Fluorescent Excimer Formation by α,ω-Diaminoalkanes and Related Compounds

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The fluorescence properties of a number of α,ω-diaminoalkanes have been studied in which the amino groups include diethylamino, pyrrolidino, piperidino, and morpholino residues. Intramolecular excimer formation was usually observed when di- and tri-methylene chains separated the amino groups. α,ω-Dimorpholinoalkanes having chain lengths of varying size between the morpholino groups, exhibited fluorescent excimer formation. Owing to the high concentrations employed it could not be ascertained whether the emission was the result of inter- or intra-molecular complex formation. In all cases the excimer fluorescence was considerably red shifted by a change of solvent from cyclohexane to tetrahydrofuran. This solvent dependency leads to the conclusion that amine excimers have some charge-transfer character.

Halpern and co-workers have shown that many cage tertiary amines, *e.g.*, 1-azabicyclo[2.2.2]octane and 1-aza-adamantane, form fluorescent excimers in the vapour phase and in non-polar solvents (*e.g.*, n-hexane).[1,2] Other cage amines, often possessing a less rigid structure, display concentration quenching but this is not attended by the formation of a fluorescent excimer,[3] *e.g.*, 1-azabicyclo[3.3.3]undecane.

Not surprisingly the fluorescence of many acyclic amines is subject to concentration quenching[2] and this also does not result in fluorescent excimer formation. However, some α,ω-dimethylaminoalkanes show intramolecular fluorescent excimer formation in both the solution[4] and vapour state.[4,5] In the light of earlier work on intramolecular excimers and exciplexes,[6] it is not surprising to find that the intramolecular amine complex formation is highly favoured when a trimethylene unit links the amino groups. An intriguing aspect of these fluorescent excimers is the nature of their binding. The binding energies (in n-hexane) of 1-azabicyclo[2.2.2]octane and 4-methyl-1-aza-bicyclo[2.2.2]octane have been determined and found to be *ca.* 11.4 and 10.2 kcal mol⁻¹, respectively. The large negative entropies of formation for the excimers (*ca.* −17 and *ca.* −19 e.u., respectively) imply a rather tight and discrete conformation for the excimer. Spectroscopic data suggests that the binding cannot be due to a dipole–dipole (exciton resonance) interaction. Binding *via* a coulombic interaction between the excited and ground-state species was ruled out on the basis that application of equation (1) would require the amine to have an

$$W_R = I - A - C(r) \qquad (1)$$

unacceptably high electron affinity (> +1.7 eV) where W_R = stabilisation energy, I and A = ionisation potential and reduction potential of the amine, respectively, and $C(r)$ = coulombic interaction between the radical ions at a separation r between the point charges. However, equation (1) takes no account of the fact that the excited amine will have an electron affinity that far exceeds that of the ground-state amine. We now report that a number of α,ω-diaminoalkanes exhibit intramolecular excimer formation, and fluorescence quenching, and also the observation that the wavelength for maximum intensity of the excimer fluorescence is highly solvent dependent, indicating that the complexes have some charge-transfer character.

Results

A series of *N,N,N',N'*-tetraethyl-α,ω-diaminoalkanes was examined in cyclohexane solution. Some of the fluorescence spectra obtained are shown in Figure 1 and values of their
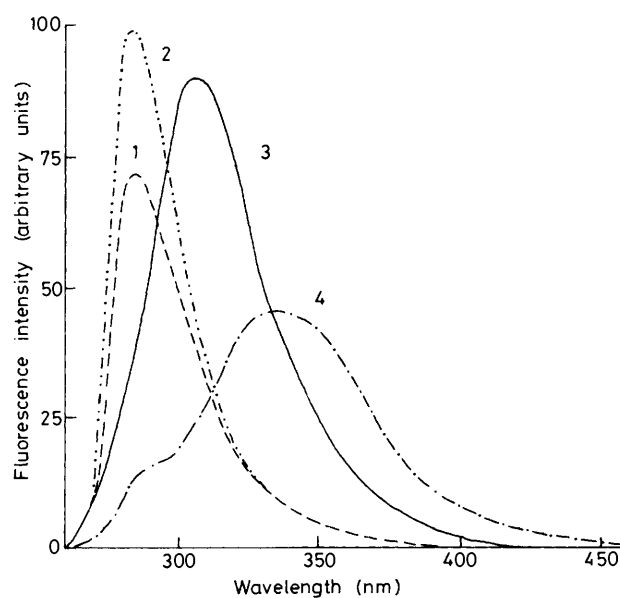

