bons to be slightly less accessible to the paramagnetic chelate.

Conclusions

This investigation clearly points to the fact that some precautions must be taken before using paramagnetic additives such as $Cr(acac)_3$ in order to obtain quantitative results in ^{13}C NMR. First, it is necessary to have a rough estimate of the spin–lattice relaxation times for the sample. This estimate of the T_1's serves two purposes: (1) it would give supplementary evidence for spectral peak assignments and (2) it would indicate the amount of paramagnetic relaxation reagent (PARR) needed to quench the NOE. If the dipole–dipole interaction is efficient enough then it will be impossible to effectively suppress NOE's with relaxation reagents without causing considerable line broadening. Also, spectral sensitivity is lowered for this application of PARR materials, since it is in this case particularly that NOE's are at or near the theoretical maximum[5,6] (Figure 3 is illustrative).

In addition to the problems cited above, there is the possibility of solution complex formation between the metal chelate and substrate functional groups (e.g., OH, NH_2, CX_2H).[1f,3] In this case the T_1 leveling effect is not present; relaxation times for carbons close to the site of complexation are shortened preferentially and individual carbon NOE's may be variably affected.

In cases where T_1's are longer than several seconds this method can be valuable for obtaining quantitative ^{13}C NMR results, provided discretion is used in the design and execution of the experiment. Also chemical suppression will allow accurate and rapid calculation of nuclear Overhauser enhancements for these molecules in laboratories where instrumental NOE suppression is not available.

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(10) The solution viscosities for cholesteryl chloride, 1 M, in CCl_4 at 42° and benzene-d_6 at 38° are 2.87 and 1.48 cP, respectively.

A Change in Mechanism During Fluorescence Quenching of Substituted Anthracenes by Triphenylphosphine

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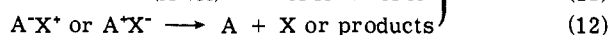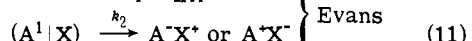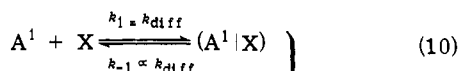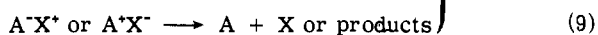
Abstract: The rate constants, k_q, for the fluorescence quenching of anthracene and ten mono- and disubstituted anthracenes by triphenylphosphine have been measured. The k_q values are correlated with the singlet energies and half-wave reduction potentials of the anthracenes according to the treatments of Weller, Evans, and Hammond. It is found that the anthracenes substituted with electronegative groups undergo quenching by a charge transfer mechanism. The anthracenes with electropositive groups are quenched by a different mechanism which probably involves formation of an excitation resonance stabilized exciplex.

It is known that the fluorescence of many aromatic molecules, A, which possess low-lying singlet states, is quenched by compounds, X, whose first excited singlets are much higher in energy.[2] Direct or indirect evidence has indicated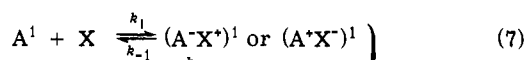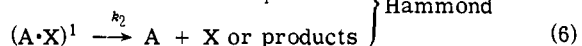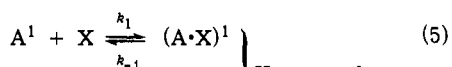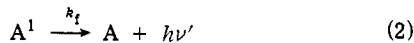 that exciplexes, excited state complexes between electronically different molecules which are dissociative in the ground states, are often formed during the quenching process.[2] The nature of the binding energy in exciplexes and the electronic nature of the nonclassical quenching step are still subjects of controversy. While Weller[3] and Evans,[4] especially, agree that charge transfer interactions contribute most, their mechanisms for exciplex formation differ. Hammond[5] believes that charge transfer interactions need not always be important: in some cases, resonance excitation may be the dominant stabilizing force; in others, many factors may contribute.

