# Preparation of a Range of *NNN'N'*-Tetrasubstituted 1,8-Diaminonaphthalenes

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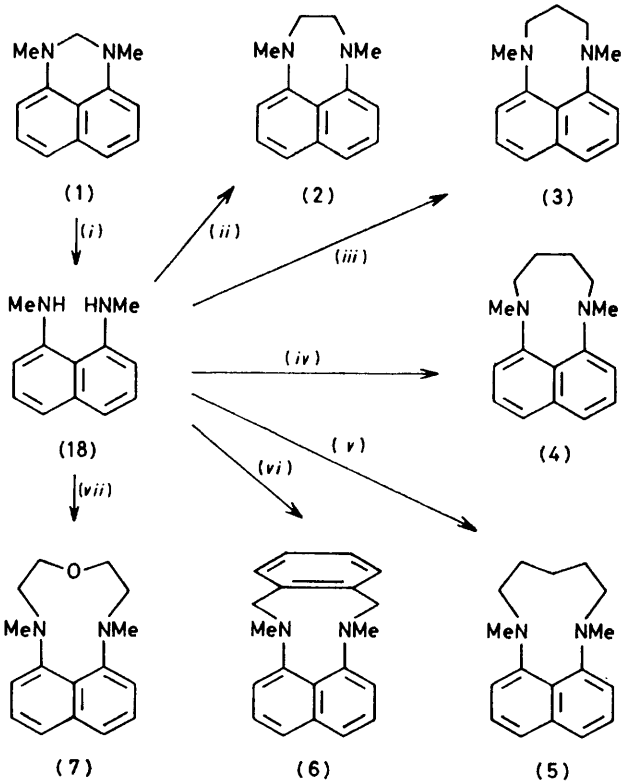
Alkylation of 1,8-bis(methylamino)naphthalene with difunctional reagents leads to a series of 1,5-dimethylnaphtho[1,8-*bc*]-1,5-diazacycloalkanes (1)—(5), to 1,5-dimethylbenzo[*g*]naphtho[1,8-*bc*]-1,5-diazacyclononane (6), and to 1,5-dimethylnaphtho[1,8-*bc*]-1,5-diaza-8-oxacyclodecane (7). A variety of attempts to develop a selective preparation of 1,8-bis(methylamino)naphthalene are reported. The preparation of 9,9-dimethylnaphtho[1,8-*bc*]-1,5-diazabicyclo[3.3.1]nonane (8), naphtho[1,8-*bc*]-1,5-diazabicyclo[3.2.2]nonane (9), and naphtho[1,8-*bc*]-1,5-diazabicyclo[3.3.3]undecane (10) from 1,8-diaminonaphthalene are described. Reaction of appropriate 1,4- and 1,5-dihalides with 1,8-diaminonaphthalene leads to 1,8-bis-(1-pyrrolidinyl)naphthalene (11), 1,8-bis(1,3-dihydroisoindol-2-yl)naphthalene (12), 1,8-bis-(1-piperidinyl)naphthalene (13), and 1,8-dimorpholinonaphthalene (14). Nitration of 2,7-dimethylnaphthalene gives a mixture from which 2,7-dimethyl-1,8-dinitronaphthalene may be isolated; this is reduced and alkylated to give 1,8-bis(dimethylamino)-2,7-dimethylnaphthalene (15). 1,8-Bis(dimethylamino)-2,7-dimethoxynaphthalene (16) and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene (17) are similarly prepared by reduction and alkylation of 1,8-dinitro-2,7-dimethoxynaphthalene. Reaction of 2,2-dimethyl-1,3-dihydroperimidine with αα'-dibromo-*o*-xylene led, surprisingly, to (12) and 5-(2-propyl)benzo[*g*]naphtho[1,8-*bc*]-1,5-diazabicyclo[4.3.0]nonane (24).

SINCE our demonstration in 1968 of the remarkable basicity of 1,8-bis(dimethylamino)naphthalene,[1] there has been continuing interest in this and related compounds.[2–15],† It is clear that the alignment and hybridisation of the lone pairs on the nitrogen atoms play a crucial role in the properties of these compounds. In this paper we describe the preparation of a range of *NNN'N'*-tetrasubstituted 1,8-diaminonaphthalenes in which the lone pair orientation is varied by ring formation and buttressing effects. Full accounts of the properties of the molecules will appear in later papers. A study of a comparable set of substituted *o*-phenylenediamines has recently appeared.[16]

## RESULTS AND DISCUSSION

We wanted first to make a series of diamines (1)—(5) in which the alicyclic ring would control the lone-pair orientation. These molecules are not, in general, available *via* reaction of 1,8-diaminonaphthalene with $X[CH_2]_nY$, since further alkylation occurs too readily (see below) to give (9), (10), (11), and (13). We made (1)—(5) instead from 1,8-bis(methylamino)naphthalene (18). The preparation of this compound by partial alkylation of 1,8-diaminonaphthalene with dimethyl sulphate was a major impediment in this work, since the yield is low and isolation involves chromatography. A substantial effort was therefore made to find a selective synthesis of this compound, and although all our efforts were unsuccessful we feel these should be detailed. Thus 1,8-bis-(*N*-methyl-*N*-tosylamino)naphthalene was prepared from 1,8-bis(tosylamino)naphthalene and dimethyl sulphate, but the tosyl groups could not be removed[17] with (*a*) concentrated $H_2SO_4$; (*b*) refluxing $H_2SO_4$–HOAc; (*c*) refluxing 66% HI; (*d*) Na in HMPA; (*e*) Na in liquid $NH_3$; or (*f*) Na in 1,2-dimethoxyethane. Less surprisingly, attempts to make 1,8-bis(ethoxycarbonylamino)naphthalene led only to 1,2-dihydro-

