

Crystal and Molecular Structure of 1,4,8,11-Tetramethyl-1,4,8,11-Tetraazacyclotetradecane: Energy and Structural Relationships for This Tetraazamacrocycle in Its Neutral and Protonated Forms

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Abstract. The X-ray crystal structure of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane has been determined. The neutral ligand crystallises in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.467(4)$, $b = 10.057(5)$, $c = 10.637(5)$ Å, $\alpha = 67.68(3)$, $\beta = 75.38(4)$, $\gamma = 76.34(4)^\circ$, $V = 800.75$ Å³ and $D_c = 1.063$ g cm⁻³ for $Z = 2$. $R = 0.047$ for 2140 unique observed ($I/\sigma(I) \geq 2.0$) reflections ($R_w = 0.052$). Two crystallographically independent molecules are observed. Both are centrosymmetric and adopt a mesodentate conformation. Molecule (1) is identified as the (*R*, *S*, *S*, *R*)-[*trans*-IV] isomer and molecule (2) as the (*R*, *R*, *S*, *S*)-[*trans*-III] isomer. Molecular mechanics calculations provide a basis for understanding the structural and energetic relationships between the neutral and protonated forms of this tetraazamacrocyclic ligand.

Supplementary Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K. as Supplementary Publication No. 82149 (13 pages).

Key words: X-ray crystal structure, tetramethylcyclam, ring conformation, molecular modelling.

1. Introduction

1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (*N*-tetramethylcyclam, Tmc), forms complexes with a wide range of metal ions and neutral metallo-species. Tetradentate *N*-coordination to the metal leaves the macrocycle either in a regular square-planar N_4 arrangement e.g. six-coordinate $[\text{Ni}(\text{Tmc})(\text{OH}_2)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ [1] (*R*, *R*, *S*, *S*)-[*trans*-III], or in a folded form e.g. five-coordinate $[\text{Ni}(\text{Tmc})(\text{O}_2\text{COCH}_3)][\text{ClO}_4]$ [2], (*R*, *S*, *R*, *S*)-[*trans*-I]. Alternatively the N_4 -azamacrocycle can effectively turn itself inside-out to assume an exodentate conformation in which each of the tertiary amine centres binds to a separate metal e.g. $[(\text{Tmc})\cdot 4\text{AlMe}_3]$ [3]. In addition to metal complexation Tmc can also form protonated species; in a very recent structure determination of the di-cation

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$[(\text{Tmc})\text{H}_2]^{2+}$ [4] the two hydrogen atoms are bonded to alternate nitrogen atoms and form intracavity $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding; the tetraazamacrocycle assumes an endodentate geometry.

Surprisingly, there has been no crystallographic study of the uncomplexed ligand. In the light of this omission we report here the structure of Tmc and examine the conformational versatility shown by this ubiquitous tetraazamacrocycle.

2. Experimental

Tmc was prepared as described in the literature [5] (m.p. 41–42°C) and purified by vacuum distillation (Vigreux column, 200°C/0.01 mm Hg). Colourless block crystals of suitable quality for X-ray diffraction studies were obtained from the resulting solid by physical separation.

2.1. X-RAY STRUCTURE DETERMINATION

2.1.1. *Crystal Data*

$\text{C}_{14}\text{H}_{32}\text{N}_4$, $M = 256.44$, triclinic, $P\bar{1}$, $a = 8.467(4)$, $b = 10.057(5)$, $c = 10.637(5)$ Å, $\alpha = 67.68(3)$, $\beta = 75.38(4)$, $\gamma = 76.34(4)^\circ$, $V = 800.75$ Å³, $Z = 2$, $D_c = 1.063$ g cm⁻³, Mo K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo}K_\alpha) = 0.06$ mm⁻¹, $T = 260$ K, $R = 0.047$ for 2140 unique observed ($I/\sigma(I) \geq 2.0$) reflections.

The selected crystal was mounted under dinitrogen in a Lindemann capillary.

Data were collected with a Siemens R3m four circle diffractometer in $\omega - 2\theta$ mode. The crystal was held at 260 K with an Oxford Cryosystems Cryostream Cooler [6]. Maximum 2θ was 50° with scan range $\pm 0.07^\circ$ (ω) around the $K_{\alpha 1} - K_{\alpha 2}$ angles, scan speed $2 - 15^\circ$ (ω) min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. hkl Ranges were: 0/10, -11/11, -12/12. Three standard reflections were monitored every 200 reflections, and showed a slight decrease during data collection. The data were rescaled to correct for this. Unit cell dimensions and standard deviations were obtained by least-squares fit to 12 reflections ($24 < 2\theta < 26^\circ$).

The 3106 reflections collected were processed using profile analysis to give 2830 unique reflections ($R_{\text{int}} = 0.07$), of which 2090 were considered observed ($I/\sigma(I) \geq 2.0$). These were corrected for Lorentz, polarization and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.973 and 0.987. Crystal dimensions were $0.17 \times 0.19 \times 0.40$ mm.

