Synthesis and structures of 1,3,1′,3′-tetrabenzyl-2,2′-biimidazolidinylidenes (electron-rich alkenes), their aminal intermediates and their degradation products

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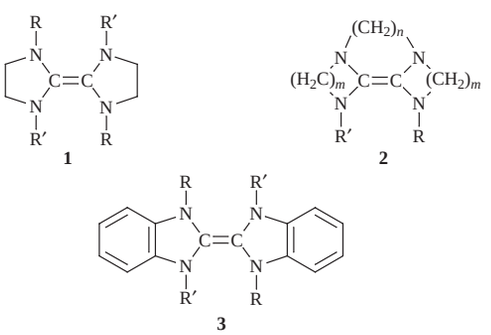
Benzyl (R) substituted enetetramines 9 and 3 have been studied. From $HNR(CH_2)_2NRH$ and $CH(NMe_2)_2OBu^t$ or $CH(OMe)_2NMe_2$, two new intermediates along the pathway to 9, namely the orthoamide 11 and the bis(orthoamide) 12 were isolated. Each of 11 and 12 was converted into 9 by refluxing in toluene. Photolysis of 9 yielded the isomer 10, while thermolysis of 9 gave the di(debenzylated) product 1,1′-dibenzyl-2,2′-biimidazoline 13. A route to 3 (R = R′ = CH_2Ph) similar to those used for 9, involving the condensation of 1,2-$C_6H_4[N(R)H]_2$ with $CH(OMe)_2NMe_2$, or the reaction between 1,3-dibenzylbenzimidazolium chloride 8 (X = Cl) and NaH, did not give the expected enetetramine 3 (the dibenzo-analogue of 9), the bis(debenzylated) product 15 being obtained instead. Heating the orthoamide 1,2-$RN\overline{C_6H_4N(R)C}(H)NMe_2$, prepared from $CH(NMe_2)_2OBu^t$ and 1,2-$C_6H_4[N(H)R]_2$, also gave 15. The reactions of S_8, PhNCS or KOH with a mixture of 8 (X = Cl) and NaH gave 17, 18 or 19, respectively, consistent with the transient formation in each reaction of the tetrabenzylenetetramine 3 (R = R′ = CH_2Ph). The molecular structure of each of the crystalline compounds 10, 11, 12 and 13 was established by X-ray diffraction.

For some years we have used enetetramines (electron-rich olefins) such as **1**, **2** and **3** as (i) sources of carbenetransition



1 **2** **3**

metal complexes,[1–3] (ii) powerful reducing agents, especially chlorine atom-abstractors,[2,4,5] or (iii) benzoin catalysts.[6] The compounds have an extensive organic chemistry.[7] They do not dissociate into imidazolidinylidenes (electron-rich carbenes), although scrambling reactions between two different compounds **1** (*e.g.* R = R′ = Ph with R = R′ = *p*-MeC_6H_4) were shown to occur in the presence of Rh^I catalysts;[8] carbene-rhodium(I) complexes were isolable intermediates in the catalytic cycle; this was the first example of model experiments implicating carbenemetal complexes in olefin metathesis. Thermally stable electron-rich carbenes such as $\overline{CNRCH{=}CHNR}$ (R = adamantyl) have recently gained prominence.[9]

The general route to compounds **1** involves interaction of the appropriate *N*,*N*′-disubstituted 1,2-diaminoethane, $HNR(CH_2)_2NRH$ (R = a primary alkyl or an unhindered aryl group) with the dimethyl acetal of *N*,*N*-dimethylformamide in an inert atmosphere, eqn. (1).[10] The equilibrium is driven to the right by

$$2HN(R)(CH_2)_2N(R)H + 2CH(NMe_2)(OMe)_2 \rightleftharpoons \mathbf{1}\ (R = R') + 2Me_2NH + 4MeOH \quad (1)$$

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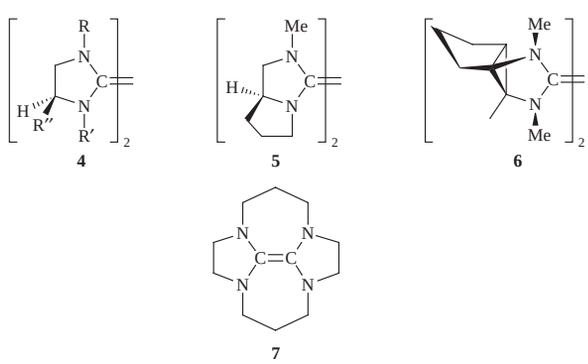
continuous removal by distillation of MeOH and Me_2NH. The reaction has been extended to (i) six-membered bicyclic analogues of **1**,[11] (ii) compounds **2**[12] and **3**,[3] (iii) optically active compounds **4**–**6**,[13] (iv) the macrocycle **7**,[14] (v) functional-



4 **5** **6**

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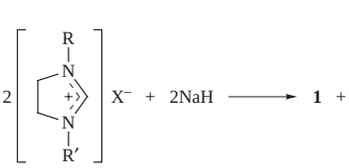
ised analogues of **1** [R = $(CH_2)_2CH{=}CH_2$,[15] $CH_2CH{=}CHMe$[15] and $(CH_2)_3PPh_2$[16]] and (vi) unsymmetrical analogues of **1** ($R \neq R'$).[12] Symmetrical tetraarylenetetramines (**1**, R = an unhindered aryl group, *e.g.* R = Ph) have been prepared by a similar procedure (EtOH elimination) from the orthoester $CH(OEt)_3$ and $HN(R)(CH_2)_2N(R)H$,[17a] or by heating $PhN\overline{(CH_2)_2N(Ph)C}(H)CCl_3$ ($CHCl_3$ elimination).[17b]

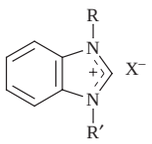
We have described a useful alternative method for preparing compounds **1** and **2**, from sodium hydride and either a 4,5-dihydroimidazolium halide, eqn. (2) [*e.g.* for **1** or **2**, $n = m = 2$,



$$2\ [\ \ ]\ X^- + 2NaH \longrightarrow \mathbf{1} + H_2 + 2NaX \quad (2)$$

R = CH_2Ph] or a bis(tetrahydropyridinium) salt [*e.g.* for **2**, $n = 2$, $m = 3$, R = CH_2Ph].[12] This procedure was adopted for

the synthesis of the enetetramine **3** (R = R′ = Me) from 1,3-dimethylbenzimidazolium iodide **8** (X = I) and NaH;[3] it has the



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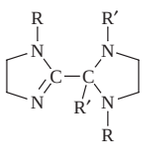
advantages that it requires extremely mild conditions, affords the products in high yield and is particularly suitable for unsymmetrical enetetramines, *e.g.* **1** and **2** (R ≠ R′).