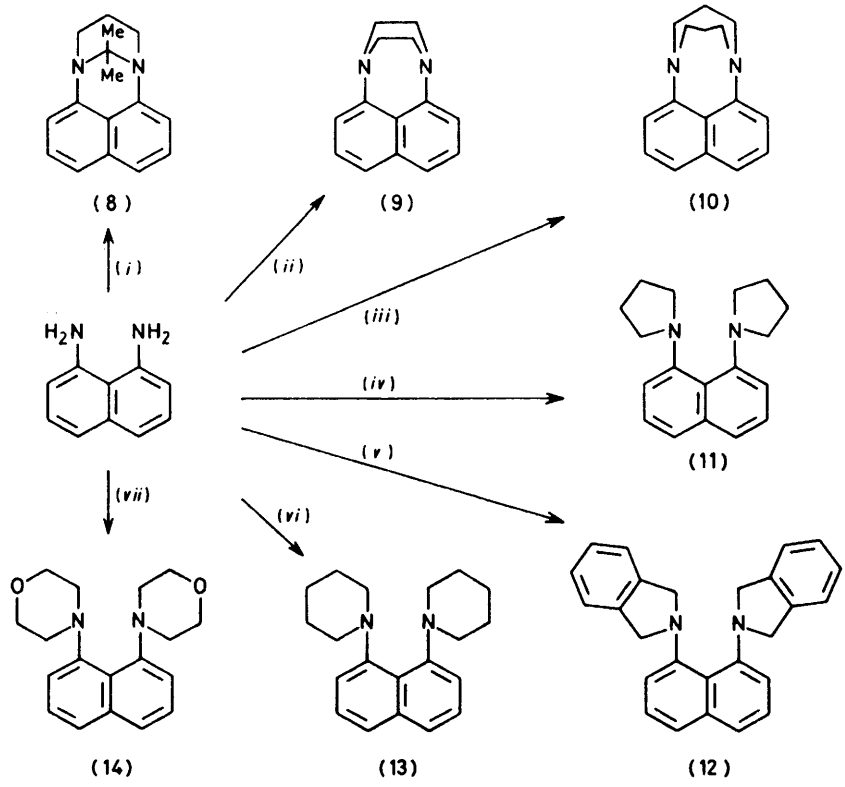



SCHEME 1 *Reagents and yields:* (*i*) $H_2CO$–EtOH–$H_2O$ (80%); (*ii*) $Br[CH_2]_2Br$–$NaHCO_3$–DMF (25%), or $Br[CH_2]_2Br$–NaH–THF (80%); (*iii*) $Br[CH_2]_3Br$–$NaHCO_3$–diglyme (43%), or $Br[CH_2]_3Br$–NaH–THF (1%); (*iv*) $Br[CH_2]_4Br$–$NaHCO_3$–diglyme (58%); (*v*) $Br[CH_2]_5Br$–$Na_2CO_3$–diglyme (25%); (*vi*) αα'-dibromo-*o*-xylene–$Na_2CO_3$–DMF (13%); (*vii*) $ClCH_2CH_2OCH_2CH_2Cl$–$Na_2CO_3$–diglyme (77%)

† 1,8-Bis(dimethylamino)naphthalene has achieved some popularity as a non-nucleophilic base, sold by the Aldrich Chem. Co. as 'Proton Sponge,' although its usefulness is limited by the very slow rates of proton transfer to it (see references 6 and 13) and possibly by its relatively easy oxidation. The name 'Proton Sponge' is indeed apt; sponges are not kinetically active in seeking water, they merely mop it up when it is presented to them.

perimidone. Reaction of 1,8-bis(trimethylsilylamino)-naphthalene [18] with potassium hydride and methyl iodide led, frustratingly, to 1-amino-8-dimethylamino-naphthalene! This reaction presumably involves the shift of a trimethylsilyl group, probably *via* a pentaco-ordinate silicon anion, and has analogies in the chemistry of silylhydrazines.[19] Reaction of 1,8-diaminonaph-thalene with dichlorodimethylsilane under the same conditions used for the reaction with chlorotrimethyl-silane [18] failed to produce any material recognisable as 2,2-dimethyl-2-sila-1,2-dihydroperimidine. 2,2-Di-methyl-1,2-dihydroperimidine (22), readily available from 1,8-diaminonaphthalene and acetone,[20a] failed to reported that the readily available 1,2,3-trimethyl-perimidinium iodide can be hydrolysed to 1,8-bis(methyl-amino)naphthalene with KOH in ethanol.

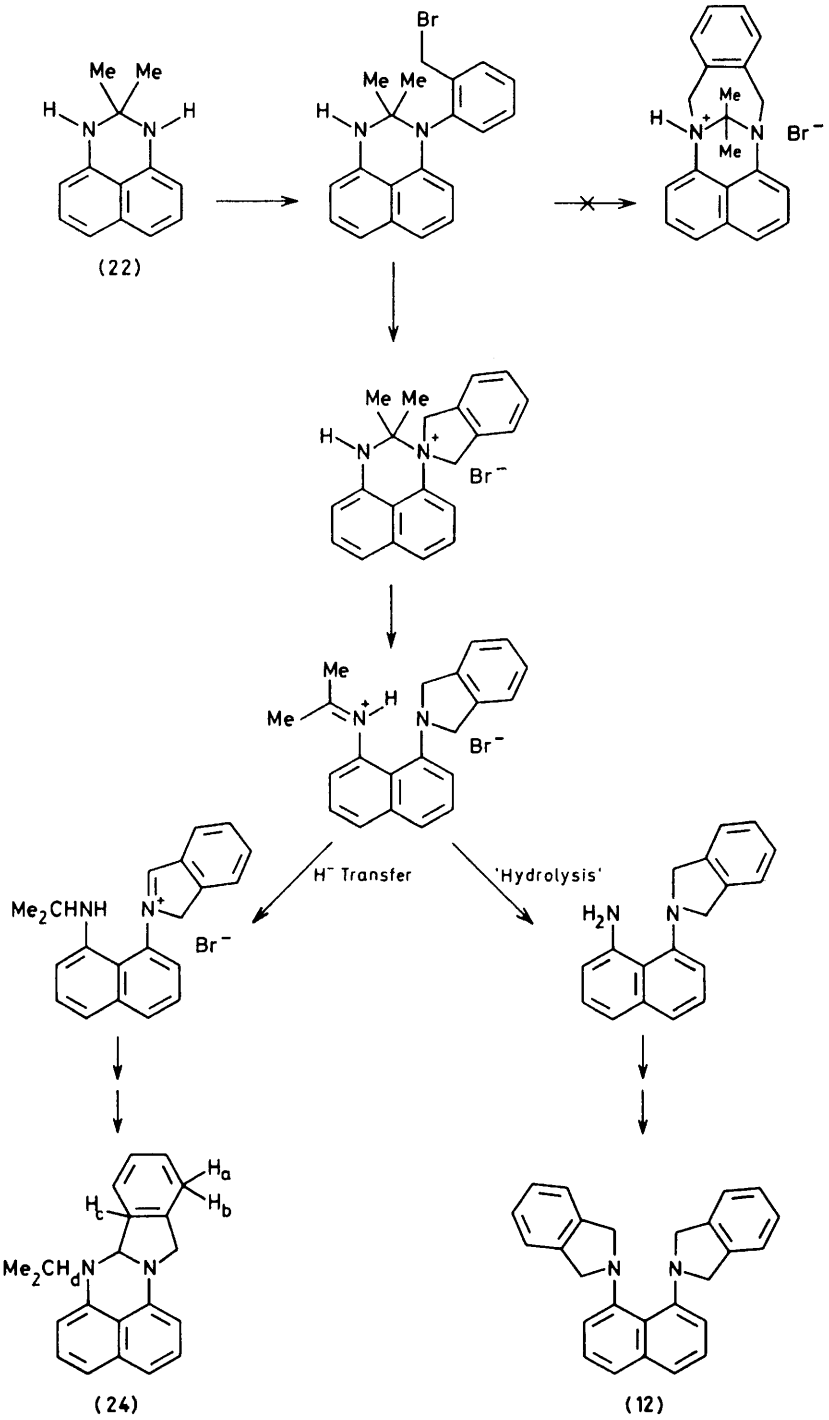
Compounds (1)—(7) were obtained by the methods shown in Scheme 1. Their structures followed directly and unambiguously from analytical and spectroscopic data: in particular the $^{13}C$ n.m.r. spectra showed the derivatives were symmetrically bridged. The crude reaction product was invariably a complex mixture by t.l.c. and g.l.c., so yields of the desired compounds were generally quite low: this could partly be due to the ready oxidation of (18). The diazacyclodecane (5) appeared to decompose on an alumina column and during the usual




SCHEME 2 *Reagents and yields:* (*i*) $Me_2CO$ then $Br[CH_2]_3Br$–$Na_2CO_3$–DMF (38%); (*ii*) $Br[CH_2]_2Br$–$Na_2CO_3$–DMF (42%); (*iii*) $Br[CH_2]_3Br$–$Na_2CO_3$–sulpholan (5%) (see Table); (*iv*) $Br[CH_2]_4Br$–$Na_2CO_3$(60%); (*v*) αα′-dibromo-*o*-xylene, $Na_2CO_3$–DMF (5%); (*vi*) $Br[CH_2]_5Br$–$Na_2CO_3$(20%); (*vii*) $ClCH_2CH_2OCH_2CH_2Cl$–$Na_2CO_3$ (10%)

hydrolyse in 6N HCl, even in the presence of 2,4-dinitro-phenylhydrazine. We hoped that an appropriate quaternary salt might hydrolyse more readily. Accord-ingly (8), prepared as described below, was mono-quaternised with $MeOSO_2F$, but hydrolysis of this salt with sodium hydroxide did not result in the desired loss of the $Me_2C$ bridge. We were able to prepare 1,8-bis-(ethylamino)naphthalene in good yield by reduction of 1,8-bis(acetamido)naphthalene [20b] with $BH_3$–THF, but unfortunately were unable to find a good preparation of 1,8-bis(formamido)naphthalene, *e.g.* by reaction of ethyl formate or formic acetic anhydride–triethylamine with the diamine. However, a solution to this problem is now at hand, for Pozharskii *et al.*[21] have very recently acid/base extraction procedure. It was best purified by short-path distillation, but it could not be obtained crystalline or entirely free of starting diamine.

