

the observed structure depends not only on the number of gauche interactions but also on the distance between the interacting groups. For these types of molecules, one must consider three types of interactions: (1) electron pair–electron pair, (2) electron pair–polar bond, and (3) polar bond–polar bond. From a comparison of the relative stabilities of the conformers of molecules of the type X_2Y_2 and X_2Y_4 , it has been concluded³³ that the electron pair–polar bond interactions are stabilizing for the X_2Y_4 molecules. The experimental dihedral angle in biphosphine is consistent with this stability.

In our observed gauche conformer, the dihedral angle between the nearest symmetry equivalent hydrogens is 18.7° leading to a dihedral angle from the cis conformation of 74.0° . This dihedral angle is very similar in value to the dihedral angles measured for other X_2Y_4 molecules of the group VA elements.¹³

The dipole moment is considerably larger than one would predict from a simple bond moment calculation.²⁴ The difference is presumably due to effects of the lone pairs. The experimental value of 0.92 D is considerably lower than the calculated value of 3.22 D reported by Cowley, *et al.*²⁸

It was not possible to obtain qualitative or quantitative information on the potential function governing

the internal rotation. First, the qualitative nature of the potential function is not known and is likely a mixture of $\cos \theta$, $\cos 2\theta$, and $\cos 3\theta$ terms. Secondly, the rotational transitions of the first excited state of the torsion could not be located, presumably because of the very large splitting.

In conclusion, it would appear that further quantitative structural determinations for these X_2Y_4 molecules are warranted, since the “gauche effect”³³ seems adequate to determine the symmetries of molecules whose structures have been determined. However, it should be pointed out that one predicts with this model the electron pair–electron pair interactions in these molecules to be stabilizing which is inconsistent with the usual qualitative concepts currently accepted. Simple MO calculations indicate³⁴ that molecules of the type $X_2Y_2Z_2$ should be exclusively trans on the basis of the orbital symmetries which was found to be the case for the phosphinodifluorophosphine molecule.²⁷ Thus, studies of these molecules may not provide as much information on the “gauche effect.”

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The Geometry of Intermolecular Aromatic Hydrocarbon–Dialkylaniline Exciplexes

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Abstract: The geometry of intermolecular aromatic hydrocarbon–*N,N*-dimethylaniline exciplexes was investigated by comparing the singlet quenching rate constants, exciplex energies, and heats of formation of the exciplexes formed upon quenching pyrene excited singlets by *N,N*-dimethylaniline (**1**) and 3,5-di-*tert*-butyl-*N,N*-dimethylaniline (**2**). The results are in accord with a sandwich-pair geometry for the **1** exciplex and a localized-pair geometry for the **2** exciplex in which the aromatic rings are adjacent but not parallel as in the sandwich-pair case. The dramatic second-order quenching behavior exhibited by **2** also is in accord with the localized-pair geometry. It is shown that about one-half of the exciplex binding energy can be attributed to localized interactions.

Studies of the fluorescence spectra of aromatic hydrocarbon crystals,¹ sandwich dimers,^{2,3} and intramolecular excimers^{4,5} have shown that a perfectly overlapping sandwich geometry is preferred for excimers which are stabilized by excitation resonance binding. Recent investigations of intramolecular aromatic hydrocarbon–amine exciplexes^{6,7} (both anilines and tertiary aliphatic amines) suggest that such specific geometries are not required when charge resonance provides the

major stabilizing interaction. It has generally been assumed that the sandwich-pair geometry is preferred for those intermolecular exciplexes in which both partners have π electrons, *i.e.*, aromatic hydrocarbon exciplexes with aromatic amines.⁸ This is reasonable if one looks at the nature of the highest occupied molecular orbital of the aniline quencher which acts as the electron donor in these polar exciplexes.

