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THE PHOTOPHYSICS OF SOME INTRAMOLECULAR TERNARY COMPLEXES FORMED BETWEEN ARYL AND AMINO GROUPS

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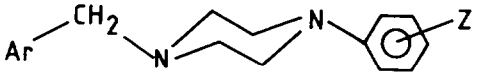
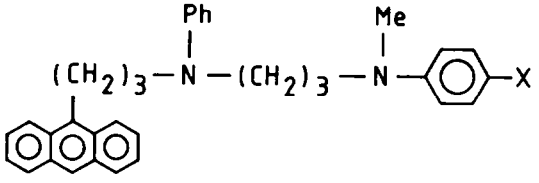
Abstract - The fluorescence properties of (3)-(6) in solvents of varying polarity have been examined and the conclusion reached that in non-polar solvents they exhibit fluorescence (low quantum yield) from an intramolecular ternary complex. In polar solvents very little fluorescence is observable. Although each compound exhibits extensive intramolecular fluorescence quenching, the quantum yield of localised triplet naphthalene in non-polar solvents remains relatively high indicating that intersystem crossing occurs in the non-relaxed exciplex.

In the early work on the quenching of the fluorescence of aromatic hydrocarbons in non-polar solvents by tertiary amines, it was found that there was an optimal concentration of amine for fluorescent exciplex formation [1]. Use of high concentrations of the amine led to a diminution in the intensity of the exciplex fluorescence and the appearance of a new emission band further to the red. It was suggested that this new band was associated with a termolecular complex formed between two molecules of the amine and one of the aromatic hydrocarbon (a ternary complex, sometimes called an exterplex). Beens and Weller [2] have also shown that the fluorescence emanating from the naphthalene (NpH)—1,4-dicyanobenzene (DCB) exciplex is quenched by naphthalene to give emission characteristic of an excited ternary complex. Examination of the effect of solvent upon this emission band led to the conclusion that the ternary complex had a very high dipole moment [3] which is indicative of the complex having a DDA structure, i.e. NpH, NpH, DCB rather than NpH, DCB, NpH. The formation of ternary complexes can be aided by linking the reaction partners together by means of a suitable chain of atoms. Thus 1,3-di(1-naphthyl)propane, which readily forms an intramolecular excimer, interacts with 1,4-dicyanobenzene to give a ternary complex [4] (trichromophoric). It was found that this complex was 0.4 eV more stable than the excimer and 0.2 eV more stable than the naphthalene—1,4-dicyanobenzene exciplex. Some totally intramolecular systems have also been investigated. Cyclophane systems have been used to demonstrate the difference between DDA and DAD systems [5] and it was found, as expected, that the DAD system has a dipole moment of zero. Less work has been done on intramolecular acyclic ternary systems [6]. Recently Verhoeven and co-workers [7] studied the intramolecular electron transfer process which accrues upon excitation of (1) and Yang and co-workers [8] have proposed that (2) exhibits excited intramolecular ternary complex formation.



where Ar = 1,2-Naphthyl or 9-Anthryl
and Z = H,2-OMe or 4-OMe

[1]



where X = H, OMe or Me

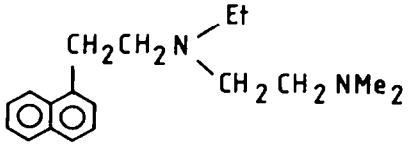
[2]

Whilst the photophysics of ternary complexes is of interest in its own right, the formation of such complexes is of importance to those carrying out product studies. Often to obtain sufficient amounts of material for characterisation purposes, high concentrations of reactants are used. This can lead to product formation via ternary complexes or exciplexes undergoing substitution reactions (S_{EX} reactions). Examples of product formation via a ternary complex appear to be the photodimerisation of anthracene in the presence of N,N-dimethylaniline [9] and the cycloaddition of dienes to octafluoronaphthalene [10] and 9,10-dichloroanthracene [11]. The chemistry of S_{EX} reactions is legion [12]. The formation and photophysics of ternary complexes is also attracting the attention of polymer chemists, as so often multicomponent complexes are formed in polymer systems [13]. A survey of the ternary systems [14] indicates that the majority are of the DDA type. Very few DAD systems have been characterised and those which have are totally rigid structures. To date, there are no well characterised DAA or ADA systems.

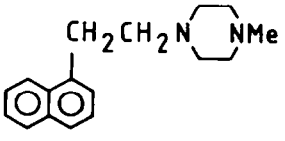
The purpose of this paper is to explore more fully, the photophysics of excited ternary complexes and to compare them with the more familiar binary systems.

