The Quenching of Aromatic Hydrocarbon Fluorescence by α,ω-Diaminoalkanes and the Formation of Excited Ternary Complexes

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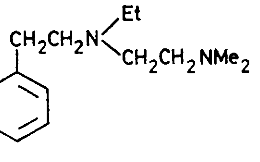
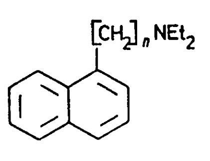
Summary The quenching of the fluorescence of aromatic hydrocarbons in cyclohexane by *NNN'N'*-tetra-alkyl-α,ω-diaminoalkanes is extremely efficient and is dependent on chain length; in certain cases fluorescent ternary complexes are formed and in the case of (**1**) a truly intramolecular excited ternary complex is produced.

The quenching of the fluorescence of aromatic hydrocarbons by aliphatic and aromatic amines and the related subject of exciplex formation is well documented.[1,2] It is known that in these bimolecular systems, formation of fluorescent exciplexes is preceded by the reversible formation of an encounter complex. We now report that *NNN'N'*-tetra-alkyl-α,ω-diaminoalkanes quench the fluorescence of aromatic hydrocarbons[3] with extraordinary efficiency and in some cases fluorescence from excited ternary complexes (*i.e.* complexes involving the interaction of three groups) can be detected. In the case of (**1**) an intramolecular excited ternary complex is produced.



(1)



(2) *n* = 2
(3) *n* = 4

The rate constants for quenching of the fluorescence of naphthalene in cyclohexane solution by *NNN'N'*-tetraethyl-α,ω-diaminoalkanes are given in Table 1. In all cases the rate constants are substantially higher than those for quenching by triethylamine. Examination of the fluorescence emission from these systems shows that for the amines having $n = 2$–4, exciplex emission is less efficient than that for triethylamine whereas for $n \geqslant 5$ it is enhanced (see I_E/I_M† values in Table 1). Another feature which can be seen from the emission spectra (Figure 1 and Table 1) is that the wavelength of the maximal excited complex fluorescence for diamines having $n = 2$ or 3 is to the red of the emission from the exciplexes observed for $n \geqslant 5$.

Table 1. Rate constants for the quenching of naphthalene fluorescence by diamines. Wavelengths at which maximal emission from the exciplexes occurs and I_E/I_M values (all values for degassed cyclohexane solutions at 20 °C).

n	$10^{-9} \times k_q$/ (l mol^{-1} s^{-1})	λ_{max}/nm exciplex	I_E/I_M (for $1{\cdot}5 \times 10^{-2}$M amine)
	$\mathrm{Et_2N[CH_2]_nNEt_2}$[a]		
2	6·1	415	0·1
3	6·1	413	0·3
4	6·05	410	0·26
5	5·8	410	0·47
6	4·0	408	0·85
7	4·3	407	0·89
8	4·2	407	0·84
10	4·45	406	0·9
		$\mathrm{CH_2[CH_2]_3N[CH_2]_nN[CH_2]_3CH_2}$[b]	
2	5·9	425	0·5
3	5·7	435	0·48
8	6·0	414	1·2
		$\mathrm{CH_2[CH_2]_4N[CH_2]_nN[CH_2]_4CH_2}$[c]	
3	3·5	421	0·2
8	2·1	410	0·4

[a] Values for $\mathrm{Et_3N}$: k_q $1{\cdot}9 \times 10^9$; λ_{max} 406; I_E/I_M 0·4. [b] Values for *N*-methylpyrrolidine: k_q $3{\cdot}2 \times 10^9$; λ_{max} 411; I_E/I_M 0·82. [c] Values for *N*-methylpiperidine: k_q $0{\cdot}3 \times 10^9$; λ_{max} 410; I_E/I_M 0·06.

