Quenching of Aromatic Hydrocarbon Fluorescence by α,ω-Diamino-alkanes

R. Stephen Davidson *
Department of Chemistry, The City University, Northampton Square, London EC1V 0HB
Terence D. Whelan
Department of Chemistry, The University, Leicester LE1 7RH

α,ω-Bisdiethylamino-, α,ω-dipyrrolidino-, and α,ω-dipiperidino-alkanes quench the fluorescence of aromatic hydrocarbons in cyclohexane solution. The efficiency of quenching is dependent upon the length of the chain linking the two nitrogen atoms. For chains containing <6 methylene groups, quenching is proposed to occur via a complex in which both nitrogen atoms interact with the aromatic hydrocarbon. Spectroscopic evidence for the formation of such complexes is presented. Complex formation markedly attenuates the quantum yield of exciplex fluorescence. For diamines having >6 methylene groups linking the nitrogen atoms, quenching is proposed to occur via a multi-collisional process. These diamines are more effective quenchers than their monoamine counterparts. The effect of chain length is barely noticeable when solvents more polar than cyclohexane are used. α,ω-Bis-(N-methylanilino)-alkanes are efficient quenchers of aromatic hydrocarbon fluorescence, but the efficiency does not depend on the length of the linking chain. The quantum yield of exciplex fluorscence is attentuated when the linking chain contains two or three methylene groups.

In early work on the quenching of the fluorescence of aromatic hydrocarbons by tertiary amines, it was found that there was an optimal concentration of amine for fluorescent exciplex formation.[1] Use of high concentrations of amine led to a diminution in the intensity of the fluorescence and a red-shift in its maximal emission wavelength. It was suggested that, under these conditions, termolecular complex formation occurred, and that this gave rise to exciplex emission to the red of the normal bimolecular exciplex emission. Naphthalene fluorescence is quenched by 1,4-dicyanobenzene, and when high concentrations of naphthalene are used fluorescence is produced; this was attributed to a triple complex composed of two naphthalene molecules and one of the dicyanobenzene.[2] By linking two naphthalene nuclei together via an insulating polymethylene chain of appropriate length it is possible to detect a similar type of emission without having to resort to high concentrations of the aromatic hydrocarbon.[3] Formation of complexes involving three interacting groups has also been observed in polymer systems, e.g. in polyvinylcarbazole containing benzanthrone.[4] A particularly elegant way of examining triple complexes involves the use of cyclophanes in which the assemblage, whether it be donor–donor–acceptor or donor–acceptor–donor, can be controlled.[5] Studies employing such cyclophanes showed that symmetrical complexes of the type donor–acceptor–donor have a zero dipole moment, whilst the unsymmetrical complexes of the type donor–donor–acceptor have a high dipole moment. A further feature of the unsymmetrical complexes is that their wavelength of maximum exciplex fluorescence is to the red of that for the corresponding donor–acceptor–donor complex.

The formation of complexes involving three interacting groups is also of photochemical importance. Anthracene is photoreduced by NN-dimethylaniline.[6] Subsequently, it was shown[7] that the ability of the amine to quench the photodimerisation of anthracene is dependent upon the anthracene concentration. To account for this, it was proposed that at high anthracene concentrations a termolecular excited complex composed of two molecules of the hydrocarbon and one of the amine was formed, and that this complex decayed by reaction to give the anthracene dimer. The formation of triple complexes has been utilised to design an effective method for determining whether exciplexes are intermediates in a

variety of reactions.[8] A number of cycloaddition reactions have been proposed to occur via triple complexes.[9]

It has been reported previously that a number of diamines, e.g. 1,4-diazabicyclo[2.2.2]octane, NN'-dimethylpiperazine, and NNN'N'-tetramethylethylenediamine quench the fluorescence of aromatic hydrocarbons.[10] Only weak exciplex fluorescence was observed. We now report the quenching of the fluorescence of aromatic hydrocarbons by a variety of α,ω-diamino-alkanes in an attempt to ascertain whether such compounds quench via a complex containing three interacting groups.[11] Since it is known that many α,ω-diamino-alkanes exhibit excimer emissions,[12] it is not unreasonable to suppose that such compounds should form complexes of the type donor–donor–acceptor.

