminum plate connected to the moderator flange with aluminum stand-offs. There are four feedthroughs in the flange that allow biasing of the moderator. The moderator is constructed with EV parts.

The low energy positrons are guided around a 90° turn by a solenoidal field (100-200 Gauss) to lose nonmoderated particles, which go straight through the chamber walls. The solenoidal field leads to the reaction region. The solenoid has not been constructed at this time.

The Reaction Region

The reaction region consists of four grids attached to an aluminum plate held from the detection flange with aluminum stand-offs. The reaction region is constructed with EV parts. The grids are Ni mesh from Buckbee-Mears. The four grids are parallel and perpendicular to the axis of the vacuum chamber. The grids, in order, are referred to as RET (retardation), P1, P2 and EXT (extraction). RET is closest to the source region; EXT is on the detection flange side. EXT should be grounded.

As the positrons encounter RET, they are slowed down if RET is not held at ground. The total electric field between P2 and RET should be large enough to stop and turn around the positrons between P1 and P2. When the positrons are turning around and have zero kinetic energy (or nearly so) is the time when we expect the attachment process to take place. Attachment, annihilation and detection of the emitted gamma ray should take place in effectively zero time, before the ion has time to escape the space between P1 and P2.

Once the gamma ray is detected with the scintillator, the electronics is triggered and very rapidly changes the biases on P1

and P2. This must also happen before the ion has time to move. The voltages between on P1 and P2 will now force the ion toward the EXT plate . The ions are then accelerated between P2 and EXT and speed toward the detector.

Typical bias voltages in the reaction region are: EXT(0,0), P2(-10,-100), P1(0,-105), where the two numbers refer to the normal and triggered biases, respectively, in volts. This example provides 100 eV ions with a potential kinetic energy spread of 5 eV. This limits the resolution of the mass spectrum, and the triggered P1-P2 difference should be minimized.

The target gas is introduced into the reaction region via a steel needle. It fits onto an adapter at the end of a copper tube that extends from the detector flange. On the outside of the flange, a Cajon adapter connects the tube to a simple, one-port inlet system with a leak valve. The target gas is aimed toward the center of the gap between P1 and P2, where the attachment is expected. There is currently no means of measuring the actual pressure in the reaction region; only the overall pressure of the vacuum chamber is known.

The Detector.

The detector consists of two microchannel plates (MCPs) in a tandem, chevron configuration. The literature on MCPs is clear, and the background on their operation will not be given here. Our MCPs were purchased from the Varian Image Division. The MCP assembly, as received from Comstock, was of poor design and has been adapted. The major change is the introduction of separate assembly screws

and voltage feed screws. Also, a grounded faceplate/grid with a large opening has been introduced to accelerate the positive ions to keV energies before they strike the front MCP. This will increase their probability of detection. The faceplate is attached to the detector flange with aluminum stand-offs.

Resistors inside the vacuum chamber connected to the MCP assembly fill two functions; two limit the possible current passing through the MCPs and a third is part of a high-pass filter. The capacitor associated with the filter is outside the chamber. The resistors are of either 10MΩ or 15MΩ, from the Victoreen company. They are special glass-enclosed resistors that neither "leak" and cause noise nor have an appreciable vapor pressure.

The MCPs operate well without noticeable noise at applied voltages of at least 2300V. They are triggered by ions or electrons emitted by the ion gauge, and the gauge must be turned off when one is trying to detect ions. The ion gauge can, however, be used to "scrub" the MCPs. To scrub the plates, put about 1300V across them at $<10^{-6}$ torr and turn on the ion gauge. The bombardment of ions cleans the plates and improves signal-to-noise. MCPs should be kept under vacuum if at all possible and if nothing else, away from humidity. MCP output is fed to an Amptek A101 preamplifier/discriminator. The best high-pass filter arrangement I could find for the signal coming off the MCP collector plate consists of: a 10MΩ resistor inside the vacuum chamber between the collector and the high-voltage input, an HV 0.01μF capacitor outside

the flange after the feedthrough and a 10pF capacitor directly before the A101 input pin.

Eight high-voltage feedthroughs, identical to those on the moderator flange, are in the detector flange. These feedthroughs were cannibalized off an old Bendix TOF instrument. Connections between the feedthroughs and the MCP assembly and the reaction region are made with shielded coaxial cable obtained from the Electronics Shop. It has a very low vapor pressure. Pins and cables are attached by either golden Burndy pins from the Instrument Shop or custom-made connects (as on the moderator flange).

