

FLUORESCENCE QUENCHING OF ANTHRACENES BY N,N-DIMETHYLANILINE: A COMPARISON WITH QUENCHING BY TRIPHENYLPHOSPHINE†

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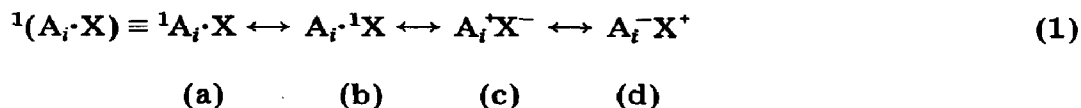
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Summary

Rate constants k_q for fluorescence quenching by N,N-dimethylaniline (DMA) of eleven anthracenes (A_i) substituted at the 9 or 9, 10 positions have been measured in benzene and acetonitrile. The results are compared with k_q obtained for the anthracenes with triphenylphosphine (P) as quencher. Emissions in benzene were observed for the exciplexes between DMA and $A_4 - A_{11}$. The data are correlated with physical constants for A_i , DMA, P and solvent according to the charge-transfer model of Weller and the excitation-resonance model of Hammond. It is shown that neither theory can explain all of the data. It is suggested that the A_i -DMA and A_i -P exciplexes may be of different geometries.

1. Introduction

The general electronic description of a singlet exciplex [1] $^1(A_i \cdot X)$ (X is the exciplex partner not excited initially) is given by [2]



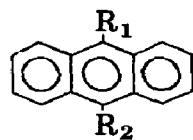
where the a and b pair and the c and d pair represent excitation-resonance and charge-transfer interactions respectively. While some exciplexes can be described primarily by c or d, accurate descriptions of others require the inclusion of a and b. In an attempt to determine the validity of the several theories for predicting the nature of a series of electronically dissimilar but sterically and geometrically similar exciplexes, we reported previously

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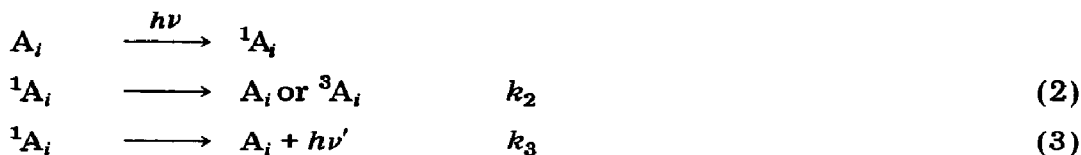
the rate constants k_q for fluorescence quenching of eleven anthracenes (A_i), with substituents at the 9 or 9, 10 positions, by triphenylphosphine P [3, 4]. It was shown that charge-transfer models [5] offer adequate descriptions of exciplexes between P and A_i with electron-withdrawing substituents. The singlet exciplexes between P and A_i with electron-donating substituents appeared more compatible with an excitation-resonance model [6]. In this paper we report results for quenching of A_i singlets by *N,N*-dimethylaniline (DMA) in benzene and acetonitrile and compare them with the data obtained from the A_i -P systems.

As noted earlier [3, 4] the series of A_i are well suited to systematic investigation of the electronic properties of exciplexes since each A_i singlet is structurally similar, described by similar wave functions and solvated similarly. On this basis the entropy of solvation for all of the A_i -DMA exciplexes should be similar as long as they are electronically similar and iso-structural[†].

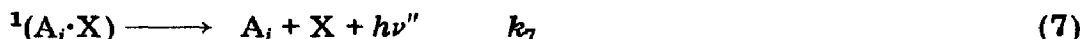
Of the A_i , only singlet exciplexes between amines and A_7 have been investigated in great detail. An important exciplex decay mode with primary or secondary amines is a reaction leading to addition products [8]. Exciplexes between singlets of A_7 and tertiary amines undergo charge-transfer interactions [9] (especially in solvents of high dielectric constants) which lead to triplets [10] of A_7 and radical ions [11]. A general mechanism for the quenching of A_i singlets by tertiary amines is presented in Scheme 1.

