

## FLUORESCENCE QUENCHING OF SUBSTITUTED ANTHRACENES BY TRIS(PENTAFLUOROPHENYL)PHOSPHINE<sup>†</sup>

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### Summary

Rate constants  $k_q$  for fluorescence quenching of eleven 9 and 9,10 substituted anthracenes ( $A_i$ ) by tris(pentafluorophenyl)phosphine (FP) are reported. Correlations of  $k_q$  with the electronic properties of  $A_i$  and FP reveal that  $A^+FP^-$  charge-transfer interactions are important in the quenching process for several of the  $A_i$ . No one quenching mechanism is able to explain all of the data. The quenching mechanism of anthracene, 9-methylanthracene and 9,10-dimethylantracene in benzene appears to lack a pathway available to anthracenes whose substituents contain a lone pair of electrons.

### 1. Introduction

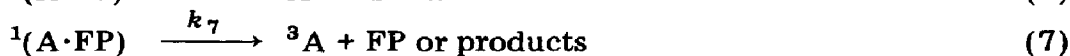
We have previously [1, 2] described the fluorescence quenching of eleven 9 or 9,10 substituted anthracenes ( $A_i$ ) by triphenylphosphine (P) and N,N-dimethylaniline (DMA) which proceeds via formation of exciplexes. Correlations between the observed quenching rate constants  $k_q$  and electronic properties of the  $A_i$  and quencher led to a number of conclusions concerning the mechanisms which are operative. It was shown that the degree of  $A^-X^+$  ( $X=P$  or DMA) charge-transfer character in the quenching steps increases with solvent dielectric and with the electron-withdrawing ability of the substituents on the anthracene rings. In some experiments, especially those conducted in benzene and with  $A_i$  containing electron-donating sub-

<sup>†</sup> A preliminary account of this work was presented at the 169th ACS National Meeting, Philadelphia, Pa., April 6 - 11, 1975, ORGN 12. Portions of this paper have been abstracted from the Ph.D. thesis of M. E. R. Marcondes, Universidade de São Paulo, São Paulo, Brazil, 1976.

stituents, the quenching mechanism appeared to involve exciplexes in which charge transfer is less important than excitation-resonance stabilization. However, in no case was it necessary to include  $A^+X^-$  charge-transfer contributions in order to describe the exciplexes adequately.

To determine whether further electronic modification of either  $A_i$  or quencher, without grossly altering the structure of either, can yield exciplexes in which the  $A^+X^-$  stabilization is evident, we have extended our study to include tris(pentafluorophenyl)phosphine (FP) as quencher. The choice of FP represents a logical extension of our previous work with P: FP and P contain a lone pair of electrons on their phosphorus heteroatoms (potential electron donors) and are similar in structure. However, the substitution of fluorines for the ring hydrogens of P should make FP a potent electron acceptor<sup>†</sup>.

Assuming a standard exciplex kinetic scheme like the following,



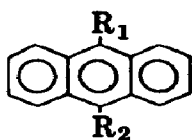
$$\frac{I_0}{I} = 1 + \frac{k_4(k_6 + k_7 + k_8)[FP]}{(k_5 + k_6 + k_7 + k_8)(k_2 + k_3)} = 1 + k_q\tau[FP] \quad (9)$$

$k_q$  can be determined conveniently via Stern–Volmer treatment of the fluorescence intensities in the absence ( $I_0$ ) and presence ( $I$ ) of FP (see eqn. (9)).

Since  $k_q$  is really a composite of several rate constants, determination of the dependence of each component rate constant on the solvent and the nature of the substituents on  $A_i$  would offer the maximum information. This type of analysis, although possible, is difficult, tedious and has been performed in only a limited number of cases (*e.g.* ref. 4 and references cited therein). Alternatively, conclusions can be drawn from the dependence of  $k_q$  on the electronic properties of  $A_i$  and FP. In this work we have followed the latter course in order to develop a structure–reactivity relation for the quenching mechanism. Our results demonstrate clearly that the trends of  $k_q$

<sup>†</sup>The electronegativities of H and F on the electrostatic scale are 2.1 and 4.1 respectively [3].

observed in the  $A_i$ -P or  $A_i$ -DMA systems [1, 2] are reversed when FP is the quencher.



