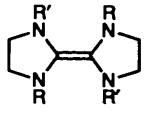
Synthesis and Characterisation of Unusual Tetraaminoalkenes (Enetetramines)

Engin Çetinkaya,† Peter B. Hitchcock, Hatam A. Jasim, Michael F. Lappert and Kostas Spyropoulos
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

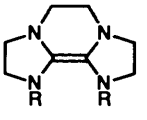
Two general routes are described for the synthesis of the title compounds from the reaction of either (A) the dimethyl acetal of *N,N*-dimethylformamide and an appropriate *N,N'*-bis(secondary amine), or (B) sodium hydride and a 4,5-dihydroimidazolium or tetrahydropyrimidinium salt. The following new compounds have been made: *trans*-$RN(CH_2)_2N(R')C{=}CN(R')(CH_2)_2NR$ [R = Et and R' = Me (**1a**) or CH_2Ph (**1b**)] and $RN(CH_2)_nNC(CH_2)_m{=}CN(CH_2)_nNR$ [$n = m = 2$ and R = Me (**2a**) or CH_2Ph (**2b**); $n = 3$, $m = 2$, and R = CH_2Ph (**3**); or $n = 2$, $m = 3$, and R = CH_2Ph (**4**)].

X-Ray data on crystalline $[CN(R)(CH_2)_2NR]_2$ (R = CH_2Ph) and (**2b**) [data in parentheses] show a short C=C bond, 1.319(8) Å [1.329(5) Å], long C_{sp^2}–N bonds, av. 1.437(11) Å [1.424(4) Å], with each of the four nitrogen atoms in a pyramidal sp^3 environment.

Although an extensive chemistry of symmetrical enetetramines (electron-rich olefins) of the type $[CN(R)CH_2CH_2NR]_2$ **I** (**1**; R = R') and $[CN(R)(CH_2)_3NR]_2$ has been developed,[1] relatively little is known of the chemistry of analogues. A tetracyclic compound **II** has been reported.[2] In this paper we describe the synthesis of (i) some less symmetrical analogues **1** of **I**, and (ii) the tricyclic enetetramines **2**–**4**. As for (i), we have previously described in outline the synthesis of the optically active enetetramines **III**–**V** and their use for the preparation of carbenemetal complexes.[3] Tetraaminoalkenes have an extensive chemistry being diaminocarbene synthons and extremely powerful reducing agents.[1]



1a R = Et, R' = Me
1b R = Et, R' = CH_2Ph



2a R = Me
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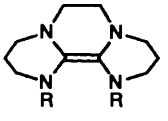
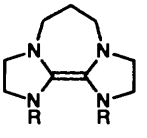


3 R = CH_2Ph

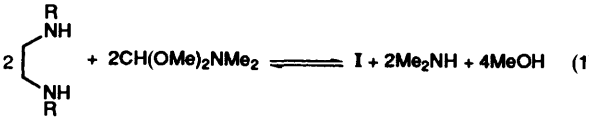


4 R = CH_2Ph

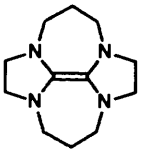
A general preparative route (Method A) adopted for the synthesis of compounds **I** was discovered by Winberg and co-workers.[4] It involved the reaction of a 1,2-bis(dialkylamino)-ethane with *N,N*-dimethylformamide dimethyl acetal in an inert atmosphere, under ambient conditions; upon distillation, the eliminated methanol and dimethylamine were removed in order to drive the equilibrium towards the desired enetetramine **I**, eqn. (1).

A limitation of reaction (1) is that it applies only for the case of R being a relatively unhindered primary alkyl group, such as Me, Et, Bu or $PhCH_2$,[5] or an alkenyl group such as $CH_2CH_2CH{=}CH_2$ or $CH_2CH{=}CHMe$.[6] However, for R = R' = $CH_2CH{=}CHMe$, the formation of the appropriate enetetramine **1** was accompanied by the amino-Claisen isomer **VI** [R = R' = CH_2Ph or $CH_2CH{=}CHMe$ (or R' = $CH_2CMe{=}CH_2$)], while for R = R' = $CH_2CH{=}CH_2$, **VI** (R' = R) was the sole product.[6]

† *Present address:* Inönü University, Malatya, Turkey.



(1)



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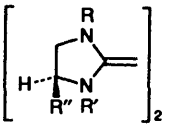
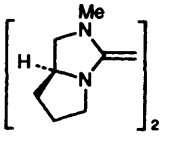
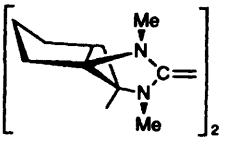


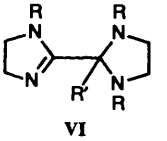
III (*e.g.*, R = Me, R' = Et, R'' = Bu^t)



IV

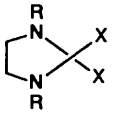


V

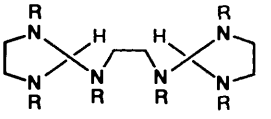


VI

Wanzlick and co-workers have reported the preparation of some aryl compounds, such as $[CN(Ph)(CH_2)_2NPh]_2$, by a similar ethanol-elimination reaction from $CH(OEt)_3$ and the appropriate 1,2-di(arylamino)ethane,[7] or by thermolysis of $PhN(CH_2)_2N(Ph)C(H)CCl_3$.[8] In general, it is assumed that an aminal **VII** (X = OEt or NMe_2) is an intermediate in such reactions or those of eqn. (1). Recently, a further (binuclear) intermediate **VIII** was isolated for the case of R = CH_2Ph from a reaction of type (1).[9] Another method, used for $C_2(NMe_2)_4$ or **1** (R = R' = Me) (≡ **13**) involved the aminolysis of $CF_2{=}CFCl$.[10]



VII



VIII

Table 1 Yields, m.p.s (b.p.), and analytical data for the new enetetramines

Compd. no.	M.p. (°C) (B.p. °C/ mmHg)	Yield (%) Method A[a]	Yield (%) Method B[b]	Found (required) (%) C	H	N
1a	(64–66/ 3×10^{-1})	*c*	69	*d*	*d*	*d*
1b	60–63	*c*	41[e]	77.0 (76.6)	8.0 (8.5)	15.1 (14.9)
2a	36–38	72	74	60.0 (61.8)	9.1 (9.3)	29.1 (28.8)
2b	110–113	92	88	76.3 (76.3)	7.6 (7.5)	15.8 (16.2)
3	120–123	91	75	77.1 (77.0)	7.9 (8.0)	15.2 (15.0)
4	115–117	87	*c*	77.0 (76.6)	7.8 (7.8)	15.2 (15.3)

[a] Based on the secondary amine. [b] Based on the imidazolium or tetrahydropyrimidium salt. [c] Not employed. [d] Not determined (compound extremely air-sensitive). [e] The low yield is attributed to the high solubility of **1b** in pentane.