	A_i			
	$i =$	1	$R_1 = \text{CN}$	$R_2 = \text{CN}$
		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	

Scheme 1



[†]Exciplexes between some of the A_i and substituted benzenes have been studied recently [7].



Application of a Stern-Volmer treatment to the fluorescence quenching of the A_i according to Scheme 1 gives eqn. (8): the ratio I_0/I of the fluorescence intensities in the absence and presence of X is equal to the corresponding quantum yield ratio ϕ_f^0/ϕ_f ; $(k_2 + k_3)^{-1}$ is the lifetime τ of 1A_i ; $k_4(k_5 + k_6 + k_7)/(k_5 + k_6 + k_7) = k_q$, the observed rate constant for fluorescence quenching; $k_6 = k_{6a} + k_{6b} + k_{6c}$. Then

$$\frac{I^0}{I} = \frac{\phi_f^0}{\phi_f} = 1 + \frac{k_4(k_5 + k_7) [X]}{(k_5 + k_6 + k_7)(k_2 + k_3)} = 1 + k_q\tau[X] \quad (8)$$

2. Experimental

Methods, chemicals and equipment are, for the most part, as described previously [3]. DMA (Eastman, "monofree") was vacuum distilled several times at 2 Torr pressure and stored under nitrogen.

The A_i were irradiated at $\lambda > 350$ nm, where no correction for competitive DMA excitation is necessary. Uncorrected exciplex emission spectra were obtained at room temperature with solutions of about 10^{-4} M A_i in DMA in sealed Pyrex tubes of outside diameter 12 mm. Spectra of solutions containing A_1 , A_2 or A_3 and DMA displayed new bands attributed to ground state complexes. With benzene as solvent, isosbestic points between the fluorescence of the other anthracenes and their DMA exciplexes were observed.

Solutions of A_i and DMA in benzene irradiated for 10 min under conditions employed to measure the emission spectra (*i.e.* in the cavity of our spectrophotofluorimeter) lost less than 5% of their initial emission intensity.

Correlation coefficients for slopes of the Stern-Volmer plots constructed from the fluorescence quenching data are all above about 0.997.

3. Results

Rate constants k_q for the suppression of A_i fluorescence by DMA and P are summarized in Table 1. The k_q were calculated by Stern-Volmer

techniques, using previously measured singlet lifetimes [3][†]. We estimate the errors in k_q to be $\pm 20\%$ for k_q near $k_{\text{diffusion}}$ and $\pm 40\%$ for $k_q \ll k_{\text{diffusion}}$.

The addition of DMA to benzene solutions of $A_4 - A_{11}$ resulted in A_i fluorescence quenching and the appearance of a new broad red-shifted emission ascribed to the exciplex. Intensities of the new emission increased as the monomer fluorescence decreased. Wavelength maxima for the exciplex emissions, calculated by subtracting the monomer fluorescence from the spectra, are listed in Table 1 in column 6.

The half-wave oxidation potential of P *versus* an Ag/Ag⁺ reference electrode in acetonitrile has been found to be 1.00 V [13]. This value is in reasonable agreement with 1.09 V, the oxidation potential of P calculated [14] from its vertical ionization potential [15]. The half-wave oxidation potential of DMA *versus* a standard calomel electrode was taken to be 0.78 V [5]. Half-wave potentials were adjusted (where necessary) to make all of the electrochemical data refer to the same experimental conditions: acetonitrile as solvent and calomel as the standard electrode. To do so, +0.3 V was added to data obtained with Ag/Ag⁺ reference electrode and -0.5 V was added to potentials measured *versus* a mercury pool [16]^{††}. The singlet excitation energy of DMA, which is calculated from the intersection of its normalized absorption and fluorescence spectra (cyclohexane), is 3.9 eV [17].

4. Discussion

Qualitatively, the k_q measured with either DMA or P as quencher follow the same trend, the A_i with the more electron-withdrawing substituents being quenched more rapidly. This suggests that the quenching acts involve substantial charge transfer with the A_i singlets acting as electron acceptors. However, as has been noted previously, the rate constants for fluorescence quenching of aromatic hydrocarbons [18] or aromatic ketones [19] by group V quenchers do not always follow the order predicted from charge-transfer treatments (but see ref. 20).