$A_i$		
$i$	$R_1$	$R_2$
1	CN	CN
2	H	CN
3	Br	Br
4	H	Br
5	Cl	Cl
6	H	Cl
7	H	H
8	H	Me
9	Me	Me
10	H	OMe
11	OMe	OMe

## 2. Experimental

The methods, chemicals and apparatus are, for the most part, as described previously [1].

FP was synthesized by the method of Wall *et al.* [5]. The product, with melting point 109 - 114 °C (literature value [5], 116 - 117 °C), was obtained in 30% yield after sublimation at 3 Torr. Resublimation resulted in a white solid, with melting point 113 - 114 °C, whose UV spectrum (methanol) displayed  $\lambda_{\max} = 253$  nm ( $\epsilon = 10\,600$ ) and  $\lambda_{\min} = 240$  nm ( $\epsilon = 8960$ ) (literature values [5],  $\lambda_{\max} = 253$  nm ( $\epsilon = 10\,400$ ) and  $\lambda_{\min} = 241$  nm ( $\epsilon = 8900$ )).

Half-wave oxidation potentials of the  $A_i$  were measured with Sargent Model III and Model XV polarographs. Internal resistances in the solutions were less than 300  $\Omega$  in all cases. Acetonitrile solutions, containing  $10^{-2}$  -  $10^{-3}$  M  $A_i$  and 0.5 M dry sodium perchlorate as electrolyte, were thermostatted at 26 °C and were deoxygenated by bubbling dry nitrogen through the liquid. All measurements were performed in duplicate. The reference electrode was an Ag/AgNO<sub>3</sub> (0.1 M) couple and the working electrode was a platinum wire spun at 1800 rev min<sup>-1</sup>. The half-wave reduction potential of FP at 26 °C in a deoxygenated acetonitrile solution (0.1 M dry tetraethylammonium iodide as electrolyte) was found to be -1.15 V *versus* a mercury pool.

No new UV absorptions were observed when the  $A_i$  were mixed in benzene with the largest concentration of FP employed in the Stern-Volmer

TABLE 1

Data related to the quenching of  $A_i$  singlets by FP

$A_i$	$k_q \times 10^{-8} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$		$E(A^+/A)$ (V vs. Ag/Ag <sup>+</sup> in acetonitrile)	$\frac{k_q^i(\text{acetonitrile})}{k_q^i(\text{benzene})}$
	Observed <sup>a</sup>	Calculated <sup>b</sup>		
$A_1$	< 0.1		1.43	
$A_2$	0.42 (0.32)	17	1.14	0.8
$A_3$	2.5		1.08	
$A_4$	9.3		0.98	
$A_5$	1.1 (2.7)	46	1.04	2.5
$A_6$	7.0		0.97	
$A_7$	3.7 (49)	130	0.85	13
$A_8$	2.8		0.75	
$A_9$	4.0 (93)	130	0.69	23
$A_{10}$	14		0.65	
$A_{11}$	17 (43)	130	0.59	2.5

<sup>a</sup>Numbers in parentheses are from experiments performed in acetonitrile; all other rate constants were determined in benzene.

<sup>b</sup>According to the method of Weller [14] (eqn. (10)).

experiments. These same samples were irradiated in the sample chamber of our spectrophotofluorometer (Hg-Xe lamp) for 15 min at the excitation wavelengths corresponding to the 0,0 bands of the  $A_i$  employed in the Stern-Volmer experiments. The decreases in fluorescence intensities ranged from about 1% for  $A_7$  to about 5% for  $A_{10}$ .

All  $A_i$  excitations were at  $\lambda > 350$  nm, where FP absorption is almost zero. No emissions other than those from  $A_i$  were observed when degassed sealed benzene or acetonitrile solutions of  $A_i$  and FP were irradiated. Direct excitation of FP in degassed cyclohexane at ambient temperatures and in the absence of  $A_i$  resulted in no discernible emissions.