The biimidazolidinylidene **1** (R = R′ = allyl) was not accessible using the procedure of eqn. (1) and, if formed, spontaneously rearranged to the isomer **1′** (R = R′ = allyl).[15] This



1′

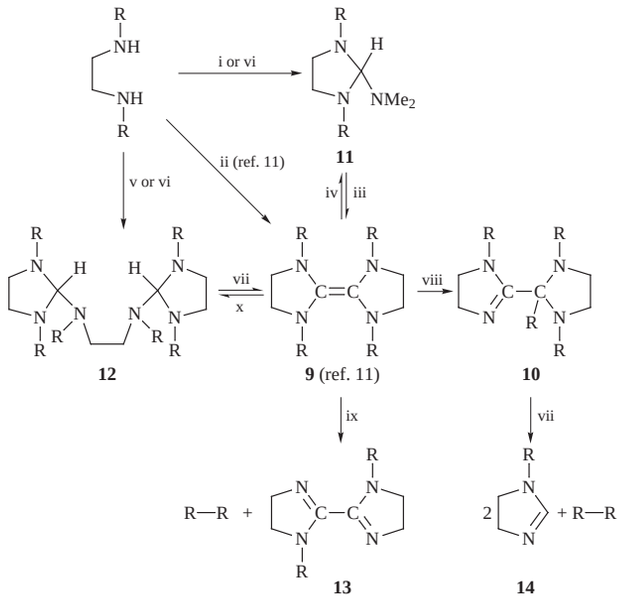
thermal amino-Claisen rearrangement was believed to be [3,3]-sigmatropic, because the corresponding thermal transformation of the tetracrotyl analogue **1** (R = R′ = CH_2CH=CHMe) regiospecifically yielded **1′** [R = CH_2CH=CHMe, R′ = CH(Me)-CH=CH_2], while its photochemical isomerisation gave not only the latter but also the isomer **1′** (R = R′ = crotyl). In a preliminary publication we noted that a similar **1** ⟶ **1′** isomerisation (**9** ⟶ **10**, viii in Scheme 1) occurred for the case of R = CH_2Ph and outline X-ray data were also shown for **10**;[15] full details are now provided.

Tetrakis(*N*-piperidyl)ethene [together with bis(*N*-piperidyl)-carbene] has been obtained by deprotonation of the amidinium salt $[(C_5H_{12}N)_2CH][BF_4]$ with $LiNPr^i_2$.[18a] Reduction of oxalic amidines with metallic lithium and addition of an electrophile yielded enetetramines; *e.g.* [Me(Ph)N][Me(4-MeC_6H_4)N]C=C-[N(4-MeC_6H_4)][N(Ph)Me] from [Me(Ph)N][4-MeC_6H_4N]C=C-[N(4-MeC_6H_4)][Me(Ph)N] and successively Li and MeI.[18b] Treatment of the thiourea $RN\overline{(CH_2)_2NR}CS$ with potassium yielded the carbene (R = Bu′) or its dimer **1** (R = R′ = Me, Et or Pr^i).[18c]

The objectives of the present study were to (i) identify aminal intermediates in the reaction of eqn. (1); (ii) study the thermal and photochemical degradation reactions of the enetetramine **9** (**1**, R = R′ = CH_2Ph); and (iii) attempt to obtain the tetrabenzyl compound **3** (R = R′ = CH_2Ph) and study its reactivity. In the event, the latter compound proved to be elusive, but trapping and decomposition reactions support the notion that it has a transient existence.

Results and discussion

The tetrabenzylenetetramine **9** has previously been described, having been prepared from the diamine $HN(CH_2Ph)$-$(CH_2)_2N(CH_2Ph)H$ and the aminal $CH(NMe_2)(OMe)_2$ (ii in Scheme 1);[11] its X-ray structure has also been reported.[12] It has been suggested that in similar reactions, an orthoamide such as **11** (R = CH_2Ph) might be an intermediate.[10] We now show that, from equimolar portions of the diamine and the orthoamide $CH(NMe_2)_3$ or $CH(NMe_2)_2OBu^t$, the monocyclic orthoamide **11** was formed (i or vi in Scheme 1) [an analogue of **11** (R = Me) had previously been made similarly [19]]; while using the Bredereck reagent $CH(NMe_2)_2OBu^t$, or under more forcing conditions $CH(NMe_2)(OMe)_2$, and the diamine in appropriate stoichiometry, gave the bicyclic orthoamide **12** (v or vi in Scheme 1). Each of **11** and **12** upon heating gave **9** (iii and vii in Scheme 1), and the latter in turn upon treatment with Me_2NH



Scheme 1 Routes to enetetramine **9** and its thermal or photochemical degradation or aminolysis (R = CH_2Ph). *Reagents and conditions*: i, $CH(NMe_2)_3$, C_5H_{12}, 36 °C, 2 h; ii, $CH(NMe_2)(OMe)_2$, MeC_6H_{11}, 110 °C (distn), 3 h; iii, C_6H_{12}, 80 °C, 1.5 h; iv, 4 Me_2NH, THF, 20 °C, 18 h; v, $CH(NMe_2)(OMe)_2$, C_6H_{12}, 80 °C, 3 h; vi, $CH(NMe_2)_2(OBu^t)$, *ca*. 25 °C, 2 h; vii, PhMe, 110 °C, 3 h; viii, *hν*, Et_2O, 20 °C, 18 h; ix, $Me_2C_6H_4$, 140 °C, 6 h; x, $RN(H)(CH_2)_2NHR$, THF, 20 °C, 40 h.

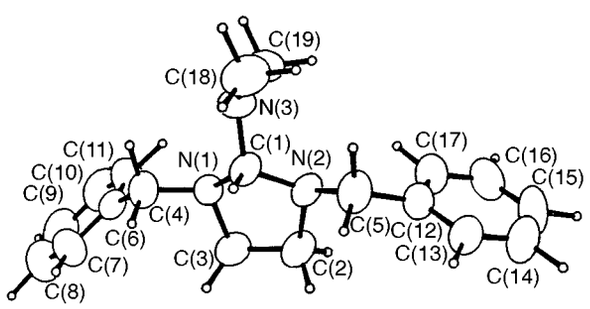


Fig. 1 X-Ray crystal structure of **11**

or 1,2-bis(benzylamino)ethane was converted into **11** or **12**, respectively (iv and x in Scheme 1). Photolysis of **9** yielded the isomer **10** (viii in Scheme 1). Thermolysis of **9** or **10** afforded dibenzyl and the debenzylated products, the bis(dihydroimidazole) **13** or dihydroimidazole **14** (ix and vii in Scheme 1).

Ethyl and allyl analogues of the orthoamide **11** (R = Et **11a** and R = CH_2CH=CH_2 **11b**) were obtained from the appropriate diamine and $CH(NMe_2)_2OBu^t$; upon heating, the former gave an enetetramine (**9**, R = Et),[7] and the latter an isomer (**10**, R = CH_2CH=CH_2).[15]

Characterisation of the new compounds **10**, **11**, **11a**, **11b**, **12** and **13** is shown in Tables 1 (colours, mps and analytical data), 2 (^{1}H NMR spectral data), 3 (^{13}C NMR spectral data) and 4 (selected IR spectral and MS data). The molecular structures of the crystalline orthoamide **11** (Fig. 1), the bis(orthoamide) **12** (Fig. 2), the rearrangement product **10** (Fig. 3) of the enetetramine **9** and the biimidazoline **13** (Fig. 4) have been determined from single crystal X-ray diffraction data.‡ Selected bond lengths and angles are listed in Tables 5 (**11**), 6 (**12**), 7 (**10**) and 8 (**13**).