Figure 1. Fluorescence spectra of selected *N,N,N',N'*-tetraethyl-α,ω-diaminoalkanes in degassed cyclohexane solution (absorbance 0.1 at 250 nm): 1, NEt₃; 2, Et₂N(CH₂)₈NEt₂; 3, Et₂N(CH₂)₂NEt₂; 4, Et₂N(CH₂)₃NEt₂

fluorescence quantum yields are shown in Table 1. Similarly some α,ω-dipyrrolidino-, -dipiperidino-, and -dimorpholino-alkanes were examined in cyclohexane solution. Some of the fluorescence spectra are shown in Figure 2 and the quantum yield measurements are shown in Table 1. The fluorescence properties of the α,ω-di(alicyclic amino)alkanes in tetrahydrofuran solution were also studied. In this solvent the weakness of the fluorescence emission often precluded the accurate determination of quantum yields. However, values of the maximum wavelength of emission could be determined (Table 2) and some representative spectra are shown in Figure 3. The fact that very high slit widths had to be employed to observe fluorescence decreases the accuracy of the measurements and this problem is accentuated where more than one emitting species was observed (*e.g.*, monomer and excimer) and where these emissions overlapped to some extent. In the case of 1,3-dipyr-rolidinopropane in tetrahydrofuran solution, the position of the $\lambda_{max.}$ fluorescence was found to change from 335 nm in aerated solution to 350 nm upon degassing. This suggests that two

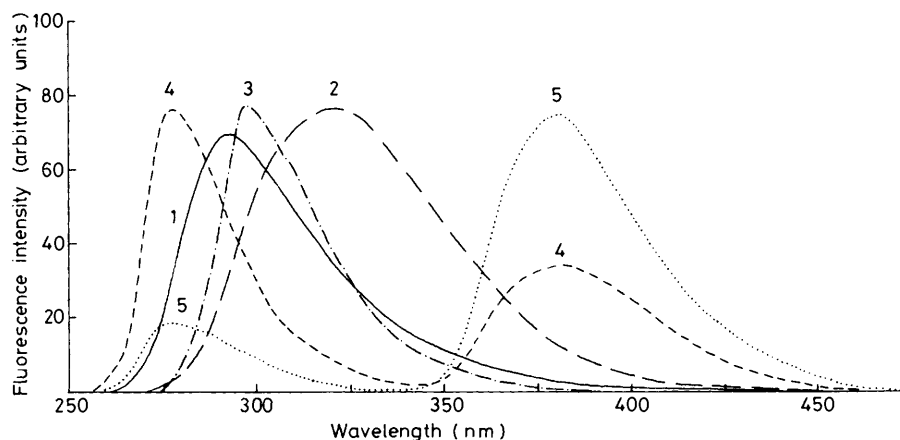**Figure 2.** Fluorescence spectra of selected α,ω-diaminoalkanes in degassed cyclohexane solution (absorbance 0.1 at 250 nm): 1, $CH_2(CH_2)_4N(CH_2)_8N(CH_2)_4CH_2$; 2, $CH_2(CH_2)_4N(CH_2)_3N(CH_2)_3CH_2$; 3, $CH_2(CH_2)_4N(CH_2)_{10}N(CH_2)_3CH_2$; 4, $CH_2CH_2O(CH_2)_2N(CH_2)_8N(CH_2)_2OCH_2CH_2$; 5, $CH_2CH_2O(CH_2)_2N(CH_2)_{10}N(CH_2)_2OCH_2CH_2$
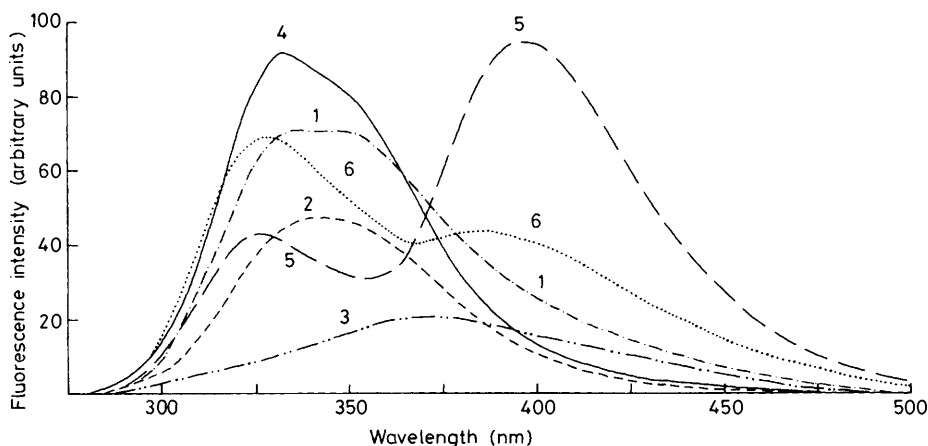