In Scheme I are listed the kinetic steps which describe the three hypotheses. Equations 1-4 (excitation, fluores-

Scheme I

$$A \xrightarrow{h\nu} A^1 \qquad (1)$$

$$A^1 \xrightarrow{k_f} A + h\nu' \qquad (2)$$

$$A^1 \xrightarrow{k_\Delta} A + \Delta \qquad (3)$$

$$A^1 \xrightarrow{k_{isc}} A^3 \qquad (4)$$

$$A^1 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (A \cdot X)^1 \qquad (5)$$

$$(A \cdot X)^1 \xrightarrow{k_2} A + X \text{ or products} \qquad (6)$$

$\left.\right\}$ Hammond

$$A^1 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (A^- X^+)^1 \text{ or } (A^+ X^-)^1 \qquad (7)$$

$$(A^- X^+)^1 \text{ or } (A^+ X^-)^1 \xrightarrow{k_2} A^- X^+ \text{ or } A^+ X^- \qquad (8)$$

$$A^- X^+ \text{ or } A^+ X^- \longrightarrow A + X \text{ or products} \qquad (9)$$

$\left.\right\}$ Weller

$$A^1 + X \underset{k_{-1} \,\propto\, k_{diff}}{\overset{k_1 = k_{diff}}{\rightleftharpoons}} (A^1 | X) \qquad (10)$$

$$(A^1 | X) \xrightarrow{k_2} A^- X^+ \text{ or } A^+ X^- \qquad (11)$$

$$A^- X^+ \text{ or } A^+ X^- \longrightarrow A + X \text{ or products} \qquad (12)$$

$\left.\right\}$ Evans
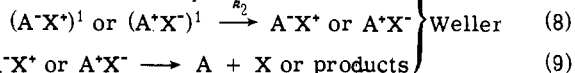
$$\frac{I_0}{I} = \frac{\Phi_f^0}{\Phi_f} = 1 + \frac{1}{k_f + k_\Delta + k_{isc}} \frac{k_1 k_2}{k_{-1} + k_2}[X] \qquad (13a)$$

$$= 1 + \tau_A \cdot k_q [X] \qquad (13b)$$

cence, internal conversion, and intersystem crossing) are common to all treatments. The remaining equations describe formation of the exciplex, its electronic nature, and quenching of A^1. For all cases, k_q, the observed rate constant for fluorescence quenching of A^1 by X, as determined from the Stern–Volmer equation,[6] is kinetically equal to $k_1 k_2/(k_{-1} + k_2)$. To determine which mechanism is most consistent with the data, a number of correlations between log k_q and energy related parameters have been derived.

According to Hammond,[5] A^1 and X collide to form the exciplex $(A \cdot X)^1$ reversibly (eq 5). The exciplex can be represented by a series of resonance structures:

$$(A \cdot X)^1 \equiv A^1 \cdot X \longleftrightarrow A \cdot X^1 \longleftrightarrow A^+ X^- \longleftrightarrow A^- X^+ \qquad (14)$$
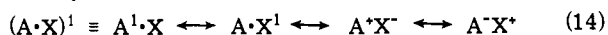
Depending upon the nature of A and X, one of the resonance forms may be much more important than the others. For instance, the first two structures at the left would be dominant in an excitation resonance stabilized exciplex. In this case, at least a rough correlation between log k_q and ^1E_A, the excited singlet energy of A, would be expected. For a series of similar exciplexes, slight deviations in the ratio log $k_q/^1E_A$ could be rationalized on the bases of variations in steric factors or the ratio k_2/k_{-1}.

In the limiting treatment of Weller,[3] the exciplex is depicted as a charge-separated, excited-state complex in which the free energy for electron transfer is the rate-determining factor for A^1 quenching (eq 7). It is assumed that k_2 is approximately constant and much smaller than k_{-1} and that a pseudo-equilibrium exists between the k_1 and k_{-1} reactions. Then, for electron transfer from X to A^1,

$$\Delta \log k_q \simeq \Delta \log k_1/k_{-1} \propto \Delta(IP_X - EA_A - {}^1E_A) \qquad (15a)$$

or from A^1 to X,

$$\Delta \log k_q \simeq \Delta \log k_1/k_{-1} \propto \Delta(IP_A - EA_X - {}^1E_A) \qquad (15b)$$

where IP is the first ionization potential and EA is the electron affinity. For a series of A quenched by one X, eq 15 simplifies to eq 16. Another term which includes steric and

$$\Delta \log k_q \propto \Delta(-EA_A - {}^1E_A) \qquad (16a)$$

$$\Delta \log k_q \propto \Delta(IP_A - {}^1E_A) \qquad (16b)$$

coulombic contributions may affect log k_q slightly. In general, it is considered constant for a given solvent.