The initial photoelectron spectroscopic data for *N,N*-dimethylaniline and its derivatives were interpreted as having a π_3 , π_2 , n molecular orbital ordering^{9,10} due to the interaction of the lone-pair n electrons with the

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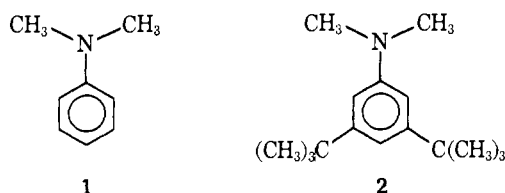
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π_3 degenerate orbital of the benzene ring. Another investigation has suggested the reverse ordering: n , π_2 , π_3 .¹¹ However, from the recent photoelectron spectroscopic data and calculations of Streets, Hall, and Caesar¹² on aniline and the phenylenediamines, it is clear that neither the first (highest) nor the third occupied orbitals can be assigned as either pure n or pure π ; the nitrogen lone-pair electrons are considerably delocalized into the ring. These results suggest that the sandwich-pair geometry should be preferred for charge-resonance stabilized exciplexes with these quenchers since orbital overlap would be maximized for such a geometry. On the other hand, the localized orbital description suggests that specific interaction at nitrogen should also be possible but that such an interaction should be somewhat less favored energetically since total overlap of the interacting orbitals would not be as great.

A test for localized interactions in intermolecular exciplexes would be to compare the singlet quenching rate constants, exciplex luminescence spectra and exciplex formation enthalpies for two *N,N*-dialkylaniline quenchers in which one of the quenchers contains substituent groups which sterically prohibit maximum π overlap. For our study we chose the interaction of excited pyrene singlets with *N,N*-dimethylaniline (**1**) and 3,5-di-*tert*-butyl-*N,N*-dimethylaniline (**2**). In the



latter compound the bulky *tert*-butyl groups effectively prevent π - π overlap with an aromatic hydrocarbon for the sandwich-pair geometry at the interaction distance thought to be preferred for excited state complexes (3.0–4.0 Å),^{13,14} since the sum of the van der Waals radii of the *tert*-butyl group (calculated as 3.9 Å from group increments to van der Waals volumes for the model compound neopentane¹⁵) and the 1.77-Å value for aromatic carbon exceed this preferred distance by about 1.7 Å. However, the *tert*-butyl groups are sufficiently removed from the nitrogen lone pair on **2** such that n - π overlap is not sterically prohibited. Thus if a localized interaction were possible one would expect similar quenching rate constants and emission maxima upon quenching by **1** or **2** and a lower enthalpy of formation for **2** if π - π overlap contributes to the stabilization of the exciplex.

Experimental Section

N,N-Dimethylaniline was distilled from calcium hydride under vacuum. 3,5-Di-*tert*-butyl-*N,N*-dimethylaniline was synthesized from 3,5-di-*tert*-butylbromobenzene¹⁶ by reaction with excess lithium dimethylamide in ether. The amine was isolated as the hydrochloride salt, mp 194–196°. Anal. Calcd for $C_{16}H_{23}ClN$:

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(12) D. G. Streets, W. E. Hall, and G. P. Caesar, *Chem. Phys. Lett.*, **17**, 90 (1972).

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(16) P. D. Bartlett, M. Rohm, and M. Stiles, *J. Amer. Chem. Soc.*, **76**, 2349 (1954).

C, 71.21; H, 10.45; N, 5.19. Found: C, 71.20; H, 10.48; N, 5.27. The free amine was regenerated from the salt by reaction with aqueous sodium hydroxide. The solution was extracted with ether and the combined extracts were washed with water and dried (Na_2SO_4). The ether was removed under high vacuum to give the desired amine **2** as an oil.

The structure of the amine was confirmed by nmr (CCl_4) τ 3.21 (t, 1 H, $J = 1$ Hz, para-aromatic proton), 3.47 (d, 2 H, $J = 1$ Hz, ortho-aromatic protons), 7.13 (s, 6 H, *N*-methyl protons), 8.75 (s, 18 H, *tert*-butyl protons). Solvents were Fisher Spectroquality grade. Zone-refined pyrene was maintained at a concentration of 2×10^{-6} M in all samples. Fluorescence spectra of degassed samples (four freeze-pump-thaw cycles at 1×10^{-4} Torr) were taken in Pyrex tubes using 334-nm excitation. The spectrometer employed has been previously described.¹⁷ Temperatures were controlled to $\pm 0.2^\circ$ using a variable temperature dewar having an inlet for cooled dry nitrogen and a heating element coupled to a Honeywell thermocontroller.