A similar incompatibility with predominantly charge-transfer quenching has been observed in the suppression of aromatic singlets by alkyl disulphides [21]. Quenching of triplets of trisbipyridyl ruthenium(II) complexes by N-heteroaromatics can be accommodated by a charge-transfer

[†] Singlet lifetimes in acetonitrile, not reported previously, are $\tau_2 = 15.5$ ns, $\tau_8 = 7.8$ ns, $\tau_9 = 16.9$ ns and $\tau_{10} = 3.4$ ns.

^{††} The adjustment cited for mercury actually applies to dimethylformamide as solvent. However, half-wave potentials in acetonitrile and dimethylformamide should be similar. Support for this contention is found in the value $E(A_7^-/A_7) = -1.96$ V measured *versus* a standard calomel electrode in acetonitrile by Weller and coworkers [5] compared with $E(A_7^-/A_7) = -1.46$ V measured *versus* a mercury pool (tetraethylammonium iodide as the supporting electrolyte) by us [3, 4].

TABLE 1

Data associated with quenching of A_i singlets by DMA and P^a

A_i	DMA		$\Delta H^{d,e}$ (kJ mol ⁻¹)	λ_{max}^c (nm) in benzene	P ^b		$\Delta H^{d,e}$ (kJ mol ⁻¹)	
	$10^{-9} k_q$ (M ⁻¹ s ⁻¹) in benzene	$10^{-9} k_q$ (M ⁻¹ s ⁻¹) in acetonitrile			$10^{-9} k_q$ (M ⁻¹ s ⁻¹) in benzene	$10^{-9} k_q$ (M ⁻¹ s ⁻¹) in acetonitrile		
1	25.3				11	27	14	-84
2	18.8				5.1			
3	16.8				3.9			
4	16.6			532	3.7			
5	12.9			560	2.5			
6	12.2			537	1.9			
7	11.3	22.8	13	513(512.8)	2.2	7.4	4.7	-8
8	4.1	20.3	13	512(507.6)	0.47			
9	0.45	16.2	11	508(500)	0.11			
10	2.1	16.0	13	523	0.36			
11	0.71	16.0	11	515	0.06	0.15	0.06	+13

^a At 25 °C.^b Ref. 3.^c Exciplex emissions; the wavelengths in parentheses refer to the data in ref. 12.^d Ref. 6.^e Calculated free energy change for step (6c) of Scheme 1.