An even stricter control of lone-pair orientation can be achieved by making the nitrogens the bridgehead atoms in a bicyclic system. Compounds (8)—(14) were pre-pared as shown in Scheme 2. Evidence that (9) has the structure shown rather than the isomeric 1,8-bis(aziri-dinyl)naphthalene comes from the total lack of con-jugation of the nitrogen lone pairs with the aromatic rings shown by the downfield position of the *ortho* and *para* carbons and attached hydrogens in the n.m.r. spectra compared with 1,8-bis(dimethylamino)naph-thalene, the lack of long wavelength u.v. absorption, and




SCHEME 3

the temperature-independent AA'BB' pattern for the $CH_2CH_2$ groups in the $^1H$ n.m.r. spectrum of (9).

Reaction of 1,8-diaminonaphthalene with 1,3-dibromopropane was run under a variety of conditions, summarised in the Table, and some rather surprising products [(3), (8), (19), (20), and (21)] were obtained along with low yields of the desired product, naphtho-[1,8-*bc*]-1,5-diazabicyclo[3.3.3]undecane (10), which was easily isolated because it was always the first product off an alumina column. Compound (21) is the only case where we have seen cyclisation onto the naphthalene ring. No evidence for the formation of 1,8-bis(azetidinyl)naphthalene was found. The structural evidence for (10) rests on its unique properties [4,5] and *X*-ray crystallography.[4]

Reaction of 1,8-diaminonaphthalene with 1,4- and

1,5-dihalogeno-compounds resulted in the formation of compounds (11)—(14). Evidence for the 1,1;8,8 rather than 1,8;1,8 bridging and for the structures of (11)—(14) comes from comparison of spectra with 1,8-bis(dimethylamino)naphthalene and the corresponding heterocycle (pyrrolidine *etc.*) and most convincingly from variable-temperature $^1$H n.m.r. studies, which show the occurrence of dynamic processes [2] which render the protons of the methylene groups equivalent. A detailed report on these effects will appear elsewhere. In addition the properties of *e.g.* (11) make it quite plain that this compound is not a naphtho-derivative of 1,6-diazabicyclo[4.4.3]tridecane.[22]

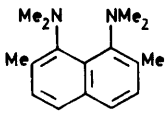
symmetrical product (12). Similar reactions were not observed for the three-carbon system (8), and would not be expected, as here cyclisation onto the same nitrogen would produce a strained azete ring.

Another way to influence the conformation of 1,8-bis-(dialkylamino)naphthalenes would seem to be through the buttressing effects of 2,7-disubstitution, and the extraordinarily high basicities of compounds (15)—(17) have been reported.[6] Details of the preparations of these compounds are now given. 2,7-Dimethylnaphthalene [23] was nitrated with 85% nitric acid to give mainly the desired 1,8-dinitro-compound [24] along with some 2,7-dimethyl-1-nitronaphthalene [25] and what was probably

Reactions of 1,8-diaminonaphthalene with 1,3-dibromopropane

| Reaction conditions | | | | 1,8-Diamino-naphthalene | 1,3-Dibromo-propane | | | Products | |
|---|---|---|---|---|---|---|---|---|---|
| Temp. (°C) | Time/h | Solvent | Volume/ml | (mmol) | (mmol) | $NaHCO_3$ (mmol) | $Na_2CO_3$ (mmol) | mmol | % yield |
| 150 | 70 | sulpholan | 90 | 19.9 | 20 | 11.6 | | (19) 4.6 | 23 |
| | | | | | | | | (10) 0.20 | 1 |
| 150 | 70 | sulpholan | 150 | 60 | 120 | | 120 | (8) 4.8 | 8 |
| | | | | | | | | (20) 0.60 | 1 |
| 150 | 46 | sulpholan | 150 | 30 | 60 | 60 | | (19) 5.4 | 18 |
| | | | | | | | | (21) 0.30 | 1 |
| 150[f] | 52 | sulpholan | 80 | 50 | 60 | | 79 | (20) 0.15 | 1 |
| | | | | | | | | (10) 2.6 | 5 |
| | | | | | | | | (21) 0.24 | 1 |
| 150 | 72 | diglyme | 150 | 19.9 | 40 | 80 | | (3) 7.4 | 37 |
| | | | | | | | | (21) 0.32 | 2 |
| 180 | 1 | DMF | 15 | 10 | 25 | | 20 | (10) 0.32 | 3 |
| 200 | 1 | DMF | 30 | 40 | 99 | | 40 | (10) 1.6 | 4 |
| Reflux | 2 | neat | | 2.9 | 3.5 | | 6.0 | (20) 0.21 | 7 |
| Reflux | 2 | neat | | 10 | 40 | | 20 | (20) 1.0 | 10 |
| | | | | | | | | (10) 0.15 | 2 |
| | | | | | | | | (8) 0.08 | 1 |

In an attempt to prepare 10,10-dimethylbenzo[*c*]-naphtho[1,8-*gh*]-1,5-diazabicyclo[4.3.1]decane (23), 2,2-dimethyl-1,2-dihydroperimidine (22) was reacted with αα′-dibromo-*o*-xylene. No (23) was obtained however; instead we isolated two other products. Chromatography of the reaction mixture on an alumina column separated 1,8-bis-(1,3-dihydroisoindol-2-yl)naphthalene (12) (26% yield) as greenish crystals, m.p. 166—169 °C. The next fractions afforded a brown crystalline solid, m.p. 112—114 °C. Analysis indicated the molecular formula $C_{21}H_{20}N_2$, and the $^1$H n.m.r. spectrum revealed the presence of an isopropyl group (two methyl doublets at δ 1.34 and 0.50, and a proton septet at δ 3.46). These data and the rest of the n.m.r. spectrum are wholly consistent with structure (24), 5-isopropylbenzo[*g*]naphtho-[1,8-*bc*]-1,5-diazabicyclo[4.3.0]nonane. A possible mechanism for this reaction is outlined in Scheme 3. Models suggest that (23) will possess large interactions between the upward methyl group and either the benzene ring or the upward benzylic protons, depending on which way the benzene ring is flipped. Thus the transition state that should lead to (23) is destabilised and so cyclisation preferentially occurs onto the same nitrogen atom. The methyl groups on the carbon bridge presumably produce the isopropyl group in (24) by ring opening and hydride transfer followed by ring closure. In an alternative pathway, the bridge is completely removed and reaction with a second molecule of the xylene then gives the 2,7-dimethyl-1,5-dinitronaphthalene. The 1,8-dinitro-compound was reduced with hydrogen and 10% palladium–charcoal, and the diamine formed was alkylated with NaH–MeI in THF to give a 27% yield of (15). Nitration of the readily available 2,7-dimethoxynaph-



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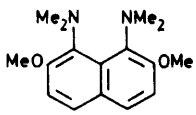

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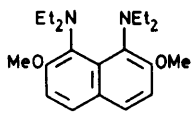

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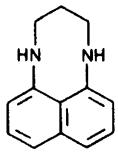

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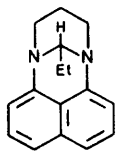

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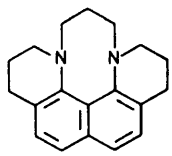

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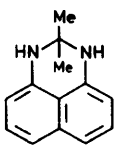

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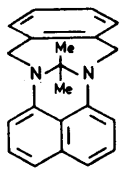

(23)

thalene yielded the 1,8-dinitro-compound [26] which was reduced with tin(II) chloride to give 1,8-diamino-2,7-dimethoxynaphthalene.[27] This compound was then methylated and ethylated using the sodium hydride method.