‡ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/221.

Table 1 Colours, yields, mps and analytical data for the new compounds

Compound no.	Colour	Mp (°C)	Yield (%)	Found (required) (%)		
				C	H	N
10	White	98–99	92	81.0 (81.6)	7.0 (7.2)	11.0 (11.2)
10a (**10**, R = CH_2CHCH_2)	White	oil	58	72.2 (72.0)	9.4 (9.3)	18.6 (18.7)
11	White	49–50	83[b]	77.0 (77.3)	8.1 (8.5)	14.0 (14.2)
11a (**11**, R = Et)	White	oil	56[c]	63.3 (63.2)	12.1 (12.3)	24.8 (24.6)
11b (**11**, R = CH_2CHCH_2)	White		87	67.3 (67.7)	10.2 (10.8)	19.9 (21.5)
12	White	65–70[a]	56	81.4 (81.6)	7.2 (7.2)	11.4 (11.2)
13	Cream	105–106	70	76.0 (75.5)	7.3 (6.9)	17.2 (17.6)
16	Yellow	70–71	58	79.1 (80.4)	6.9 (7.2)	11.9 (12.2)
15	White	215–217	80[d]	80.6 (81.1)	5.3 (5.3)	13.3 (13.5)
20	Cream	143–145	14	83.7 (84.6)	6.1 (6.4)	9.2 (9.4)
17	White	190–191	65	75.1 (76.4)	5.3 (5.4)	8.4 (8.5)
18	Yellow	203–205	52	77.6 (77.6)	5.3 (5.3)	9.6 (9.7)
19	White	114–115	76	79.7 (79.7)	6.2 (6.4)	8.9 (8.9)

[a] The compound first melted then resolidified. [b] 50% based on i in Scheme 1. [c] 50% based on vi and 47% based on x in Scheme 1. [d] The yield calculated from the acetal method.

Table 2 ^{1}H NMR spectroscopic chemical shift (δ) data, with assignments for the new compounds;[a] *J* values in Hz

Compound no.	Ring CH_2	CH_2 Ph	Aromatics	Others
11[b]	2.33 (m), 2.83 (m, AA′BB′)	3.68 (q, AB)	7.23 (m, C_6H_5)	2.48 (s, Me_2N) 4.12 (s, *H*-C^2)
11a				2.37 (NMe_2), 3.58 (2-C*H*)
11b				2.19 (NMe_2), 3.47 (2-C*H*)
12[b]	2.20–2.30 (m, AA′BB′)[d] 3.10 (s)[e]	*f*	7.00–7.50 (m, C_6H_5)	4.37 (s, C*H*)
13[b]	2.90 (t, CH_2N=)[g] 3.70 (t, CH_2NR)	4.80 (s)	7.00–7.60 (m, C_6H_5)	
16[c]	—	4.10 (s)	6.30–6.70 (m) 7.14 (s)	2.12 (s, NMe_2) 5.48 (s, C*H*)
15[c]	—	6.25 (s)	7.15–7.34 (m) 7.88 (m)	
20[c]	—	4.27 (s), 5.19 (s)	6.94–7.26 (m) 7.83 (d)	
17[c]	—	5.66 (s)	7.09–7.32 (m) 7.42 (m)	
18[c]	—	5.81 (s)	7.10–7.63 (m)	
19[c]	—	4.18 (d),[h] 4.81 (s)	6.79–6.82 (m) 7.26–7.31 (m)	4.10 (t, N*H*)[i] 8.21 (s, C*H*O)

[a] Chemical shifts (δ) relative to $SiMe_4$; abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. [b] Spectra recorded in C_6D_6. [c] Spectra recorded in $CDCl_3$. [d] CH_2's of the orthoamide rings. [e] CH_2's of the ethylenediamine bridge. [f] The other signals (singlets) at δ 3.10, 3.30, 3.70, 4.10 and 4.20 are not assigned. [g] J = 10. [h] J = 6. [i] J = 6.

Table 3 ^{13}C NMR spectroscopic chemical shift (δ) data, with assignments, for the new compounds[a]

Compound no.	Ring CH_2	*C*H_2Ph	Aromatics	Other
11[b]	49.6	58.4	128.1, 128.6, 129.3, 140.8	101.2 (*C*-2)
11a	49.5	—	—	102.2 (*C*-2), 38.8 [N(*C*H$_3$)$_2$], 14.5 (CH_2CH_3), 48.4 (CH_2CH_3)
11b	49.7	—	—	38.8 [N(*C*H$_3$)$_2$], 101.2 (*C*-2), 115.8 (*C*H=CH_2), 137.3 (CH_2=CH)
12b	48.6,[d] 50.7	54.7, 57.5[f]	126.4, 126.6, 126.9, 127.3	100.4 (*C*-2)
13[b]	50.0, 52.5	54.6	128.0, 128.3, 128.5, 128.6, 128.7	99.5 (*C*-bridging)
16[c]	—	51.0	118.7, 127.1, 127.4, 128.7, 139.2, 140.5	37.3, 112.8
15[c]	—	48.5	110.8, 120.5, 122.9, 124.1, 126.8, 127.4, 128.6, 135.5, 136.9, 142.6, 142.8	
20[c]	—	34.5, 47.0	109.6, 119.5, 122.5, 126.1, 127.4, 128.6, 135.5, 136.6, 142.6, 153.3	
17[c]	—	49.0	110.1, 123.5, 127.9, 128.3, 129.2, 136.1	132.5
18[c]	—	50.1	113.3, 122.4, 122.9, 123.9, 126.2, 128.4, 128.5, 128.8, 129.1, 130.4, 133.4	165.7, 150.7
19[c]	*e*	47.6, 48.6	111.7, 117.0, 127.1, 128.5, 126.6, 129.2, 129.8, 129.9, 136.7, 138.4, 144.9	163.8

[a] Chemical shifts (δ) relative to $SiMe_4$ = 0. [b] Spectra recorded in C_6D_6. [c] Spectra recorded in $CDCl_3$. [d] C of the orthoamide. [e] ^{15}N = −249.1 (*N* CHO), −323.0 (*N* H). [f] Attached to ring N.