The Vacuum Chamber

The vacuum chamber is constructed of nonmagnetic 304 steel with standard 4 $^{5}/_{8}$ Conflat flanges. The source region's five-way cross and the 90^{o} elbow are standard products from MCB or Huntington. A six-inch Varian diffusion pump is attached to the main chamber through a 12-hour liquid nitrogen trap that usually lasts closer to 11 hours. Seals are made on both ends of the trap with O-rings. A roughing pump is connected to both the diff pump foreline and the source region.

A glass-enclosed ion gauge (also MCB or Huntington) with a one-inch diameter arm and a thermocouple gauge with a Varian 843 controller measure the chamber pressures. Another thermocouple gauge is on the diff pump foreline to measure the backing pressure. This gauge does not read true pressure and should be replaced.

Once the trap is filled, the system given overnight on the diff pump and the ion gauge degassed, the pressure should be down to 1.5×10^{-7}. Baking out the chamber will give an even lower background pressure. Be careful baking out with the MCPs.

The Computer

The computer is an XT Clone with a hard disk and two floppy drives. The program that was going to be used to collect data is named PAMS and is adapted from Dave Dearden's PES program. It is written in Profort fortran. The various subroutines and Profort devices are in the PAMS directory. L.BAT is a batch file used to link all the various object files and libraries necessary to run PAMS successfully. PAMS has been through several hands before this incarnation and may seem cumbersome, but it works. As of now, it does not save data but it should not be difficult to correct this deficiency. The code listing for the main program and subroutines are attached, as are diskettes with all relevant software.

Data are collected by the computer through a Metrabyte MDB64 board in the body of the computer, which talks to the external Metrabyte MCN8 counter board (discussed under Electronics). The Metrabyte manual is relatively clear, and the Metrabyte people are willing to answer questions.

The Electronics

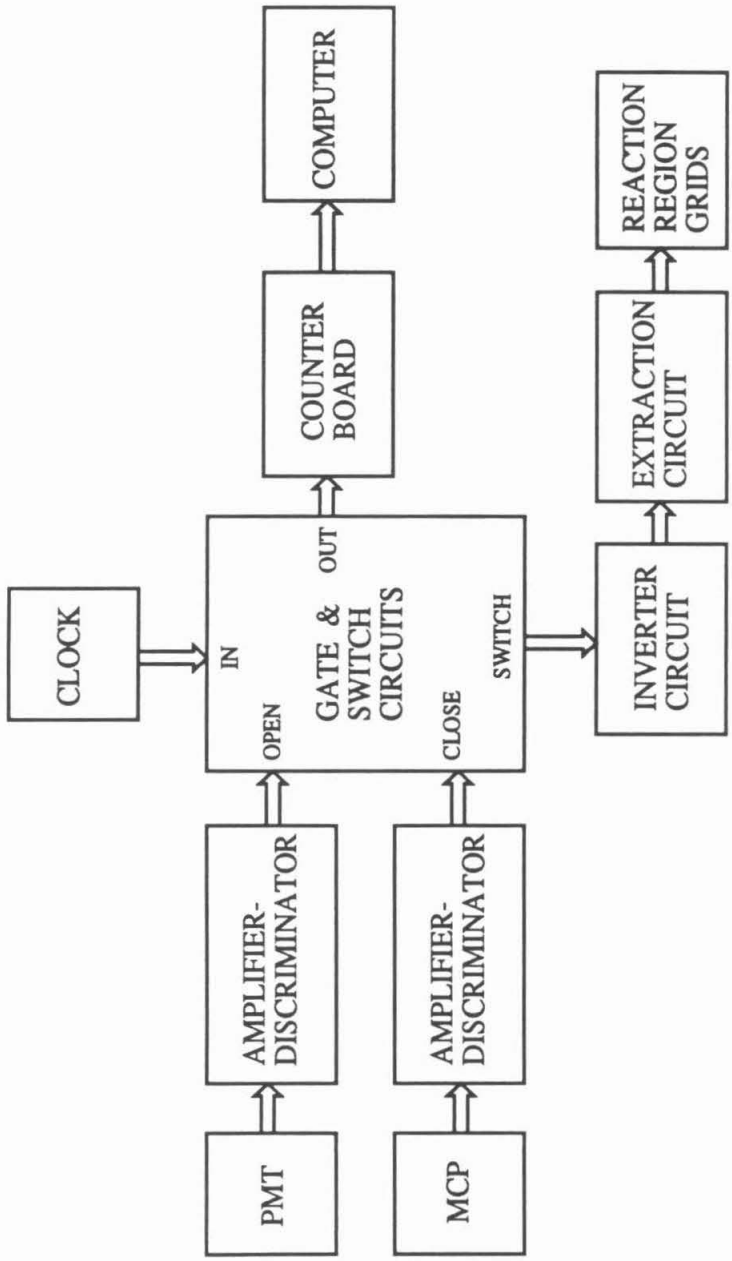
The electronics has main functions: detect annihilation events, switch the voltage on P1 and P2 and detect ions for a TOF analysis of their mass. The detection function will be discussed under Scintillator. (See flowchart, Figure 4.)