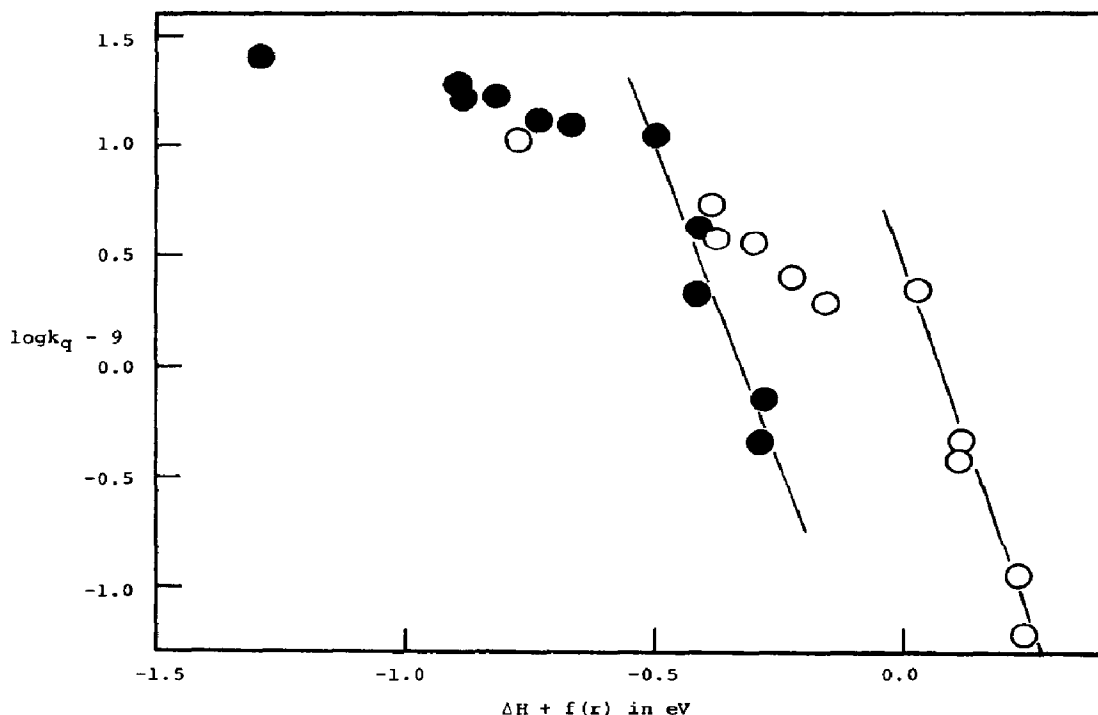


Fig. 1. Log k_q vs. $\Delta H + f(r)$ for quenching of 1A_i by DMA (●) and by P (○) in benzene. Line segments described by the quenching of singlets of $A_7 - A_{11}$ are shown.

model even though energy transfer is equally efficient [22]. The large endothermicity of electronic energy transfer from any singlet of A_i to DMA precludes its occurring at a rate competitive with exciplex formation.

The total free enthalpy change associated with reaction (6c) is given by [5]

$$\Delta H = -E(A^-/A) + E(X^+/X) - {}^1E_{00} - f(r) \quad (9)$$

where $E(A^-/A)$ is the half-wave reduction potential of A_i , $E(X^+/X)$ is the half-wave oxidation potential of X, ${}^1E_{00}$ is the 0,0 singlet excitation energy of A_i and $f(r)$ is a coulombic term. Although the slope from a plot of $\log k_{sc}$ versus ΔH is predicted to be a straight line, a similar plot of $\log k_q$ versus ΔH is not since k_q is a composite of several rate constants (eqn. 8). In Fig. 1 we have constructed a graph of $\log k_q$ versus $\Delta H + f(r)$ from data obtained with P and DMA in benzene solutions.

In a non-polar medium like benzene, $f(r) = e^2/er$ (where e is the electron charge, r is the ${}^1A_i-X$ separation at the moment of electron transfer and ϵ is the solvent dielectric constant) is large (since $\epsilon = 2.3$). Therefore, a part of the point scatter in Fig. 1 may be due to small variations in r . A careful examination of Fig. 1 shows that such a set of points can be accommodated

by two line segments[†]. Transposition of the P points by -0.4 eV brings the segments of higher slope into congruence. However, no single change in $\Delta H + f(r)$ can make the sets of points for P and DMA lie along one curve.

The work of Chuang and Eisenthal [25] suggests that electronic interaction between 1A_7 and DMA should occur when r is as large as 8 \AA^\ddagger . We expect that if reaction (6c) were occurring in benzene, a substantially smaller value of r would be appropriate. A small change from $r = 4 \text{ \AA}$ with P to $r = 5 \text{ \AA}$ with DMA would compensate for the lack of congruency between the two high slope segments of Fig. 1. All terms in ΔH other than $f(r)$ and the quencher half-wave oxidation potentials appear equally in both the A_7 -DMA and A_7 -P calculations and cannot therefore contribute to a non-systematic error in the ΔH calculations.[¶] Even if an error in the quencher half-wave potentials or a quencher-dependent variation in r exists, the data indicate that one charge-transfer model cannot explain the 1A_7 suppression by both DMA and P.