Correlation coefficients for slopes of Stern-Volmer plots constructed from the fluorescence quenching data were not less than 0.98 except for  $A_2$  in acetonitrile ( $r = 0.94$ ). Each plot comprised at least six data points.

### 3. Results and discussion

Rate constants  $k_q$  for the suppression of  $A_i$  fluorescence, half-wave oxidation potentials for  $A_i$  and other pertinent data not reported elsewhere [1, 2] are summarized in Table 1. The estimated errors in  $k_q$  near  $k_{\text{diffusion}}$  and much less than  $k_{\text{diffusion}}$  are  $\pm 20\%$  and  $\pm 40\%$  respectively. The fluorescence quenching of  $A_1$  by FP was insufficient to allow a  $k_q$  to be calculated. An upper limit of  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  was estimated based upon the sensitivity of our spectrophotofluorometer.

The trend of  $k_q$  to increase as the substituents on  $A_i$  become more electropositive as defined by Ingold [6] is incompatible with exciplex formation

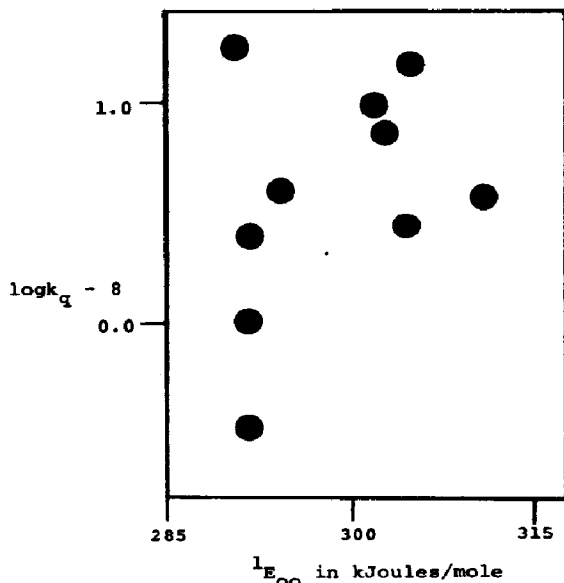


Fig. 1. Plot of  $\log k_q$  vs.  ${}^1E_{00}$  for  $A_i$  singlet quenching by FP in benzene.

in which  $A^- FP^+$  charge-transfer interactions are important: the  $k_q$  increase as the electron-donating ability of the  $A_i$  increases. Our previous studies with P and DMA as quenchers showed a completely different trend which indicated the lack of importance of  $A^+ P^-$  and  $A^+ DMA^-$  exciplex interactions.

Similar reversals in the charge-transfer character of quenching mechanisms have been observed by others when singlets of naphthalene derivatives are suppressed by carbon tetrachloride and diethylamine [7], when singlets of anthracene derivatives are intercepted by benzonitrile and anisole [8] or by 4,4'-dimethoxy-1,1-diphenylethylene and 4,4'-dinitro-1,1-diphenylethylene [9], and when triplets of benzophenone derivatives are quenched by substituted benzenes [10].

We have reported that the Hammett plot of  $\log (k_q'/k_q^7)$  versus  $\sigma$  for  $A_i$  fluorescence quenching by P has two positive  $\rho$  slopes [11]<sup>†</sup>. A Hammett correlation, employing FP as quencher, yields a reasonable fit to a single straight line whose slope is unmistakably negative:  $\rho = -1.15$  ( $r = 0.937$ );  $\rho^* = -0.78$  ( $r = 0.939$ ). While these results are of qualitative interest, especially with regard to the change of sign of the  $\rho$  slopes, we are reluctant to discuss them quantitatively since it is unclear whether or not ground state  $\sigma$ s can be applied directly to excited states<sup>††</sup>.

As has been noted by Hammond and coworkers [13], a correlation between  $\log k_q$  and the  $A_i$  singlet excitation energies  ${}^1E_{00}$  should exist for a series of exciplexes which are primarily excitation-resonance stabilized. The resonance contribution from excitation resonance will be a maximum when

<sup>†</sup>Two positive  $\rho$  slopes, similar in magnitude to those reported for P, are found when DMA is the quencher.