Once a gamma ray has been detected, the PMT PAD (see later) sends a 5V, 220 nsec pulse to the MCN8 BOX. The MCN8 box holds three circuits: the MCN8 board, the gate circuit (Figure 5) and an external clock. This box has three inputs: a 5V source power, the PMT input and the MCP input. The latter two come directly from the appropriate Amptek A101 Preamplifier Discriminator (PAD). The two outputs are 200 μsec 5V pulses that are triggered by the rising edge of the PMT pulse. One output goes HI from ground to 5V and one goes LO from 5V to ground.

In the gate circuit, the PMT pulse also opens a gate that passes clock pulses through to a MCN8 counter. The clock is used to time the ion's flight down the tube and is on the same vectorboard as the rest of the circuit. Clock pulses are passed through the gate until a pulse is received from the MCP. This closes the gate. The MCP and PMT pulses are also fed into counters. The clock gate may also be closed by another pulse, from either the external clock or by a pulse from the MCN8 internal clocks.

The PAMS program proceeds as follows: Once the PMT pulse is received by its counter and read as a nonzero count by the computer, the computer looks at the MCP counter and waits for that pulse to

Figure 4. A flowchart describing the electronic controls of the Positron Annihilation Mass Spectrometer.



arrive. Once it is counted, the computer looks at the clock counter and records the number of clock pulses that made it to the counter. This number, multiplied by the amount of time between each pulse, provides the time of the ion's flight. Once the clock counter is read, all counters are zeroed and the sequence begins again. Thus, a TOF spectrum is collected.

The two output pulses from the MCN8 box are used to switch P1 and P2. One output (labeled SWITCH, Figure 6) passes through an inverter box (Figure 7), which switches polarity of the pulse and amplifies it with an op-amp. The inverter output passes to the extractor box. (Figure 8) The extractor box controls the voltage on P1 and P2 and is responsible for rapidly switching the voltages on the plates for as long as the input pulse lasts (i.e., 200 msec). Two trimpots (or variable resistors) in the extractor box allow one to vary the biases on P2 for maximizing resolution and signal. The extractor serves as a gate/voltage divider for another input, which may range up to about 300V. This voltage is approximately the triggered bias on P2 and therefore approximately the kinetic energy of the ion.

The PADs are Amptek A101 chips on Amptek circuitboards. The triggering threshold of the A101 is too low and must be raised by an added resistor, as described in the Amptek literature. Shielding of all inputs into the A101 is absolutely required.

Figure 5. The Gate circuit.