Results and Discussion

The Stern–Volmer quenching constants (k_q) were determined from the change in pyrene fluorescence intensity with quencher concentration [Q] using the Stern–Volmer equation (eq 1) and the reported pyrene

$$I_0/I = 1 + k_q\tau_s[Q] \quad (1)$$

fluorescence lifetimes (τ_s). The data summarized in Table I show that, in hexane, **2** is a slightly better

Table I. Stern–Volmer Quenching Constants and Exciplex Emission Maxima for Quenching Pyrene Fluorescence at 23° ^a

Quencher	Exciplex emission maximum, eV ^b	$k_q \times 10^{-8}$, l./msec	
		Hexane $\tau_s = 450$ nsec ^c	Acetonitrile $\tau_s = 270$ nsec ^c
1	2.85 ^{c,d}	1.0, 0.4 ^c	12, 10 ^c
2	2.78	6.4	14

^a Neither of the quenchers absorbed the exciting light for the concentration ranges used (10^{-1} – 10^{-5} M). ^b In hexane at 23° .

^c N. Mataga, T. Okada, and K. Ezumi, *Mol. Phys.*, **10**, 203 (1966).

^d N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970, p 437.

^e D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

quencher than **1** and forms an exciplex having a slightly lower energy luminescence maximum. Other studies of the effect of *tert*-butyl substituents on singlet quenching processes, presumed to proceed through exciplex intermediates stabilized by π - π overlap,^{18,19} have always noted a *reduction* in rate constant upon introduction of the bulky *tert*-butyl groups except for one case in which a conformational change was invoked to explain the small rate enhancement observed.¹⁸ Thus, the small rate enhancement found for **2** in hexane is more consistent with a localized interaction for this case.

Related to this is the fact that the quenching constants in the more polar solvent acetonitrile are almost identical for **1** and **2** and quenching occurs at approximately the diffusion-controlled rate. Since quenching in this medium is thought to occur by electron transfer over larger distances (7 Å) than in nonpolar media,²⁰

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(18) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(19) G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 1486 (1972).

(20) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

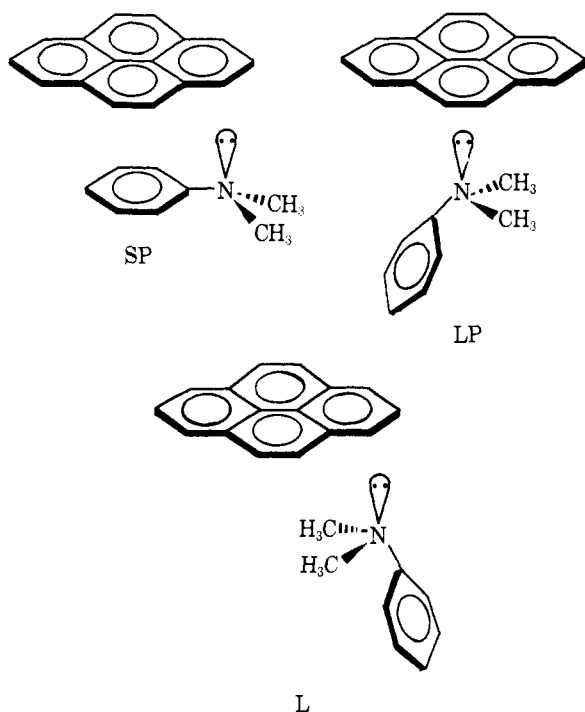
steric effects would be expected to be attenuated substantially, giving nearly identical quenching rate constants as is observed.