The trend that a given 1A_i is quenched more rapidly by DMA than by P can be accommodated by a number of hypotheses, *e.g.* (1) k_5 is larger with P than with DMA and (2) a component (or components) of k_6 is smaller with P than with DMA. Since the individual rate constants of k_q have been measured only for the A_7 -DMA exciplex [25 - 27], no comparison of these hypotheses for any A_j -DMA and A_j -P is possible. However, it is reasonable to assume that k_5 will increase[§] and that k_{6b} and k_{6c} will decrease as ΔH increases. This, in turn, will cause internal conversion (eqn. (6a)) and exciplex emission (eqn. (7)) to become more important. Both the absence of fluorescence from A_j -P exciplexes and their lower k_q relative to the corresponding A_j -DMA exciplexes suggest that $k_5/(k_6 + k_7)$ with P is greater than with DMA. The presence of emissions from the A_j -DMA exciplexes ($j = 4 - 11$) indicates, further, that k_7 cannot be much less than $k_5 + k_6$.

The semi-empirical charge-transfer model of Weller and coworkers [5] allows the shape of a plot like Fig. 1 to be calculated when the resonance structures c or d describe $^1(A_i \cdot X)$ primarily and when acetonitrile is the solvent. The model predicts a curve with two limiting slope regions and that k_q will approach $k_{\text{diffusion}}$ as reaction (6c) becomes increasingly exothermic.

We have measured a representative number of k_q for A_i singlets being quenched by DMA^{††} and P in acetonitrile (see Table 1). The ΔH for electron

[†] Others [23, 24], studying completely different exciplexes, have found parallel slopes for plots of $\log k_q$ versus ΔG .

[‡] In the work of Chuang and Eisenthal diethylamine was the exciplex partner of anthracene.

[¶] Application of half-wave reduction potentials measured in acetonitrile to experiments conducted in benzene is a systematic error which affects the abscissa of Fig. 1 but not the placement of points relative to one another.

[§] The possible role of k_5 influencing the observed static rate constant for fluorescence quenching has been discussed elsewhere [6, 28].

^{††} We assume that $A_1 - A_6$ singlets will be quenched by DMA at diffusion-controlled rates in acetonitrile. A_7 and A_8 singlets, which are predicted to be less efficient electron acceptors, have $k_q \approx k_{\text{diffusion}}$.

TABLE 2

Effects of medium on k_q

A_i 2	$k_q(\text{CH}_3\text{CN})/k_q(\text{PhH})$	
	P	DMA
1	2.5	
7	3.4	2
7		5
9		35
10		8
11	2.5	23

transfer were calculated as before, assuming an interaction distance between 1A_i and quencher of 6 Å and $f(r) = 6.3 \text{ kJ mol}^{-1}$.

The discrepancy between the k_q calculated from ΔH and the measured values are either within or close to Weller's self-imposed tolerance of $\pm 100\%$ for all of the data. Although the data are not extensive, they clearly show that in acetonitrile the k_q of the A_i -DMA and A_i -P exciplexes are affected similarly by variations in ΔH . From this it would appear that in acetonitrile fluorescence quenching of 1A_i by P and DMA occurs via charge-transfer-dominated pathways.

Comparisons between the k_q for a given exciplex in acetonitrile and benzene help to reveal further the nature of the quenching processes. It is known that the k_q of only certain types of exciplexes are sensitive to medium polarity (dielectric constant). For instance, the ratio of quenching constants for perylene singlets by DMA in acetonitrile ($\epsilon = 38.8$) and benzene ($\epsilon = 2.28$) is 12 [29], even though the ratio of their self-diffusion rate constants, as calculated from the Debye equation [30], is 2.2. However, piperylene quenching of naphthalene singlets is virtually insensitive to solvent polarity: the ratio of quenching rate constants in acetonitrile and n-hexane ($\epsilon = 1.9$) is 1.7 for the *trans* and 1.4 for the *cis* while the ratio of the self-diffusion constants for the two solvents is unity [6]. Various explanations, kinetic [28] and phenomenological [6, 29], have been advanced to explain these differences.