Table 2 1H NMR spectroscopic data, with assignments, for the new enetetramines:[a] *J* values in Hz

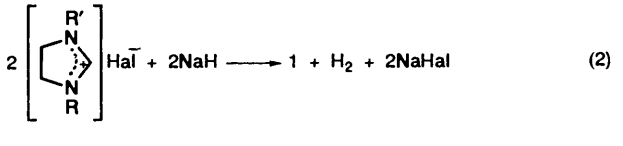
Compd. no.	Ring CH_2	CH_2Ph	Others
1a	2.75 (s) 2.58 (s)		1.01 (t, CH_3CH_2) 2.75 (s, CH_3N) 2.96 (qa, CH_3CH_2)
1b	2.68–2.79 (m)[b]	4.31 (2) 4.37 (s)	0.98 (t, CH_3CH_2) 1.03 (t, CH_3CH_2) 7.04–7.42 (m, $PhCH_2$)
2a	2.92 (s)[c] 2.83 (m)[d]		2.67 (s, NCH_3)
2b	3.17 (s)[c] (2.56–2.86)[e]	4.13 (s)	7.06 (m, $PhCH_2$)
3	2.57 (s) 2.55 (qi, J = 7)	4.26 (s)	7.19 (m, $PhCH_2$), 1.48 (qi, J = 7)
4	2.75 (m)	4.37 (s)	7.18 (m, $PhCH_2$), 1.69 (qi, J = 7)

[a] Spectra recorded in C_6D_6 at 360 MHz and 305 K; chemical shifts (δ) relative to $Si(CH_3)_4$ = 0; abbreviations: s = singlet, d = doublet, qa = quartet, qi = quintet, m = multiplet. [b] This multiplet includes the signal from RCH_2 (R = Me or Ph). [c] CH_2 of six-membered ring. [d] CH_2 of five-membered ring. [e] These signals centred at δ 2.56 and 2.86 arise from the 4 CH_2's of the non-bridging rings which appear as an AA'BB' spin system with J = 6.1.

Results and Discussion

The enetetramines **1** can be prepared (Method A) from the interaction of the acetal with the appropriate secondary amine [a modification of eqn. (1)]. Alternatively (Method B), they may be obtained by the reaction between sodium hydride and a dihydroimidazolium halide, as in eqn. (2); by using a tetrahydropyrimidinium salt, the six-membered ring analogue of **1** is derived.

These methods are illustrated in Scheme 1 for the case of the tricyclic enetetramine **2b**. Isolable intermediates for Route A (Method A) are the Schiff base **5**, the imidazolidine **6**, and the *N*,*N*′,α,ω-dibenzyltetramine **8** (and its tetrahydrochloride **7**).



(2)

Table 3 ^{13}C NMR spectroscopic data, with assignments, for the new enetetramines[a]

Compd. no.	C=C	Ring CH_2	CH_2	Others
1a	90.4	53.8 49.4	—	46.4, 41.0 13.3
1b	*b*	48.7, 48.8 49.4, 49.7	56.4 55.7	12.9, 13.0 45.6, 46.5 126.6–140.9
2a	122.2	54.2, 51.1 48.4		39.9
2b	139.4	51.5, 51.3 48.7	57.0	128.8, 128.3 128.0, 126.8 125.8
3	140.7	53.2, 47.5 20.9	58.9	129.5, 128.9 127.9, 126.5
4	139.9	54.1, 52.5 50.6, 29.7	56.6	129.2, 128.3 127.9, 126.7

[a] Spectra recorded in C_6D_6 and 90.55 MHz at 305 K; chemical shifts (δ) relative to $Si(CH_3)_4$ = 0. [b] Overlapping with aromatics.

Table 4 Selected IR[a] and mass spectral data for the new enetetramines

Compd. no.	ν(C=C)/ cm^{-1}	ν(CN_2)/ cm^{-1}	*m*/*z* (rel. intensity, %; assignment; M^+ = parent molecular ion)
1a	*b*	1494w	224 (66, M^+), 209 (40, $[M - 15]^+$), 195 (100, $[M - 29]^+$), 113 (28, $[M/2 + 1]^+$)
1b	*b*	1495w	376 (17, M^+), 285 (65, $[M - CH_2Ph]^+$), 189 (82, $[M/2 + 1]^+$), 91 (100, $[M - 285]^+$)
2a	*b*	1495w	
2b	1660w	1492s	346 (1, M^+), 255 (13, $[M - CH_2Ph]^+$), 164 (s, $[M - 2CH_2Ph]^+$), 91 (100, $[M - 255]^+$)
3	1650w	1492s	
4	1644w	1498s	

[a] Spectra recorded as Nujol mulls; abbreviations: s = strong, m = medium, w = weak. [b] Not identified [IR inactive (?)].