## EXPERIMENTAL

U.v. spectra were recorded on a Pye-Unicam SP1800 spectrophotometer. Mass spectra were recorded on an AEI MS 902 double-focusing spectrometer operating at an ionising energy of 70 eV. $^1$H N.m.r. spectra were recorded at 100 MHz on a Varian Associates HA 100 or a JEOL PFT 100 spectrometer; $^{13}$C n.m.r. spectra were obtained using a JEOL FX 90Q spectrometer. Chemical shifts are quoted downfield from internal tetramethylsilane. Micro-analyses were obtained on a Perkin-Elmer 240 elemental analyser. Melting points were recorded on a Kofler micro-heating stage and are uncorrected. G.l.c. analyses were performed on a 2-m column of 5% polyimide 110 on 100—120 mesh Gas-Chrom Q at an oven temperature of 210 °C. Column chromatography was performed on alumina Brockman activity II. All chemicals were used as supplied unless otherwise stated. Dimethylformamide (DMF), diglyme, and tetrahydrofuran (THF) were dried and distilled before use. 1,8-Diaminonaphthalene was purified by Soxhlet extraction into n-hexane and recrystallised from n-hexane. Light petroleum refers to the fraction having b.p. 40—60 °C.

*General Procedures.—Extraction of the amines.* The procedure for extraction of the amines was the same in all cases except for compound (5) as stated. The crude reaction mixtures were shaken with 2M hydrochloric acid and extracted with an organic solvent to remove alkylating agents. The amines were liberated from their salts by basifying the aqueous layer to pH 14 with 2M sodium hydroxide, and were then extracted into a suitable organic solvent.

*Preparation of salts.* The hydrogen trifluoroacetate salts were obtained by dissolving the amine in diethyl ether, adding an ethereal solution of trifluoroacetic acid (1 equiv.) and collecting the precipitate. The hydrogen tetrafluoroborate salts were prepared by dissolving the trifluoroacetate salt in the minimum volume of hot water and adding an excess of sodium tetrafluoroborate, also in hot water. The precipitate was recrystallised from water.

1,8-*Bis(methylamino)naphthalene* (18).—1,8-Diaminonaphthalene (30.0 g, 0.188 mol) was suspended in sodium hydroxide solution (60 g in 400 ml water) and dimethyl sulphate (48.0 g, 0.381 mol) was added during 20 min with stirring. The mixture was then heated for a further 20 min on a steam-bath. The cool solution was extracted with enough 10% acetic acid to produce a final pH of 7, in order to remove any 1,8-bis(dimethylamino)naphthalene formed. The rest of the mixture was chromatographed on alumina with light petroleum–ether (98 : 2 v/v) as eluant. The first product eluted was 8-methylamino-1-dimethylaminonaphthalene (4.2 g, 13%), followed by (18) (3.5 g, 10%), white *crystals*, m.p. 103—104 °C after sublimation (85 °C/0.5 mmHg) and recrystallisation from light petroleum (Found: C, 77.15; H, 7.7; N, 14.9. $C_{12}H_{14}N_2$ requires C, 77.42; H, 7.53; N, 15.05%); *m/e* 186 ($M^+$); $\lambda_{max.}$ (iso-octane) 338 and 348 nm ($\log_{10}$ ε 4.03, 4.02); δ ($CCl_4$) 7.02 (H-3), 6.96 (H-4), 6.30 (H-2), 5.01 (NH), and 2.70 (Me).

1,3-*Dimethyl*-1,2-*dihydroperimidine* (1).—To a solution of diamine (18) (0.186 g, 1.0 mmol) in hot ethanol (6 ml) was added formalin (2 ml of 40% formaldehyde). The precipitate was collected and recrystallised from ethanol to give (1) (0.160 g, 80%) as white *plates*, m.p. 148—149 °C (Found: C, 78.65; H, 7.3; N, 14.0. $C_{13}H_{14}N_2$ requires C, 78.79; H, 7.07; N, 14.14%); *m/e* 198 ($M^+$); $\lambda_{max.}$ (iso-octane) 345 and 343 nm ($\log_{10}$ ε 4.04, 4.02); $\delta_H$ ($CCl_4$) 7.09 (H-3), 6.98 (H-4), 6.28 (H-2), 3.95 ($CH_2$), and 2.85 (Me) ($J_{2,3}$ 7.6, $J_{2,4}$ 0.9, $J_{3,4}$ 8.2 Hz); $\delta_C$ ($CDCl_3$) 144.4 (C-1), 134.7 (C-10), 126.7 (C-3), 120.4 (C-9), 117.5 (C-4), 103.2 (C-2), 70.4 ($CH_2$), and 36.7 (Me).

1,5-*Dimethylnaphtho*[1,8-bc]-1,5-*diazacycloheptane* (2).—*Route* (*i*). 1,2-Dibromoethane (0.63 g, 3.3 mmol) and (18) (0.46 g, 2.4 mmol) were dissolved in DMF (15 ml). Sodium hydrogencarbonate (0.42 g, 5 mmol) was added and the mixture stirred at reflux under nitrogen for 50 min. The amines were extracted from the basic solution into ether and chromatographed on alumina with hexane–ether (99 : 1 v/v). First eluted was unchanged (18) (0.907 g, 20%) followed by (2) which was recrystallised from n-hexane and sublimed (100 °C/0.4 mmHg) to give white *needles* (0.127 g, 25%), m.p. 88—90 °C (Found: C, 79.4; H, 7.7; N, 13.6. $C_{14}H_{16}N_2$ requires C, 79.24; H, 7.54; N, 13.20%); *m/e* 212 ($M^+$); $\lambda_{max.}$ (iso-octane) 330 and 350 nm ($\log_{10}$ ε 3.98, 4.03). $\delta_H$ ($CCl_4$) 7.26 (H-3), 7.26 (H-4), 6.67 (H-2), 3.34 ($CH_2$), and 3.00 (Me) ($J_{2,3}$ 7.0, $J_{2,4}$ 0.8, $J_{3,4}$ 8.0 Hz); $\delta_C$ ($CDCl_3$) 149.1 (C-1), 136.7 (C-10), 125.6 (C-3), 123.5 (C-9), 120.3 (C-4), 109.9 (C-2), 57.3 ($CH_2$), and 41.9 (Me). Later fractions contained (1) (0.061 g, 13%).

*Route* (*ii*). To a solution of (18) (0.188 g, 1 mmol) in THF (10 ml) under nitrogen was added a suspension of petroleum-washed sodium hydride (0.300 g, 12.5 mmol). The mixture was warmed to reflux and 1,2-dibromoethane (0.192 g, 1 mmol) was added dropwise. After refluxing for 24 h the reaction mixture was quenched with water and extracted into ether. Chromatography on alumina separated (2) (0.169 g, 80%), identical with the sample described above.