RESULTS

Compounds (3) and (4) were synthesised by standard routes and their fluorescence spectra in a number of solvents, are shown in Figures 1 and 2.



[3]



[4]

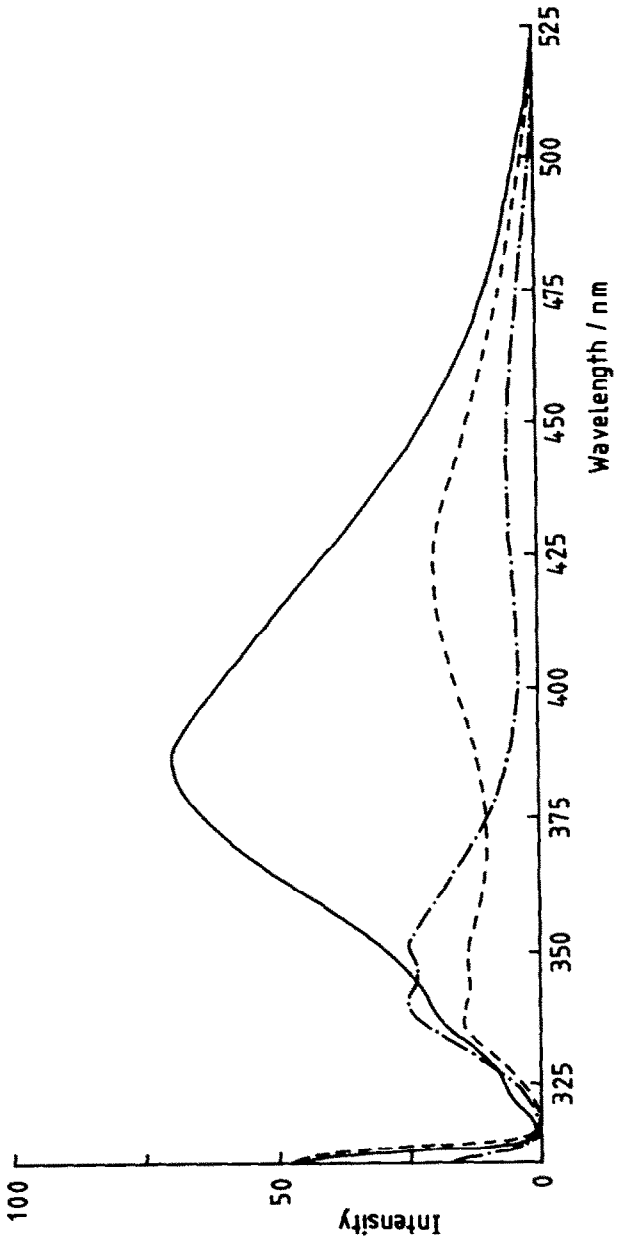


Figure (1) Fluorescence spectra of 1-$NpCH_2CH_2N(Et)CH_2CH_2NMe_2$ in degassed (——) cyclohexane, (---) benzene and (-•-) tetrahydrofuran solutions at 20°