The Evans[4] exciplex consists of an encounter complex between A^1 and X in which electronic interactions are small. Charge transfer from the encounter complex leads to other than excited species directly, without intervention of a Weller-type exciplex. The rate constant for the formation of the encounter complex $(A^1 | X)$ should be controlled by diffusion properties of the solvent (i.e., $k_1 \simeq k_{diff}$). The rate of the reverse step, separation of the encounter pair to A^1 and X, should be proportional to the same solvent properties (i.e., $k_{-1} \propto k_{diff}$). Then, log k_2/k_{-1} = log $k_q/(k_{diff} - k_q)$. Since k_{-1} is assumed to be constant for a given solvent, log k_2/k_{-1} is proportional to the free energy of activation for electron transfer (eq 11). The work of Weller[3] indicates that this quantity is directly proportional to the free energy for formation of ions from the encounter complex. Accordingly, for a series of quenchers and one excited singlet, log $k_q/(k_{diff} - k_q) \propto IP_X$ when electron transfer is from X to A^1 and $\propto EA_X$ when from A^1 to X.

Although examples which are compatible, at least, with each treatment have been found, one series of sensitizers or quenchers has not been shown to form exciplexes or to undergo fluorescence quenching by two electronically distinct mechanisms. A study of the effect of k_q of varying greatly the electronic, but not steric, properties of a series of A molecules with one X which is capable of acting as an electron donor or acceptor may yield valuable information concerning the possibility that mechanisms for exciplex formation and fluorescence quenching can change with subtle modifications in A or X. Herein, we report the results of such an experiment.[7] The rate constants for quenching the fluorescence of eleven anthracenes, Aa–k, by triphenylphos-
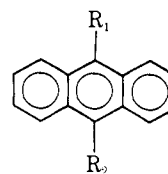
Aa, $R_1 = CN$; $R_2 = CN$
b, $R_1 = H$; $R_2 = CN$
c, $R_1 = Br$; $R_2 = Br$
d, $R_1 = H$; $R_2 = Br$
e, $R_1 = Cl$; $R_2 = Cl$
f, $R_1 = H$; $R_2 = Cl$
g, $R_1 = H$; $R_2 = H$
h, $R_1 = H$; $R_2 = Me$
i, $R_1 = Me$; $R_2 = Me$
j, $R_1 = H$; $R_2 = OMe$
k, $R_1 = OMe$; $R_2 = OMe$

phine, P, were measured and the treatments of Hammond, Evans, and Weller are applied critically.

Experimental Section

All boiling points and melting points are uncorrected. Ultraviolet absorption spectra were recorded on a Cary 14 or Zeiss DMR-21 spectrophotometer.

Triphenylphosphine (Ventron), mp 82° (lit.[8] mp 79-81°), was recrystallized twice from absolute alcohol and sublimed twice (3 mm). Anthracene (Merck, scintillation grade) was used as received. 9,10-Dicyanoanthracene (Eastman), mp 335° (lit.[9] mp 335°), was recrystallized five times from chloroform. 9-Cyanoanthracene (Aldrich), mp 177° (lit.[10] mp 175°), was recrystallized from alcohol and sublimed (3 mm). 9,10-Dibromoanthracene (Aldrich), mp 221-222° (lit.[11] mp 221-222°), was recrystallized from chloroform and sublimed (3 mm). 9,10-Dichloroanthracene (Eastman), mp 211-212° (lit.[12] mp 210°), was recrystallized from benzene and sublimed (3 mm). 9-Methoxyanthracene (Eastman), mp

Table I. Precision of Stern-Volmer Plots

A	Intercept[a]	Correlation coefficient[b]
a	0.81	0.999
b	0.79	0.999
c	0.99	0.988
d	1.04	0.993
e	1.12	0.995
f	0.93	0.999
g	0.98	0.995
h	1.00	0.995
i	1.01	0.999
j	0.97	0.998
k	1.01	0.998

[a] Predicted to be unity if mechanism is described completely by Scheme I. [b] Slope fitted to a straight line.

79° (lit.[10] mp 78–79°), was recrystallized from benzene and sublimed (3 mm). 9,10-Dimethylanthracene (K & K), mp 177° (lit.[13] mp 177–180°), was recrystallized twice from benzene and sublimed (3 mm). 9-Methoxyanthracene, mp 94–96° (lit.[14] mp 95–96°), was prepared from anthrone according to the literature,[14] recrystallized twice from 2-propanol, and sublimed (3 mm). 9,10-Dimethoxyanthracene, mp 200–201° (lit.[14] mp 198–199°), was prepared from anthraquinone according to the literature,[14] recrystallized twice from benzene, and sublimed (3 mm). 9-Chloroanthracene, mp 104–106° (lit.[15] mp 106°), and 9-bromoanthracene, mp 98–100° (lit.[16] mp 99–100°), were synthesized from anthracene by the method of Nonhebel[15] and were sublimed (2 mm). Benzene (Merck, spectrograde) was used as received. Acetonitrile was purified by the method of Mann et al.[17]