The starting materials $H_2N(CH_2)_nN(H)(CH_2)_mN(H)(CH_2)_n$-$NH_2$ for the three tricyclic enetetramines **2b**, **3**, and **4** were readily available for the case of (a), n = 2 = m and (b) n = 3, m = 2, while for (c), n = 2, m = 3, the tetraamine was made by a literature procedure from $Br(CH_2)_3Br$ and $2H_2N(CH_2)_2NH_2$.[11]

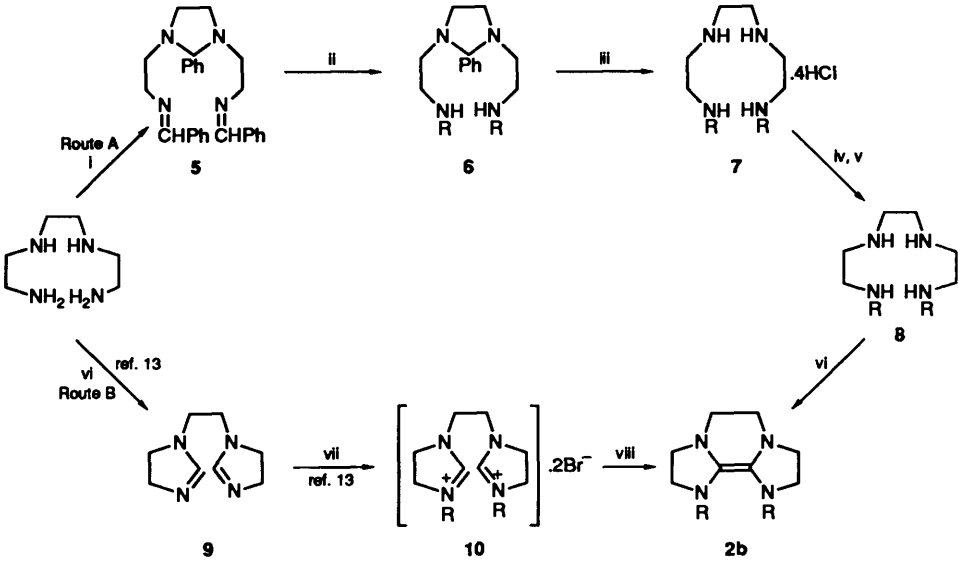
Yields, m.p.s (or b.p.), and analytical data for the new enetetramines **1a**, **1b**, **2a**, **2b**, **3** and **4** are listed in Table 1, while ^1H NMR, ^{13}C NMR, and selected IR and MS data are in Tables 2–4, respectively. Similar data on the new intermediates for the synthesis of the tricyclic enetetramines **2b**, **3** and **4** are in Table 5: (i) the three Schiff bases (*e.g.* **5**), (ii) the imidazolidines (*e.g.* **6**), and (iii) their hydrochlorides (*e.g.* **7**). The dimethyl analogue of **8**, $MeN(H)(CH_2)_2N(H)(CH_2)_2N(H)CH_2CH_2NHMe$ has previously been reported.[12]

As for Method B, the starting imidazolium or tetrahydropyrimidinium salts are readily prepared in a two-step process from the appropriate 1-alkylamino-2- (or 3-)amino-ethene(or propene), as illustrated in Scheme 1 (Route B) for the bis(2-imidazolium) bromide **10** *via* the bis(2-imidazolidine) **9**.[13] The hydrogen atom attached to C(2) of an imidazolium or tetrahydropyrimidinium salt has considerable protic character (as evident from ^1H NMR data[13]) and hence the high reactivity to the base-induced protic acid-elimination is not surprising. Thus, they reacted smoothly and in excellent yield (Table 1) with an excess (*ca.* 50%) of sodium hydride in tetrahydrofuran at ambient temperature within 12–20 h, as in *e.g.* **2**; only the

Table 5 Yields, m.p.s, analytical, IR [ν(NH)], and NMR [$\delta(^1H)$ and $\delta(^{13}C)$] data for (i) Schiff bases, (ii) imidazolidines and tetrahydropyrimidine, and (iii) tetramines

	Yield (%)	M.p. (°C) B.p. (°C/8 mmHg)	Found (required) (%) C	H	N	ν(NH)/cm^{-1} [δ(Ph^{13}CH=N]	δ(N^{1}H) [δ(C^{1}H=N]
[PhCH=N(CH$_2$)$_2$]$_2$[N(CH$_2$)$_2$NCHPh]	85	86–88	78.9 (78.9)	7.4 (7.4)	13.7 (13.6)	[161.4]	[8.07 (s)]
[PhCH=N(CH$_2$)$_2$]$_2$[N(CH$_2$)$_3$NCHPh]	89	110–112	79.9 (79.2)	7.7 (7.6)	13.2 (13.2)	[161.4]	[8.07 (s)]
[PhCH=N(CH$_2$)$_3$]$_2$[N(CH$_2$)$_2$NCHPh]	88	101–102	79.0 (79.4)	7.7 (7.8)	12.8 (12.8)	[160.9]	[8.10 (s)]
[PhCH$_2$N(H)(CH$_2$)$_2$]$_2$[N(CH$_2$)$_2$NCHPh]	50	137–139	78.0 (78.2)	8.2 (8.2)	13.5 (13.5)	3380br	4.00 (br)
[PhCH$_2$N(H)(CH$_2$)$_2$]$_2$][N(CH$_2$)$_3$NCHPh]	56	125–127	79.1 (78.5)	8.4 (8.5)	12.9 (13.0)	3450br	4.00 (br)
[PhCH$_2$N(H)(CH$_2$)$_3$]$_2$[N(CH$_2$)$_2$NCHPh]	57	100–103	78.3 (78.7)	8.7 (8.6)	12.6 (12.6)	3430br	4.18 (br)
[PhCH$_2$N(H)(CH$_2$)$_2$]$_2$[N(H)(CH$_2$)$_2$NH]^a	33^b	(144–148)	50.6 (50.9)	7.1 (7.2)	12.1 (11.9)	3300br	1.37 (s)
[PhCH$_2$N(H)(CH$_2$)$_2$]$_2$[N(H)(CH$_2$)$_3$NH]^a	31^b	(164–168)	51.4^b (51.8)	7.4 (7.4)	11.6 (11.5)	3300br	1.02 (br)
[PhCH$_2$N(H)(CH$_2$)$_3$][N(H)(CH$_2$)$_2$NH]^a	35^b	(170–172)	52.9 (52.8)	7.6 (7.6)	11.1 (11.2)	3290br	1.14 (br)

^{a} Analytical data are for the 4HCl adduct. ^{b} This is the overall yield based on $H_2N(CH_2)_nN(H)(CH_2)_mN(H)(CH_2)_nNH_2$.