Figure 3. Fluorescence spectra of selected α,ω-diaminoalkanes in degassed tetrahydrofuran solution (absorbance 0.1 at 250 nm): 1, $CH_2(CH_2)_4N(CH_2)_3N(CH_2)_4CH_2$; 2, $CH_2(CH_2)_3N(CH_2)_6N(CH_2)_3CH_2$; 3, $CH_2(CH_2)_4N(CH_2)_3$ $N(CH_2)_4CH_2$; 4, $CH_2CH_2O(CH_2)_2N(CH_2)_8N(CH_2)_2OCH_2CH_2$; 5, $CH_2CH_2O(CH_2)_2N(CH_2)_8N(CH_2)_2OCH_2CH_2$; 6, $CH_2CH_2O(CH_2)_2N(CH_2)_{12}$ $N(CH_2)_2OCH_2CH_2$

emitting species, having different lifetimes, are present,[7] *i.e.*, monomer and excimer. Our assignment of the emission for the dipyrrolidino- and dipiperidino-ethanes and -propanes being mainly excimeric comes from the fact that the emission is red shifted with respect to that for the compounds containing hexamethylene, octamethylene, and decamethylene linking groups. For the dimorpholino compounds the rather strange situation arises where all the compounds studied exhibited excimer emission.
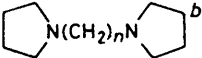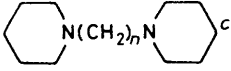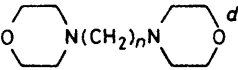
Discussion

As with the *N,N,N',N'*-tetramethyl-α,ω-diaminoalkanes, fluorescent excimer formation for the corresponding tetraethyl compounds was observed when three methylene groups linked the amino groups. The emission of the diaminoethane also suggests that excimer formation is taking place although the $\lambda_{max.}$ of fluorescence for this amine is somewhat blue shifted from that of the propane derivative. This may either be due to the very different geometry of the complex formed by the ethane compared with that of the propane derivative or, possibly, the
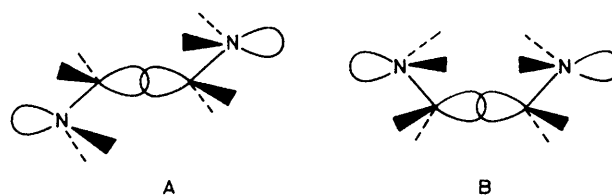
amino groups in the diaminoethane see each other *via* a 'through bond' interaction. For a 'through bond' interaction to occur the diamine would need to adopt some specific conformations, *i.e.*, (A) or (B) in Figure 4. Such 'through bond' interactions have been observed for 1,4-diazabicyclo-[2.2.2]octane,[8,9] for *N,N'*-dimethylpiperazine,[9,10] and for rigid piperazines.[10]

The quantum yield measurements (Table 1) show that substantial fluorescence quenching is occurring when four and five methylene groups are interposed between the diethylamino groups. This quenching gradually falls off in efficiency as the chain is further increased in length although even with ten methylene units the quantum yield of fluorescence is significantly less than that for triethylamine. Halpern,[1] using fluorescence lifetime measurements, observed a similar effect. This situation is reminiscent of that found for intramolecular exciplexes but not usually for excimers. In the case of (1-naphthyl)aminoalkanes, intramolecular fluorescence quenching is efficient for quite long chains but this is not the case for fluorescent exciplex formation.[11] It was proposed that quenching *via* electron transfer can occur over quite large distances,[12] these