Neither the trifluoroacetate nor the tetrafluoroborate salt of (2) could be obtained crystalline.

1,8-*Dimethylnaphtho*[1,8-bc]-1,5-*diazacyclo-octane* (3).—*Route* (*i*). Diamine (18) (0.776 g, 4.1 mmol) was dissolved in diglyme (15 ml) in which sodium hydrogencarbonate (0.701 g, 8.3 mmol) was suspended. 1,3-Dibromopropane (1.26 g, 15.1 mmol) was added and the reactants heated under nitrogen at 190 °C for 1.25 h. The cooled solution was filtered and evaporated to dryness under vacuum. Column chromatography on alumina with n-hexane removed unchanged (18) (0.029 g, 4%); n-hexane–ether (95 : 5 v/v) eluted (3) which was recrystallised from methanol at −80 °C and then sublimed (100 °C/0.1 mmHg) to give yellow *crystals*, m.p. 77—79 °C (0.405 g, 43%) (Found: C, 79.2; H, 8.0; N, 12.25. $C_{15}H_{18}N_2$ requires C, 79.61; H, 8.02; N, 12.38%); *m/e* 226 ($M^+$). $\lambda_{max.}$ (iso-octane) 350 nm ($\log_{10}$ ε 3.97); $\delta_H$ ($CCl_4$) 7.35 (H-4), 7.22 (H-3), 6.95 (H-2), 2.90 ($CH_2$-α), 2.85 (Me), and 1.56 ($CH_2$-β) ($J_{2,3}$ 7.2, $J_{2,4}$ 1.8, $J_{3,4}$ 8.2 Hz); $\delta_C$ ($CDCl_3$) 149.0 (C-1), 136.2 (C-10), 130.5 (C-9), 125.7 (C-3), 123.9 (C-4), 116.9 (C-2), 59.3 ($CH_2$-α), 44.3 (Me), and 26.1 ($CH_2$-β). When DMF was used as solvent for the reaction (3) (*ca.* 25% yield) was obtained along with (1) (*ca.* 10%).

*Route* (*ii*). The method described above for (2) was followed using (18) (1.5 g, 8.0 mmol), sodium hydride (3.8 g, 158 mmol), and 1,3-dibromopropane (20 g, 99 mmol) in THF and refluxing for 36 h. A 1% yield of (3) was obtained. The tetrafluoroborate salt of (3) had m.p. 171—173 °C.

1,5-*Dimethylnaphtho*[1,8-bc]-1,5-*diazacyclononane* (4).—A mixture of (18) (0.56 g, 3.0 mmol), 1,4-dibromobutane (1.29 g, 5.9 mmol), and sodium hydrogencarbonate (3.8 g, 45 mmol) was refluxed together in diglyme (25 ml) under nitrogen for 46 h, by which time g.l.c. indicated no (18) remained. The solution was filtered and evaporated *in vacuo* to leave a dark red gum. The hexane extract was dried and evaporated onto chromatographic alumina which on elution with light petroleum–ether (9 : 1 v/v) yielded a yellow, oily solid which could not be purified by recrystallisation or sublimation. Instead (4) was purified as its *tetrafluoroborate salt*; white crystals [58% yield from (18)], m.p. 211—214 °C (Found: C, 58.5; H, 6.35; N, 8.40. $C_{16}H_{21}BF_4N_2$ requires C, 58.70; H, 6.42; N, 8.56%). A solution of the salt (0.090 g) in 2M NaOH was extracted into ether. The ether layer was dried and evaporated to return the free amine (4) (0.049 g, 74%) as a white gum which would not crystallise; *m/e* 240 ($M^+$); $\delta_H$ ($CDCl_3$) 7.25—6.77 (6 H, m, Ar-H), 3.1 (4 H, m, $CH_2$-α), 2.67 (6 H, s, Me), and 1.7 (4 H, m, $CH_2$-β); $\delta_C$ ($CDCl_3$) 150.8 (C-1), 137.7 (C-10), 125.3 (C-3), 122.9 (C-9), 121.3 (C-4), 115.6 (C-2), 56.4 ($CH_2$-α), 39.2 (Me), and 25.2 ($CH_2$-β).

1,5-*Dimethyl*[1,8-bc]-1,5-*diazacyclodecane* (5).—A mixture of (18) (0.40 g, 2.15 mmol), 1,5-dibromopentane (0.74 g, 3.2 mmol), and sodium carbonate (2.7 g, 30 mmol) in diglyme (*ca.* 20 ml) was refluxed under nitrogen for 26 h. The mixture was cooled, filtered, and evaporated *in vacuo*; the residue was dissolved in light petroleum, washed with water, dried, and evaporated to a red tar (0.53 g). Short-path distillation of this (oil bath, 140 °C/0.6 mmHg) produced an oil which on redistillation gave (5) (*ca.* 0.14 g, 25%) as a pale yellow, viscous *oil* which would not crystallise (Found: $M^+$, 254.1783; $C_{17}H_{22}N_2$ requires *M*, 254.1784); $\delta_H$ ($CDCl_3$) 7.5—6.9 (Ar-H), 3.4—3.1 ($CH_2$-α), 2.71 (Me), 3.0—2.6 and 2.0—1.2 (other $CH_2$) (the spectrum at room temperature is poorly resolved due to broadening; the variable-temperature spectra will be discussed in detail elsewhere); $\delta_C$ ($CDCl_3$), 150.0 (C-1), 137.6 (C-10), 125.4 (C-3), 122.5 (C-4 or C-9), 122.3 (C-4 or C-9), 114.5 (C-2), 56.0 ($CH_2$-α), 41.6 (Me), 26.9 ($CH_2$-β), and 25.8 ($CH_2$-γ). The n.m.r. spectra showed that (5) was contaminated with a small amount of starting amine (18). Compound (5) could not be purified by column chromatography on alumina; light petroleum–ether eluted dark oils that were a complex mixture by g.l.c. and n.m.r. Attempts to isolate (5) by the usual extraction procedure resulted in reduced yields.

1,6-*Dimethylbenzo*[c]*naphtho*[1,8-gh]1,6-*diazacyclononane* (6).—A mixture of (18) (0.782 g, 4.20 mmol), αα′-dibromo-*o*-xylene (2.3 g, 8.71 mmol), and sodium carbonate (0.45 g, 4.24 mmol) was refluxed overnight in DMF. The amines were extracted into ether and chromatographed on alumina with light petroleum–ether (95 : 5 v/v) as eluant. The first material eluted was (6), a yellow oil (0.161 g, 13%). It was purified as the *tetrafluoroborate salt*; white crystals, m.p. 232—235 °C (Found: C, 62.9; H, 5.75; N, 7.75. $C_{20}H_{21}BF_4N_2$ requires C, 63.69; H, 5.49; N, 7.27%. Found: $M^+$, 288.1621; $C_{20}H_{20}N_2^+$ (the free-base molecular ion) requires *M*, 288.1626); $\delta_H$ ($CDCl_3$), 7.29 (H-4), 7.18 (H-3), 6.98 (H-2), 6.00 (Ar-H on bridge, s), and 2.25 (N-Me) ($J_{2,3}$ 7.75, $J_{2,4}$ 1.09, $J_{3,4}$ 8.00 Hz). The $CH_2$ protons are broadened to invisibility at room temperature but can be observed at −30 °C.