The ratios of the k_q in acetonitrile and benzene for several A_i -X are given in Table 2. Although the standard deviation for each ratio is large, the trends are unmistakable. The absence of a ratio significantly greater than predicted for self-diffusion in the A_i -P and A_7 -DMA pairs is reasonable since each $k_q \approx k_{\text{diffusion}}$. The remainder of the ratios contain at least one $k_q \ll k_{\text{diffusion}}$ and therefore will be near the self-diffusion ratio only if one of two kinetic conditions — that the important individual rate constants of k_q are insensitive to changes in the dielectric medium or that changes in solvent dielectric cause compensating changes in the individual components of k_q — is met. The improbability of the latter condition establishes the former condition as the probable explanation for the observations with the A_7 -P and

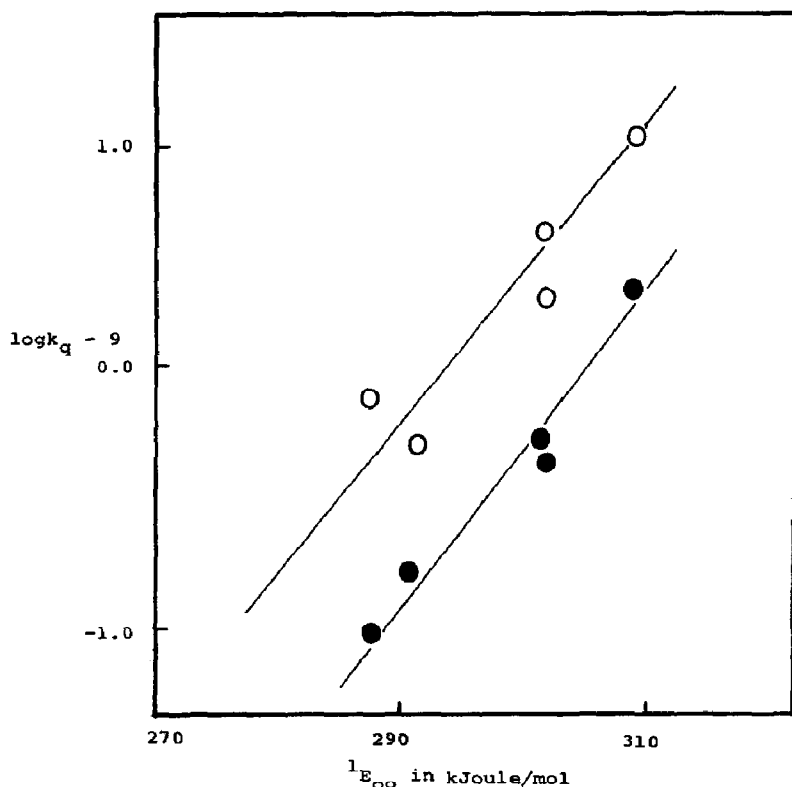


Fig. 2. $\log k_q$ vs. ${}^1E_{00}$ for quenching of ${}^1A_7 - {}^1A_{11}$ by DMA (\circ) and P (\bullet) in benzene.

A_{11} -P systems (and, by extrapolation, in the exciplexes between P and either A_8 , A_9 or A_{10}). This suggests that processes other than charge transfer are important in the quenching of A_i singlets by P. In contrast, the A_i -DMA exciplexes display solvent-dependent quenching behavior typical of other charge-transfer-dominated excited state complexes; the large ratios with $A_8 - A_{11}$ are consistent with a decreased efficiency of charge-transfer quenching in benzene without a corresponding increase in other quenching processes (e.g. eqns. (6a) and (7)).

The treatment of fluorescence quenching via exciplexes by Hammond and coworkers [6] predicts a linear correlation between $\log k_q$ and ${}^1E_{00}$ if excitation-resonance interactions are dominant. Presumably these would lead to enhanced internal conversion (eqn. (6a)). As seen in Fig. 2, excellent fits to straight lines are obtained from both P and DMA quenching of singlets of $A_7 - A_{11}$ in benzene. It should be noted that the near invariance of $E(A^-/A)$ for $A_7 - A_{11}$ allows a good correlation between $\log k_q$ and ${}^1E_{00}$ for both excitation-resonance and charge-transfer-stabilized exciplexes: when $E(A^-/A)$ is a constant, both the Weller and Hammond models predict that with one quencher $\log k_q$ will be directly proportional to ${}^1E_{00}$. Confirmation of this is found in the excellent correlations obtained between $\log k_q$ and $\Delta H +$