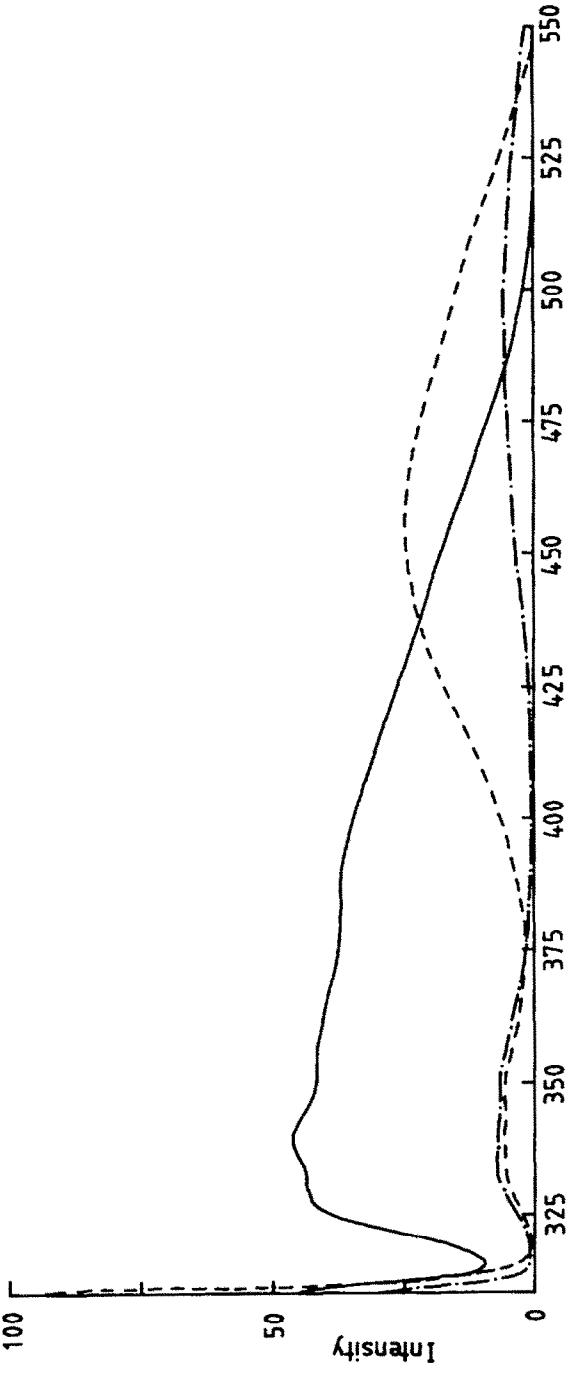


Figure (2) Fluorescence spectra of 1-$NpCH_2CH_2$--NMe in degassed (——) cyclohexane, (---) benzene and (-•-) tetrahydrofuran solutions at 20°

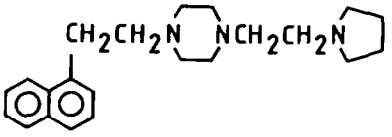
In benzene and tetrahydrofuran solutions, (3) exhibits some residual naphthalene fluorescence, whilst with (4), some residual naphthalene and piperazine fluorescence can be seen in cyclohexane solution and residual piperazine fluorescence is present in both benzene and tetrahydrofuran solutions. Exciplex fluorescence from (3) and (4) is clearly visible in each solvent. The wavelengths for maximal fluorescence emission for these compounds in the various solvents and for a number of related compounds are shown in Table 1, whilst Table 2 gives details of fluorescence quantum yields. The data in Table 1, reveal that compounds (3) and (4) exhibit fluorescent exciplex formation and that the fluorescence occurs to the red of that displayed by the related binary systems. Unlike the binary systems however, the ternary chromophoric systems

Table 1 Fluorescence λ_{max} Values (nm) for Compounds (3)-(6) and Related Compounds in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions at 20°

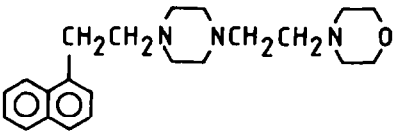
Compound	λ_{max} (nm) C_6H_{12}	C_6H_6	THF	MeCN
1-Np$(CH_2)_2$N(Et)$(CH_2)_2NMe_2$	386	420	445	(a)
1-Np$(CH_2)_2$N(piperidine)NMe	395	458	502	(a)
1-Np$(CH_2)_2$N(piperidine)NCH_2CH_2N(pyrrolidine)	405	460	505	(a)
1-Np$(CH_2)_2$N(piperidine)NCH_2CH_2N(morpholine)	405	455	500	(a)
1-Np$(CH_2)_2NEt_2$	365	408	433	482
1-Np$(CH_2)_4NEt_2$	400			520

(a) No exciplex emission observed.

fail to exhibit exciplex fluorescence in highly polar solvents. Furthermore, the data in Table 2 show that the quantum yield of exciplex fluorescence from (3) and (4) is very low and that the quenching of the fluorescence of the aromatic hydrocarbon by the diamine system is extremely efficient. A similar situation obtains for (5) and (6), where in principle complexes involving



[5]



[6]

four interacting groups can occur (Tables 2 and 3).

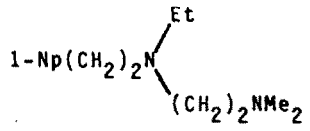
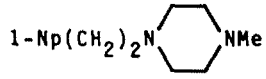
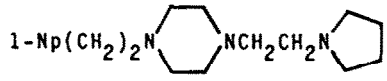
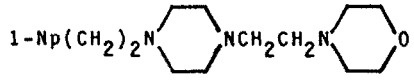
Table 2 Quantum Yields of Residual Monomer Fluorescence[a] (ϕ_F^M) and Fluorescent Exciplex Formation (ϕ_f^E) for Compounds (3)-(6) and Related Compounds in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions at 20°