Results and Discussion

(I) *Quenching of Naphthalene Fluorescence by α,ω-Diamino-alkanes in Cyclohexane.*—α,ω-Bisdiethylamino-alkanes and other α,ω-diamino-alkanes quench the fluorescence of naphthalene, giving rise to a new, structureless fluorescence band which is red-shifted relative to that of the naphthalene fluorescence.[11] The results (Table 1) show that the wavelength of emission is dependent upon the structure of the amine. The greatest red shift is observed for the diamines having two or three methylene groups between the nitrogen atoms. The emission spectra observed with bisdiethylamino-octane and -decane are similar to that with triethylamine. Since the shapes of the emission spectra are not affected by the presence of oxygen,[13] we conclude that only one species is responsible for the red-shifted fluorescence bands. The observation that both α,ω-dipyrrolidino- and α,ω-dipiperidino-alkanes behave in a similar way (Table 1) supports the view that the described results are not peculiar to any one type of amino group. In the case of the pyrrolidino- and piperidino-compounds there is a marked difference in the maximum wavelength of exciplex fluorescence between the diamino-ethanes and -propanes on the one hand and the octanes and the parent N-methylpyrrolidine and N-methylpiperidine on the other.

(a) *Quenching by diaminoalkanes having >6 methylene groups between the nitrogen atoms.* The similarity in behaviour of these compounds and the parent N-methyl compounds
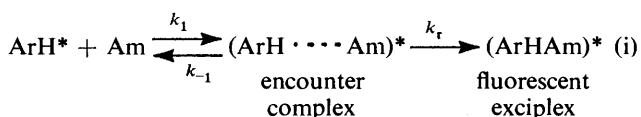
Table 1. Quenching of naphthalene fluorescence by α,ω-diamino-alkanes and related compounds in degassed cyclohexane solution at 20 °C

Amine	n	Stern–Volmer quenching rate constant (l mol⁻¹ s⁻¹ × 10⁻⁹)	k_r/k_{-1}	I_E/I_M [a]	I_E^∞/I_M^0	Exciplex $\lambda_{max.}$/nm	
Triethylamine		1.9	0.21	0.4	0.134	406	(436) [b]
Et₂N[CH₂]ₙNEt₂	2	6.1	1.245	0.1	0.01	415	
	3	6.1	1.245	0.3	0.03	413	(440) [b]
	4	6.05	1.222	0.26	0.026	410	(438) [b]
	5	5.8	1.12	0.47	0.05	410	
	6	4.0	0.57	0.85	0.13	408	
	7	4.3	0.64	0.89	0.125	407	
	8	4.2	0.62	0.84	0.122	407	
	10	4.45	0.68	0.90	0.123	406	
[CH₂]₄NMe		3.2	0.41	0.82	0.16	411	
[CH₂]₄N[CH₂]ₙN[CH₂]₄	2	5.9	1.16	0.5	0.05	425	
	3	5.7	1.08	0.48	0.05	435	
	8	6.0	1.2	1.2	0.12	414	
[CH₂]₅NMe		0.3	0.028	0.06	0.11	410	
[CH₂]₅N[CH₂]ₙN[CH₂]₅	2	3.5	0.467	0.2	0.035	421	
	8	2.1	0.230	0.4	0.12	410	

[a] Exciplex/monomer fluorescence intensity ratio for [amine] 0.15 mol l⁻¹. [b] Exciplex emission wavelength when toluene is used as solvent.