Table 1. Fluorescence wavelength maxima ($\lambda_{max.}$/nm) and quantum yields of fluorescence (φ_f) for some α,ω-diaminoalkanes in degassed cyclohexane solution ($\lambda_{exc.}$ 250 nm)

Compound $Et_2N(CH_2)_nNEt_2$[a]	$\lambda_{max.}$/nm	Assignment	φ_f (± 0.01)
$n = 2$	312	Excimer	0.08
$n = 3$	287	Monomer	0.01
	336	Excimer	0.25
$n = 4$	290	Monomer	0.02
$n = 5$	293	Monomer plus a little excimer	0.01
$n = 6$	287	Monomer	0.13
$n = 10$	285	Monomer	0.17

$\begin{array}{c}\text{(pyrrolidine)}N(CH_2)_nN\text{(piperidine)}\end{array}$[b]

$n = 2$	305	Monomer plus eximer	0.02
$n = 3$	330	Excimer	0.05
$n = 6$	297	Monomer	0.04
$n = 8$	298	Monomer	0.22

$\begin{array}{c}\text{(piperidine)}N(CH_2)_nN\text{(piperidine)}\end{array}$[c]

$n = 2$	334	Excimer	0.04
$n = 3$	340	Excimer	0.20
$n = 6$	292	Monomer	0.09

$\begin{array}{c}O\text{(morpholine)}N(CH_2)_nN\text{(morpholine)}O\end{array}$[d]

$n = 2$	380	Excimer	0.19
$n = 3$	380	Excimer	0.22
$n = 8$	275	Monomer	0.06
	380	Excimer	0.05
$n = 10$	278	Monomer	0.01
	380	Excimer	0.11
$n = 12$	278	Monomer	<0.01
	380	Excimer	0.05
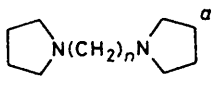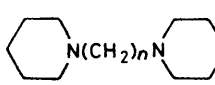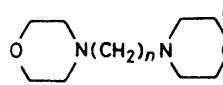
[a] Et_3N, $\lambda_{max.}$ 285 nm, φ_f 0.44. [b] Pyrrolidinomethane, $\lambda_{max.}$ 295 nm, φ_f, 0.48. [c] Piperidinomethane, $\lambda_{max.}$ 295 nm, φ_f, 0.28. [d] Morpholinomethane, $\lambda_{max.}$ 280 nm, φ_f 0.04.

Figure 4. Specific conformations of the diamine for 'through bond' interaction to occur

being greater than the optimum separation in the fluorescent exciplexes. That quenching can occur over quite large distances has recently been confirmed by several workers.[12] In the case of diarylethanes and similar compounds, little fluorescence quenching occurs unless fluorescent excimer formation takes place.[13] Since similar results were obtained for the α,ω-di(pyrrolidino)- and -(piperidino)-alkanes, it appears that the phenomenon of quenching of excited states over quite large distances in the α,ω-diaminoalkanes is quite general. Halpern[1] has considered whether this quenching is similar to that which occurs during the concentration quenching of acyclic amines. There appear to be two possible situations which can give rise to fluorescence quenching. If the amino groups or amine molecules can come to encounter distance then the quenching may be the result of an excimeric or exciplex interaction. On the other hand, if the excited state of an amine can be quenched by an electron-transfer process, this may occur at distances greater than the encounter distances and thereby inhibit excimer formation. That quenching can occur *via* electron transfer is not unreasonable if one accepts that the best description of the excited state of the amine in solution approximates to a Rydberg state.* If in the excited state some electron detachment from the nucleus has occurred, then electron transfer to the electron-deficient nucleus from an external source should be possible. As the polarity of the medium is increased, the degree of electron detachment in the excited amine should increase. All the spectroscopic studies on amines are in accord with this view.[14,15] Under these circumstances electron-transfer quenching should become even more favourable. The diaminoalkanes were found to fluoresce in tetrahydrofuran solution, albeit extremely weakly. It would appear that the change to a more

* The word approximate has been used since it may be impossible to have Rydberg states in solution which are similar in all respects to their gas-phase counterparts.