Compound	Solvent							
	C_6H_{12}		C_6H_6		THF		MeCN	
	ϕ_F^M	ϕ_F^E	ϕ_F^M	ϕ_F^E	ϕ_F^M	ϕ_F^E	ϕ_F^M	ϕ_F^E
1-Np$(CH_2)_2$N(Et)(CH_2)NMe$_2$	0.002	0.128	0.007	0.028	0.016	0.007	0.005	0
1-Np$(CH_2)_2$N(piperidine)NMe	0.019	0.052	0.004	0.031	0.004	0.010	0.014	0
1-Np$(CH_2)_2$N(piperazine)CH_2CH_2N(pyrrolidine)	0.008	0.043	0.005	0.036	0.003	0.011	0.005	0
1-Np$(CH_2)_2$N(piperazine)CH_2CH_2N(morpholine)	0.008	0.039	0.006	0.032	0.005	0.013	0.001	0
1-Np$(CH_2)_2NEt_2$	0.001	0.406	0.001	0.220	0.019	0.097	0.008	0.040
1-Np$(CH_2)_4NEt_2$	0.030	0.034					0.009	0.002

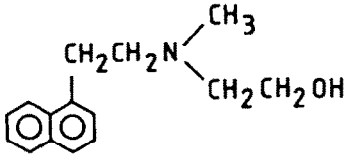
(a) In some cases the monomer emission was composed of both naphthalene and amine emission.

Since the fluorescence quantum yields are so low for (3)-(6), attempts were made to discover how the excitation energy was being dissipated. It is well known that singlet exciplexes undergo intersystem crossing [14,15,16] to produce localised triplet states. The quantum yields of triplet production for (3)-(6) were therefore determined utilising the technique of nanosecond laser flash photolysis. The results are summarised in Table 3 and show that in cyclohexane solution, ternary complex formation leads to efficient triplet production. However, as the solvent polarity is increased the triplet yield drops quite markedly. The laser flash photolysis studies gave no indication of the formation of radical ions or radicals. Compounds (3)-(6) were also found to be relatively photostable in degassed solution.

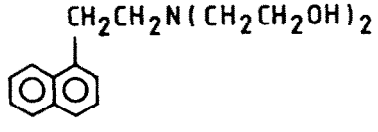
Table 3 Quantum Yields of Triplet Formation (Φ_T) for (3)-(6) and Related Compounds in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions

Compound	Φ_T		
	C_6H_{12}	THF	MeCN
	0.25	0.04	0.018
	0.43	0.09	0.009
	0.41	0.05	0.012
	0.42	0.05	0.008
1-Np$(CH_2)_2NEt_2$	0.29	0.33	0.22

Irradiation in aerated solution does lead to some decomposition. It could be argued that for compounds (3) and (4), the normal exciplex is formed (i.e. between the naphthalene group and the nearest nitrogen atom) and that the second amino group acts as a small polar molecule [17,18] which solvates the exciplex, thereby causing a bathochromic shift in the exciplex fluorescence. To see whether a single or two polar groups can act as a solvent for intramolecular exciplexes, compounds (7) and (8) were synthesised.



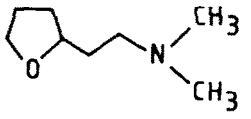
[7]



[8]

The hydroxyl groups cause only a small shift in the wavelengths for maximal exciplex fluorescence (Table 4). Thus the hydroxyl group, which is more polar than a tertiary amine (based on dipole moments), has a much smaller effect upon the wavelength maximum of the exciplex. Recently, Halpern [19] has shown that

for amino ethers such as (9a) and (9b) the ether linkage is unable to solvate the excited state of the amine. It appears that for solvation of exciplexes

$Me_2NCH_2CH_2CH_2OCH_3$ 

[9a] [9b]

by small polar molecules to be effective, several such molecules are required to form the solvation shell [18,20].

Table 4 Fluorescence λ_{max} values (nm) for (1) 1-$NpCH_2CH_2NEt_2$, (2) 1-$NpCH_2CH_2NMe(CH_2CH_2OH)$, (3) 1-$NpCH_2CH_2N(CH_2CH_2OH)_2$, in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions as 20°

Compound	λ_{max} (nm)			
	C_6H_{12}	C_6H_6	THF	MeCN
1-$NpCH_2CH_2NEt_2$	365	408	433	482
1-$NpCH_2CH_2NMe(CH_2CH_2OH)$	370	415	-	490
1-$NpCH_2CH_2N(CH_2CH_2OH)_2$	370	-	437	470

DISCUSSION

It can be seen from Figures 1 and 2 and Tables 1 and 2 that the presence of a diamine unit leads to efficient quenching of the naphthalene fluorescence in compounds (3) and (4). The question arises as to whether the fluorescent complexes formed by these compounds involve both amino groups and the aromatic hydrocarbon nucleus. The fact that the wavelength of maximal fluorescence emission for these compounds is red shifted when compared with compounds such as (10), suggests that the terminal amino group plays a part. If on the other hand only the terminal amino group and the aromatic hydrocarbon were involved