<sup>††</sup>This question is being investigated [12].

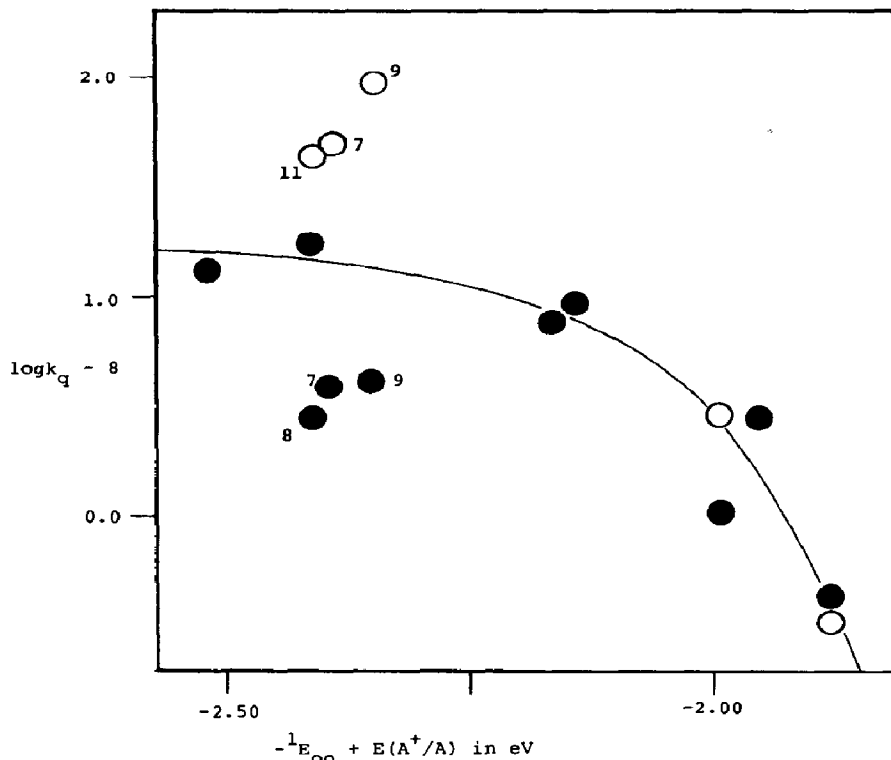


Fig. 2. Plot of  $\log k_q$  vs.  $-{}^1E_{00} + E(A^+/A)$  for  $A_i$  singlet quenching in benzene ( $\bullet$ ) and in acetonitrile ( $\circ$ ). An approximate best fit curve is drawn for the benzene points from  $A_i$  with substituents containing lone pairs of electrons.

charge-transfer resonance is minimized (*i.e.* in non-polar solvents). Figure 1 shows a plot of  $\log k_q$  versus  ${}^1E_{00}$  for the  $A_i$  being quenched by FP. As can be seen, no clear trend exists, although  $\log k_q$  appears to increase as  ${}^1E_{00}$  increases.

Weller's semi-empirical theory of fluorescence quenching via exciplex formation applies when  $A^+ FP^-$  charge-transfer interactions dominate [14]. The theory predicts that two limiting slopes should be observed when  $k_q$  (as  $\log k_q$ ), which varies from near  $k_{\text{diffusion}}$  to much less than  $k_{\text{diffusion}}$ , is plotted against  $-{}^1E_{00} + E(A^+/A)$ . Figure 2 shows such a plot for  $k_q$  obtained in benzene, a non-polar solvent ( $\epsilon = 2.28$ ), and in acetonitrile, a polar solvent ( $\epsilon = 38.8$ ). Since only five points in acetonitrile were obtained, no best fit line was attempted. At first glance the data in benzene do not appear to allow a reasonable best fit line. However, a curve whose shape is near that predicted [14] can be drawn for the seven points for which the substituents contain an unshared pair or electrons. The  $A_i$  ( $i = 7 - 9$ ) for which no unshared electrons are on the substituents fall far below the curve. That  $A_7 - A_9$  do exhibit  $k_q$  lower than "normal" is supported by the ratio of the  $k_q$  in acetonitrile and benzene (Table 1). Of the five ratios measured, only those of  $A_7$  and  $A_9$  are much larger than the value of 2.2 obtained for the self-diffu-