Scheme 1 *Synthesis of the enetetramine* **2b** (R = CH_2Ph). Route A comprises steps i–vi and Route B steps vi, vii and viii. *Reagents and conditions:* i, 3PhCHO, 20 °C; ii, Na, EtOH, 20 °C; iii, HCl, EtOH; iv, KOH, H_2O; v, P_2O_5; vi, $CH(OMe)_2NMe_2$, 100 °C; vii, $PhCH_2Br$, EtOH; viii, NaH, THF, 20 °C.

reaction with tetrahydropyrimidinium bromide leading to **3** was somewhat sluggish.

Base (Et_3N)-induced HBr or HOTos elimination from an *N*-benzylbenzothiazolium salt to yield the appropriate electron-rich alkene $\ddagger$[CS(C$_6$H$_4$-*o*)NCH$_2$Ph]$_2$ or its [1,3]sigmatropic rearrangement product has been reported;[14] as has the action of a strong base (including NaH) on a 1,3-diphenylbenzimidazolium salt to give *in situ* supposedly $\ddagger$[CN(Ph)(C$_6$H$_4$-*o*)NPh]$_2$, which was not isolated but captured by various co-reactants.[15]

Comparing Methods A and B, we find that the latter is invariably superior, involving fewer steps, milder reaction conditions, greater ease of work-up and better yields.

The ^1H and ^{13}C NMR data for the *N,N″*-dimethyl-*N′,N‴*-diethyltetraaminoalkene **1a** show that the *trans*-isomer was formed stereospecifically; moreover the CH_2 ^1H signal of the ethyl group was found as an AB quartet, indicating that there is restriction to rotation about the N–CH_2CH_3 bond. The corresponding diethyl-dibenzyl analogue **1b** was obtained as a mixture of *cis*/*trans*-isomers as evident from the observed CH_3CH_2 ^1H NMR signal, two triplets in the ratio of 1:1.2.

The $^{13}C_{sp^2}$ NMR signal was found at the lowest frequency for **1a**, δ 90.4, consistent with **1a** being the most reactive of the enetetramines **1**–**4** to nucleophilic attack (*vide* its extreme water-sensitivity).

The mass spectra of each of **1a**, **1b**, and **2b** showed prominent $[P - R]^+$ ions (R = Me, Et, or CH_2Ph; P^+ = parent molecular ion). Whereas $[P/2 + 1]^+$ was a significantly abundant fragment ion for **1a** and **1b**, it was not observed for **2b**.

The $\nu(CN_2)$ asymmetric stretching modes for the enetetramines are assigned to bands at *ca.* 1495 cm^{-1}, while the low intensity absorption found in the IR spectra of **2b**, **3**, and **4** at *ca.* 1650 cm^{-1} is attributed to ν(C=C).

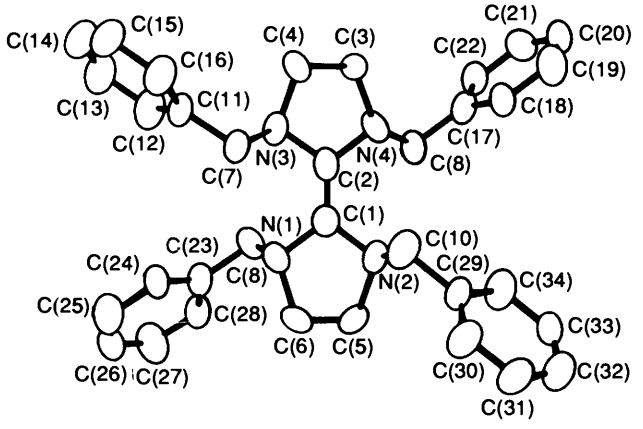


Fig. 1 X-Ray structure of $[CN(CH_2Ph)(CH_2)_2NCH_2Ph]_2$ **11**, showing the atom numbering scheme

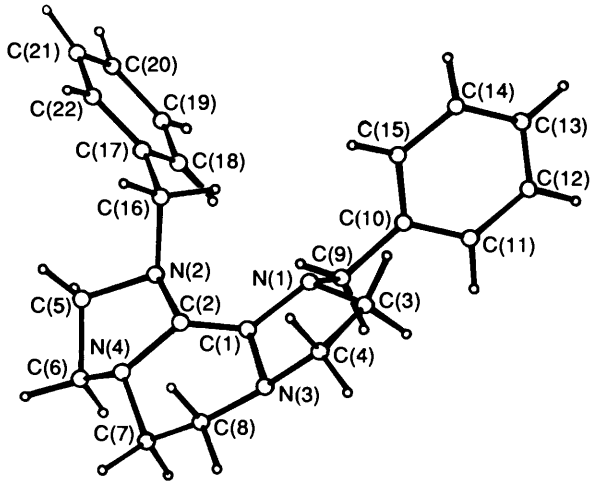


Fig. 2 X-Ray structure of the tricyclic alkene **2b**, showing the atom numbering scheme

Table 6 Selected intramolecular distances (Å) and angles (°), with estimated standard deviations in parentheses for $[CN(R)(CH_2)_2NR]_2$ (R = CH_2Ph) **11**

(a) Bonds			
N(1)–C(1)	1.438(5)	N(1)–C(6)	1.457(8)
N(1)–C(9)	1.478(7)	N(2)–C(1)	1.449(6)
N(2)–C(5)	1.464(7)	N(2)–C(10)	1.482(8)
N(3)–C(2)	1.442(7)	N(3)–C(4)	1.476(7)
N(3)–C(7)	1.480(7)	N(4)–C(2)	1.419(5)
N(4)–C(3)	1.477(8)	N(4)–C(8)	1.489(7)
C(1)–C(2)	1.319(8)	C(3)–C(4)	1.512(8)
(b) Angles			
C(1)–N(1)–C(6)	104.6(4)	C(1)–N(1)–C(9)	111.7(4)
C(6)–N(1)–C(9)	114.4(5)	C(1)–N(2)–C(5)	104.1(3)
C(1)–N(2)–C(10)	111.5(5)	C(5)–N(2)–C(10)	113.9(5)
C(2)–N(3)–C(4)	106.4(3)	C(2)–N(3)–C(7)	114.6(5)
C(4)–N(3)–C(7)	111.1(5)	C(2)–N(4)–C(3)	105.9(4)
C(2)–N(4)–C(8)	113.2(4)	C(3)–N(4)–C(8)	110.7(5)
N(1)–C(1)–N(2)	110.9(5)	N(1)–C(1)–C(2)	124.6(4)
N(2)–C(1)–C(2)	124.4(4)	N(3)–C(2)–N(4)	109.2(4)
N(3)–C(2)–C(1)	124.8(4)	N(4)–C(2)–C(1)	125.9(4)
N(4)–C(3)–C(4)	102.7(5)	N(3)–C(4)–C(3)	102.4(5)