The exciplex energy, E_E , as characterized by the exciplex luminescence maximum, $h\nu_{\max}$, is a function of the energy of the pyrene first excited singlet state, E_S , the exciplex formation enthalpy, ΔH_E , and the ground-state repulsion, E_R , at the distance for maximum exciplex binding (eq 2). The substitution of *tert*-

$$E_E = h\nu_{\max} = {}^1E_S + \Delta H_E - E_R \quad (2)$$

butyl groups on the aniline nucleus is expected to affect E_E in two ways. In addition to the steric effects mentioned previously, the inductive effect of the *tert*-butyl groups is expected to change E_E . The inductive effect should lead to a decrease in the ionization potential of **2** by about 0.1–0.2 eV, making it a better donor. This enhanced charge-donating ability should be reflected in a more favorable ΔH_E as is observed for ground-state charge-transfer complexes.²¹ Although there are insufficient data to confirm such a trend for exciplexes stabilized by charge resonance interactions, it seems reasonable to expect a similar correlation. Therefore, for the three types of geometries discussed below, the inductive effect of the *tert*-butyl groups is expected to make ΔH_E more favorable (negative) and shift E_E to lower energies. This effect is then modified by the steric effects.

Several situations now present themselves, depending upon whether the pyrene-1 and pyrene-2 exciplexes adopt the sandwich-pair (SP), the localized-pair (LP), or localized (L) geometries. These geometries differ



in the contribution of π - π overlap to the total exciplex binding energy. The SP case has maximum π - π overlap due to the coplanar arrangement of the π -electron clouds. In the LP case π - π overlap is only possible at the aromatic carbon atom α to the amino group, and total π - π overlap would be less than in the

SP case. For the purely localized geometry (L) π - π overlap is not possible. For the case in which both exciplexes adopt the SP geometry (SP₁, SP₂) the steric bulk of the *tert*-butyl groups would hold the partners so far apart that there could be little orbital overlap and $\Delta H_E \approx 0$. Simultaneously, the E_R term would be somewhat increased. Overall, one would probably expect the enthalpy term to be more important and the emission maximum for **2** would be shifted to *higher* energy by a maximum of about 0.3 eV.

For the case where both exciplexes adopt the LP geometry, the energy of the **2** exciplex would be *lower* (by more than 0.15 eV) due to the lower ionization potential of **2** and a somewhat larger E_R term. For the L₁, L₂ case the E_R terms should be the same and E_E for the **2** exciplex would again be at *lower* energy because of the inductive effects of the *tert*-butyl groups. In this instance, however, the decrease in E_E would not be as great (~ 0.15 eV) as for the LP₁, LP₂ example.

Finally, we must consider the SP₁, LP₂ and SP₁, L₂ cases as it seems reasonable to exclude the LP₁, SP₂ and L₁, SP₂ cases on the basis of both steric and orbital overlap considerations. For the SP₁, LP₂ case the inductive effect of the *tert*-butyl groups should lead to a more negative ΔH_E for the **2** exciplex. This is counterbalanced by decreased total overlap relative to that available in SP₁. In addition, models suggest that the E_R term for LP₂ would be much larger than that for SP₁. The overall result is difficult to predict quantitatively but, as a first approximation, one might expect to see *little change* in $h\nu_{\max}$ in the exciplex with either **1** or **2**. For the SP₁, L₂ case approximately the same values for ΔH_E are expected, but the E_R values are much different. The E_R value for SP₁ should be greater than that for L₂, and the overall result would be a *higher* energy exciplex emission for the pyrene-2 exciplex.

The results in Table I reveal that the pyrene-2 exciplex has an emission maximum in hexane 0.07 eV lower than that for the pyrene-1 exciplex. These results seem most compatible with the SP₁, LP₂ case.