suggests that the exciplex emission emanates, in the case of the diamino-compounds, from the interaction of one amino group with the aromatic hydrocarbon. It is interesting that the I_E/I_M values for such diamines are greater than those for the parent amines (triethylamine, N-methylpyrrolidine, N-methylpiperidine). The I_E/I_M values were obtained by using an amine concentration of 1.5×10^{-2} mol l⁻¹, since this concentration gave a measurable amount of exciplex emission and yet was low enough to avoid complications caused by quenching of the exciplex fluorescence produced by the formation of termolecular species. The significance of the I_E/I_M values is that they show, for a particular amine concentration, a larger amount of exciplex fluorescence in the case of the diamines than of their parent amines. In the case of the tetraethylalkanes and pyrrolidino-alkanes, the increase in efficiency appears to be a purely statistical effect, but this is not so for the piperidino-octane where the I_E/I_M value is considerably higher than that for N-methylpiperidine. Table 1 shows that both triethylamine and N-methylpyrrolidine quench the fluorescence of naphthalene in cyclohexane at close to the diffusion-controlled rate, whereas an N-methylpiperidine is a far less efficient quencher.[14]

The quenching properties of diamines having >6 methylene groups between the nitrogen atoms can be rationalised on the following basis. 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,[1] radical ions, triplet states and products [equation (i)]. For diamines, in

$$\text{ArH}^* + \text{Am} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{\text{encounter} \\ \text{complex}}}{(\text{ArH} \cdots \text{Am})^*} \xrightarrow{k_r} \underset{\substack{\text{fluorescent} \\ \text{exciplex}}}{(\text{ArHAm})^*} \quad \text{(i)}$$

which there is the possibility of only one amino group interacting with the hydrocarbon in the encounter complex, dissociation *via* the reaction having rate constant k_{-1} will generate the excited aromatic hydrocarbon in the vicinity of a second amino group, with which it can react and so reform the encounter complex. In other words, the presence of a second amino group increases the probability of fluorescent exciplex formation by creating an artificially high local concentration

of the amine. We have given the name ' multi-collisional quenching ' to this process. The effect becomes particularly apparent when amines such as N-methylpiperidine, having low quenching efficiencies, are used and is reflected in the values of the quenching rate constants.

The kinetics of fluorescence quenching by a process such as that shown by equation (i) have been examined by Evans,[15] who obtained equation (ii), relating the various rate constants.

$$\varphi_0/\varphi = 1 + \tau[\text{Am}] \, k_1 \, k_r/(k_{-1} + k_r) \quad \text{(ii)}$$

If the measured Stern–Volmer quenching rate constant is k_{q^1}, then $k_{q^1} = k_1 \, k_r/(k_{-1} + k_r)$ and hence $k_r/k_{-1} = k_{q^1}/(k_{-1} - k_{q^1})$. Values of k_r/k_{-1} were calculated for the quenching of naphthalene fluorescence by α,ω-bisdiethylamino-alkanes in cyclohexane solution (Table 1). The values were calculated using a value of 1.1×10^{10} l mol⁻¹ s⁻¹ for k_1 in cyclohexane.[16] As one can see from Table 1, the diamines containing six or more methylene groups between the nitrogen atoms have larger k_r/k_{-1} values than that for triethylamine, showing that the overall efficiency of the back reaction (rate constant k_{-1}) is lower for the diamines. This is consistent with the view that the presence of a second nitrogen atom in the diamine increases the probability of quenching.

Table 1 also lists I_E^∞/I_M^0 values, evaluated from equation

$$I_E^\infty/I_M^0 = I_E/I_M K_{SV}[\text{c}] \quad \text{(iii)}$$

where [c] = concentration of amine

(iii).[1,17] For the diamines having >6 methylene groups between the nitrogen atoms, there is little difference between the I_E^∞/I_M^0 values for the parent amines and those for the diamines. This is not surprising since at infinite concentration, whether or not the amine contains one or two amino groups will be of no consequence. However the utility of aliphatic diamines lies in the fact that under reasonable experimental conditions it is easier to observe the exciplex emission than with the parent monoamines.

(b) *Quenching by diamino-alkanes having <6 methylene groups between the nitrogen atoms.* As already noted, the quenching by diamino-ethanes and -propanes leads to exciplex emission, which is red-shifted in comparison with that produced by the parent amine.