The X-ray structure of crystalline $[CN(CH_2Ph)(CH_2)_2NCH_2Ph]_2$ **11** and of **2b** are shown in Figs. 1 and 2, respectively, together with the numbering schemes. Similar data for **4** were of poor quality and hence are not published, but confirmed the proposed structure.[16] Intramolecular geometric parameters for **11** are in Table 6 and atomic coordinates in Table 7. Comparison of (i) C_{sp^2}–C_{sp^2} and C_{sp^2}–N bond lengths, and (ii) geometry at the N atoms as judged by the sum of the angles at each N, are in Table 8, incorporating also X-ray data on $[CN(Ph)(CH_2)_2NPh]_2$ **12**[17] and electron diffraction results of gaseous $[CN(Me)(CH_2)_2NMe]_2$ **13**.[8]

Table 7 Atomic coordinates ($\times 10^4$) for carbon and nitrogen atoms, and ($\times 10^3$) for hydrogen atoms, with estimated standard deviations in parentheses for $[CN(R)(CH_2)_2NR]_2$ (R = CH_2Ph) **11**

	x	*y*	*z*
N(1)	9 125(2)	1 518(8)	7 154(2)
N(2)	8 039(2)	1 691(10)	6 401(2)
N(3)	9 497(2)	899(9)	6 087(2)
N(4)	8 482(2)	2 103(9)	5 373(2)
C(1)	8 696(2)	1 631(12)	6 489(2)
C(2)	8 875(2)	1 595(11)	6 021(2)
C(3)	8 917(2)	2 337(13)	5 063(2)
C(4)	9 446(2)	652(12)	5 435(2)
C(5)	8 087(2)	1 963(16)	7 045(2)
C(6)	8 711(2)	1 354(18)	7 478(2)
C(7)	9 746(2)	−1 256(11)	6 460(2)
C(8)	8 095(2)	4 254(11)	5 284(2)
C(9)	9 568(2)	3 517(11)	7 352(2)
C(10)	7 687(2)	−418(12)	6 067(3)
C(11)	10 427(2)	−1 715(11)	6 561(2)
C(12)	10 900(2)	−38(12)	6 860(3)
C(13)	11 529(2)	−527(14)	6 953(3)
C(14)	11 679(2)	−2 573(14)	6 750(3)
C(15)	11 213(3)	−4 221(12)	6 464(3)
C(16)	10 585(2)	−3 766(11)	6 363(3)
C(17)	7 662(2)	4 655(11)	4 583(2)
C(18)	7 227(2)	3 005(12)	4 234(2)
C(19)	6 821(2)	3 399(12)	3 598(2)
C(20)	6 862(2)	5 442(13)	3 319(3)
C(21)	7 292(3)	7 106(13)	3 657(3)
C(22)	7 706(2)	6 745(11)	4 304(3)
C(23)	10 032(2)	3 339(11)	8 048(2)
C(24)	10 406(2)	1 413(12)	8 290(2)
C(25)	10 831(3)	1 296(13)	8 928(3)
C(26)	10 872(2)	3 096(14)	9 315(3)
C(27)	10 511(3)	5 086(15)	9 084(3)
C(28)	10 077(2)	5 173(12)	8 440(2)
C(29)	7 000(2)	−365(11)	5 984(2)
C(30)	6 769(2)	−2 214(13)	6 192(3)
C(31)	6 145(3)	−2 252(14)	6 115(3)
C(32)	5 753(2)	−416(15)	5 841(3)
C(33)	5 973(2)	1 469(13)	5 628(3)
C(34)	6 608(2)	1 513(12)	5 703(3)

Table 8 Selected bond lengths (Å) and the sum (Σ, °) of the angles at each nitrogen atom for four enetetramines *

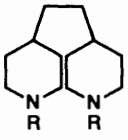
	11	**2b**	**12**[a]	**13**[b]
C(1)–C(2)	1.319(8)	1.329(5)	1.372(6)	1.387(11)
C–N	1.438(5)	1.425(4)	1.403(3)	1.401(4)
C–N	1.449(6)	1.429(4)	1.395(3)	1.401(4)
C–N	1.442(7)	1.420(4)	1.395(3)	1.401(4)
C–N	1.419(5)	1.424(4)	1.403(3)	1.401(4)
ΣN(1)	330.7	334.0	354.1	[c]
ΣN(2)	329.5	336.2	358.1	[c]
ΣN(3)	332.1	334.8	358.1	[c]
ΣN(4)	329.8	334.9	354.1	[c]

* The gas phase electron and low temperature X-ray diffraction structure of $C_2(NMe_2)_4$ has recently been published (H. Bock, H. Borrmann, Z. Harlas, H. Oberhammer, K. Ruppert and A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1678.

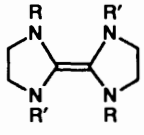
[a] $[CN(Ph)(CH_2)_2NPh]_2$. [b] $[CN(Me)(CH_2)_2NMe]_2$ (gas-electron diffraction). [c] Shallow pyrimidal configuration at N atoms, ΣN 342.2° (overall D_2 molecular symmetry).