More concrete evidence for the localized-pair geometry lies in the heat of formation data since it should lead to a smaller but nonzero ΔH_E and a larger value of E_R for the **2** exciplex. We have found this to be the case. The emission spectra obtained upon quenching pyrene singlets by **2** (Figure 1) reveal a more complex behavior than that normally found. The isoemissive point characteristic of a 1:1 complex is not maintained upon quenching pyrene singlets with **2** in hexane at concentrations greater than 5×10^{-4} M. The slope of the Stern-Volmer plot also curves upward at concentrations higher than this value. Such behavior is indicative of another exciplex intermediate containing one molecule of pyrene and two molecules of di-*tert*-butyl-N,N-dimethylaniline. This interaction manifests itself further at higher quencher concentrations by distorting the luminescence curve, shifting the emission maximum to lower energy, and, finally, in decreasing the exciplex luminescence intensity. Mataga and coworkers²² have observed a somewhat similar effect for quenching by **1**, but in this instance the concentration required for the onset of second-order effects is greater than that for **2** by more than a factor of 100. These and our results

(21) R. Foster, "Organic Charge Transfer Complexes," Academic Press, New York, N. Y., 1969, p 211.

(22) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970, p 445.

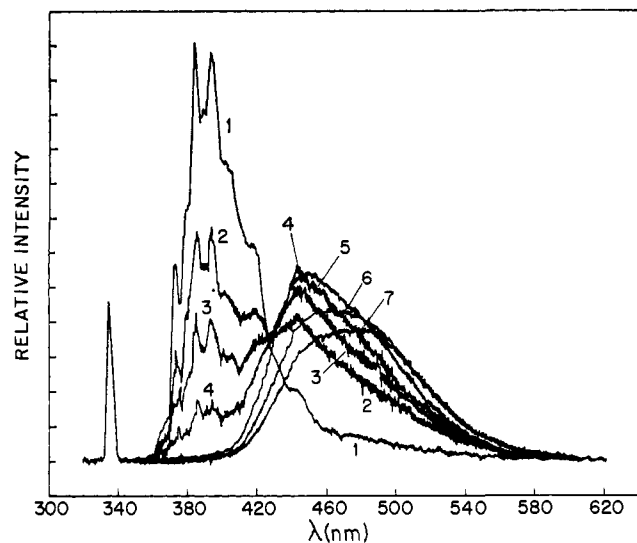


Figure 1. Quenching of pyrene ($2 \times 10^{-5} M$) fluorescence by *N,N*-dimethyl-3,5-di-*tert*-butylaniline. Quencher concentrations (M): (1) 0.0, (2) 3.67×10^{-4} , (3) 6.45×10^{-4} , (4) 2.02×10^{-3} , (5) 2.64×10^{-2} , (6) 1.06×10^{-1} , (7) 1.85×10^{-1} . The exciting light is observed as the sharp scattered mercury line at 334 nm.

are reminiscent of the findings of Chandross and Thomas²³ who observed that small dipolar molecules quenched the fluorescence of long-lived polar exciplexes often with the appearance of a new lower energy luminescence. They attributed such effects to formation of another exciplex stabilized by dipole-dipole and polarization interactions of the polar initial exciplex with the added dipolar solutes. It seems likely that a similar situation is also occurring with both 1 and 2. Since these solutes do not have large permanent dipoles we believe that the interactions, which are most dramatic for 2, arise primarily from polarization forces.

The difference in second-order quenching for 1 and 2 is most clearly demonstrated by the concentration dependence of their formation enthalpies determined by the method of Stevens and Ban²⁴ using eq 3, where I_E

$$\ln \frac{I_E}{I_M [Q]} = \frac{\Delta S_E}{R} - \frac{\Delta H_E}{RT} + \text{const} \quad (3)$$

and I_M are the exciplex and monomer emission intensities at fixed wavelengths, $[Q]$ is the quencher concentration, and the constant is the ratio of the exciplex (k_f') and aromatic hydrocarbon (k_f) fluorescence rate constants (k_f'/k_f). For a 1:1 interaction ΔH_E should be independent of concentration. From the data in Table II we note that, within the concentration range investigated, the *N,N*-dimethylaniline-pyrene exciplex has a concentration independent heat of formation of 8.2 ± 0.4 kcal/mol, which is consistent with a 1:1 interaction between the partners. However, the 3,5-di-*tert*-butyl-*N,N*-dimethylaniline-pyrene exciplex exhibits a marked change in formation enthalpy with increasing quencher concentration. This is evident from the data presented in Table II and the changes in the slopes of the Stevens and Ban plots presented in Figure 2. In fact for 2 the enthalpy becomes more negative (favorable) by a factor of 2 upon going from the lowest concentration investigated to $2 \times 10^{-3} M$ quencher.