Space group $P\bar{1}$ was chosen and deemed correct by successful refinement. The structure was solved by direct methods using SHELXTL (TREF). Refinement was by E-map expansion and successive Fourier syntheses. The asymmetric unit consists of two half-molecules. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were refined with isotropic thermal parameters. Final refinement was on F by least-squares methods refining 291 parameters.

TABLE I

Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
N(11)	6387.2(18)	7399.7(15)	-268.2(14)	44(1)*
C(12)	4872(3)	7160(2)	-498(2)	55(1)*
C(13)	3321(2)	8127(2)	-110(2)	49(1)*
N(14)	3036.0(18)	8145.1(15)	1287.6(14)	42(1)*
C(15)	1591(2)	9194(2)	1548(2)	52(1)*
C(16)	1818(2)	10774(2)	762(2)	51(1)*
C(17)	3212(3)	11166(2)	1138(2)	46(1)*
C(18)	7724(3)	6259(2)	-474(3)	65(1)*
C(19)	2838(3)	6709(2)	2298(2)	58(1)*
N(21)	7301(2)	2320(2)	4573(2)	50(1)*
C(22)	5897(3)	1535(2)	5021(2)	55(1)*
C(23)	4574(3)	1868(2)	6157(2)	49(1)*
N(24)	3430.7(18)	3218.9(16)	5736.5(14)	45(1)*
C(25)	2474(2)	3624(2)	6917(2)	51(1)*
C(26)	1803(2)	5237(2)	6536(2)	56(1)*
C(27)	3167(2)	6142(2)	6172(2)	48(1)*
C(28)	8622(4)	1658(3)	3720(3)	77(1)*
C(29)	2343(3)	3130(3)	4922(3)	68(1)*

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Largest positive and negative peaks on a final difference Fourier synthesis were of height $\pm 0.13 \text{ e \AA}^{-3}$.

A weighting scheme of the form $W = 1/(\sigma^2(F) + gF^2)$ with $g = 0.00400$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.047$, $R_w = 0.052$, $S = 0.8945$; $R_{(\text{all reflections})} = 0.070$. The maximum shift/error in the final cycle was 0.008. All the calculations were carried out using SHELXTL PLUS [7] on a DEC Microvax-II computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from Ref. [8]. Final atomic co-ordinates are given in Table I, and bond lengths and angles in Table II.

2.2 MOLECULAR MODELLING

Calculations were carried out using the program PCMODEL versions 3.2 and 4.0 [9], running on an IBM compatible PC with an 80486 processor. The force field was MMX [10], which is an extension of Allinger's MM2 [11]. The crystallographic coordinates of the main atoms were read in, hydrogen atoms and lone pairs were

TABLE II
Dimensions*

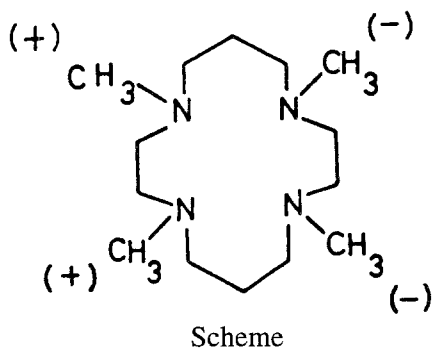
Bond lengths (Å)			
N(11)–C(12)	1.453(3)	N(11)–C(18)	1.448(3)
N(11)–C(17a)	1.453(2)	C(12)–C(13)	1.506(3)
C(13)–N(14)	1.451(3)	N(14)–C(15)	1.459(2)
N(14)–C(19)	1.454(2)	C(15)–C(16)	1.521(3)
C(16)–C(17)	1.513(4)		
N(21)–C(22)	1.461(3)	N(21)–C(28)	1.453(4)
N(21)–C(27a)	1.454(2)	C(22)–C(23)	1.509(3)
C(23)–N(24)	1.456(2)	N(24)–C(25)	1.456(3)
N(24)–C(29)	1.452(4)	C(25)–C(26)	1.517(3)
C(26)–C(27)	1.522(3)		
Bond angles (deg.)			
C(12)–N(11)–C(18)	109.7(2)	C(12)–N(11)–C(17a)	111.8(1)
C(18)–N(11)–C(17a)	111.6(1)	N(11)–C(12)–C(13)	115.7(2)
C(12)–C(13)–N(14)	114.9(2)	C(13)–N(14)–C(15)	111.7(2)
C(13)–N(14)–C(19)	111.0(2)	C(15)–N(14)–C(19)	109.6(1)
N(14)–C(15)–C(16)	114.0(2)	C(15)–C(16)–C(17)	112.1(2)
C(16)–C(17)–N(11a)	113.4(2)	C(22)–N(21)–C(28)	109.2(2)
C(22)–N(21)–C(27a)	111.6(2)	C(28)–N(21)–C(27a)	110.8(2)
N(21)–C(22)–C(23)	115.8(2)	C(22)–C(23)–N(24)	115.9(1)
C(23)–N(24)–C(25)	111.8(1)	C(23)–N(24)–C(29)	111.3(2)
C(25)–N(24)–C(29)	110.5(2)	N(24)–C(25)–C(26)	113.0(1)
C(25)–C(26)–C(27)	111.8(2)	C(26)–C(27)–N(21a)	114.0(2)