Table 9 Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses, for **2b**

(a) Bonds			
N(1)–C(1)	1.425(4)	N(1)–C(3)	1.495(4)
N(1)–C(9)	1.470(5)	N(2)–C(2)	1.429(4)
N(2)–C(5)	1.483(4)	N(2)–C(16)	1.462(4)
N(3)–C(1)	1.420(4)	N(3)–C(4)	1.478(5)
N(3)–C(8)	1.457(5)	N(4)–C(2)	1.424(4)
N(4)–C(6)	1.468(5)	N(4)–C(7)	1.465(4)
C(1)–C(2)	1.329(5)	C(3)–C(4)	1.527(5)
C(5)–C(6)	1.531(5)	C(7)–C(8)	1.527(5)
C(9)–C(10)	1.513(5)	C(10)–C(11)	1.386(5)
C(10)–C(15)	1.401(5)	C(11)–C(12)	1.402(5)
C(12)–C(13)	1.381(5)	C(13)–C(14)	1.388(6)
C(14)–C(15)	1.394(5)	C(16)–C(17)	1.518(5)
C(17)–C(18)	1.396(5)	C(17)–C(22)	1.377(5)
C(18)–C(19)	1.389(5)	C(19)–C(20)	1.384(5)
C(20)–C(21)	1.381(5)	C(21)–C(22)	1.392(5)
(b) Angles			
C(1)–N(1)–C(3)	106.3(2)	C(1)–N(1)–C(9)	115.1(3)
C(3)–N(1)–C(9)	112.6(3)	C(2)–N(2)–C(5)	106.6(2)
C(2)–N(2)–C(16)	115.2(3)	C(5)–N(2)–C(16)	114.4(3)
C(1)–N(3)–C(4)	104.7(2)	C(1)–N(3)–C(8)	113.2(3)
C(4)–N(3)–C(8)	116.9(3)	C(2)–N(4)–C(6)	105.0(3)
C(2)–N(4)–C(7)	113.1(3)	C(6)–N(4)–C(7)	116.8(3)
N(1)–C(1)–N(3)	109.0(3)	N(1)–C(1)–C(2)	128.1(3)
N(3)–C(1)–C(2)	122.7(3)	N(2)–C(2)–N(4)	108.2(3)
N(2)–C(2)–C(1)	128.8(3)	N(4)–C(2)–C(1)	122.5(3)
N(1)–C(3)–C(4)	103.6(3)	N(3)–C(4)–C(3)	100.9(3)
N(2)–C(5)–C(6)	102.9(3)	N(4)–C(6)–C(5)	100.1(3)
N(4)–C(7)–C(8)	108.4(3)	N(3)–C(8)–C(7)	108.5(3)
N(1)–C(9)–C(10)	111.5(3)	C(9)–C(10)–C(11)	120.2(3)
C(9)–C(10)–C(15)	121.0(3)	C(11)–C(10)–C(15)	118.9(3)
C(10)–C(11)–C(12)	120.4(3)	C(11)–C(12)–C(13)	120.6(3)
C(12)–C(13)–C(14)	119.3(3)	C(13)–C(14)–C(15)	120.5(3)
C(10)–C(15)–C(14)	120.4(3)	N(2)–C(16)–C(17)	111.3(3)
C(16)–C(17)–C(18)	120.2(3)	C(16)–C(17)–C(22)	121.5(3)
C(18)–C(17)–C(22)	118.2(3)	C(17)–C(18)–C(19)	120.9(3)
C(18)–C(19)–C(20)	119.9(3)	C(19)–C(20)–C(21)	119.7(3)
C(20)–C(21)–C(22)	119.9(3)	C(17)–C(22)–C(21)	121.2(3)



2b′



2b″

The X-ray data on **2b** (Tables 9 and 10) unequivocally demonstrate its molecular structure and hence rules out that of the alternative isomer **2b′** (R = CH_2Ph) or that of the partially condensed product **2b″** (R′ = CH_2CH_2NHR).

The enetetramine **11** has no crystallographically imposed symmetry. The 5-membered rings are non-planar, C(3) being below and C(4) above the C(2)N(3)N(4) plane, with the benzyl groups axial. It is thus clear that the nitrogen lone pairs are stereochemically active (and accessible, for example, to ready protonation; many such reactions are known for other enetetramines). The C=C bond is twisted by 17° with respect to the two sets of CN_2 planes. The *cis*-benzyl groups are bent away from one another (and would certainly not sterically hinder attack at C_{sp^2}).

The comparative data of Table 8 show that for the *N*-benzylic enetetramines **11** and **2b** there is little conjugation involving nitrogen lone pairs and the C=C alkene bond. This is evident from the short $C_{sp^2}-C_{sp^2}$ bond lengths (in contrast to those in **12** or **13**), the rather long C_{sp^2}–N bonds (*cf.* **12** and **13**), and the pyramidal rather than planar (as in **12**) configuration at each nitrogen atom for **11** and **2b**.

The molecules of **2b** have approximate two-fold rotational symmetry about the line through the mid points of the C(1)–C(2) and C(7)–C(8) bonds. The bonds at the nitrogen atoms are pyramidally arranged with C(8) and C(16) above, and C(6) and C(9) below the plane defined by C(1), C(2), and the four N atoms. As in **11**, the benzyl groups are bent away from each other. Because of the C_2H_4 group connecting N(3) and N(4), the twist of 5° about the double bond in **2b** is lower than that in **11**.

The new enetetramines are exceptionally air-sensitive. The methyl compounds are spontaneously inflammable, but even the *N*-benzylic derivatives fume in air, and subsequently display a green chemiluminescence.

Table 10 Fractional atomic coordinates (× 10^4), for **2b**

	x	*y*	*z*
N(1)	4665(2)	2137(3)	5564(2)
N(2)	2467(2)	1549(3)	6562(2)
N(3)	3361(2)	1835(3)	4416(2)
N(4)	1392(2)	1115(3)	5337(2)
C(1)	3454(3)	1830(3)	5276(2)
C(2)	2547(3)	1477(3)	5706(2)
C(3)	5380(3)	2146(4)	4837(2)
C(4)	4567(3)	1425(4)	4194(2)
C(5)	1184(3)	1313(4)	6703(2)
C(6)	524(3)	1635(4)	5879(2)
C(7)	1214(3)	1495(4)	4481(2)
C(8)	2330(3)	1088(4)	4062(2)
C(9)	4810(3)	3356(4)	6040(2)
C(10)	6106(3)	3556(3)	6371(2)
C(11)	6639(3)	4785(4)	6332(2)
C(12)	7849(3)	4968(4)	6621(2)
C(13)	8528(3)	3928(4)	6944(2)
C(14)	7996(3)	2698(4)	6990(2)
C(15)	6794(3)	2507(3)	6707(2)
C(16)	3325(3)	721(3)	7048(2)
C(17)	3279(3)	990(3)	7947(2)
C(18)	3330(3)	2280(3)	8238(2)
C(19)	3279(3)	2542(4)	9059(2)
C(20)	3186(3)	1517(4)	9600(2)
C(21)	3133(3)	237(4)	9319(2)
C(22)	3163(3)	−15(4)	8494(2)

Experimental

General Procedures and Starting Materials.—All experiments (except those involving water) were carried out under argon or nitrogen gas using Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded using a Bruker WM360 spectrometer. Ir and mass spectra were obtained on a Perkin-Elmer 597 and a Kratos MS902 instrument, respectively. Microanalytical data were provided by the University of Sussex Analytical Department.