(23) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971).

(24) B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, **60**, 1515 (1964).

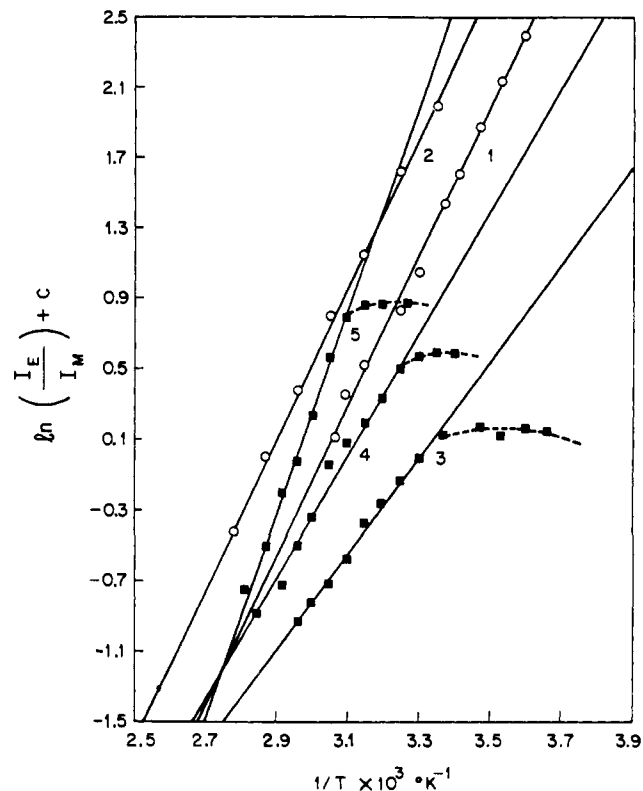


Figure 2. Plot of $\ln(I_E/I_M) + C$ vs. $1/T$ for pyrene excited singlets quenched by *N,N*-dimethylaniline (line 1, $2.48 \times 10^{-3} M$, and line 2, $1.46 \times 10^{-2} M$) and *N,N*-dimethyl-3,5-di-*tert*-butylaniline (line 3, $3.67 \times 10^{-4} M$, line 4, $6.45 \times 10^{-4} M$, and line 5, $2.02 \times 10^{-3} M$). The constant C has been arbitrarily adjusted in order to fit all of the data on one graph. I_E and I_M were measured at 374 and 460 nm, respectively.

Table II. Formation Enthalpies for Pyrene *N,N*-Dimethylaniline Exciplexes as a Function of Quencher and Concentration in Hexane^a

Quencher	Concentration, $M \times 10^3$	$-\Delta H_E^b$, kcal/mol
1	2.48	7.9 ± 0.2 Lit. 6.9^c
1	14.6	8.5 ± 0.5
2	0.367	5.6 ± 0.2
2	0.645	7.5 ± 0.3
2	2.02	10.9 ± 0.4

^a Intensities for the pyrene and exciplex luminescences were measured at 374 and 460 nm, respectively. For each temperature an emission spectrum was run for pyrene ($2 \times 10^{-5} M$) in the absence of quencher and the intensities were corrected for the overlapping of the two emission spectra. ^b Calculated by least-squares treatment of the data obtained from the linear portion of the curve for which a true equilibrium of the exciplex and its components was established. Entropies are not presented since the errors inherent in determining ΔH_E would constitute a significant fraction of the values. ^c T. Okada, H. Matsui, H. Oohari, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, **49**, 4717 (1968).

The difference in the structures proposed for the two exciplexes (SP₁, LP₂) is compatible with the observation that the 2 exciplex forms a 2:1 complex at lower concentrations than does the 1 exciplex. Presumably, in the SP structure of the 1 exciplex the lone pair interaction is responsible for a major portion of the binding energy, but further stabilization is gained through π -electron overlap which would facilitate the transfer of charge from the aniline to the pyrene. This overlap may be

viewed as a back donation of charge and would result in the delocalization of more of the positive charge into the benzene ring of the aniline than is possible for the LP geometry of the **2** exciplex. In the LP structure more of the positive charge is expected to be localized on the nitrogen atom. Consequently, one would expect the amine nitrogen atom to be more readily solvated by an additional Lewis-base molecule.