Irradiations of A and P. Benzene solutions of ca. 10^{-4} M anthracene, 9,10-dimethoxyanthracene, or 9,10-dicyanoanthracene and 0.19 M triphenylphosphine were prepared. Aliquots were placed in quartz cuvettes and nitrogen was bubbled slowly through for 15 min. The cuvettes were closed tightly with Teflon stoppers and were irradiated for 125 min with a Pyrex-filtered Hanovia 450 W medium pressure mercury arc lamp. The progress of the reactions, which was followed spectrophotometrically, indicated that ca. 45% of anthracene, ca. 25% of dicyanoanthracene, and ca. 35% of dimethoxyanthracene had been consumed. An orangish color which developed during irradiation was destroyed partially when oxygen was bubbled through the solutions. A nonirradiated aliquot of the degassed solution of anthracene and triphenylphosphine was unaltered spectroscopically after standing in the dark at room temperature for 2 days.

Fluorescence Quenching of A by P. Aliquots, 1.0 ml, of A in benzene (concentrations corresponding to an optical density of 0.6–0.8 at the 0–0 absorption band) were pipetted into at least six dry, clean 12 mm (o.d.) Pyrex test tubes with constricted necks. Various volumes of a standard solution of P and enough benzene to make total volumes of 3.0 ml were added. The tubes were degassed by the freeze–pump–thaw method (3 cycles at $\leq 2 \times 10^{-4}$ Torr) and sealed under vacuum on a mercury free vacuum line.

Fluorescence spectra were obtained on a Perkin-Elmer Hitachi MPF-2A spectrofluorimeter at 26° by irradiating at λ_{max} of the 0–0 bands. Relative intensity ratios for fluorescence were measured by comparing the heights of emission maxima. Excitation spectra for each A were recorded by monitoring the intensities of the emission maxima as a function of excitation wavelength. Information pertinent to the Stern–Volmer plots derived from the data is summarized in Table I.

In our hands, no fluorescence attributable to triphenylphosphine was observed, even under conditions where strong phosphorescence was obtained. Solutions in cyclohexane at room temperature and in ether–isopentane–alcohol at −196° and room temperature were measured.

Singlet Lifetime Measurements. A TRW Model 31A nanosecond lifetime machine equipped with a deuterium excitation lamp and appropriate excitation and emission filters was used to measure the singlet lifetimes of all compounds except Ad and Af which were measured via the single photon counting technique. The degassed samples of A, prepared as before in sealed Pyrex tubes, were the same concentration as in the fluorescent quenching stud-

ies. The average of at least five determinations per tube is reported. Decay of the fluorescence intensities versus time, displayed as a stationary image on a Tektronix 556 dual-beam oscilloscope, appeared exponential. Due to practical considerations, it was not possible to measure the decay curves in the presence of triphenylphosphine. This would have allowed an alternate method to obtain k_q and an upper limit to be placed on the exciplex lifetime.[18]

Reduction Potentials of A. The half-wave reduction potentials of A were measured on a Sargent Model III polarograph using a Metrohn Herison E-510 potentiometer.

Measurements were performed at 25° under nitrogen on 10^{-3}–10^{-4} M solutions of A in deoxygenated acetonitrile containing 0.1 M dry tetraethylammonium iodide as the supporting electrolyte. The electrodes were a pool of mercury (reference) and dropping mercury (working). Internal resistances, measured with a Metrohn AG E-382 conductance meter, were found to be less than 300 Ω. No correction was applied. In all cases, at least the onset of a second wave was observed.[19]

It was not possible to measure the reduction potential of triphenylphosphine since waves due to reduction of solvent impurities began to appear at ca. −2.2 eV. Under different conditions, the half-wave potential was found to be −2.08 eV.[20]

Excited Singlet State Energies. The singlet energies of A were calculated from the crossing points of the normalized room temperature absorption and emission spectra in benzene solutions. Where vibrational structure was absent, the exciting wavelengths in the quenching studies (vide ante) were the crossing point values.