Table 1 shows that these compounds and the one diamino-butane studied have I_E/I_M values significantly lower than those for the parent amine. In addition, these compounds and the 1,5-diaminopentane have I_E^∞/I_M^0 values much lower than those for the parent amine. These parameters, together with the quenching rate constant and the k_r/k_{-1} values, all demonstrate that these compounds are far more effective quenchers than the parent amines, and that the quantum yield of exciplex fluorescence for these systems is far lower than that for the parent amines or the diamines having 6 or more methylene groups between the nitrogen atoms. We suggest that these effects, together with the effect of structure of the diamine upon the wavelength of exciplex formation, are consistent with the view that quenching by these diamines involves the interaction of both amino groups with the excited aromatic hydrocarbon (see Figure).

For such an interaction, the diamino-alkane chain has to fold, and it is therefore not surprising to find that the diamino-propanes are particularly effective quenchers. The fact that the diamino-ethanes and -butanes are also effective quenchers suggests that the line-up of nitrogen lone pair orbitals (which in the complex may have considerable p-character) may be more dependent upon internuclear separation than on the extent of orbital overlap. Recently, it has been shown that in
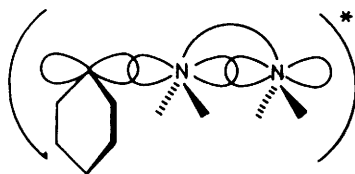

Figure.

exciplexes the extent of separation between the donor and acceptor groups is more important than the geometry and extent of orbital overlap.[18]

We believe that the reason for the low quantum yield of exciplex emission for these systems is due to the fact that the complex involves three interacting groups. Such a complex is more likely to break up than one involving only two interacting groups. Since these complexes are likely[3] to be lower in energy than the complex formed between the aryl group and its nearest amine groups, they are less likely to dissociate, regenerating the excited aromatic hydrocarbon. Break-up of the complexes involving three interacting groups may lead to an enhancement in intersystem crossing to generate the triplet hydrocarbon, besides other non-radioactive processes.

(II) *Quenching of the Fluorescence of Pyrene and other Aromatic Hydrocarbons by* α,ω-*Diamino-alkanes in Cyclohexane.*—Pyrene fluorescence is quenched by various α,ω-diamino-alkanes (Table 2). The diamines are more efficient quenchers than their monoamine counterparts; indeed their quenching efficiency exceeds the statistical factor. For the diamino-octanes we attribute this efficiency to multicollisional quenching, and the quenching by the diamino-ethanes and -propanes to complex formation involving both nitrogen atoms. The emission spectra of the complexes formed by the dipyrrolidino-compounds show that the amino-ethanes and -propanes form complexes involving three interacting groups. Interestingly the dipyrrolidino-alkanes produce fluorescent exciplexes which are more easy to detect than the complex formed by N-methylpyrrolidine.

Dipyrrolidino-alkanes quench the fluorescence of many polycyclic aromatic hydrocarbons and substituted aromatic hydrocarbons, and often exciplex fluorescence can be observed (see Table 3). In some cases, probably where charge transfer is extensive, exciplex fluorescence is difficult to detect.

(III) *Quenching of Anthracene Fluorescence by* α,ω-*Bis-diethylamino-alkanes in Various Solvents.*—The diamines were found to quench anthracene fluorescence and quenching rate constants were measured (Table 4). For cyclohexane the usual pattern is observed, *i.e.* the diamines quench more efficiently than triethylamine and the diamines having 2—5 methylene groups between the nitrogen atoms are more efficient quenchers than those containing 6 or more methylene groups. However, the effect of the length of the chain connecting the two amino groups appears to be totally negated in solvents more polar than cyclohexane, *i.e.* benzene and methanol. In such solvents, the diamines are still more effective quenchers than triethylamine. The similarity in quenching efficiency shown by the diamines in benzene and methanol may well be due to the ability of both amino groups to interact with the excited hydrocarbon. The distance over which quenching by electron transfer can occur increases as the polarity of the solvent is increased, in benzene and methanol,[19] and consequently the

Table 2. Rate constants for the quenching of pyrene fluorescence by diamines in degassed cyclohexane at 20 °C