The conformations of the five-membered rings in the orthoamide **11** and the bicyclic orthoamide **12** have an envelope-like shape. The methine carbon [C(1)] in **11** is *ca*. 0.56 Å below the N(1)–C(3)–C(2)–N(2) plane; the three substituent atoms C(4), C(5) and N(3) [attached to N(1), N(2) and C(1), respectively] are equatorial to this plane, with C(4) and C(5) *ca*. 0.6 Å out of this plane. In **12**, by contrast, one of the ring carbons [C(3)] is *ca*. 0.6 Å above the N(1)–C(1)–N(2)–C(4) plane; the C(5) sub-

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

Compound no.	ν(C=N)/cm^{-1}	*m*/*z* (rel. intensity, %; assignment; M^+ = parent molecular ion)
11	—	*b*
12	—	*b*
13	1522	318 (13, M^+), 227 (43, $[M - 91]^+$), 186 (15, $[M - 132]^+$), 159 (5, $[M^+/2]$), 132 (15, $[M - 18]^+$), 91 (100, $[M - 227]^+$)
16	—	343 (15, M^+), 299 (100, $[M - 44]^+$)
15	1603	414 (55, M^+), 323 (100, $[M - 91]^+$)
20	1610	298 (50, M^+), 207 (100, $[M - 91]^+$), 91 (100, $[M - 207]^+$)
17	1612	330 (100, M^+), 297 (20, $[M - 33]^+$), 239 (80, $[M - 91]^+$)
18	1601	434 (80, $[M + 1]^+$), 402 (18, $[M - 32]^+$), 310 (75, $[M - 123]^+$), 298 (30, $[M - 135]^+$)
19	*c*	316 (18, M^+), 299 (25, $[M - 17]^+$), 197 (20, $[M - 119]^+$), 91 (100, $[M - 225]^+$)

[a] Spectra recorded as Nujol mulls. [b] Parent ion was not observed; fragmentation similar to that of **1**, with different intensities. [c] $\nu_{CO} = 1657$ cm^{-1}.

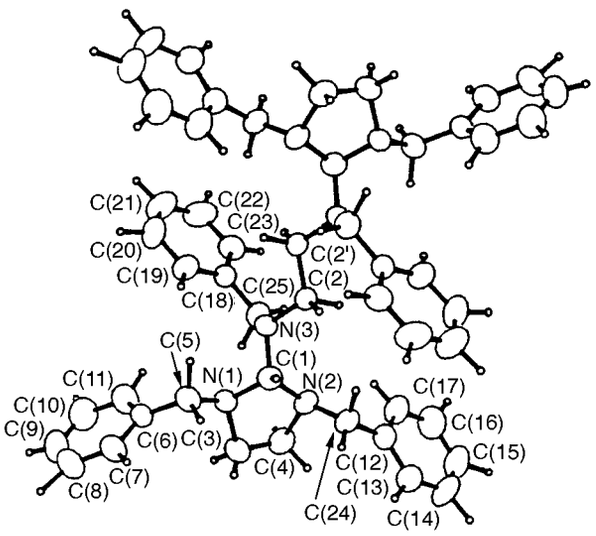


Fig. 2 X-Ray crystal structure of **12**

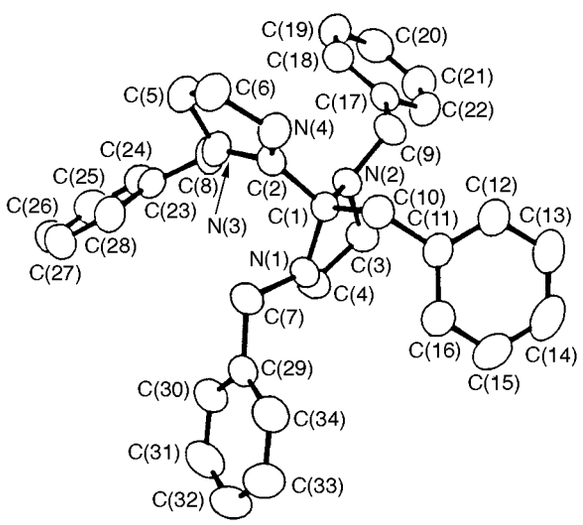


Fig. 3 X-Ray crystal structure of **10**

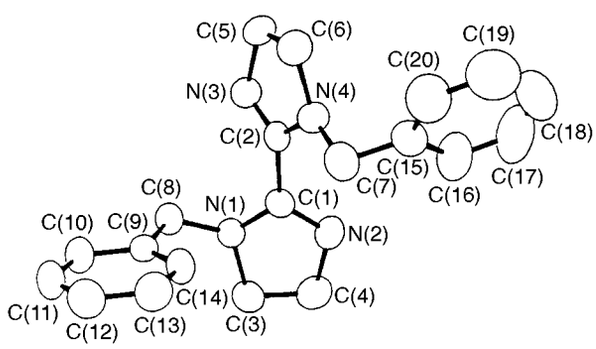


Fig. 4 X-Ray crystal structure of **13**

Table 5 Selected bond lengths (Å) and angles (°) for the ortho-amide **11**

N(1)–C(1)	1.457(6)	N(1)–C(3)	1.450(6)
N(1)–C(4)	1.461(6)	N(2)–C(1)	1.458(6)
N(2)–C(2)	1.465(7)	N(2)–C(5)	1.455(6)
N(3)–C(1)	1.432(6)	N(3)–C(18)	1.451(7)
N(3)–C(19)	1.453(7)	C(2)–C(3)	1.489(7)
C(1)–N(1)–C(3)	106.0(3)	C(1)–N(1)–C(4)	113.4(4)
C(3)–N(1)–C(4)	113.6(4)	C(1)–N(2)–C(2)	106.9(4)
C(1)–N(2)–C(5)	114.7(4)	C(2)–N(2)–C(5)	113.8(4)
C(1)–N(3)–C(18)	115.0(4)	C(1)–N(3)–C(19)	117.2(4)
C(18)–N(3)–C(19)	114.0(4)	N(1)–C(1)–N(2)	101.0(4)
N(1)–C(1)–N(3)	110.0(4)	N(2)–C(1)–N(3)	116.5(4)

Table 6 Selected bond lengths (Å) and angles (°) for the bicyclic orthoamide **12**

N(1)–C(1)	1.446(6)	N(1)–C(3)	1.454(6)
N(1)–C(5)	1.451(6)	N(2)–C(1)	1.468(6)
N(2)–C(4)	1.486(7)	N(2)–C(24)	1.474(7)
N(3)–C(1)	1.461(6)	N(3)–C(2)	1.460(6)
N(3)–C(25)	1.459(7)	C(3)–C(4)	1.509(8)
C(1)–N(1)–C(3)	106.2(4)	C(1)–N(1)–C(5)	114.6(4)
C(3)–N(1)–C(5)	112.7(4)	C(1)–N(2)–C(4)	105.9(3)
C(1)–N(2)–C(24)	114.5(4)	C(4)–N(2)–C(24)	111.3(4)
C(1)–N(3)–C(2)	112.0(4)	C(1)–N(3)–C(25)	111.5(4)
C(2)–N(3)–C(25)	113.2(4)	N(1)–C(1)–N(2)	106.1(4)
N(1)–C(1)–N(3)	109.7(4)	N(2)–C(1)–N(3)	115.6(4)