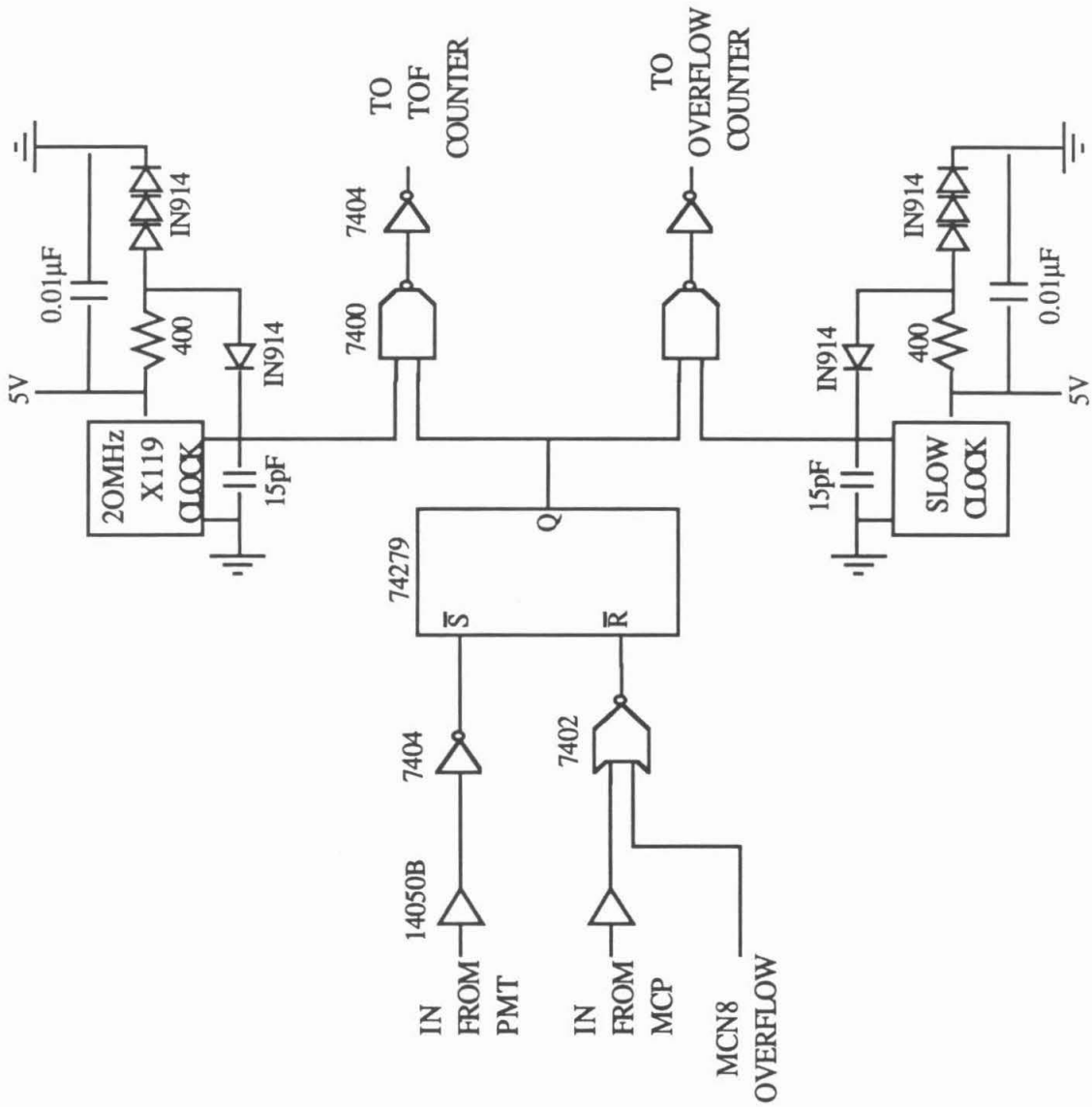


Figure 6. The Switch circuit.