Results

The data are summarized in Table II. The apparent rate constants, k_q, were calculated by standard Stern–Volmer (eq 13) procedures; ratios of I^0/I (the intensity for fluorescence of A in the absence of P divided by the intensity at a given concentration of P) were plotted against the concentration of P. Least-squares fits of the data to straight lines gave the products of $k_q\tau_A$, where τ_A is the lifetime of A[1] in the absence of P. Since the τ_A values were measured independently (vide ante), k_q values were obtained.

Quenching cannot be attributed to ground state complexation between A and P since the first electronic absorptions of all A were unchanged in the presence of the maximum concentration of P employed in the quenching experiments. The extremely dilute concentrations of A diminish the possibility that self-quenching[21] can compete with quenching by P. Also, the shapes of the excitation spectra of A were unchanged in the presence of P and were similar to the absorption spectra of A. Unfortunately, no exciplex emissions were observed although the spectra were examined carefully from 350 to 700 nm.

McClure[22] has reported ^1E_P, the singlet excitation energy of P, to lie 110 kcal/mol above its ground state and more recently, the 0–0 emission band was found to be at 275 nm (104 kcal/mol).[23] We have been unable to repeat Dori's work and did not find fluorescence from P under a number of other conditions. The unstructured nature of the absorption spectrum requires that both absorption and emission spectra be employed to place the excited singlet energy accurately. We are squeamish about using either published number. However, since the ^1E_A are less than 76 kcal/mol and, almost certainly, ^1E_P is 25 kcal/mol higher, it is not critical that we know the exact excited energy of P; it is sufficient that ^1E_P is much greater than ^1E_A.

The major pathway for deactivation of A[1] by P does not appear to be product formation. The intensity if Aa, Ag, or Ak fluorescence was not changed noticeably when tubes employed in the quenching experiments and containing the maximum concentrations of P were irradiated by the spectrofluorimeter excitation lamp for 5 min. Also, in the irradiations conducted with a 450 W medium pressure lamp, the per cent of disappearance of A did not follow the per cent of A[1] quenched by P: at 0.19 M P, >99, 64, and 35%

Table II.[a] Data for Quenching of Fluorescence of Anthracenes by Triphenylphosphine

A	$k_q \times 10^{-9}$, M^{-1} sec^{-1} (in benzene)	$-E(A^-/A)$, eV vs. Hg (in CH$_3$CN)	^1E_A, eV (in benzene)	τ_A, nsec (in benzene)
a	11 (27)	0.30	2.87	15.2 (16.0)
b	5.1	0.84	3.02	15.9
c	3.9	0.86	3.03	2.5
d	3.7	1.04	3.14	0.65
e	2.5	1.01	3.03	12.3
f	1.9	1.20	3.15	6.5
g	2.2 (7.4)	1.46	3.24	4.1 (5.3)
h	0.47	1.47	3.16	11.6
i	0.11	1.48	3.05	13.5
j	0.36	1.47	3.17	6.8
k	0.060 (0.15)	1.44	3.00	15.5 (13.1)

[a] Numbers in parentheses refer to data obtained in acetonitrile solutions.
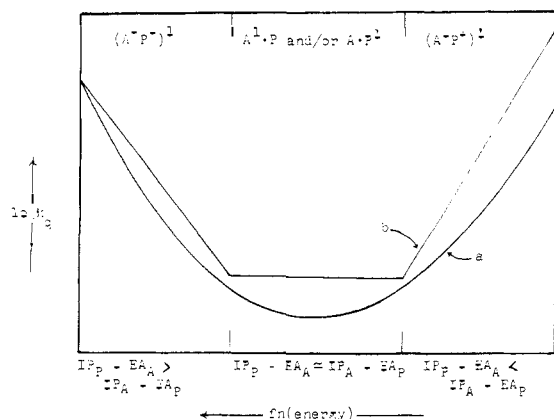

Figure 1.

Figure 2. Evans treatment of quenching data.

of the Aa, Ag, and Ak fluorescence is quenched, whereas after 125 min of irradiation, ca. 25, 45, and 35% of the Aa, Ag, and Ak were destroyed. The low rate of disappearance of A upon irradiation with the very intense medium pressure lamp is perhaps the strongest qualitative evidence against the importance of product formation in the fluorescence quenching.