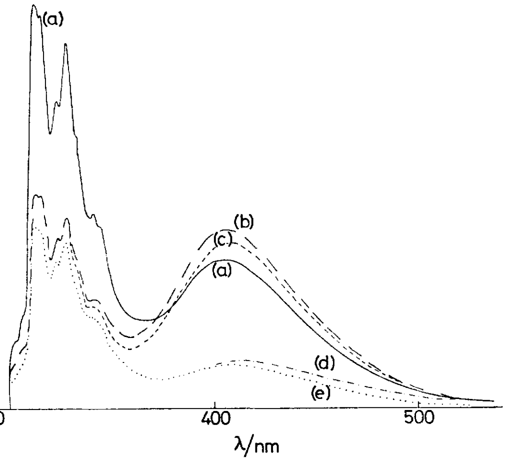


Figure 1. Quenching of the fluorescence of naphthalene in degassed cyclohexane solution by amines ($1{\cdot}5 \times 10^{-2}$M): (a) triethylamine; (b) 1,10-*NNN'N'*tetraethyldiamino-decane; (c) 1,6-*NNN'N'*-tetraethyldiaminohexane; (d) 1,3-*NNN'N'*-tetraethyldiaminopropane; (e) 1,4-*NNN'N'*-tetraethyldiaminobutane.

The quenching efficiency of an amine is crucially dependent upon the efficiency of formation (rate constant k_1) and reversal (rate constant k_{-1}) of encounter complex formation and upon the efficiency with which this complex decays to an emissive complex, radical ions, triplet states, and products [equation (1)]. When the quenching involves

$$\mathrm{ArH}^* + \mathrm{Am} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Encounter complex}}{(\mathrm{ArH}\text{ - - - }\mathrm{Am})^*} \rightarrow \underset{\text{Fluorescent exciplex}}{(\mathrm{ArHAm})^*} \qquad (1)$$

α,ω-diaminoalkanes there is the possibility that either formation of an encounter complex involves the hydrocarbon and both amino groups or that encounter complex formation occurs involving only one of the amino groups. If the latter is the case, dissociation of the complex will generate the excited aromatic hydrocarbon in the

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† I_E/I_M refers to the ratio of the intensity of the complex emission to that of the monomer emission when the naphthalene is photoexcited in the presence of the amine at the stated concentration.

vicinity of a second amino group with which it can interact and so reform the encounter complex [equation (2)].

$$\begin{tikzcd}
\mathrm{ArH^* + Am^1 \sim Am^2} \arrow[r] & \mathrm{(ArH \text{ - - - } Am^1 \sim Am^2)^*} \arrow[d] \\
\mathrm{(ArH \text{ - - - } Am^2 \sim Am^1)^*} \arrow[u] & \mathrm{ArH^* + Am^2 \sim Am^1} \arrow[l]
\end{tikzcd} \quad (2)$$

Even if the first reformation of the encounter complex fails to lead to fluorescence quenching or fluorescent exciplex formation, further collisions to reform the encounter complex are highly probable. Thus, the quenching efficiency by the diamino compounds may often exceed the statistical factor of two and we use the term multi-collisional quenching to describe this process.

We attribute the high I_E/I_M values for the diamines having $n \geqslant 5$ as being due to the multi-collisional process. Quenching by the diamino-ethanes, -propanes, and -butanes is also extremely efficient, but in these systems the I_E/I_M values are lower than for the triethylamine–naphthalene system. It is probable that in these systems, the second amino group in the diaminoalkanes can interact with either the initially formed encounter complex or fluorescent exciplex, thus resulting in ternary complex formation. The ternary complex species will be of lower energy than the initially formed encounter complex and therefore reformation of the fluorescent hydrocarbon is less likely. This will not only increase the efficiency of quenching but also bring into question the relative efficiencies for fluorescent excited ternary complex and exciplex emission. Our measurements indicate that excited ternary complex formation lowers the quantum yields for fluorescent excited complex formation and this is not surprising when one considers that ternary complexes are more likely to undergo radiationless decay by dissociation than are binary complexes.[4]

The fluorescence emission for complexes formed between the naphthalene and *NNN'N'*-tetraethyl-α,ω-diamines having $n = 2$ and $n = 3$ show a slight red shift compared with those for the diamines having $n \geqslant 5$, and also triethylamine. We consider that the observed broad structureless emissions (see Figure 1) may be due to emission from both exciplex and excited ternary complexes. Examination of several α,ω-diaminoalkanes having $n = 2$ and 3 revealed that α,ω-*NN'*-dipyrrolidinyl- and *NN'*-dipiperidyl-alkanes produce excited complexes which emit to the red of the normal exciplexes (see Figure 2 and Table 1).