1-$NpCH_2CH_2NEt_2$ 1-$Np(CH_2)_4NEt_2$

[10] [11]

in exciplex formation, the exciplex formed may well have fluoresced at a similar wavelength to that found for (11) [7]. However in the case of (3) complexation with the terminal nitrogen would have produced an exciplex with five atoms interposed between the donor and acceptor groups. Unless special structural features are present [14], intramolecular exciplex formation in

non-polar solvents is only efficient when two or three atoms are interposed and is highly inefficient when five atoms are interposed . Thus, the fact that intramolecular fluorescence quenching in (3) is highly efficient in such solvents and the exciplex fluorescence is red shifted compared with (10), is strongly indicative that both amino groups and the hydrocarbon are involved in the exciplex. In the case of (4) a slightly different situation obtains since there is a through bond interaction between the nitrogen atoms [21]. Furthermore, if the piperazine ring adopts a boat conformation, the nitrogen atoms can interact via a through space process. The fluorescence spectra and quantum yields of fluorescence for (5) and (6) are similar to those for (4). The small red shift in the wavelength for maximal fluorescence emission displayed by (5) and (6) in cyclohexane solution compared with (3) and (4) may possibly indicate that in (5) and (6) the three amino groups participate in the exciplex. The extra stabilisation gained by delocalising the positive charge over three atoms is probably relatively small and in solvents such as benzene and tetrahydrofuran where solvent stabilisation is important, this effect is probably insignificant.

The experiments carried out with (7) and (8) show that a single or two polar groups strategically placed within a molecule are insufficient to cause any marked stabilisation of an exciplex. Consequently the red shifted fluorescent emission in (3)-(6) are interpreted as involving ternary complexes and the case of (5) and (6) possibly quaternary complexes.

It will be noted that for (3)-(6) efficient intramolecular quenching of fluorescence occurs. Our earlier proposal [22] that quenching can occur over long distances has been substantiated by a growing body of evidence [7,23]. As a consequence we cannot be certain as to whether the quenching observed for (3)-(6) is due to both amino groups interacting with the excited naphthalene chromophore or whether the amino groups act independently of each other.

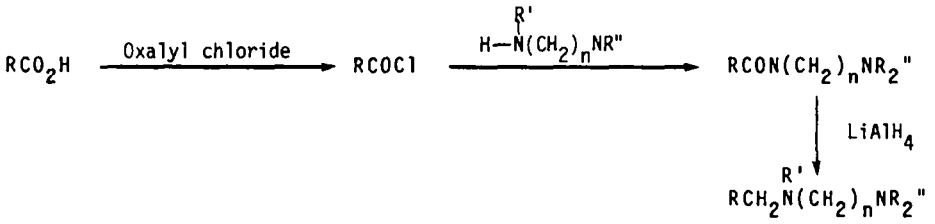
The quantum yields of fluorescence for (3) to (6) are relatively low indicating that some efficient non-radiative decay pathways are available to these compounds. The measurements of triplet yield formation indicate that in cyclohexane solution triplet formation is quite efficient. In view of the low quantum yields of fluorescence, most of the triplets would appear to be produced via the non-relaxed exciplex or the long range electron transfer process which does not necessarily lead to fluorescent exciplex formation. The low triplet yields in acetonitrile may either be due to inefficient triplet population or else the triplet state being efficiently quenched by the diamine unit. Preliminary experiments have indicated that diamines can quench aromatic hydrocarbon triplet states [15]. For these ternary systems however, the possibility that in polar solvents the energy of the exciplex and/or the intramolecular ion pair lie below that of the triplet hydrocarbon cannot be ignored.

The results obtained indicate that ternary complexes are highly effective at dissipating electronic energy via, as yet, unidentified non-radiative pathways. It is likely therefore that the use of reactants at concentrations high enough to produce ternary complexes may either totally change the course of chemical reactions or reduce the efficiency of the reaction occurring via a binary complex.

EXPERIMENTAL

Details of i.r., u.v. and fluorimetric instrumentation and methods have been described previously [24]. The laser flash photolysis system and method for obtaining triplet yields have also been previously described [25].

The arylalkylamines were synthesised via the following general method:



2-(1'-naphthyl)ethanoyl chloride

2-(1'-naphthyl)ethanoic acid (0.01 mole) was dissolved in sodium-dried benzene (100 cm^3) and oxalyl chloride (0.03 mole) added. The mixture was refluxed under a nitrogen atmosphere for 2.5 h and the solvent removed under reduced pressure using a rotary evaporator to give the crude acid chloride.