1,5-*Dimethylnaphtho*[1,8-bc]-1,5-*diaza*-8-*oxacyclodecane* (7).—Diamine (18) (0.56 g, 3.0 mmol) and ββ′-dichlorodiethyl ether (0.35 g, 2.5 mmol) were dissolved in diglyme, sodium carbonate (0.320 g, 3.0 mmol) was added, and the mixture was heated to reflux. Reaction was followed by g.l.c. and more alkylating agent (4 × 0.63 g, 4.5 mmol) was added after 4, 26, 119, and 139 h. After 151 h the mixture was cooled, filtered, and evaporated. The light petroleum extract was dried and evaporated to yield (7) as a yellow oil (0.59 g, 77%). The *trifluoroacetate salt* of (7) was isolated as a white solid, m.p. 178—182 °C (Found: C, 58.55; H, 5.90; N, 7.35. $C_{18}H_{21}N_2F_3O_3$ requires C, 58.34; H, 5.67; N, 7.56%); $\delta_H$ ($CDCl_3$) 7.4—6.85 (6 H, m, Ar-H), 4.0—3.1. (8 H, m, $CH_2$-α and $CH_2$-β), and 2.8 (6 H, s, Me).

9,9-*Dimethylnaphtho*[1,8-bc]-1,5-*diazabicyclo*[3.3.1]*nonane* (8).—1,8-Diaminonaphthalene (0.320 g, 2.0 mmol), 1,3-dibromopropane (0.60 g, 3.0 mmol) and sodium carbonate (0.24 g, 2.27 mmol) were refluxed with stirring in acetone for 8 h. The ether extract was dried and chromatographed on alumina; light petroleum–ether (95 : 5 v/v) eluted (8) (0.16 g, 34%) as white *plates*, m.p. 67—70 °C (from n-hexane) (Found: C, 80.95; H, 7.8; N, 11.75. $C_{16}H_{18}N_2$ requires C, 80.67: H, 7.56; N, 11.77%); *m/e* 238 ($M^+$). $\lambda_{max.}$ (iso-octane) 330 nm ($\log_{10}$ ε 3.85); $\delta_H$ ($CDCl_3$) 7.61 (H-4), 7.44 (H-3), and 7.15 (H-2) ($J_{2,3}$ 7.3, $J_{2,4}$ 1.0, $J_{3,4}$ 8.25 Hz). The aliphatic region is complex as there are two sets of $CH_2$-α protons and the $CH_2$-β protons are inequivalent: δ 4.08 and 3.11 (both $CH_2$-α), 1.50 and 0.80 (both $CH_2$-β), 1.90 and 1.07 (s, Me).

Compound (8) was also prepared as follows: 2,2-dimethyl-1,2-dihydroperimidine (22) (0.396 g, 2.00 mmol) was dissolved in DMF (5 ml) and heated at 150 °C for 3 h with 1,3-dibromopropane (0.56 g, 2.77 mmol) and sodium carbonate (0.24 g, 2.27 mmol). Chromatography separated (8) (0.18 g, 38%), identical with the sample described above.

*Naphtho*[1,8-bc]-1,5-*diazabicyclo*[3.2.2]*nonane* (9).—1,8-Diaminonaphthalene (5.3 g, 33.1 mmol), 1,2-dibromoethane (13.0 g, 69 mmol), and sodium carbonate (7.3 g, 69 mmol) were refluxed for 1 h in DMF (20 ml). The basic material was extracted into dichloromethane, which was evaporated to give a solid which on recrystallisation from n-hexane and sublimation (100 °C/0.1 mmHg) afforded (9) (2.90 g, 42%) as white *plates*, m.p. 82—85 °C (Found: C, 79.8; H, 13.1; N, 6.65. $C_{14}H_{14}N_2$ requires C, 79.97; H, 13.32; N, 6.71%); *m/e* 210 ($M^+$); $\lambda_{max.}$ (iso-octane) 277 and 280 nm ($\log_{10}$ ε 3.83, 3.85); $\delta_H$ ($CCl_4$), 7.57 (H-4), 7.18 (H-2), 7.09 (H-3) ($J_{2,3}$ 7.25, $J_{2,4}$ 1.35, $J_{3,4}$ 8.10 Hz) (the aliphatic region is an AA′BB′ spectrum centred at δ ($CDCl_3$) 3.26; $\delta_C$ ($CDCl_3$) 151.3 (C-1), 136.5 (C-10), 135.7 (C-9), 126.2 (C-3), 126.2 (C-4), 124.7 (C-2), 51.4 ($CH_2$-α). The mono-trifluoroacetate salt was obtained as white plates, m.p. 127—130 °C (from benzene–n-hexane).

*Naphtho*[1,8-bc]-1,5-*diazabicyclo*[3.3.3]*undecane* (10).—The various reactions attempted are summarised in the Table. They were all carried out under nitrogen. In all cases the total basic mixture was chromatographed on a column of alumina. Light petroleum eluted (10) as yellow *needles*, m.p. 67—69 °C after recrystallisation at low temperature from methanol followed by sublimation (100 °C/0.5 mmHg) (Found: C, 79.95; H, 7.65; N, 11.45. $C_{16}H_{18}N_2$ requires C, 80.67; H, 7.56; N, 11.77%); *m/e* 238 ($M^+$); $\lambda_{max.}$ (iso-octane) 276, 286, and 379 nm ($\log_{10}$ ε 3.76, 3.80, 2.37); $\delta_H$ ($CCl_4$) 7.57 (H-4), 7.21 (H-2), 7.19 (H-3) ($J_{2,3}$ 7.2, $J_{2,4}$ 1.35, $J_{3,4}$ 8.4 Hz); there are complex signals centred at δ 3.33 ($CH_2$-α) and 1.30 ($CH_2$-β); $\delta_C$ ($CDCl_3$), 145.5 (C-1), 138.9 (C-10), 137.2 (C-9), 131.2 (C-3), 128.0 (C-4), 126.9 (C-2), 54.3 ($CH_2$-α), and 26.2 ($CH_2$-β). The material was purified as its *trifluoroacetate salt*, m.p. 103—105 °C, white plates (from benzene–n-nexane) (Found: C, 61.5; H, 5.55; N,

7.95. $C_{17}H_{19}F_3N_2O_2$ requires C, 61.36; H, 5.40; N, 7.96%).

Elution with light petroleum–ether (98 : 2 v/v) gave 9-*ethylnaphtho*[1,8-bc]-1,5-*diazabicyclo*[3.3.1]*nonane* (20) as yellow needles, m.p. 67—70 °C after recrystallisation from n-hexane and sublimation (80 °C/0.2 mmHg) (Found: C, 80.2; H, 7.7; N, 11.5. $C_{16}H_{18}N_2$ requires C, 80.67; H, 7.56; N, 11.77%); *m/e* 238 ($M^+$); $\lambda_{max.}$ (iso-octane) 330 ($\log_{10}$ ε 3.85); $\delta_H$ ($CDCl_3$) 7.61 (H-4), 7.44 (H-3), and 7.15 (H-2) ($J_{2,3}$ 7.3, $J_{2,4}$ 1.0, $J_{3,4}$ 8.25 Hz). As with (8) the aliphatic region is complex: $\delta_H$ 4.31 (C*H*Et), 3.84 and 3.46 (both $CH_2$-α), 1.50 and 0.80 (both $CH_2$-β), 1.34 and 0.90 (both ethyl). Light petroleum–ether (95 : 5 v/v) removed (8), identical with the sample described above. Light petroleum–ether (90 : 10 v/v) eluted the pentacyclic compound (21) as white *crystals*, m.p. 126—129 °C after recrystallisation from methanol and sublimation (150 °C/0.3 mmHg) (Found: C, 82.15; H, 10.3; N, 8.15. $C_{19}H_{22}N_2$ requires C, 82.01; H, 10.07; N, 7.91%); *m/e* 278 ($M^+$); $\lambda_{max.}$ (iso-octane) 356 nm ($\log_{10}$ ε 3.75); $\delta_H$ ($CDCl_3$) 7.28 (H-4) and 7.00 (H-3) ($J_{3,4}$ 8.4 Hz); the aliphatic region is complex, $\delta_H$ 3.34 (4 H), 3.18 (4 H), 2.88 (4 H,) 1.92 (4 H), and 1.58 (2 H).