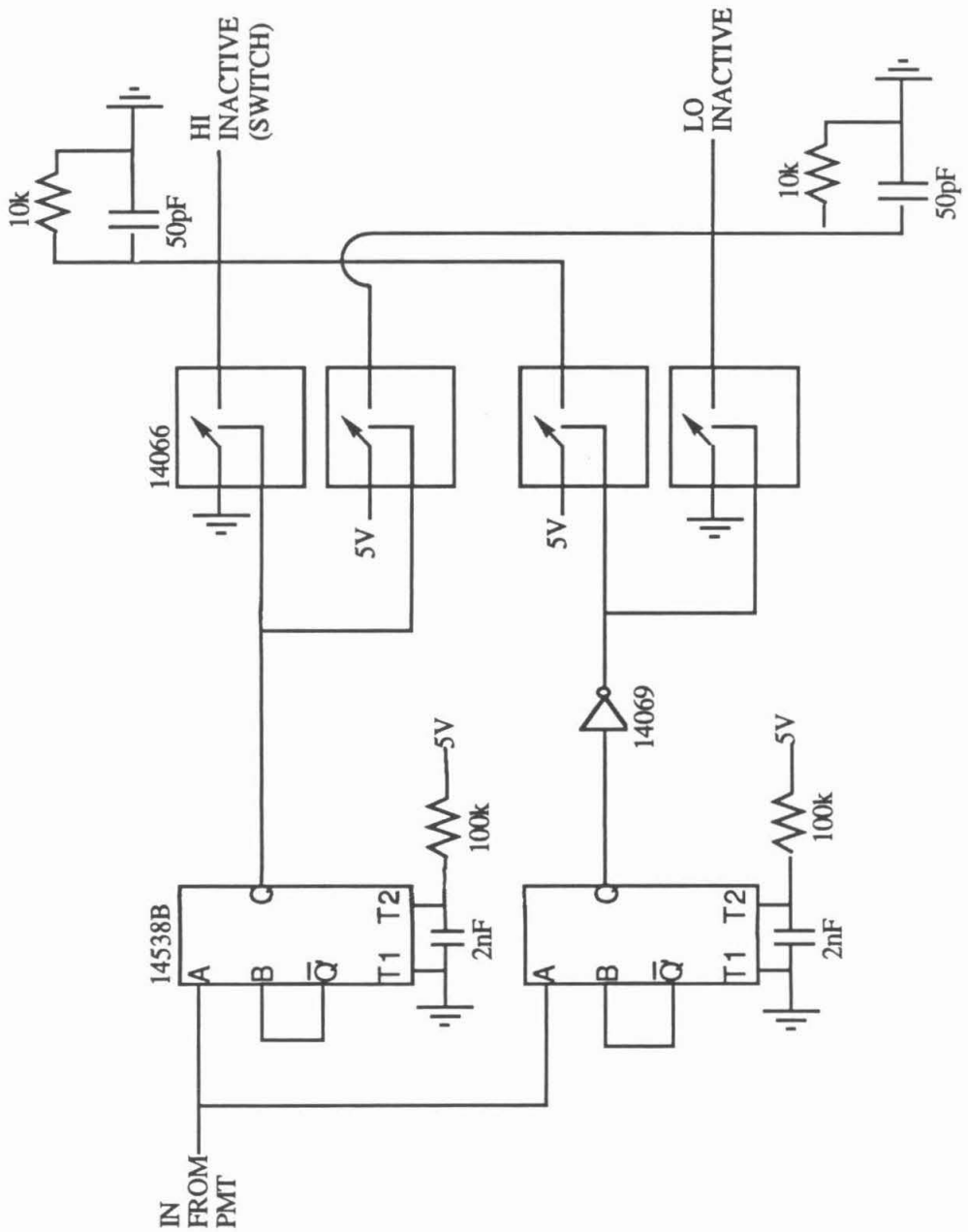
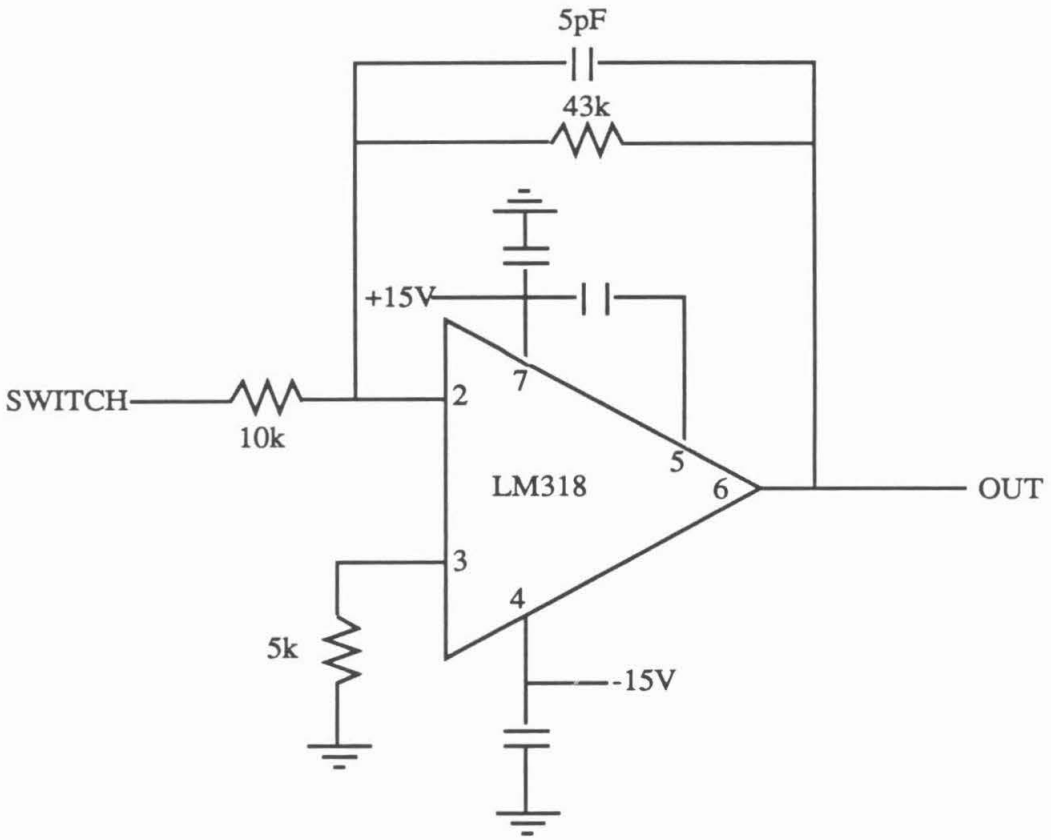
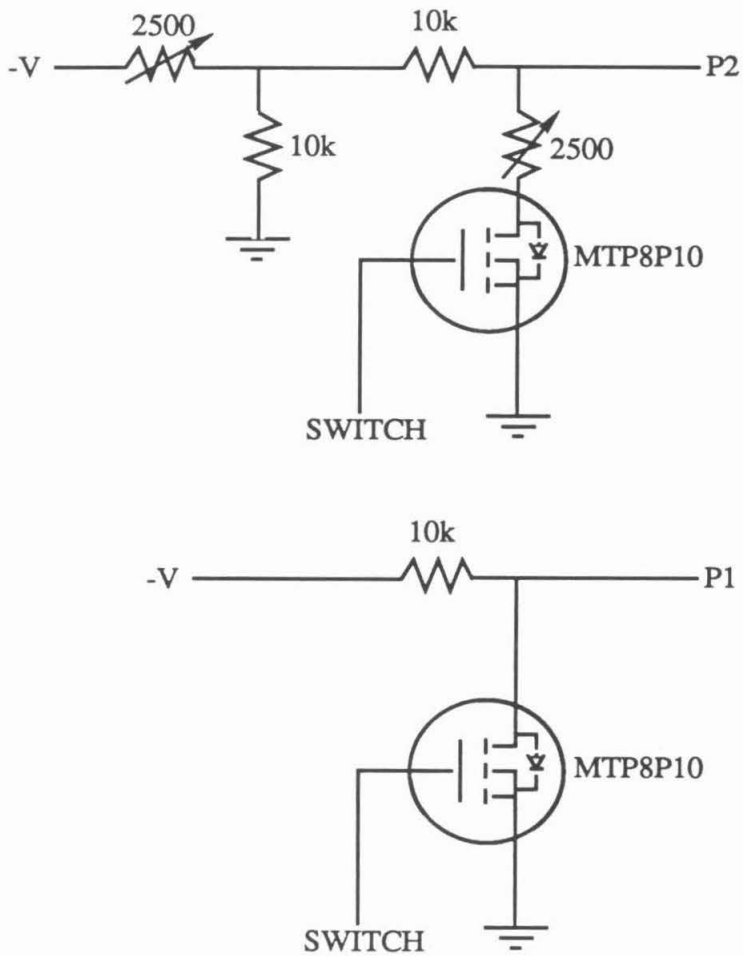