Amine	n	Quenching rate constant $(1\ mol^{-1}\ s^{-1} \times 10^{-9})$	Exciplex $\lambda_{max.}/nm$
Triethylamine		0.017	
$Et_2N[CH_2]_nNEt_2$	2	2.8	
	3	1.1	
	8	0.07	
$[CH_2]_4NMe$		0.074	
$[CH_2]_4N[CH_2]_nN[CH_2]_4$	2	2.7	490
	3	2.75	495
	8	0.78	470
$[CH_2]_5NMe$		0.0004	
$[CH_2]_5N[CH_2]_nN[CH_2]_5$	3	0.35	
	8	0.03	

Table 3. Wavelengths of maximum emission (nm) from excited complexes formed between α,ω-dipyrrolidino-alkanes and aromatic hydrocarbons in degassed cyclohexane solution at 20 °C [a]

Amine	Naphthalene	Pyrene	9-Cyano-phenanthrene	Anthracene	9-Cyano-anthracene
$[CH_2]_4NMe$	411 (450)[b]				
$[CH_2]_4N[CH_2]_2N[CH_2]_4$	425	490			
$[CH_2]_4N[CH_2]_3N[CH_2]_4$	435 (465)[b]	495	ca. 500	v.w.	n.o.
$[CH_2]_4N[CH_2]_8N[CH_2]_4$	414	470	495	ca. 500	n.o.

v.w. = very weak; n.o. = not observed. [b] Benzene as solvent.

Table 4. Rate constants for the quenching of anthracene by α,ω-bisdiethylamino-alkanes in various degassed solvents at 20 °C

| | Quenching rate constants (l mol^{-1} s^{-1} $\times$ 10^{-9}) | | |
Amine	Cyclohexane	Benzene	Methanol
Triethylamine	0.32	2.8	0.58
Et$_2$N[CH$_2$]$_n$NEt$_2$			
$n = 2$	4.7	4.4	2.1
$n = 3$	4.1	4.2	2.3
$n = 4$	3.3	4.0	2.0
$n = 5$	2.9	4.8	2.2
$n = 6$	1.4	4.2	1.75
$n = 7$	1.3	4.7	1.7
$n = 8$	1.3	5.1	1.7
$n = 10$	1.4	4.8	1.8

Table 5. Quenching of pyrene and anthracene fluorescence by α,ω-bis-(N-methylanilino)-alkanes in degassed cyclohexane solution at 20 °C

Pyrene

Amine	I_E^∞/I_M^0 [a]	$10^{-9}k_q/$ l mol^{-1} s^{-1}
NN-Diethylaniline	0.24	1.7
PhMeN[CH$_2$]$_n$NMePh		
$n = 2$	0.06	4.6
$n = 3$	0.08	5.8
$n = 5$	0.22	5.4
$n = 8$	0.26	4.9

Anthracene

Amine	$10^{-9}k_q/$l mol^{-1} s^{-1}
NN-Diethylaniline	
PhMeN[CH$_2$]$_n$NMePh	
$n = 2$	8.1
$n = 3$	8.8
$n = 5$	14.8
$n = 8$	12.6

[a] Exciplex fluorescence with pyrene is observed for all amines, the $\lambda_{max.}$ of 445 nm being the same in each case.

amino group in diaminodecane may be able to act synergistically. Alternatively the use of more polar solvents may increase the efficiency of multi-collisional quenching to the same level as that involving three interacting groups.

(IV) *Quenching of Pyrene and Anthracene Fluorescence by* α,ω-*Bis*-(N-*methylanilino*)-*alkanes in Cyclohexane.*—It has been known for many years that aromatic amines quench the fluoresence of polycyclic aromatic hydrocarbons, giving rise to exciplex fluorescence;[1,20] aromatic diamines are no exception. Quenching rate constants determined for pyrene and anthracene are shown in Table 5. The diamines have higher quenching rate constants than the corresponding monoamines, but there is no marked variation in the rate constants. The I_E^∞/I_M^0 values show that the diamino-ethane and -propane probably quench *via* a complex involving three interacting groups. Whether this or the multi-collisional process is responsible for quenching by the pentane and the octane cannot as yet be ascertained.