We suggest that much if not all the emission from these complexes arises from excited ternary complexes. Unfortunately steady state measurements do not allow us to state categorically that the emission arises solely from the excited ternary complexes. The observation that the emission spectra have the same shape in both degassed and aerated solutions is evidence in favour of the emission coming solely from one species.[5] The wavelength of emission from the complexes is solvent dependent. Increasing the polarity of the solvent shifts the position of maximal emission from the complex to the red. This observation shows that the complexes have charge transfer character and that the excited ternary complex is more likely to have an unsymmetrical rather than a symmetrical structure.[6]

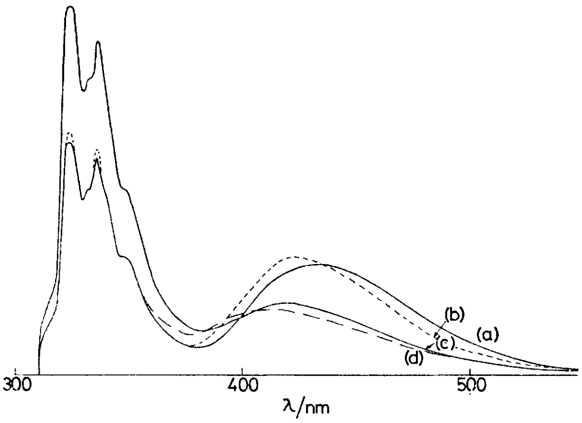

FIGURE 2. Quenching of the fluorescence of naphthalene in degassed cyclohexane solution by amines ($1{\cdot}5 \times 10^{-2}$M): (a) 1,3-*NN'*-dipyrrolidinopropane; (b) 1,2-*NN'*-dipyrrolidinoethane; (c) 1,3-*NN'*-dipiperidinopropane; (d) 1,3-*NNN'N'*-tetraethyldiaminopropane.

In order to favour excited ternary complex formation compound (**1**) was prepared and its fluorescence properties examined (Table 2).

From Table 2 it can be seen that for (**1**) the quantum yield of exciplex fluorescence is lower than that for (**2**). This is not due to the inability of the amino-groups in (**1**) to quench the fluorescence of the naphthalene unit since the emission spectra of (**2**) show hardly any fluorescence from the naphthalene unit. Another feature of the fluorescence spectrum of (**1**) in cyclohexane and benzene is that emission from the complex is to the red of the emission from the complex of (**2**). This is to be expected if an excited ternary complex is formed. Excited ternary complex formation also accounts for the low quantum yield of fluorescence complex formation in (**1**). It is anticipated that the excited ternary complex will be relatively more stable than the conventional intramolecular exciplex by a relatively small factor[7] and therefore the observable broad emission from (**1**) may be due to contribution from exciplex and excited ternary complex. The shape of the broad emission from (**1**) in cyclohexane is the same in aerated and degassed solutions and this indicates that the emission is due to one species, this being the excited ternary complex.[5]

TABLE 2. Quantum yields[a] for fluorescence from the naphthalene unit (M) and exciplex (E) for compounds (**1**)—(**3**)

Compound	Cyclohexane		Methylcyclohexane		Benzene		Acetonitrile		Dichloromethane	
	M	E	M	E	M	E	M	E	M	E
(**1**)			0·006	0·05	0·007	0·02	0·005	—	0·034	0·0075
(**2**)	<0·001	0·41			<0·001	0·22	0·008	0·04		
(**3**)	0·03	0·034					0·009	0·002		

[a] Determined by use of 1-methylnaphthalene as standard

A particularly interesting feature of (**2**) and (**3**) is that emission from the exciplexes can be observed when acetonitrile is used as solvent. In the case of (**1**) no such emission can be observed in polar solvents such as acetonitrile. This lack of emission is probably due to more than one cause which includes the greater probability of quenching by electron transfer in (**1**) compared with (**2**) and the enhanced favourability of radiationless decay of excited ternary complexes compared with binary complexes.

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