Ether eluted *naphtho*[1,8-bc]-1,5-*diazacyclo-octane* (19) as white crystals, m.p. 82—84 °C after recrystallisation from benzene–n-hexane mixture and sublimation (120 °C/0.1 mmHg) (Found: C, 78.5; H, 7.25; N, 14.35. $C_{13}H_{14}N_2$ requires C, 78.78; H, 7.07; N, 14.14%); *m/e* 198 ($M^+$); $\nu_{max.}$ (Nujol) 3 250 and 3 280 $cm^{-1}$ (both NH); $\delta_H$ ($CDCl_3$) 7.57 (H-4), 7.34 (H-3), 7.03 (H-2), 4.6 (NH), 3.32 ($CH_2$-α), and 1.54 ($CH_2$-β) ($J_{2,3}$ 7.2, $J_{2,4}$ 1.4, $J_{3,4}$ 8.0 Hz).

1,8-*Bis*-(1-*pyrrolidinyl*)*naphthalene* (11).—1,8-Diaminonaphthalene (5.0 g, 31 mmol) was dissolved in the minimum volume of 1,4-dibromobutane (*ca.* 30 g, 137 mmol) and sodium carbonate (7.0 g, 66 mmol) was added. The solution was stirred under nitrogen at 160 °C for 40 min. The amines were extracted into n-hexane; the extract was dried and evaporated onto chromatographic alumina from which light petroleum eluted (11) (5.0 g, 60%) as pale yellow *needles*, m.p. 143—146 °C (from n-hexane) (Found: C, 81.2; H, 8.25; N, 10.5. $C_{18}H_{22}N_2$ requires C, 81.16; H, 8.56; N, 10.28%); *m/e* 266 ($M^+$). $\lambda_{max.}$ (iso-octane) 342 nm ($\log_{10}$ ε 4.04); $\delta_H$ ($CDCl_3$) 7.21 (H-3), 7.19 (H-4), 6.73 (H-2), 2.96 ($CH_2$-α), and 1.62 ($CH_2$-β) ($J_{2,3}$ 8.0, $J_{2,4}$ 0.95, $J_{3,4}$ 8.1 Hz) (*cf.* pyrrolidine,[28] δ 2.75 and 1.46); $\delta_C$ ($CDCl_3$) 147.7 (C-1), 137.4 (C-10), 125.4 (C-3), 119.2 (C-4), 119.2 (C-9), 108.2 (C-2), 51.2 ($CH_2$-α), and 24.8 ($CH_2$-β). The tetrafluoroborate salt of (11) was prepared, m.p. 177—180 °C.

1,8-*Bis*(1,3-*dihydroisoindol*-2-*yl*)*naphthalene* (12).—A mixture of 1,8-diaminonaphthalene (1.58 g, 1.0 mmol), αα′-dibromo-*o*-xylene (5.3 g, 2.0 mmol), and sodium carbonate (2.12 g, 2.0 mmol) was refluxed in DMF (35 ml) for 1 h. The basic materials were extracted into ether and chromatographed on alumina. Light petroleum eluted (12) (0.16 g, 5%) as greenish *crystals*, m.p. 166—169 °C (from methanol) (Found: C, 85.9; H, 6.2; N, 7.45. $C_{26}H_{22}N_2$ requires C, 86.15; H, 6.12; N, 7.73%); *m/e* 362 ($M^+$). $\lambda_{max.}$ (iso-octane) 350 nm ($\log_{10}$ ε 4.29); δ ($CDCl_3$), 7.37 (H-4), 7.34 (H-3), 7.32 (other Ar-H), 6.99 (H-2), and 4.95 ($CH_2$) ($J_{2,3}$ 7.60, $J_{2,4}$ 1.35, $J_{3,4}$ 8.1 Hz).

1,8-*Bis*-(1-*piperidinyl*)*naphthalene* (13).—To a solution of 1,8-diaminonaphthalene (2.2 g, 1.4 mmol) in 1,5-dibromopentane (15 g, 64 mmol) was added sodium carbonate (2.9 g, 27 mmol). The mixture was stirred and heated to 150 °C under nitrogen for 50 min. The basic layer was extracted into n-hexane; the extract was dried and chromatographed on alumina with light petroleum as eluant. The first fractions were recrystallised from n-hexane and then sublimed (150 °C/0.2 mmHg) to give (13) (0.82 g, 20%) as white *needles*, m.p. 135—138 °C (Found: C, 81.35; H, 9.0; N, 9.35. $C_{20}H_{26}N_2$ requires C, 81.58; H, 8.90; N, 9.51%); *m/e* 294 ($M^+$). $\lambda_{max.}$ (iso-octane) 322 nm ($\log_{10}$ ε 3.88); $\delta_H$ ($CDCl_3$), 7.40 (H-4), 7.32 (H-3), 7.04 (H-2), 3.40 and 2.52 ($CH_2$-α), and 2.18—2.10 ($CH_2$-β and $CH_2$-γ) ($J_{2,3}$ 7.7, $J_{2,4}$ 1.0, $J_{3,4}$ 8.0 Hz) (*cf.* piperidine,[29] δ 2.71 and 1.59); $\delta_C$ ($CDCl_3$), 151.2 (C-1), 137.7 (C-10), 125.3 (C-3), 123.6 (C-4), 120.8 (C-9), 113.0 (C-2), 54.3 ($CH_2$-α), 25.8 ($CH_2$-β), and 24.7 ($CH_2$-γ) (*cf.* piperidine,[29] δ 47.9, 27.7, 25.8). The tetrafluoroborate salt of (13) was obtained as white needles, m.p. 246—249 °C.

1,8-*Dimorpholinonaphthalene* (14).—A mixture of 1,8-diaminonaphthalene (2.19 g, 13.6 mmol), ββ′-dichlorodiethyl ether (20 g, 144 mmol), and sodium carbonate (2.9 g, 27 mmol) was stirred at 150 °C under nitrogen for 1.25 h. The amines were extracted into ether, and the extracts were dried and chromatographed on alumina. Light petroleum–ether (7 : 3 v/v) removed a yellow oil (2.21 g). Continued elution gave (14) as white needles (0.29 g, 10%), m.p. 196—198 °C (from methanol) (Found: C, 72.4; H, 7.35; N, 9.1. $C_{18}H_{22}N_2O_2$ requires, C, 72.48; H, 7.38; N, 9.39%); *m/e* 298 ($M^+$); $\lambda_{max.}$ (iso-octane) 317 nm ($\log_{10}$ ε 3.97); $\delta_H$ ($CDCl_3$) 7.38 (H-4), 7.34 (H-3), 7.14 (H-2), 3.28 and 2.78 ($CH_2$ α to N), and 4.06 ($CH_2$ β to N) ($J_{2,3}$ 7.9, $J_{2,4}$ 1.1, $J_{3,4}$ 8.2 Hz (*cf.* morpholine,[30] δ 2.73 and 3.55); $\delta_C$ ($CDCl_3$) 149.6 (C-1), 137.8 (C-10), 125.6 (C-3), 123.8 (C-4), 120.0 (C-9), 113.2 (C-2), 66.6 ($CH_2$-β), and 53.5 ($CH_2$-α). The tetrafluoroborate salt of (14) was obtained as white needles, m.p. 246—249 °C.