Reagents and solvents were rigorously purified by standard procedures. The bicyclic enetetramine $\overline{[CN(R)(CH_2)_2NR]}_2$ (R = CH_2Ph) **11**, required for an X-ray study, was prepared as described previously.[5]

Preparation of 1,1′-*Diethyl*-3,3′-*dimethyl*-2-′-*biimidazolidin*-2-*ylidene* **1a**.—1-Ethyl-3-methyl-4,5-dihydroimidazolium iodide (13 g, 54.17 mmol) was added to a suspension of sodium hydride (2.16 g, 90 mmol) in THF (60 cm^3). The mixture was stirred at 20 °C for 12 h and the volatiles were removed under reduced pressure. Pentane (15 cm^3) was added to the resultant oily residue and the suspension was filtered. After removal of the solvent from the filtrate, the residue was distilled to give the colourless liquid title compound **1a** (4.02 g).

Preparation of 1,1′-*Dibenzyl*-3,3′-*diethyl*-2,2′-*biimidazolidin*-2-*ylidene* **1b**.—A mixture of 1-benzyl-3-ethyl-4,5-dihydroimidazolium bromide (8.15 g, 30.30 mmol) and sodium hydride

Table 11 Crystallographic data for the structural analyses of **11** and **2b**

	11	**2b**
Formula	$C_{34}H_{36}N_4$	$C_{22}H_{26}N_4$
Formula weight	500.7	346.5
Crystal dimensions (mm)	0.17 × 0.30 × 0.40	0.2 × 0.2 × 0.2
Crystal system	Monoclinic	Monoclinic
a/Å	23.202(9)	11.112(3)
b/Å	5.747(1)	10.166(2)
c/Å	23.251(8)	16.546(6)
β/°	115.32(3)	94.62(3)
V/Å^3	2802.5	1863.1
Z	4	4
Space group	*P*2/*n*	$P2_1/n$
D_{calc}/g cm^{-3}	1.19	1.24
μ/cm^{-1}	0.6	0.7
Number of observed reflections	2223	1637
Rejection criterion[a]	$\|F^2\| < \sigma(F^2)$	$\|F^2\| < 2\sigma(F^2)$
R	0.080	0.048
R_w	0.080	0.059
λ(Mo-Kα)/Å	0.710 69	0.710 69
$\Delta\rho_{max}$ on final difference map	0.28	0.20
T/K	293	173

[a] $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/Lp$.

(1.16 g, 66.6 mmol) in THF (50 cm^3) was stirred at 20 °C for 12 h. Volatiles were removed under reduced pressure. The yellow oily residue was dissolved in pentane (30 cm^3) and the suspension was filtered. The volume of the filtrate was reduced to *ca.* 10 cm^3. Upon cooling of the latter to −30 °C pale yellow crystals of the title compound **1b** (2.31 g) were obtained; these were washed with cold hexane (2 × 5 cm^3) and dried.

Preparation of the Diimidazo[1,2-a:2′,1′-c]*pyrazines* **2a**, **2b** *and Dipyrimido*[1,2-a:2′,1′-c]*pyrazine* **3** *by Method B.*—Using a procedure similar to that described for compound **1a** (Method B), 3,3′-dimethyl-1,1′-ethylenedi(4,5-dihydroimidazolium) diiodide (3.76 g, 8.36 mmol), sodium hydride (0.50 g, 20.8 mmol), and THF (30 cm^3), were stirred for 12 h to afford the title compound **2a** as a pale yellow liquid (1.22 g), which slowly solidified.

Similarly, using a procedure similar to that described for **1b** (Method B), 3,3′-dibenzyl-1,1′-ethylenedi(4,5-dihydroimidazolium) dibromide (31.5 g, 62.1 mmol), sodium hydride (5.13 g, 213 mmol), and THF (200 cm^3), were stirred for 12 h to yield cream crystals of the title compound **2b** (18.10 g).

Likewise a mixture of 3,3′-dibenzyl-1,1′-ethylenedi(1,4,5,6-tetrahydropyrimidinium) dibromide (7.34 g, 13.69 mmol), sodium hydride (1.00 g, 41.6 mmol), and THF (100 cm^3) when stirred for 20 h gave colourless crystals of the title compound **3** (3.84 g).

Preparation of the Schiff Base PhCH=N(CH$_2$)$_2$N[CH(Ph)](CH$_2$)$_2$N(CH$_2$)$_2$N=CHPh **5**.—Benzaldehyde (32.6 g, 308 mmol) was slowly added to *N,N′*-bis(3-aminopropyl)ethylenediamine[11] (18.4 g, 102 mmol) in an ice-bath with vigorous stirring. After completing the addition (*ca.* 0.5 h), stirring was continued for *ca.* 1 h. The reaction mixture was extracted with diethyl ether. The organic extracts were dried (MgSO$_4$, *ca.* 12 h), filtered, and evaporated under reduced pressure to give an orange oil. Crystallisation (EtOH) of the latter afforded white needles of the title product **5** (38.3 g, 85%).

Preparation of the Imidazolidine PhCH$_2$(H)N(CH$_2$)$_2$N[CH(Ph)](CH$_2$)$_2$N(CH$_2$)$_2$N(H)CH$_2$Ph **6**.—Sodium (15.0 g), 652 mmol) was rapidly added to a vigorously stirred solution of the Schiff base **5** (35.0 g, 79.7 mmol) in ethanol (500 cm^3) in a 1 dm^3 3-necked round-bottomed flask equipped with a mechanical stirrer and an efficient reflux condenser. Water (50 cm^3) was added and the reaction mixture was stirred for 0.5 h. Volatiles were removed at 25 °C/10^{-1} mmHg to give an orange oil. This was extracted with diethyl ether and the extracts were dried (MgSO$_4$, *ca.* 12 h), filtered, and evaporated under reduced pressure to give a yellow oil. Crystallisation (EtOH) of the latter afforded white needles of the title product **6** (17.6 g, 50%).