Procedure for preparing amides

N-(2-(1'-naphthyl)-1-oxo-ethyl)N'-methyl-1,4-diazacyclohexane

The crude 2-(1'-naphthyl)ethanoyl chloride was dissolved in sodium-dried ether (50 cm^3) and this solution added slowly to a stirred solution of N-methyl-1,4-diazacyclohexane (2.5 equivalents) in sodium-dried ether (75 cm^3) under a nitrogen atmosphere. The mixture was stirred at 20° for 20 h and then aqueous potassium hydroxide solution (2 M, 100 cm^3) added. Extraction with ether (3 x 50 cm^3) followed by washing the ethereal layer with water (2 x 50 cm^3), drying over anhydrous sodium sulphate and removal of the solvent under reduced pressure gave the product as a white solid (90% yield) M.p. 116-118° (from petroleum spirit (B.p. 60-80°)), found C, 76.10; H, 7.37; N, 10.22; $C_{17}H_{20}N_2O$ requires C, 76.09; H, 7.51; N, 10.44%, m/z 268.1560, I.r. (Nujol), 3030 (w), 2830 (br,s), 1630 (s), 1460-1430 (s), 1375 (s), 780 (s), ^1H nmr ($CDCl_3$), 2.20 δ (3H, s, NCH_3), 2.00-2.50 δ (4H, m, NCH_2), 3.26-3.83 δ (4H, m, $CONCH_2$), 4.08 δ (2H, s, $Np\underline{CH_2}CO$), 7.20-8.07 δ (7H, m, aromatics).

Procedure for preparation of amines

N-Methyl-N'-(2-(1'-naphthyl)ethyl)-1,4-diazacyclohexane (4)

A slurry of the amide prepared above (0.01 mole) in sodium-dried ether (50 cm^3) was added slowly, to an ice-cooled stirred suspension of lithium aluminium hydride (3 equivalents) under a nitrogen atmosphere. The mixture was allowed to warm up to room temperature and then heated under reflux for 4 h. The reaction mixture was cooled to 0° and the excess lithium aluminium hydride destroyed by the cautious addition of water (5 cm^3). The ethereal layer was separated, washed with water (1 x 25 cm^3), dried over anhydrous sodium sulphate and the solvent removed under reduced pressure to give the crude amine (90% yield). Purification was carried out by chromatography on alumina (UG1) with petroleum spirit as the eluant. The amine was distilled prior to use. B.p. 201-203° at 0.03 mm, found C, 80.32; H, 8.65; N, 11.00; $C_{17}H_{22}N_2$ requires C, 80.27; H, 8.72; N, 11.01%, m/z 254.1683. I.r. (neat) 3040 (m), 2920 (s), 2846-2740 (vs), 1600 (s), 1510 (s), 1470 (s), 800-770 (vs), ^1H nmr ($CDCl_3$), 2.30 δ (3H, s, NCH_3), 2.30-2.91 δ (10H,m, NCH_2), 3.03-3.50 δ (2H, m, $Np\underline{CH_2}$), 7.23-8.20 δ (7H, m, aromatics).

N,N-dimethyl-N'-ethyl-N'-(2-(1'-naphthyl)-1-oxoethyl)-1,2-diaminoethane

This amide was prepared using the typical procedure from N,N-dimethyl-N'-ethyl-1,2-diaminoethane using triethylamine (0.03 mole) to remove the hydrogen chloride generated by the reaction. The crude amide obtained as a yellow oil (80% yield) had a satisfactory I.r. and ^1H nmr spectrum. I.r. (neat) 3050 (m), 2920 (s), 2760 (s), 1620 (s), 1600 (m), 1510 (m), 1470-1400 (br,s), 1370-1350 (s), 780-770 (s), ^1H nmr ($CDCl_3$) 1.10 and 1.16 δ (3H, t, $CH_2\underline{CH_3}$), 2.13 and 2.23 δ (6H, s, NCH_3) 2.00-2.67 δ (2H, m, $\underline{CH_2}NMe_2$), 3.10-3.69 δ (4H, m, NCH_2), 4.07 and 4.13 δ (2H, s, $Np\underline{CH_2}CO$), 7.21-8.13 δ (7H, m, aromatics).