Figure 7. The Inverter circuit.



Capacitors are 0.1μF

Figure 8. The Extract circuit.



For positive voltages, IRF731 or IRF732 take the place of the MTP8P10.

The Scintillator

The gamma rays emitted during annihilation will pass through the vacuum chamber walls with high probability. Outside the chamber, a Bicron poly(methylmethacrylate) or PMMA scintillator will "collect" the photons. Scintillators are used for this purpose because as high-energy photons pass through them, they convert the photons to low-energy, visible photons, which are easily detected with a photomultiplier tube (PMT). The PMT output is passed into an Amptek A101 similarly to the MCP output.

The scintillator must be bent to wrap around the vacuum chamber. The literature or calls to Bicron will help with this. Once bent, the scintillator must be painted with high-reflectance paint supplied by Bicron, which we have. The lucite light pipe off the scintillator should not be glued directly to the PMT face, but glued to a second lucite light pipe that is already attached to the PMT housing. Bicron has supplied an optical glue for this task. It has two components; one should be in the refrigerator.

An old EMI 6256S PMT fits into the PMT housing and should be up to the job.

Of the positron annihilation mass spectrometer project, the following were completed in this work:

1. Design of general experimental scheme
2. Design and construction of vacuum chamber and internal components
3. Design, construction and testing of electronic circuits
4. Adaptation of software
5. Adaptation, testing and maximization of MCPs

To Be Completed:

1. Construction and testing of solenoid
2. Testing and maximization of scintillator and PMT
3. Demonstration of mass spectrum collection using an electron beam in the reaction region
4. Simulation of positron attachment with electrons originating from an electron beam in the source region
5. Construction of shielding
6. Positron attachment experiments
7. Data analysis

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