Table 7 Selected bond lengths (Å) and angles (°) for the isomer **10** of the enetetramine **9**

N(1)–C(1)	1.466(4)	N(1)–C(4)	1.456(4)
N(1)–C(7)	1.456(4)	N(2)–C(1)	1.475(4)
N(2)–C(3)	1.453(4)	N(2)–C(9)	1.451(4)
N(3)–C(2)	1.392(2)	N(3)–C(5)	1.460(4)
N(3)–C(8)	1.447(3)	N(4)–C(2)	1.276(3)
N(4)–C(6)	1.469(4)	C(1)–C(2)	1.536(4)
C(1)–C(10)	1.556(3)	C(3)–C(4)	1.508(5)
C(5)–C(6)	1.506(3)		
C(1)–N(1)–C(4)	110.8(2)	C(1)–N(1)–C(7)	118.4(2)
C(4)–N(1)–C(7)	117.5(2)	C(1)–N(2)–C(3)	108.4(2)
C(1)–N(2)–C(9)	118.2(2)	C(3)–N(2)–C(9)	117.7(2)
C(2)–N(3)–C(5)	106.3(2)	C(2)–N(3)–C(8)	127.5(2)
C(5)–N(3)–C(8)	116.8(2)	C(2)–N(4)–C(6)	107.0(2)
N(1)–C(1)–N(2)	102.1(2)	N(1)–C(1)–C(2)	115.3(2)
N(1)–C(1)–C(10)	108.1(2)	N(2)–C(1)–C(2)	107.8(2)
N(2)–C(1)–C(10)	115.8(2)	C(2)–C(1)–C(10)	107.9(2)
N(3)–C(2)–N(4)	115.2(2)	N(3)–C(2)–C(1)	124.2(2)
N(4)–C(2)–C(1)	120.6(2)	N(2)–C(3)–C(4)	101.6(2)

stituent at N(1) is in an equatorial site and *ca*. 0.6 Å above this plane, while the other two substituents [C(24) and N(3)] are on opposite sides of the ring with both *ca*. 1.0 Å out of the plane. Each nitrogen atom in **11** or **12** is in a distorted pyramidal

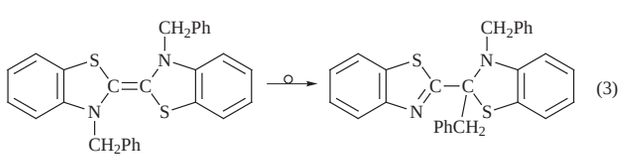
Table 8 Selected bond lengths (Å) and angles (°) for the 1,1′-dibenzyl-2,2′-biimidazoline **13**

N(1)–C(1)	1.369(5)	N(1)–C(3)	1.468(6)
N(1)–C(8)	1.453(4)	N(2)–C(1)	1.281(5)
N(2)–C(4)	1.485(6)	N(3)–C(2)	1.276(5)
N(3)–C(5)	1.481(6)	N(4)–C(2)	1.366(5)
N(4)–C(6)	1.469(6)	N(4)–C(7)	1.449(5)
C(1)–C(2)	1.480(6)	C(3)–C(4)	1.524(5)
C(5)–C(6)	1.506(6)		
C(1)–N(1)–C(3)	107.7(3)	C(1)–N(1)–C(8)	126.8(3)
C(3)–N(1)–C(8)	120.2(3)	C(1)–N(2)–C(4)	105.6(3)
C(2)–N(3)–C(5)	105.4(3)	C(2)–N(4)–C(6)	106.2(3)
C(2)–N(4)–C(7)	127.6(3)	C(6)–N(4)–C(7)	119.6(3)
N(1)–C(1)–N(2)	117.1(4)	N(1)–C(1)–C(2)	121.3(3)
N(2)–C(1)–C(2)	121.6(3)	N(3)–C(2)–N(4)	117.4(3)
N(3)–C(2)–C(1)	121.9(3)	N(4)–C(2)–C(1)	120.5(3)

environment, implying that there is a stereochemically active lone pair of electrons. The sum of the C–N–C angles at N(1) and N(2) in **11** and **12** is closely similar, but at N(3) is 9.5° greater in **11** than in **12**, presumably because of the greater steric strain in the latter. The N(2)–C(1)–N(3) bond angles are greater than N(1)–C(1)–N(3) for both **11** and **12**. The N–C bond length mean values of 1.45(1) Å in **11** and 1.46(1) in **12** are unexceptional.

The conformations of the five-membered rings in the isomer **10** of the enetetramine **9** differ. The saturated ring is envelope-like, in which C(3) is *ca*. 0.52 Å below the N(2)–C(1)–N(1)–C(4) plane and the substituent atoms on the two nitrogens are equatorial and *trans* to one another, with C(7) *ca*. 0.78 Å above and C(9) *ca*. 0.44 Å below the plane. The unsaturated ring in **10**, like both in the biimidazoline **13**, is almost planar. The sum of the angles at N(1), N(2) and N(3) in **10** and N(1) and N(4) in **13**, each bearing a benzyl group, shows that each of these nitrogen atoms is closer to being trigonal planar than pyramidal. The C=N and C(sp^2)–N bond lengths in **10** and **13** have similar values of 1.276(3) and a mean of 1.279(5) and 1.392(2) and a mean of 1.367(4) Å, respectively.

The amino-Claisen rearrangement of **9** ⟶ **10** has precedents in (i) the transformations of eqn. (3),[20] (ii) **1** ⟶ **1′**

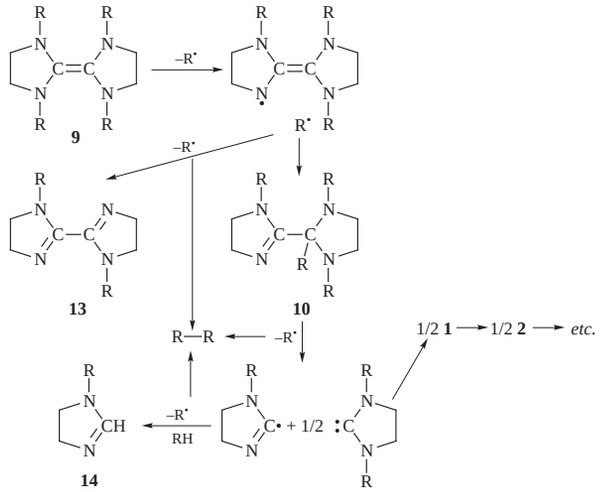


(3)