N,N-dimethyl-N'-ethyl-N'-(2-(1'-naphthyl)ethyl)-1,2-diaminoethane (3)

The crude amide from the preceeding preparation was reduced by lithium aluminium hydride using the typical procedure to give the crude amine (90% yield). Purification was effected by column chromatography on alumina (UG1) using a mixture of petroleum spirit (B.p. 60-80°) and diethyl ether (50:50 v/v) as the eluent. Further purification was effected by distillation. B.p. 172-174° at 0.05 mm, found C, 79.51; H, 9.88; N, 10.56; $C_{18}H_{26}N_2$ requires C, 79.95; H, 9.69; N, 10.36%. I.r. (neat), 3050 (m), 2920 (s), 2810 (s), 1600 (m), 1510 (m), 1460 (s), 1390 (m), 790 (s), ^{1}H nmr ($CDCl_3$) 1.10 δ (3H, t, $CH_2\underline{CH_3}$), 2.26 δ (6H, s, NMe_2), 2.76 δ (2H, q, $\underline{CH_2}CH_3$), 2.20-3.05 δ (6H, m, NCH_2), 3.05-3.46 δ (2H, m, $Np\underline{CH_2}$), 7.23-8.16 δ (7H, m, aromatic).

N-(2-(1'-naphthyl)-1-oxo-ethyl)-N'-(2-azacyclopentyl-2-oxo-ethyl)-1,4-diazacyclohexane

This amide was prepared from N-(2-azacylopentyl-2-oxo-ethyl)-1,4-diazacyclohexane using the typical procedure. Triethylamine (2 equivalents) was added to the reaction mixture to absorb the hydrogen chloride generated during the reaction. The crude amide was a white solid and obtained in 79% yield. I.r. (Nujol) 3040 (w), 2920 (vs), 2860 (s), 1640 (s), 1600 (m), 1470-1450 (s), 805 (s), 790 (m). ^{1}H nmr ($CDCl_3$), 1.72-2.06 δ (4H, m, ring CH_2), 2.34-2.72 δ (4H, m, $\underline{CH_2}NCH_2CO$), 3.10 δ (2H, s, NCH_2CON), 3.28-3.88 δ (8H, m, $CONCH_2$), 4.16 δ (2H, s, $Np\underline{CH_2}CO$), 7.22-8.04 δ (7H, m, aromatic).

N-(2-(1'-naphthyl)ethyl)-N'-(2-(azacyclopentyl)-ethyl)-1,4-diazacyclohexane(5)

This amine was prepared using the typical procedure from the crude amide. The crude amine (63% yield) was purified by vacuum distillation. M.p. 46-49°, B.p. 164-166° at 0.01 mm, found C, 78.09; H, 9.43; N, 12.34; $C_{22}H_{31}N_3$ requires C, 78.29; H, 9.26; N, 12.45%, m/z 337.2465. I.r. (Nujol) 3050 (m), 2960 (vs), 2800 (vs), 1600 (m), 1510 (m), 1460 (s), 1160-1120 (s), 800 (vs). ^{1}H nmr ($CDCl_3$), 1.68-1.88 δ (4H, m, ring CH_2), 2.44-2.80 δ (18H, m, NCH_2), 3.16-3.38 δ (2H, $Np\underline{CH_2}$), 7.28-8.10 δ (7H, m, aromatic).

N-(2-(1'-naphthyl)-1-oxo-ethyl)-N'-(2-(1-aza-4-oxa-cyclohexyl)-2-oxo-ethyl-1,4-diazacyclohexane

This amide was prepared using the typical procedure. M.p. 176-178°, (ethanol). I.r. (Nujol) 3050 (w), 2960-2920 (vs), 2860 (s), 1640 (s), 1600 (m), 1510 (m), 1470-1450 (vs), 1380 (s), 795 (s), 790 (s), 770 (s). ^{1}H nmr ($CDCl_3$) 2.28-2.58 δ (4H, m, $\underline{CH_2}NCH_2CO$), 3.16 δ (2H, s, NCH_2CO), 3.42-3.82 δ (12H, m, $O\underline{CH_2}$, $CON\underline{CH_2}$), 4.18 δ (2H, s, $Np\underline{CH_2}CO$), 7.30-8.04 δ (7H, m, aromatic).

N-(2-(1'-naphthyl)ethyl)-N'-(2-(1-aza-4-oxa-cyclohexyl)ethyl)-1,4-diazacyclohexane (6)

The crude diamide from the above preparation was reduced by lithium aluminium hydride using the typical procedure. The amine was distilled in vacuo to give an oil which eventually solidified. M.p. 52-55° (from petroleum spirit, B.p. 60°-80°), found C, 74.51; H, 9.12; N, 11.72; $C_{22}H_{31}N_3O$ requires C, 74.75; H, 8.84; N, 11.89%. I.r. (Nujol) 3050 (m), 2950 (vs), 2810 (vs), 1600 (m), 1510 (m), 1450 (s), 1160-1120 (vs), 870 (s), 800 (vs), 780 (vs). ^{1}H nmr ($CDCl_3$), 2.44-2.84 δ (18H, m, NCH_2), 3.20-3.40 δ (2H, m, $Np\underline{CH_2}$), 3.68-3.84 δ (4H, m, CH_2O), 7.28-8.16 δ (7H, m, aromatic).