Table 2. Fluorescence wavelength maxima (and quantum yields of fluorescence) for some α,ω-diaminoalkanes in degassed tetrahydrofuran solution ($\lambda_{exc.}$ 250 nm)

Chain length	Diamine $\text{(pyrrolidine)}N(CH_2)_nN\text{(pyrrolidine)}$[a] ($\lambda_{max.}$/nm)	$\text{(piperidine)}N(CH_2)_nN\text{(piperidine)}$[b] ($\lambda_{max.}$/nm)	$O\text{(morpholine)}N(CH_2)_nN\text{(morpholine)}O$[c] ($\lambda_{max.}$/nm)
2	355	355	398 (0.16)
3	350	370	399 (0.10)
6	345	335	
8	345	335	325 (0.02)
			395 (0.05)
10	345	335	395 (0.11)
12			330
			395

[a] Pyrrolidinomethane, $\lambda_{max.}$ 345 nm, φ_f 0.30. [b] Piperidinomethane, $\lambda_{max.}$ 355 nm, φ_f 0.15. [c] Morpholinomethane, $\lambda_{max.}$ 340 nm, φ_f 0.07.

polar solvent has led to a marked increase in the efficiency of the quenching process and in many cases this made it impossible to obtain reliable fluorescence quantum yields. However, it has been shown that amines fluoresce in tetrahydrofuran solution and their quantum yields of fluorescence are slightly lower and in some cases their lifetimes are slightly shorter in this more polar solvent. These effects are not sufficient to account for the weakness of emission of the diaminoalkanes in tetrahydrofuran solution. A further interesting point is that the excimeric emission observed in tetrahydrofuran solution is red shifted compared with that in cyclohexane solution, indicating that the excited complex has some charge-transfer character. Interestingly, the energy difference between the excimers and monomers in tetrahydrofuran is much less than in cyclohexane solution. This suggests that the excited state of the monoamine is very efficiently solvated in tetrahydrofuran and that complex formation leads to little stabilisation.

The dimorpholino compounds, in cyclohexane and tetrahydrofuran solution, appear to behave differently to the other diamino compounds. Thus for the α,ω-dimorpholino-octane, excimer formation appears to be taking place. We attribute this difference as being due to the fact that in order to observe any effects with the morpholino compounds, quite high concentrations had to be employed (2.5×10^{-2}M). As a consequence, both inter- and intra-molecular quenching processes may be taking place. If one accepts that intermolecular quenching is occurring, it is surprising that excimer emission can be observed, since concentration quenching of N-methylmorpholine does not, apparently, lead to excimer formation.

On the basis of fluorescence quantum yield measurements and in particular solvatochromic shifts, we propose that the excimers formed by α,ω-diaminoalkanes containing aliphatic amine groups have considerable charge-transfer character.

Experimental

Solvents used for absorption and fluorescence spectroscopy were as follows: cyclohexane (Hopkin and Williams Spectrosol grade), tetrahydrofuran (BDH Chemicals), which was distilled from lithium aluminium hydride prior to use.

The amines (Aldrich) and the diamines (preparation previously described[16]) were distilled and then purified by preparative gas–liquid chromatography (Pye Unicam 105, 20% PEG A column) prior to use.

U.v.–visible absorption spectra were recorded using a Perkin-Elmer 402 spectrometer and fluorescence spectra with an uncorrected Perkin-Elmer MPF-4 fluorescence spectrometer. The fluorescence spectra of the solvent blanks were run in each case, to check that they showed negligible emission at maximum sensitivity over the wavelengths monitored for the amine

emission experiments. For recording the amine emission spectra, solutions of the amines and diamines were made up in 1 cm pathlength quartz rectangular fluorimeter cells to an absorbance of 0.1 at the excitation wavelength (250 nm). The solutions were degassed via several freeze–pump–thaw cycles. Quantum yields were determined relative to toluene ($\varphi_f = 0.14$).[17]

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