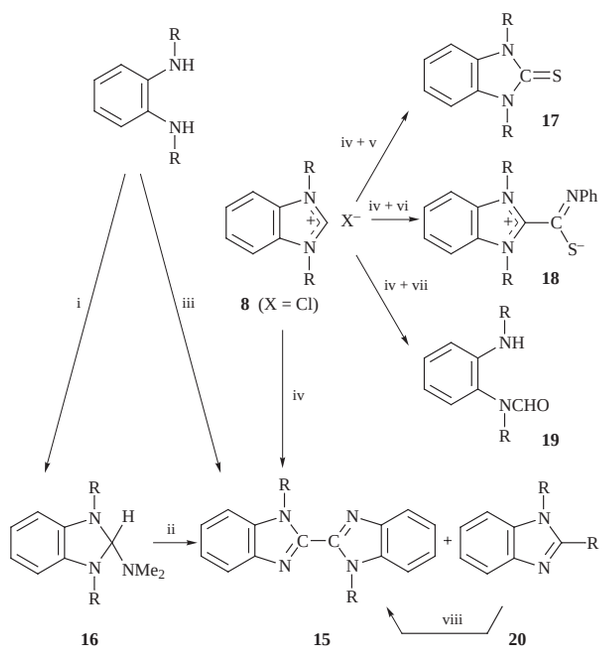
(R = $CH_2CH{=}CH_2$),[15] and (iii) **2** ($n = 2$ or 3, $m = 2$ or 3, R = CH_2Ph) to the isomer **2′**.[21] The mechanism of the photochemical isomerisation for case (ii) was considered to be at least in part intermolecular because of the nature of **1′** when R = crotyl.[15] The debenzylation reactions **9** ⟶ **13** and **10** ⟶ **14**, likewise, are almost certainly free radical in character, as evident from the concomitant formation of bibenzyl in each case.

Suggested mechanisms for the isomerisation **9** ⟶ **10** and the debenzylations **9** ⟶ **13** and **10** ⟶ **14** (viii, ix and vii, respectively in Scheme 1) are shown in Scheme 2.

Attempts to prepare the tetrabenzylenetetramine **3** (R = R′ = CH_2Ph), using either 1,2-bis(dibenzylamino)benzene and the acetal $CH(NMe_2)(OMe)_2$, or the corresponding 1,2-*N*,*N*′-dibenzylbenzimidazolium chloride **8** (X = Cl) and NaH (iii and iv in Scheme 3) proved to be unsuccessful, the bis(debenzylated) product **15** being obtained instead. This is surprising, because both methods had been effective in the preparation of the analogous tetramethylenetetramine **3** (R = R′ = Me).[3] Furthermore, an alternative strategy whereby 1,2-bis(dibenzylamino)benzene was converted into the orthoamide **16**, using



Scheme 2 Proposed mechanism for the debenzylation **9** ⟶ **13** and **10** ⟶ **14** and the isomerisation **9** ⟶ **10** (R = CH_2Ph)



Scheme 3 Routes to derivatives of the transient enetetramine **3** (R = R′ = CH_2Ph). *Reagents and conditions*: i, $CH(NMe_2)_2(OBu^t)$, 75 °C, 2 h; ii, PhMe, 110 °C, 3 h; iii, $CH(NMe_2)(OMe)_2$, PhMe, 110 °C, 2 h; iv, NaH, THF, 20 °C, 8 h; v, S_8; vi, PhNCS; vii, KOH, H_2O–EtOH, 75–80 °C, 2 h; viii, $Me_2C_6H_4$, 140 °C, 2 h.

Bredereck's reagent, and then **16** was heated (i and ii in Scheme 3) also afforded **15**. Evidence was therefore sought for at least the transient formation of the tetrabenzylenetetramine **3** (R = R′ = CH_2Ph) from **8** (X = Cl) and NaH, by trapping reactions, using S_8, PhNCS or KOH, which yielded the thiourea **17**, the zwitterion **18** and *N*,*N*′-bisbenzyl-*N*-formyl-1,2-diaminobenzene **19** (v, vi and vii in Scheme 3). The benzylbenzimidazole **20**, upon heating, underwent debenzylation and C–C coupling to give **15** (viii in Scheme 3), presumably by a radical coupling mechanism. Related bis(benzimidazoles) are known.[22]

The thermal instability of the tetrabenzylenetetramine **3** (R = R′ = CH_2Ph) is attributed to steric effects, as may be judged by examining X-ray crystallographic data on **9**[12] and **3** (R = R′ = Me),[3] both being stable in toluene up to *ca*. 100 °C. The latter has each fused bicyclic moiety coplanar, with the methyl groups bent out of the plane on opposite sides of the fused rings, the two ends of the molecules twisted with respect to one another by *ca*. 21° about the central C=C bond, thus

reducing the steric strain between adjacent methyl groups.[3] The molecular structure of **9** showed that the conformation of the five-membered rings was such that the central NCN′ planes are twisted by *ca*. 17° with respect to one another about the C=C bond, and the other two endocyclic carbon atoms are out of the NCN′ plane: above for one ring and below for the other.[12] The sum of angles at the four nitrogens is *ca*. 331° in **9**[12] and *ca*. 342° in **3** (R = R′ = Me).[3]

Experimental

General procedures and starting materials

All experiments were performed under argon or dinitrogen using freshly distilled dry solvents. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker WM360 or a Bruker AMX-500 spectrometer. *J* Values are given in Hz. IR and mass spectra were obtained on a Perkin-Elmer 597 and a Kratos MS902 instrument, respectively. Melting points were recorded using an electrothermal melting point apparatus and are uncorrected.

The starting compounds, not available commercially, were prepared according to the procedures described in the literature. But the procedure for *N*,*N*′-dibenzyl-*o*-phenylenediamine, involving the reaction of the 1,3-dibenzylbenzimidazolium chloride and aqueous KOH gave in our hands *N*-formyl-*N*,*N*′-dibenzyl-*o*-phenylenediamine **19**. Therefore, we adopted another method (*cf.* ref. 23) which has not been described in the literature.

Preparation of 1,2-bis(benzylamino)benzene

Benzoyl chloride (23 cm^3, 194.4 mmol) was added dropwise to a solution of 1,2-diaminobenzene (10 g, 92.59 mmol) and pyridine (15 cm^3) in THF (50 cm^3). The precipitate, 1,2-$C_6H_4(NHCOPh)_2$ (28.9 g, 99%) was filtered off, washed with diethyl ether (2 × 25 cm^3) and dried at 100 °C. A portion of the latter (10 g, 31.64 mmol) in THF (150 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (6 g, 163 mmol). The mixture was heated under reflux for 3 h, then cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water and then 15% aqueous NaOH (10 cm^3). The white precipitate was filtered off and thoroughly washed with diethyl ether. The combined filtrate and washings were washed with water, and dried (Na_2SO_4). Volatiles were evaporated *in vacuo* and the residue was recrystallised from ethanol to yield yellow crystals of the title amine (7.38 g, 81%).