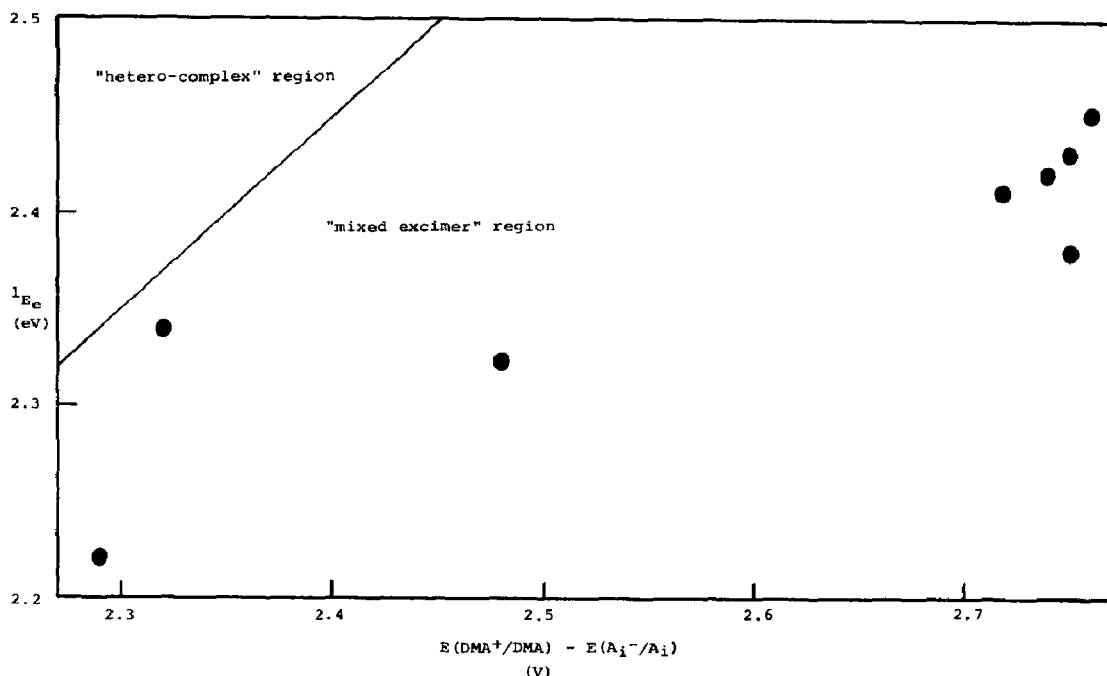


Fig. 3. Energy 1E_e of maximum emission vs. $E(\text{DMA}^+/\text{DMA}) - E(\text{A}_i^-/\text{A}_i)$ for exciplexes between DMA and $\text{A}_4 - \text{A}_{11}$ in benzene. The theoretical line between the "hetero-complex" and the "mixed-excimer" regions [31] is shown.

$f(r)$ for $\text{A}_7 - \text{A}_{11}$ in Fig. 1. When $k_q \ll k_{\text{diffusion}}$, Weller's treatment predicts that the slope of a graph between $\log k_q$ (acetonitrile) and ΔG will exhibit a slope equal to $-1/2.3kT$ ($= -0.2 \text{ kJ}^{-1}$). The slope obtained from $\text{A}_4 - \text{A}_{11}$ and P in acetonitrile can be approximated from either a two-point line or by assuming, as before, that the A_8 , A_9 and A_{10} exciplexes with P follow the order established by A_7 and A_{11} with P (*i.e.* the rate ratios for these exciplexes are near the self-diffusion ratios). Each method leads to a slope much lower in magnitude than $1/2.3kT$.

Thus, in acetonitrile we believe that charge-transfer interactions explain adequately all of the A_7 -DMA exciplexes but can explain only those exciplexes with P for which A_i contains an electron-withdrawing substituent. In benzene, charge-transfer-stabilized exciplexes seem to be formed with either P or DMA only when the A_i contain electron-withdrawing substituents while exciplexes between P and A_i with electron-donating substituents are described better by excitation-resonance structures a and b. The data discussed thus far do not allow a clear distinction between the predominantly excitation-resonance and charge-transfer models to be made for exciplexes between $\text{A}_8 - \text{A}_{11}$ and DMA formed in benzene.