Throughout this work, we have used half-wave potentials in place of the more difficult to obtain electron affinities. The proportional relationship between the two quantities has been demonstrated.[24]

Discussion

The quenching of Ag[1] by P had already been reported to proceed at close to diffusion controlled rates[25] when we began this study. By varying the substituents on A from strongly electron withdrawing groups to strongly electron donating ones, we hoped to obtain exciplexes in which IP$_P$ − EA$_A$ < IP$_A$ − EA$_P$, IP$_P$ − EA$_A$ ≃ IP$_A$ − EA$_P$, and IP$_P$ − EA$_A$ > IP$_A$ − EA$_P$. The inequalities should favor A$^-$P$^+$ and A$^+$P$^-$ type exciplexes, respectively, while excitation resonance stabilized exciplexes should be most probable when the equality obtains. If this were to occur, a plot of log k_q vs. fn(energy) should include three separate regions as depicted in Figure 1.[26] Curve a would be expected for a gradual change in mechanism (i.e., the exciplex is described well only if excitation resonance and both charge transfer structures are included as resonance contributors); curve b would indicate an abrupt change in mechanism (i.e., only charge transfer or excitation resonance structures are required to describe each exciplex well).

The existence of A$^-$X$^+$ exciplexes is well documented when X is diethylaniline or triethylamine[27] and the A$^+$X$^-$ type has been found when X is carbon tetrachloride.[28] Simi-
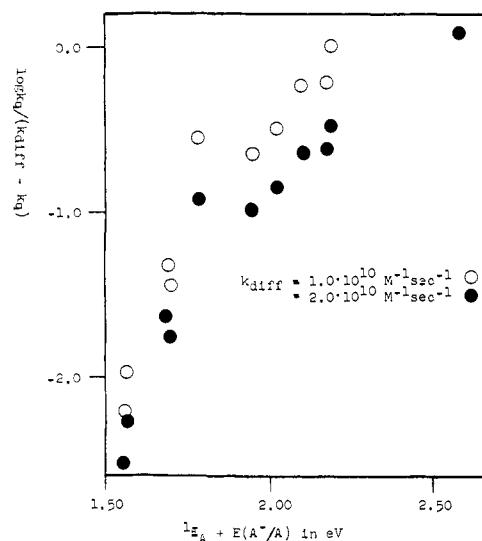
lar dependence of the quenching mechanism on the electronic nature of the quencher has been found with naphthalene, 1-methoxynaphthalene, and 1-cyanonaphthalene.[29]

In this work, substituents were placed only at the 9 or 9 and 10 positions of A since these have been shown to be the most reactive thermally,[30] electrochemically,[31] and photochemically.[32]

As can be seen from the data in Table II, k_q decreases steadily as the R$_1$ and R$_2$ groups on A become more electropositive. This is clearly inconsistent with any A[1] being quenched by a mechanism which includes an A$^+$P$^-$ type exciplex.[33]

In Figure 2, we have applied the treatment of Evans[4] to the quenching data. Since k_q of Aa is greater than k_{diff} as calculated from the Debye equation,[34] two plots using k_{diff} = 10^{10} and 2 × 10^{10} M^{-1} sec^{-1} have been constructed. In the former, Aa must be deleted. Both graphs show a fairly sharp change in slope occurring at Ag. A similar shape, but showing the change in slope more clearly, is obtained with the Weller[3] treatment (Figure 3). Similarly shaped graphs for log k_q vs. Hammett σ constants of R$_1$ and R$_2$[7] and for log k_q vs. quencher ionization potentials during fluorenone triplet quenching by substituted anilines in benzene[35] have been obtained. It is reasonable to ascribe the Aa–g lines to A$^-$P$^+$ charge transfer quenching; the strongly electronegative R$_1$ and R$_2$ should facilitate removal of an electron from P.

The Ag–k line, being of even higher positive slope, would appear to indicate A$^-$P$^+$ charge transfer quenching as well. However, if both lines represent electronically similar
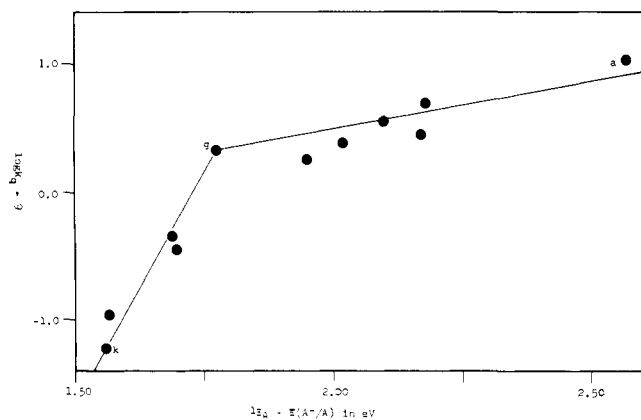
Figure 3. Weller treatment of quenching data.