Conclusion

The results show that α,ω-diamino-alkanes quench the fluorescence of aromatic hydrocarbons. The efficiency of quenching, as measured by the quenching rate constant, is dependent upon a number of factors. N-Methylpyrrolidine is

far more effective than N-methylpiperidine. This may be due to the lone pair orbital of the pyrrolidine ring having more p-character than that in the piperidine system. The greater the degree of p-character, the less structural reorganisation is required on going from the amine to its radical cation. In the Marcus–Hush treatment of the energetics of electron transfer reactions,[21] account is taken of the energy needed to bring about the necessary conformational changes. The more favourable conformation of the pyrrolidine system compared with that of the piperidine may explain why the former is the better quencher, even though the ionisation potentials of pyrrolidines are higher than those of piperidines. The nitrogen atom in triethylamine is more pyramidal than that in pyrrolidine but less than that in piperidine. The finding that triethylamine is a better quencher than N-methylpiperidine but poorer than N-methylpyrrolidine [14,22] is in accord with these views.

The α,ω-diamino-alkanes are far more efficient quenchers than their N-alkylmonoamine counterparts, and this has been attributed to quenching either by a multi-collisional process or *via* a complex involving interaction of both nitrogen atoms with the excited aromatic hydrocarbon. This latter process is particularly favoured in the α,ω-diamino-ethanes, -propanes, and -butanes. A particular feature of this quenching process is the low quantum yield of exciplex fluorescence even when non-polar solvents (*e.g.* cyclohexane) are employed. 1,4-Diazabicyclo[2.2.2]octane (DABCO) is a particularly effective quencher of aromatic hydrocarbon excited singlet states (*e.g.* naphthalenes, chrysene, anthracene, and perylene) [22] and the quenching is not accompanied by any significantly measurable exciplex fluorescence. It is known from photoelectron spectroscopic studies [23] that the nitrogen atoms in DABCO interact *via* a through-bond process which lowers the ionisation potential of the amine. The lack of exciplex emission from systems containing this amine may be due to the pyramidal nature of the nitrogen atoms precluding the formation of a relatively stable amine radical cation; consequently the photophysics (*e.g.* intersystem crossing) emanates from the encounter complex rather than from a relaxed exciplex.

That the photophysics of complexes involving two nitrogen atoms interacting with an aromatic hydrocarbon is so different from that of a complex involving only nitrogen atom is of relevance to the design of experimental conditions for reactions involving electron-transfer processes. The use of high concentrations of reactants may well lead to complexes containing more than two interacting groups and consequently the chemistry which ensues may bear little resemblance to that of complexes involving only two interacting groups.

Experimental

Fluorescence spectra were recorded using an uncorrected Perkin–Elmer MPF4 spectrofluorimeter. Unicam SP 800 and SP 1800 spectrophotometers were used to record u.v. spectra and to make up solutions of known optical density at a given wavelength. I.r. spectra for samples (thin films) were obtained with Perkin–Elmer 237 and 457 grating spectrophotometers. ^{1}H N.m.r. spectra were recorded for solutions in deuterio-chloroform (with tetramethylsilane as internal standard) on a Varian T60 spectrometer. Elemental analyses were carried out (at The City University) using a Carlo Erba Model 1106 C, H, and N analyser. The diamines were purified by preparative g.l.c. (Pye 104), using polyethylene glycol adipate in column. Mass spectra were recorded using a Macromass MS30/76 Kratos instrument.

Fluorescence spectra were recorded for solutions in cyclohexane, benzene, and acetonitrile (Merck, Uvasol) used as supplied. All solvents were checked to ensure that they did not

give any fluorescence when irradiated under conditions similar to those used for recording spectra.

Quenching studies were carried out using a quartz cell adapted in such a way that solutions could be degassed by freeze–pump–thaw cycles. Solutions of the aromatic hydrocarbons were made up to an optical density of 0.1 at the wavelength used for excitation. Solutions were degassed by at least three freeze–pump–thaw cycles and then the spectrum was recorded. Air was then admitted to the cell and the spectra were re-run. In this way the effect of oxygen upon the fluorescence spectra could be assessed.