Preparation of [PhCH$_2$(H)N(CH$_2$)$_2$N(H)(CH$_2$)$_2$N(H)-(CH$_2$)$_2$N(H)CH$_2$Ph]·4HCl **7**.—Concentrated hydrochloric acid was slowly added to a vigorously stirred solution of the imidazolidine **6** (15.0 g, 33.9 mmol) in ethanol (200 cm^3) and water (50 cm^3). A yellow precipitate formed instantly. The reaction was taken to be complete when acid addition produced no further precipitation. The precipitate was filtered off, washed with cold ethanol (3 × 30 cm^3), and twice recrystallised (H$_2$O) to afford white needles of the title product **7** (14.1 g, 83%).

Preparation of the Tetramine PhCH$_2$(H)N(CH$_2$)$_2$N(H)(CH$_2$)$_2$-N(H)(CH$_2$)$_2$N(H)CH$_2$Ph **8**.—Potassium hydroxide (8.00 g, 142 mmol) was slowly added to a saturated aqueous solution of the tetrahydrochloride **7** (14.1 g, 28.2 mmol). The reaction mixture was set aside for *ca.* 12 h. The hydrated amine separated out, as a low melting brown solid and white needles. This was filtered off, washed with cold ethanol (3 × 10 cm^3), and dried *in vacuo.* Dehydration was completed in a vacuum desiccator (over P$_2$O$_5$, *in vacuo*, 7 d). Distillation afforded the title product **8** (5.40 g, 54%), as a slightly yellow, viscous oil.

In situ Preparation of the Tetramine PhCH$_2$(H)N(CH$_2$)$_2$N-(H)(CH$_2$)$_2$N(H)(CH$_2$)$_2$N(H)CH$_2$Ph **8**.—Benzaldehyde (43.5 g, 410 mmol) was slowly added with vigorous stirring to *N,N′*-bis(3-aminopropyl)ethylenediamine (24.5 g, 137 mmol) at 0 °C. The mixture was stirred at 25 °C for *ca.* 1.5 h and then dissolved in ethanol (600 cm^3). Sodium (25.0 g, 1.08 mol) was added, and then (after *ca.* 1 h) water (50 cm^3). Careful neutralisation with hydrochloric acid afforded an orange precipitate, which was filtered off, washed with cold ethanol (3 × 40 cm^3), dissolved in boiling water, treated with activated charcoal, and filtered. Potassium hydroxide (35.0 g, 625 mmol) was added to the filtrate and the reaction mixture was set aside for *ca.* 12 h. The precipitate was filtered off, washed with cold ethanol (3 × 10 cm^3), and dried *in vacuo* (desiccator, P$_2$O$_5$, 7 d). Distillation of the resultant brown viscous oil yielded the title product **8** (17.0 g, 35%).

Preparation of the Dipyrimido[1,2-a:2′,1′-c]*pyrazine* **3** *by Method A.*—A stirred solution of *N,N′*-bis(3-benzylaminopropyl)ethylenediamine **8** (6.00 g, 16.9 mmol) and *N,N′*-dimethylformamide dimethyl acetate (6.04 g, 50.7 mmol) in ethanol (10 cm^3) was heated at 90 °C for 2 h under reflux. The reaction mixture was then heated at 130 °C under distillation conditions in an argon atmosphere, the dimethylamine and methanol produced being allowed to distil off. Pentane (2 × 30 cm^3) was added to the residual yellow oil with stirring and the volatiles were removed under reduced pressure. The residual yellow powder was extracted into pentane (60 cm^3) and the extract was concentrated and cooled (−30 °C for 2 d), to afford colourless prisms of the title product **3** (5.76 g, 91%).

Preparation of the Diimidazo[1,2-a:2′,1′-c][1,4]*diazepine* **4** *and the Diimidazo*[1,2-a:2′,1′-c]*pyrazines* **2**.—The alkene **4** was prepared from *N,N′*-bis(benzylaminoethyl)propane-1,3-diamine[12] and CH(OMe)$_2$NMe$_2$ in a manner similar to that described for the analogue **3**. The enetetramines **2a** and **2b** were

prepared similarly from $R(H)N(CH_2)_2N(H)(CH_2)_2N(H)(CH_2)_2NHR$ (R = Me or CH_2Ph) and $CH(OMe)_2NMe_2$; data on the new precursors (Schiff base, imidazolidine or pyrimidine, and tetramine) for the enetetramines **2b**, **3**, and **4** are in Table 5.

X-Ray Structures of $[CN(R)(CH_2)_2NR]_2$ (R = CH_2Ph) **11** *and of* **2b**.—Crystal and refinement data are summarised in Table 11. X-Ray quality crystals of **11** and **2b** were obtained by recrystallisation from toluene–hexane (1:1) **11** or pentane **2b** at −30 °C. Cell dimensions were derived from the setting angles of 25 reflections with $\theta \approx 14°$ on an Enraf–Nonius CAD4 diffractometer using Mo-$K\alpha$ radiation with a graphite monochromator (λ = 0.710 69 Å). Intensities for unique reflections with $2 < \theta < 25°$ for **11** or $2 < \theta < 22°$ for **2b** were measured in the $\theta/2\theta$ scan mode. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption.

Non-hydrogen atoms were located by direct methods using MULTAN[19] for **11** and SHELXS-86[20] for **2b**, and refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf–Nonius SDP package. Hydrogen atoms were held fixed at calculated positions with either B_{iso} = 8.0 Å^2 for **11** or B_{iso} = 1.3 B_{eq} for the parent atom for **2b**. With a weighting scheme of $w = \sigma^{-2}(F)$, refinements converged at the residuals shown in Table 11. Scattering factors were taken from ref. 21. Tables of thermal parameters and hydrogen atom positions are available on request from the Cambridge Crystallographic Data Centre• and structure factors are available from one of the authors (P. B. H.).

• For full details of the CCDC deposition scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

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