Figure 4. Hammond treatment of quenching data.

mechanisms, they must differ in another property, like conformation[36] or a change from endothermicity to exothermicity in the electron transfer step.[3] While conformational changes cannot be eliminated rigorously, their *reason* for occurring in these experiments would, of necessity, be related to an electronic change; sterically, all of the A are very similar. If the variations were due to changes in the energy of an electron transfer step, the Ag-k slope (Figure 3) should be 0.73 kcal^{-1}; in fact, it is 0.31 kcal^{-1}.

The effect of changing solvent gives further evidence against Ag-k[1] being quenched by a charge transfer mechanism. The ratios of k_q in acetonitrile and benzene for Aa, Ag, and Ak are 2.5, 3.4, and 2.5, respectively. These are near the ratio of $k_{diff}^{acetonitrile}/k_{diff}^{benzene} = 1.7$, as calculated from the Debye equation,[34] and indicate that the contribution of solvent dielectric changes on the k_q's of Ag-k are small: $\epsilon_{acetonitrile}/\epsilon_{benzene} = 17$ at 20°. It is known that polar solvents greatly enhance the rates of charge transfer quenching. For instance, the ratio of the rate constants for pyrene fluorescence quenching by diethylaniline in acetonitrile and benzene is 14.[37] The low ratio with Aa is probably a consequence of k_q being at the diffusion controlled limit in both solvents. That the ratios for Ag and Ak are nearly equal is more difficult to explain in terms of charge transfer; were charge transfer important during the quenching step, the ratios should be different and much larger as a result of solvent dielectric effects.

In Figure 4, the Hammond treatment[5] yields a very good correlation between $\log k_q$ and ^1E_A for Ag-k. Both classical endothermic energy transfer (assuming P has a "phantom" excited singlet state lying much lower than 100 kcal/mol above its ground state) and excitation resonance exciplex formation are expected to yield positive linear slopes. However, were classical endothermic transfer occurring, the slope of the graph should be that predicted from the Arrhenius equation, 0.73 kcal^{-1} (i.e., $1/2.3kT$). The actual slope, 0.31 kcal^{-1}, clearly eliminates this possibility.[38] Thus, excitation resonance is the most probable explanation for P quenching of Ag-k fluorescence.

The fact that Weller and Evans' treatments for Ag-k data yield very good correlations even though charge transfer exciplex formation is not important in the rate determining step points out a potential problem in basing mechanistic conclusions solely on such methods. Perhaps, the exact nature of binding energies in nonfluorescing exciplexes will be elucidated only through flash spectroscopic studies like those of Ottolenghi.[39] In any event, the data clearly indicate that two distinct quenching mechanisms are operating in this system and that one of them is probably due to formation of an excitation resonance stabilized exciplex. While it is tempting to extrapolate these results to other aromatic
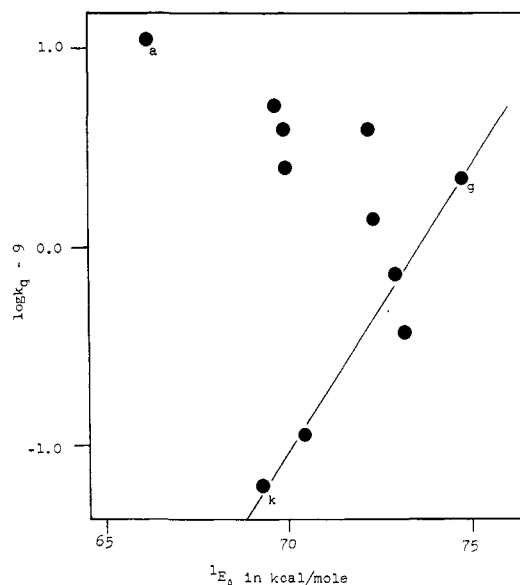
systems, we feel that insufficient data are available to warrant such speculation. For instance, there is no reason to believe that with other quenchers, a sudden change in mechanism will occur. We are presently investigating perfluorotriphenylphosphine and dimethylaniline as quenchers with A and will report the results in the future.[40]