The heat of formation of the **2** exciplex should approach that of the 1:1 complex at the lowest concentrations provided that equilibrium is maintained. That this condition is in fact realized is indicated by the linearity of the high-temperature portions of the plots in Figure 2. At lower temperatures the departure from linearity (dashed line) indicates that this condition is no longer maintained. Equation 3 can be rewritten to show the dependence of the emission intensity ratios on the exciplex lifetime (τ_0') and the temperature-dependent rate constants for exciplex formation (k_1) and dissociation (k_2) which are given by eq 5 and 6.²⁵ Equilib-

$$\ln \frac{I_E}{I_M[Q]} = \text{const} + \ln \left[\frac{k_1 \tau_0}{1 + k_2 \tau_0'} \right] \quad (4)$$

$$k_1 = k_1^0 e^{-\Delta G_1/RT} \quad (5)$$

$$k_2 = k_2^0 e^{-\Delta G_2/RT} \quad (6)$$

rium is maintained when $k_2 \tau_0'$ is much greater than unity. Deviations from it indicate that $k_2 \tau_0'$ is approaching unity. When a point is reached where $k_2 \tau_0' \lll 1$, linearity will again be observed. In this case the sign of the slope in the plot of Figure 2 will be negative. In Figure 2 we observe that the onset of nonlinearity for the **2** exciplex occurs at higher temperatures when the concentration of **2** is increasing. At the same time the formation enthalpies are becoming more favorable, *i.e.*, the exciplex is more stable at higher concentrations of **2**. Taken together these effects suggest that higher concentrations reduce k_2 by interaction of the **2** exciplex with another quencher molecule.

(25) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970, p 415-419.

We have already noted that very high concentrations of 3,5-di-*tert*-butyl-*N,N*-dimethylaniline lead to significant changes in the emission spectra of the **2** exciplex (Figure 1). These changes can result from further interactions with more quencher molecules (3:1 and 4:1 complexes, etc.). However, if for analysis purposes we assume that the highest concentration formation enthalpy for the **2** exciplex is more representative of the enthalpy of a 2:1 complex while the lowest value is most representative of a 1:1 complex, we can estimate from the enthalpy difference what the increase in binding energy might be for interaction with a second molecule of quencher. This difference is about 5 kcal/mol which is reasonable for the interaction of a Lewis base with a positive center.

Returning to the question of the sandwich-pair *vs.* a localized geometry for the pyrene-**2** exciplex, we again note that the localized-pair geometry would be expected to have a somewhat less favorable enthalpy of formation, due to decreased total overlap, and a larger ground-state repulsion term. Again taking the lowest concentration value in Table II as being exemplary of the heat of formation for the 1:1 pyrene-**2** exciplex, we observe that this exciplex is approximately 2 kcal/mol less stable than the pyrene-**1** exciplex. Allowing for the inductive effect of the *tert*-butyl groups, the destabilization is probably closer to 4 kcal/mol. The repulsion energies calculated from the ΔH_E values, the pyrene singlet energy, and the emission maxima are 3.2 kcal/mol and 7.4 kcal/mol, respectively, for the **1** and **2** exciplexes. These results are again most consistent with the sandwich-pair geometry for the pyrene-**1** exciplex and the localized-pair geometry for the pyrene-**2** exciplex. Furthermore, they suggest that approximately half of the binding energy for exciplexes formed by collision of aromatic hydrocarbon excited singlets and *N,N*-dialkylanilines results from the localized interaction and that π - π overlap, in cases where it is not sterically prohibited, provides an additional contribution to the binding energy. The sandwich-pair structure expected on the basis of simple qualitative considerations of overlap is indeed that preferred by the pyrene-dimethylaniline exciplex.