Preparation of the rearranged product 10 from the enetetramine 9 (R = CH_2Ph)

A suspension of the enetetramine **9** (1.84 g, 3.68 mmol)[11] in diethyl ether (60 cm^3) was irradiated using a medium pressure mercury UV-lamp at *ca*. 20 °C for 8 h. Volatiles were removed *in vacuo*, and the residue was dissolved in warm *n*-hexane (10 cm^3). On cooling to *ca*. 20 °C, cubic crystals of **10** (1.76 g, 96%) were obtained. $\delta_H(C_6D_6)$ 2.51 and 2.75 (AB system, dq, 4H, saturated ring-*H*, J_{HAHB} 8.35), 2.93 and 3.68 (A_2X_2 system, dt, 4H, unsaturated ring-*H*, J_{HAHX} 9.6), 3.69 and 4.10 (AB system, dd, 4H, CH_2Ph attached to saturated ring nitrogens, J_{HAHB} 13.4), 3.74 (s, 2H, CH_2Ph attached to C), 4.68 (s, 2H, CH_2Ph attached to unsaturated ring nitrogen), 7.12–7.75 (m, 20H, aromatic protons). $\delta_C(C_6D_6)$ 39.67 (*C*H_2Ph attached to C), 47.97 (C of saturated ring), 51.97, 52.39 (C of unsaturated ring), 53.30 (N*C*H_2Ph of saturated ring), 53.72 (N*C*H_2Ph of unsaturated ring), 83.59 (C-2 of saturated ring), 166.35 (C-2 of unsaturated ring).

Preparation of 10a (10, R = $CH_2CH{=}CH_2$)

A stirred solution of *N*,*N*-dimethylformamide dimethyl acetal (4.9 g, 40 mmol) and 1,2-bis(allylamino)ethane (4.37 g, 30 mmol) was heated under reflux for 3 h at 90 °C under an argon atmosphere. The reaction mixture was then heated at 120 °C under distillation conditions, allowing the produced dimethylamine and methanol to escape. From the resultant product, unreacted starting materials were eliminated *in vacuo*. Pentane was added to the yellow residual oil and the mixture was filtered through Celite. After elimination of volatiles from the filtrate *in vacuo*, **10a** (2.55 g, 58%) was obtained. $\delta_H(C_6D_6)$ 2.4 and 2.7 (AB system, dq, 4H, saturated ring-H), 2.8 and 3.3 (AB system, dt, 4H, unsaturated ring-H), 2.8 (m, 4H, NCH_2, saturated ring), 3.0 and 3.2 (AB system, m, 2H, NCH_2, rearranged group), 3.9 (d, 2H, NCH_2, unsaturated ring), 4.9 (m, 8H, $=CH_2$), 5.6 (m, 3H, =C*H*–, rearranged and attached saturated ring), 5.9 (m, 1H, =CH–, attached unsaturated ring). $\delta_C(C_6D_6)$ 39.41 (NCH_2, rearranged group), 48.93 (saturated ring), 51.96, 52.39 (unsaturated ring), 52.08 (NCH_2, attached saturated ring), 52.51 (NCH_2, attached unsaturated ring), 81.93 (C-2, saturated ring), 165.72 (C-2, unsaturated ring).

Preparation of 2-dimethylamino-1,3-dibenzylimidazolidine 11

Cooled (−30 °C) dimethylamine (1.5 cm^3, 22.6 mmol) was added to a solution of the enetetramine **9** (2.85 g, 5.7 mmol) in THF (20 cm^3). The mixture was stirred at *ca*. 20 °C for 18 h. Volatiles were removed under reduced pressure to leave a yellow oil, which was dissolved in *n*-hexane (10 cm^3) and cooled to −78 °C. The white precipitate of **11** (2.80 g, 83%) was recrystallised from Et_2O (10 cm^3) and *n*-hexane (10 cm^3) at −78 °C.

Preparation of 2-dimethylamino-1,3-diethylimidazolidine 11a (11, R = Et)

A mixture of 1,2-bis(ethylamino)ethane (3.24 g, 28 mmol) and *tert*-butoxybis(dimethylamino)methane (5.04 g, 29 mmol) was stirred at *ca*. 20 °C for 100 min. Volatile unreacted starting materials were eliminated *in vacuo*. *n*-Hexane was added to the yellow residual oil and the mixture was filtered through Celite. After hexane elimination *in vacuo* from the filtrate, **11a** (2.7 g, 56%) was obtained as a dense yellow oil.

Preparation of 2-dimethylamino-1,3-diallylimidazolidine 11b (11, R = $CH_2CH{=}CH_2$)

A mixture of 1,2-bis(allylamino)ethane (1.5 g, 10.71 mmol) and tris(dimethylamino)methane (1.6 g, 11.03 mmol) was refluxed in hexane for 2 h under distillation conditions; *ca*. half of the solvent was eliminated and the mixture cooled to −30 °C to afford, after filtration and washing with cold hexane, **11b** (1.82 g, 87%).

Isolation of the bis(orthoamide) 12

A mixture of 1,2-bis(benzylamino)ethane (10 cm^3, 41.6 mmol) and dimethylformamide dimethyl acetal (5.7 cm^3, 43 mmol) in cyclohexane (20 cm^3) was heated, keeping the bath temperature below 100 °C and allowing the formed MeOH and Me_2NH to be distilled off. In order to complete the reaction, a small portion of the cyclohexane (*ca*. 5 cm^3) was also distilled off. Volatiles were removed at *ca*. 25 °C/10^{-2} Torr. The residue was extracted into toluene (2 cm^3) and *n*-hexane (10 cm^3) and the extract was filtered. Upon cooling, the filtrate yielded white needles of the bis(orthoamide) **12** (5.85 g).

Preparation of the enetetramine 9 (*cf.* ref. 11)

The reaction described above for **12** was carried out in methylcyclohexane (100 cm^3), using the diamine (40.9 g, 170.6 mmol) and the acetal (24 cm^3, 180.9 mmol) at a higher temperature (oil bath at 90 °C for 3 h and then 120 °C for 1 h). Cream crystals of **9** (13.5 g, 31.7%) were obtained upon cooling to *ca*. 20 °C. The filtrate was evaporated *in vacuo* to give an oily residue which, upon crystallisation from *n*-hexane (30 cm^3), yielded further crystals of **9** (12.0 g).

Conversion of 12 into 9

A solution of **12** (1.8 g, 3.6 mmol) in toluene (30 cm^3) was heated under reflux for 3 h. The solution was cooled to 20 °C, the volume was reduced to *ca*. 10 cm^3 and *n*-hexane (10 cm^3) was added yielding crystals of **9** (1.71 g, 95%).