Fortunately, their electronic nature can be explored further since DMA exciplexes with $\text{A}_4 - \text{A}_{11}$ emit in benzene solutions. The energy of fluorescence of a charge-transfer exciplex should be equal (within a solvent-

dependent constant) to $E(X^+/X) - E(A^-/A)$ [12, 31]. As excitation resonance structures a and b make increasingly important contributions to the exciplex stability, the energy of fluorescence becomes progressively less than the difference between the redox potentials of its constituents. Rehm and Weller [31] have established empirical limits for this correlation below which an excited hetero complex is considered a "mixed excimer". Figure 3 shows the correlation between the fluorescence of A_i -DMA exciplexes and their redox potentials. The area above the line represents the proposed "charge-transfer" region. As can be seen, all of the exciplexes fall within the "mixed-excimer" region. It would appear then that the A_i -DMA quenching mechanism in benzene must include substantial excitation-resonance interactions for at least the A_i with electron-donating substituents.

It is surprising that two quenchers as similar as P and DMA do not always quench the 1A_i at rates which are dependent solely on their electronic differences. Obviously, factors which have not been considered must be important. Among these are the shape of the quencher molecules and the availability of their electrons for donation. If, as has been assumed thus far, only macroscopic properties of A_i and X are important in the quenching process, then exciplex formation and decay should be free of orientational constraints. This has repeatedly been shown not to be the case [32 - 38]. Good evidence has been presented to indicate that the first electron ejected from triphenylamine during its adiabatic ionization resides in a π orbital [15]. Consistent with this, the pyrene-DMA exciplex has been shown to exist preferentially in a sandwich-like arrangement [33]. However, photoelectron spectroscopy indicates that an n electron is the first ejected from P [13 - 16], and a part of the lack of correlation between the ionization potentials of series of analogous group V quenchers and their rates of quenching of carbonyl triplets has been ascribed to large differences in the "availability" of lone-pair electrons on the quenchers' central atom [19]. This, coupled with the steric difficulty of a phenyl ring on P being both near and parallel to A_i , suggests that the A_i -P and A_i -DMA exciplexes differ in their preferred geometries at least when benzene is solvent. We suggest that the A_i -P exciplexes may have the phosphorus atom centered above the central ring of A_i and that the phenyl of DMA resides over the central ring of A_i in their exciplexes. While such a structural difference would be of little importance to charge-transfer exciplexes which form at large r in polar media, it may be a significant factor in determining the k_q of excitation-resonance-stabilized exciplexes.[†]

Thus the effect on Fig. 1 of a structural change between the P and DMA exciplexes would be to invalidate the use of one $f(r)$ for both quenchers and to require a variable entropy term in addition to ΔH . While

[†]The lack of correlation noted previously [18, 19] between k_q and group V quencher ionization potentials may also be due to quencher-dependent changes in exciplex structure.

the differences necessary to bring the two sets of line segments into partial congruence are calculated easily (see earlier), they cannot be shown to be valid with the available data.

5. Conclusions

Charge-transfer and excitation-resonance models have been considered for the exciplexes formed between either DMA or P and a member of the series of anthracenes A_i . Neither model alone is capable of accommodating all of the data. Whereas in acetonitrile the charge-transfer-based theory of Weller describes adequately all of the A_i -DMA exciplexes, it is consistent with only those exciplexes of P and A_i in which the anthracenes contain electron-withdrawing substituents. Satisfactory descriptions of the other A_i -P exciplexes in both acetonitrile and benzene, as well as exciplexes between DMA and A_i with electron-donating substituents in benzene, require the inclusion of excitation-resonance interactions. In general, there appears to be a gradual decrease in the importance of charge-transfer interactions as the electron-donating abilities of the substituents on A_i increase.

It is suggested that a part of the inconsistencies between the A_i -DMA and A_i -P exciplexes may be due to their preferred structures being different.

Acknowledgments

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