Fluorescence quenching rate constants were obtained from Stern–Volmer plots of $I_0/I - 1$ versus quencher concentration where I is the intensity of fluorescence of the aromatic hydrocarbon in the presence of a quencher at a given concentration and I_0 is the fluorescence intensity in the absence of quencher. All solutions were thoroughly degassed. In order to obtain accurate values at least four different concentrations of the quencher were used. A least-squares analysis of the plots was carried out to obtain the line having the best fit. In order to calculate the quenching rate constants, the following fluorescence lifetimes were employed: naphthalene/cyclohexane 110 ns, anthracene/cyclohexane 50 ns, anthracene/benzene 4.1 ns, anthracene/methanol 5.7 ns, pyrene/cyclohexane 450 ns.[24]

Materials.—The syntheses of 1,2-bisdiethylaminoethane, 1,3-bisdiethylaminopropane, 1,5-bisdiethylaminopentane, 1,6-bisdiethylaminohexane 1,8-bisdiethylamino-octane, and 1,10-bisdiethylaminodecane have been previously described.[25] 1,4-Bisdiethylaminobutane was prepared via $NNN'N'$-tetraethylsuccinamide. Reaction of succinoyl chloride with an excess of diethylamine in ether gave the amide, which on reduction with lithium aluminium hydride gave the diamine, b.p. 65 °C at 1 mmHg, $\delta(CDCl_3)$ 1.0 (12 H, t, J 7 Hz), 1.3 (8 H br s), and 2.2—2.65 (12 H, m) * 1,2-Dipyrrolidinoethane was prepared by treating oxalyl chloride with an excess of the amine to give the diamide, which was then reduced by lithium aluminium hydride in ether to give the diamine, b.p. 70—72 °C at 0.02 mmHg, $\delta(CDCl_3)$ 1.61—2.00 (8 H, m) and 2.38—2.77 (12 H, m), m/z 168.1584 (Found: C, 71.65; H, 11.7; N, 16.4. Calc. for $C_{10}H_{20}N_2$: C, 71.35, H, 12.0; N, 16.65%). 1,3-Dipyrrolidinopropane and 1,8-dipyrrolidino-octane were prepared by treating the appropriate dibromo-alkane with an excess of pyrrolidine. The amines were distilled and purified by preparative g.l.c. 1,3-Dipyrrolidinopropane had b.p. 78—80 °C 1 at mmHg, $\delta(CDCl_3)$ 1.60—2.00 (10 H, m) and 2.30—2.67 (12 H, m), m/z 182.1637 (Found: C, 72.2; H, 12.0, N, 15.3. Calc. for $C_{11}H_{22}N_2$: C, 72.45; H, 12.15; N, 15.35%). 1,8-Dipyrroldino-octane had b.p. 116—118 °C at ca. 0.05 mmHg, $\delta(CCl_4)$ 1.32 (12 H, m), 1.8 (8 H, m), and 2.2—2.65 (12 H, m), m/z 252.2604.*
1,3-Dipiperidinopropane and 1,8-dipiperidino-octane were prepared in a similar way to the pyrrolidino-compounds and were purified by preparative g.l.c. 1,3-Dipiperidinopropane had b.p. 100—102 °C at ca. 0.02 mmHg, $\delta(CDCl_3)$ 1.40—1.88 (14 H, m), and 2.28—2.56 (12 H, m), m/z 210.2212 (Found: C, 74.05; H, 12.55; N, 13.05. Calc. for $C_{13}H_{26}N_2$: C, 74.2; H, 12.45; N, 13.3%). 1,8-Dipiperidino-octane, b.p. 118—120 °C at ca. 0.02 mmHg, $\delta(CDCl_3)$ 1.32 (12 H, m), 1.47 (12 H, m), and 2.1—2.5 (12 H, m), m/z 280.2819.*

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* Difficulty was experienced in obtaining good microanalytical data for these compounds, owing to their ability to absorb water and carbon dioxide.

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