sion ratio of the solvents<sup>†</sup>. In addition, a plot of  $\log k_q$  (benzene) versus  $-{}^1E_{00} + IP_A$  (where  $IP_A$  is the ionization potential of the  $A_i$  (obtained from ref. 15)) for  $A_2 - A_{10}$  is similar in appearance to Fig. 2. The points for  $A_7 - A_9$  fall below the curve described by the other data. Thus, it appears that an important quenching pathway available to the other  $A_i$  in benzene is not operative in  $A_7 - A_9$ . Considering the differences between  $A_7 - A_9$  and the other  $A_i$  and the electrophilic nature of the quencher FP, it seems plausible that the unavailable pathway involves a substantial charge-transfer interaction between  $A_i$  and FP.

The data in acetonitrile indicate that the more polar solvent allows the charge-transfer quenching pathway (or another of equal efficiency) to occur with  $A_7 - A_9$ . The Weller theory [14] has predictive value in that  $k_q$  in acetonitrile can be calculated for an  $A^+ FP^-$  charge-transfer-dominated quenching process as follows:

$$k_q = \frac{20 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}}{1 + 0.25 \{ \exp(\Delta H^\ddagger / RT) + \exp(\Delta H / RT) \}} \quad (10)$$

$$\Delta H = E(A^+/A) - E(FP^-/FP) - {}^1E_{00} - e^2/\epsilon r \quad (11)$$

where  $\Delta H^\ddagger$  is the enthalpy of activation for step (8) in which the exciplex ( $A \cdot FP$ ) is depicted as an encounter complex and  $\Delta H$ , given in eqn. (11), is the thermodynamic enthalpy difference for the same step.  $\Delta H^\ddagger$  is approximated by a best fit equation in which  $\Delta H$  is the only variable. The coulombic term  $e^2/\epsilon r$  in eqn. (11) is approximated also since the distance  $r$  between  $A_i$  and FP at which electron transfer occurs is unknown. Previous work indicates that  $r \approx 6 \text{ \AA}$  (and  $e^2/\epsilon r \approx 0.05 \text{ eV}$ ) is appropriate [2, 16]. The calculated  $k_q$  (Table 1) do not agree well with the observed values when  $k_q \ll k_{\text{diffusion}}$ . The observed and calculated values do approach Weller's self-imposed difference limit of  $\pm 100\%$  when  $k_q$  is near  $k_{\text{diffusion}}$ .

Interestingly,  $A_7$ ,  $A_9$  and  $A_{11}$  seem to behave similarly in acetonitrile, both on the basis of Fig. 2 and of the proximity of their observed and calculated  $k_q$ . It would appear, then, that at least the singlets of  $A_i$  with electron-donating substituents are quenched by FP in acetonitrile by a predominantly charge-transfer mechanism. In benzene only those  $A_i$  whose substituents are electron donating and which contain lone pairs of electrons undergo quenching via a similar pathway.

While it is tempting to discuss further why  $A_7 - A_9$  do not react like the other  $A_i$  in benzene, the paucity of data makes a detailed analysis inappropriate and any further conclusions speculative at best. The results obtained thus far clearly demonstrate that neither excitation-resonance nor charge-transfer models alone can account for the quenching of all of the  $A_i$  by FP. The trend in the  $k_q$ s, to increase as the electron richness of the sub-

<sup>†</sup>The error in these ratios, especially for  $A_2$ , is potentially large. The trends, however, are unmistakable and beyond possible error.

stituents on  $A_i$  increases, is opposite that found when either P or DMA was quencher. The results discussed here, combined with those reported previously, clearly show that the electronic nature of a series of exciplexes comprising structurally similar quenchers and quenchees can be altered completely by altering the electronic properties of either component: a complete spectrum of exciplex types, varying from  $A^+X^-$  to  $A^-X^+$ , has been found.

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