Table 9 Crystal data and final refinement parameters for compounds **11**, **12**, **10** and **13**

Compound	**11**	**12**	**10**	**13**
Molecular formula	$C_{19}H_{25}N_3$	$C_{50}H_{56}N_6$	$C_{34}H_{36}N_4$	$C_{20}H_{22}N_4$
M	295.45	741.04	500.69	318.42
Crystal size/mm	0.4 × 0.5 × 0.45	0.4 × 0.1 × 0.25	0.4 × 0.25 × 0.20	0.17 × 0.15 × 0.10
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.663(1)	6.153(3)	10.939(3)	6.865(4)
b/Å	5.958(2)	12.178(2)	12.107(2)	9.018(3)
c/Å	25.268(3)	14.251(2)	12.456(1)	14.560(3)
α/°	—	89.04(1)	115.27(1)	88.44(2)
β/°	98.72(1)	83.84(2)	106.47(2)	88.67(3)
γ/°	—	81.89(3)	94.11(1)	71.59(4)
U/Å^3	1735.5	1051.2	1394.8	854.8
Z	4	1	2	2
D_c/g cm^{-3}	1.13	1.17	1.19	1.29
$F(000)$	640	398	536	340
μ (cm^{-1})	0.63	0.64	0.66	0.73
θ range/°	0–22	0–25	0–25	0–25
Observed reflections with $I > \sigma(I)$	959	1926	2446	1304
R_1	0.051	0.066	0.044	0.045
wR	0.060	0.082	0.051	0.044
$\Delta\rho_{max}$/e Å^{-3}	0.2	0.2	0.2	0.5

[a] $R_1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)^2]/(\Sigma w|F_o|^2)\}^{\frac{1}{2}}$.

Conversion of 11 into 9

2-Dimethylamino-1,3-dibenzylimidazolidine **11** (0.25 g, 0.85 mmol) in cyclohexane (3 cm^3) was refluxed for 90 min. The formerly colourless solution became yellow. Upon cooling to *ca*. 20 °C, pale yellow crystals of **9** (0.2 g, 95.2%) were deposited.

Reaction of the enetetramine 9 with 1,2-bis(benzylamino)ethane

A mixture of **9** (1.27 g, 2.54 mmol) and the diamine (0.65 g, 27 mmol) in THF (10 cm^3) was stirred at *ca*. 20 °C for 4 h. Volatiles were removed *in vacuo*. *n*-Hexane (20 cm^3) was added with shaking to the cream residue. The cream precipitate was separated by filtration and identified as **12** (0.6 g, 47.2%). After 2 d at *ca*. 20 °C, the filtrate yielded white crystals of **9** (0.49 g, 33%).

Debenzylation of the enetetramine 9

A solution of **9** (0.9 g, 1.8 mmol) in xylene (10 cm^3) was heated under reflux for 6 h. The volume of the solution was reduced to *ca*. 4 cm^3 and *n*-hexane (6 cm^3) was added. Upon cooling to −30 °C, cream crystals of 1,1′-dibenzyl-2,2′-biimidazoline **13** (0.4 g, 70%) were obtained. Gas chromatographic analysis of the filtrate showed it to comprise a mixture of **13**, toluene and bibenzyl.

Preparation of 15 and 20 from 8 (X = Cl)

To a suspension of **8** (X = Cl) (5 g, 16.95 mmol) in THF (60 cm^3) was added NaH (0.4 g, 16.66 mmol). The mixture was stirred for 8 h at *ca*. 20 °C. The solvent was removed *in vacuo*, toluene (100 cm^3) was added and the suspension was filtered. The resultant bright yellow filtrate was concentrated to *ca*. 20 cm^3 and *n*-hexane (10 cm^3) was added. Upon cooling, white crystals of the bis(benzimidazole) **15** (3.8 g, 56%) were obtained. Upon further cooling of the mother liquor, 1,2-dibenzylbenzimidazole **20** (0.6 g, 14%) was obtained.

Preparation of 15 from 1,2-bis(benzylamino)benzene

A stirred solution of the diaminobenzene (5 g, 17.36 mmol) and *N*,*N*-dimethylformamide dimethyl acetal (2.5 cm^3, 19.13 mmol) in toluene (15 cm^3) was heated at 90 °C for 2 h and then at 145–150 °C under distillation conditions for 30 min in an argon atmosphere, allowing the produced dimethylamine and methanol to distil off. The volatiles were removed *in vacuo*. The oily residue in a toluene–*n*-hexane (2:1) mixture was cooled to −30 °C, yielding **15** (5.7 g, 80%). This reaction was repeated using a water bath at 90 °C for 4 h, in an attempt to avoid the debenzylation, but only **15** was obtained, rather than the enetetramine **3** (R = R′ = CH_2Ph).

Preparation of the orthoamide 16

A mixture of 1,2-bis(benzylamino)benzene (2 g, 6.94 mmol) and *tert*-butoxybis(dimethylamino)methane (2.2 cm^3, 7.94 mmol) was stirred at *ca*. 20 °C for 2 h, then heated at 75 °C for 2 h. Volatiles were eliminated *in vacuo*. *n*-Hexane (30 cm^3) was added to the residue and the mixture was filtered. The filtrate was concentrated to *ca*. half of the original volume. Upon cooling, cream crystals of compound **16** (1.38 g, 58%) were obtained.

Conversion of the orthoamide 16 into 15

A solution of compound **16** (1 g, 2.92 mmol) in toluene (10 cm^3) was refluxed for 3 h. The volume of the solution was then concentrated to *ca*. half of the initial volume and *n*-hexane (3 cm^3) was added. Upon cooling (−30 °C), white crystals of **15** (0.5 g, 85%) were obtained.

Preparations of compounds 17 and 18

In order to trap **3** (R = R′ = CH_2Ph) during the formation of **15**, elemental sulfur (0.16 g, 0.63 mmol) was added to a mixture of **8** (X = Cl) (1.7 g, 5.14 mmol) and NaH (0.13 g, 5.42 mmol). After stirring for 2 h at *ca*. 20 °C and then at 80 °C for 1 h, volatiles were removed *in vacuo* and the residue was extracted with toluene. Addition of *n*-hexane and cooling to −30 °C yielded white crystals of the thiourea **17** (1.08 g, 65%).

Similar to the above procedure, but in place of sulfur, PhNCS (0.6 cm^3, 5.03 mmol) was added to a mixture of **8** (X = Cl) (1.7 g, 5.14 mmol) and NaH (0.13 g, 5.42 mmol). Stirring for 2 h at *ca*. 20 °C and similar work-up afforded compound **18** (1.13 g, 52%).

Preparation of 19

Compound **19** (1.8 g, 76%) was isolated when **8** (X = Cl) (2.5 g, 7.47 mmol) and KOH (1.5 g, 26.78 mmol) in technical alcohol (IMS) (25 cm^3) were heated under reflux for 2 h.

X-Ray crystallography

In each case, a crystal was sealed in a Lindemann glass capillary under argon and data collected on an Enraf-Nonius CAD4 diffractometer at ambient temperature using monochromated Mo-Kα radiation (λ = 0.710 69 Å). Cell dimensions were calculated from setting angles for 25 reflections with $7 < \theta < 10°$.

Intensities were measured by $\omega - 2\theta$ scans and corrected for Lorentz and polarisation effects but not for absorption. Structure solution was by direct methods using MULTAN;[24] and refinement, using the Enraf-Nonius MOLEN[25] programs was by full-matrix least-squares on F using reflections with $I > \sigma(I)$ and weighting scheme of $w = 1/\sigma^2(F)$. Non-H atoms were refined anisotropically. For **10** and **12** the H atoms were refined isotropically, while for **11** and **13** the H atoms were fixed at calculated positions with $B_{iso} = 6.0$ Å^2. Crystal data are in Table 9.

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