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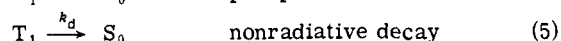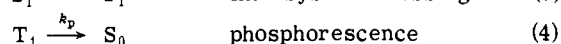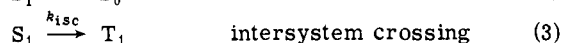# Photophysical Studies on the Benzophenones. Prompt and Delayed Fluorescences and Self-Quenching
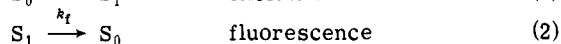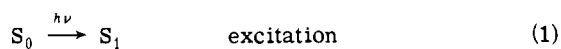
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Abstract: The photophysical pathways of benzophenone and several 4,4'-disubstituted benzophenones (fluoro, chloro, methyl, methoxy, dimethylamino) in benzene at room temperature have been investigated using time-resolved laser spectroscopy. Prompt fluorescence spectra are reported for benzophenone and 4,4'-difluoro-, 4,4'-dichloro-, 4,4'-dimethyl- and 4,4'-dimethoxybenzophenone. The relative prompt fluorescence and absolute phosphorescence quantum yields at room temperature in benzene are reported. Both thermal ($T_1 \leadsto S_1$) and P type ($T_1 + T_1 \rightarrow S_1 + S_0$) delayed fluorescence are documented for these ketones. From variable temperature data on the thermal delayed fluorescence, the singlet–triplet splittings are estimated to be: benzophenone, 4.9 ± 0.5 kcal/mol; 4,4'-difluoro-, 3.9 ± 0.4 kcal/mol; 4,4'-dichloro-, 4.1 ± 0.4 kcal/mol; 4,4'-dimethyl-, 4.5 ± 0.5 kcal/mol; 4,4'-dimethoxy-, 5.1 ± 0.5 kcal/mol. All of these ketones and also 4,4'-bis(dimethylamino)benzophenone are shown to undergo self-quenching ($T_1 + S_0 \rightarrow 2S_0(k_{SQ})$). The k_{SQ}'s vary from ca. 10^5 to 10^9 M^{-1} sec^{-1} and correlate well with σ_p^+, $\rho = -1.7$. It is proposed that self-quenching involves formation of an exciplex wherein the half-filled n orbital of T_1 is directed toward the π electron density of an aromatic ring of S_0.

The photophysical and photochemical processes in aromatic carbonyl systems have been investigated extensively.[2] In the last few years, studies using recently developed technology[3] have allowed a more complete deciphering of the photophysical pathways in these systems. In this regard, we wish to report our results of a study of benzophenone and several derivatives using nitrogen laser excitation in conjunction with an electronically gated detection system.[3g]

The typically important photophysical processes in organic systems in fluid media are:

$$S_0 \xrightarrow{h\nu} S_1 \qquad \text{excitation} \qquad (1)$$

$$S_1 \xrightarrow{k_f} S_0 \qquad \text{fluorescence} \qquad (2)$$

$$S_1 \xrightarrow{k_{isc}} T_1 \qquad \text{intersystem crossing} \qquad (3)$$

$$T_1 \xrightarrow{k_p} S_0 \qquad \text{phosphorescence} \qquad (4)$$

$$T_1 \xrightarrow{k_d} S_0 \qquad \text{nonradiative decay} \qquad (5)$$

Many aromatic aldehydes and ketones have large rates of intersystem crossing ($k_{isc} \approx 10^{10}$–10^{11} sec^{-1})[4] with result-

ing low quantum efficiencies for prompt fluorescence ($\Phi_f \lesssim 10^{-4}$).[5] Recently, for such systems, we[3g] successfully time resolved the prompt fluorescence from the total emission, and elucidated delayed thermal fluorescence (DTF) (thermal activation of $T_1 \leadsto S_1$)[6] and P type delayed fluorescence ($T_1 + T_1 \rightarrow S_1 + S_0$)[7] in solution at room temperature.

In this paper, we utilize our method of time-resolved laser spectroscopy[3g] to identify the above and other photophysical pathways in a series of substituted benzophenones. Our approach is particularly suited for this study because of the (i) high intensity (100 kW) and short duration (~8 nsec) monochromatic (3371 Å) source and the (ii) variable time gating and signal averaging capabilities of the detecting system which lead to increased sensitivity and time resolution capabilities.

Specifically, the present study includes the time resolution of prompt fluorescence from the total emission for benzophenone and 4,4'-difluoro-, 4,4'-dichloro-, 4,4'-dimethyl-, and 4,4'-dimethoxybenzophenone. Both DTF and P type delayed fluorescence are documented for all of the above ketones. The singlet–triplet energy splittings ($\Delta E_{S_1-T_1}$) for