*Reaction of* 2,2-*Dimethyl*-1,2-*dihydroperimidine* (22) *with* αα′-*Dibromo*-o-*xylene*.—The xylene derivative (3.99 g, 15.1 mmol) and (22) (1.98 g, 10.0 mmol) were dissolved in DMF (25 ml) and refluxed with a stirred suspension of sodium carbonate (1.06 g, 10.0 mmol) under nitrogen for 1 h. The basic materials were extracted into ether and chromatographed on alumina. Light petroleum eluted 1,8-bis(1,3-dihydroisoindol-2-yl)naphthalene (12) (0.93 g, 26%), identical with the sample described previously.

Elution with light petroleum–ether (95 : 5 v/v) furnished 5-*isopropylbenzo*[g]*naphtho*[1,8-bc]-1,5-*diazabicyclo*[4.3.0]-*nonane* (24) (0.287 g, 10%), brown needles, m.p. 112—114 °C (from methanol) (Found: C, 83.8; H, 6.65; N, 9.15. $C_{21}H_{20}N_2$ requires C, 84.00; H, 6.69; N, 9.30%; $\delta_H$ ($CDCl_3$) 7.68—7.06 (9 H, m, Ar-H), 6.44 (1 H, dd, Ar-H), 5.86 (1 H, dd, $H_c$), 4.76 and 4.46 (both 1 H, dd, $H_a$ and $H_b$), 3.46 (1 H, septet, $H_d$), 1.3 4(3 H, d, Me), and 0.50 (3 H, d, Me) ($J_{Hd,Me}$ 6.9, $J_{a,b}$ 13.5, $J_{a,c}$ 3.0, $J_{b,c}$ 2.2 Hz).

2,7-*Dimethyl*-1,8-*diaminonaphthalene*.—2,7-Dimethyl-1,8-dinitronaphthalene [25] (0.493 g) was suspended in ethanol (120 ml) and hydrogenated (280 ml hydrogen at S.T.P.) with 10% palladium–charcoal (0.150 g). After filtration under nitrogen the solution was evaporated to yield 2,7-*dimethyl*-1,8-*diaminonaphthalene* (0.340 g, 91%) as pale orange needles, m.p. 63—66 °C, after recrystallisation from n-hexane and sublimation (100 °C/0.1 mmHg) (Found: C, 77.4; H, 7.9; N, 15.15. $C_{12}H_{14}N_2$ requires C, 77.41; H, 7.52; N, 15.05%); $\delta_H$ ($CDCl_3$) 7.09 (H-3), 7.04 (H-4), 4.41 (NH), and 2.22 (Me) ($J_{3,4}$ 8.5 Hz); $\nu_{max.}$ ($CCl_4$) 3 460 and 3 360 $cm^{-1}$ (both NH).

2,7-*Dimethyl*-1,8-*bis*(*dimethylamino*)*naphthalene* (15).—2,7-Dimethyl-1,8-diaminonaphthalene (0.835 g, 4.49 mmol) was dissolved in THF (20 ml) and added to a suspension of

light petroleum-washed sodium hydride (2.5 g, 96 mmol) in THF. The solution was heated to 60 °C under nitrogen and an excess of methyl iodide (40 g) added dropwise. The solution was refluxed for 24 h until no starting diamine remained (by t.l.c.) and the cooled solution was carefully quenched with water. The basic extracts were taken up in diethyl ether, which on evaporation gave an oily solid which was chromatographed on alumina; n-hexane–ether (95 : 5 v/v) eluted (15) (0.290 g, 27%) as a red, oily solid which would not crystallise; $\delta_H$ ($CDCl_3$) 7.50 (H-3), 7.19 (H-4), 2.97 (N-Me), and 2.40 (C-Me) ($J_{3,4}$ 8.2 Hz).

The tetrafluoroborate salt was prepared as pale pink *needles*, m.p. 239—242 °C (Found: $M^+$, 242.1789; $C_{16}H_{22}N_2$ requires $M$, 242.1783).

2,7-Dimethoxy-1,8-diaminonaphthalene was prepared as follows. 2,7-Dimethoxynaphthalene [27] was nitrated as described [28] to give 2,7-dimethoxy-1,8-dinitronaphthalene in 90% yield. Treatment of this (7.35 g) with tin(II) chloride dihydrate (35.8 g) in concentrated HCl (40 ml) as described [29] gave a salt of 2,7-dimethoxy-1,8-diaminonaphthalene (probably the hydrochloride) (3.9 g), white crystals, m.p. 170 °C (decomp.). Dissolving this salt in sodium hydroxide and extracting into methylene chloride gave 2,7-dimethoxy-1,8-diaminonaphthalene, m.p. 110—114 °C (lit.,[29] 115 °C).

2,7-*Dimethoxy*-1,8-*bis*(*dimethylamino*)*naphthalene* (16).—The 2,7-dimethoxy-1,8-diaminonaphthalene salt (3.2 g) was suspended in THF and added dropwise to an excess of light petroleum-washed sodium hydride (8 g) in THF with stirring under nitrogen. This was heated to reflux and methyl iodide (70 g) added dropwise. After 20 h at reflux the solution was cooled, quenched with water, and basified with 2M sodium hydroxide. The amines were extracted into methylene chloride and chromatographed on alumina; elution with diethyl ether afforded (16) (1.21 g, 40%) as pale yellow *needles*, m.p. 67—70 °C after recrystallisation from n-hexane and sublimation (100 °C/0.2 mmHg) (Found: C, 69.7; H, 8.35; N, 10.05. $C_{16}H_{22}N_2O_2$ requires C, 70.07; H, 8.02; N, 10.21%); *m/e* 274 ($M^+$); $\lambda_{max.}$ (iso-octane) 318 nm ($\log_{10}\varepsilon$ 3.59); $\delta_H$ ($CDCl_3$) 7.48 (H-4), 7.06 (H-3), 3.89 (OMe), and 2.89 (NMe) ($J_{3,4}$ 9.0 Hz). The tetrafluoroborate salt was prepared, m.p. 227—230 °C.

2,7-*Dimethoxy*-1,8-*bis*(*diethylamino*)*naphthalene* (17).—The procedure detailed above for (16) was followed using the naphthalene salt (5.0 g) in THF (50 ml), potassium hydride (9.4 g) in THF (50 ml), and bromoethane (31 ml) and refluxing for 20 h. The amines were extracted into ether and chromatographed on alumina; ether eluted (17) (1.40 g, 21%) as pale orange *crystals*, m.p. 50—53 °C after sublimation at 120 °C/0.02 mmHg (Found: $M^+$, 330.2309; $C_{20}H_{30}N_2O_2$ requires $M$, 330.2307); $\delta$ ($CCl_4$), 7.52 (H-4), 7.04 (H-3), 3.85 (OMe), 3.29 ($CH_2$), and 0.93 (Me) ($J_{3,4}$ 9.0, $J_{CH_2Me}$ 7.5 Hz). The trifluoroacetate salt of (17) was obtained as white *crystals*, m.p. 77—78 °C (from ethyl acetate) (Found: C, 58.1; H, 7.2; N, 6.0; F, 13.05. $C_{18}H_{21}F_3N_2O_4$ requires C, 58.32; H, 7.23; N, 6.48; F, 13.18%).

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