N-Methyl-N-(2-(1'-naphthyl)-1-oxo-ethyl)-2-(2-(1'-naphthyl)ethanoyloxy)ethyl amine

The amido-ester was prepared by the reaction of 2 mole equivalents of 2-(1'-naphthyl)ethanoyl chloride with 1 equivalent of N-methyl-2-hydroxyethylamine, following the typical procedure. Triethylamine (2 equivalents) was added to the reaction mixture to absorb the hydrogen chloride generated during the reaction. The crude amino-ester was isolated as a viscous yellow oil and partially characterised. I.r. (Neat), 3050 (m), 2960 (s), 1720 (s), 1640 (s), 1600 (m), 1170-1120 (m), 790 (s). ^{1}H nmr ($CDCl_3$), 2.30 δ (3H, s, NCH_3), 3.45 δ (2H, t, CH_2NCO), 4.10 δ (4H, s, $Np\underline{CH_2}CO$), 4.25 δ (2H, t, CH_2OCO), 7.32-8.15 δ (7H, m, aromatics).

N-methyl-N-(2-(1'-naphthyl)ethyl)-2-hydroxyethylamine (7)

The crude amido-ester was reduced by the usual procedure, using 3 mole

equivalents of lithium aluminium hydride. The ethereal solution from the reaction was given an acid wash to separate the amino-alcohol from the 2-(1'-naphthyl)ethan-1-ol by-product. Basification and back extraction yielded the amino-alcohol as an orange oil, purified by vacuum distillation. B.p. 114-115° at 0.035 mm, found C, 78.47; H, 8.46; N, 6.09; $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11%. I.r. (Neat), 3400 (br, vs), 3050 (m), 2950 (s), 2850 (s), 1600 (m), 1520 (m), 1470 (s), 1400 (s), 1040 (br,s), 810 (s), 790 (s). ^{1}H nmr ($CDCl_3$), 2.26 δ (3H, s, NCH_3), 2.50 δ (2H, t, $N\underline{CH_2}CH_2O$), 2.68 δ (2H, m, $N\underline{CH_2}CH_2Np$), 3.14 δ (2H, m, $Np\underline{CH_2}$), 3.40 δ (1H, s, OH), 3.50 δ (2H, t, CH_2OH), 7.20-8.04 δ (7H, m, aromatics). (Signal at 3.40 δ exchanged with D_2O).

N-(2-(1'-naphthyl)-1-oxo-ethyl)-2,2-bis-(2-(1'-naphthyl)ethanoyloxy)diethylamine

The amido-diester was prepared by the reaction of 3 mole equivalents of 2-(1'-naphthyl)ethanoyl chloride with 1 equivalent of the amino-diol, (N,N-bis(2-hydroxyethyl)amine). Triethylamine (3 equivalents) was added to remove the hydrogen chloride generated by the reaction. The crude amido-diester, obtained as an orange oil was partially characterised by I.r. and ^{1}H nmr spectroscopy. I.r. (Neat) 3060 (m), 2990 (s), 1740 (s), 1645 (s), 1600 (m), 1510 (m), 1480 (s), 800 (s), 785 (s). ^{1}H nmr ($CDCl_3$), 3.30-3.40 δ (4H, m, CH_2NCO), 3.60 δ (6H, s, $Np\underline{CH_2}CO$), 4.10 δ (4H, t, CH_2O), 7.20-8.20 δ (21H, m, Np).

N-(2-(1'-naphthyl)ethyl)-N,N-bis-(2-hydroxyethyl)amine (8)

The amido-diester was reduced by the usual procedure using 4 mole equivalents of lithium aluminium hydride. The ethereal solution from the reaction was given an acid wash to separate the amino-diol from the 2-(1'-naphthyl)ethan-1-ol by-product. Basification of the aqueous layer and back extraction yielded the crude amino-diol as a yellow oil, purified by vacuum distillation. I.r. (Neat), 3400 (br,vs), 3070 (m), 2960 (s), 2890 (s), 1600 (m), 1510 (m), 1070-1050 (br,s), 880 (m), 805 (s), 785 (s). ^{1}H nmr ($CDCl_3$), 2.74 δ (2H, s, OH), 2.78 δ (2H, t, NCH_2), 2.96 δ (2H, m, $Np\underline{CH_2}CH_2$), 3.20 δ (2H, m, $Np\underline{CH_2}$), 3.60 δ (2H, t, OCH_2), 7.21-8.24 δ (7H, m, Np). (Signal at 2.74 δ exchanged with D_2O).

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