* Atoms labelled (a) are inversion-related: in molecule (1) by $(1 - x, 2 - y, -z)$; in molecule (2) by $(1 - x, 1 - y, 1 - z)$.

added and, with the main atoms fixed, the structure was minimised to give hydrogens and lone pairs at optimised rather than idealised positions. This is considered to be the 'experimental structure'. The fixed atom constraint was removed and the structure was reminimised with or without other constraints, as discussed below. The difference in energy between a structure minimised with constraints and the unconstrained minimised structure is referred to as the distortion energy of the constrained structure. Structures were compared geometrically by a least squares fitting of the atomic coordinates of the heavy atoms for a pair of structures and the RMS deviations are quoted.

3. Results and Discussion

The structure of Tmc consists of discrete molecules in which the macrocyclic rings lie about a crystallographic centre of symmetry thus placing the four nitrogen atoms in a planar array. Two crystallographically independent molecules (1 and 2) are observed and these are shown in Figure 1 (a–d); bond lengths and angles are given in Table II. The intra-ring torsion angles are listed in Table IV. Using the nomenclature proposed originally by Bosnich *et al.* [12] for metal-cyclam compounds, both molecules *could* be represented as the *trans-IV* isomer (scheme) where the (\pm) sign denotes the location of a methyl group with reference to the N_4 plane. The two sets of CH_3 groups lie on opposite sides of the N_4 plane at distances of $\pm 1.19, \pm 0.50 \text{ \AA}$ (molecule 1) and $\pm 0.64, \pm 0.27 \text{ \AA}$ (molecule 2).



However, instead of the methyl group locations we prefer to use the sequential absolute configurations of nitrogen centres to categorise these molecules in conjunction with the Bosnich nomenclature.* Inspection reveals that molecule (1) can be identified as the *R, S, S, R*-[*trans-IV*] isomer and molecule (2) as the *R, R, S, S*-[*trans-III*] isomer. Molecule (1) represents the first example of such a *trans-IV* structure.

With the structural identity of Tmc now established for both uncomplexed and protonated forms and with details of the parent molecule 1,4,8,11-tetraazacyclotetradecane (cyclam) available in the literature it is instructive to consider the structural preferences of these tetraazamacrocyclic ligands. Two aspects in particular merit comment *viz.*, conformational patterns and the extent and significance of $\text{N-H} \cdots \text{N}$ hydrogen bonding. Selected structural parameters of the several ligands under consideration are listed in Table III.

* In a metal complex the macrocyclic ligand has to adopt an endodentate geometry i.e. the lone pairs are directed towards the N_4 centroid and the N-H (cyclam) or N-Me (Tmc) bond directionality provides an unequivocal stereochemical description. In the present instance where the lone pairs are not thus constrained the directionalities of the N-Me bonds are not determined by the sequence of *N*-configurations. The labelling of the nitrogen atoms follows the IUPAC-required 1,4,8,11 pattern around the ring and not the 1,5,8,12 sequence that has often (incorrectly) been used.

TABLE III. Selected bond lengths (Å) of Tmc and cyclam ligands.

Compound	Ring Geometry	N-configuration	N-H	N-H...N separation distance	N-CH ₃		C-C _{ring} *		C-N _{ring} *		CH ₃ displacement from N ₄ plane	Ref.
					protonated	basic	protonated	basic	protonated	basic		
cyclam	<i>endo</i>						1.51			1.46		a
	<i>endo</i>		0.91	2.06	3.96		1.51		1.50			b
[(cyclam)H ₂][ClO ₄] ₂			0.94	2.61	4.22					1.47		
			0.99									
[(cyclam)H ₄](Cl) ₄	<i>exo</i>				5.13		1.51		1.50			a
					6.49							
[(cyclam)H ₄][CuCl ₆]	<i>exo</i>				5.29		1.52		1.51			c
					5.46							
[(cyclam)H ₄][ReCl ₆](Cl) ₂ · 4Me ₂ SO	<i>exo</i>		0.99		5.22		1.51		1.50			d
			1.00		5.51							
Tmc molecule (1)		(<i>R</i> , <i>S</i> , <i>S</i> , <i>R</i>)- [<i>trans</i> (IV)]			5.10	5.38		1.45		1.45	±0.27 ±0.65	
												e
— molecule (2)	<i>meso</i>	(<i>R</i> , <i>R</i> , <i>S</i> , <i>S</i>)- [<i>trans</i> (III)]										
					4.53	6.09		1.45		1.46	±0.50 ±1.19	
[[Tmc]H ₂][As ₄ O ₇ Cl ₁₀]	<i>endo</i>	(<i>R</i> , <i>S</i> , <i>R</i> , <i>S</i>)- [<i>trans</i> (I)]	1.04	2.12	4.03	1.52	1.44	1.52	1.50	1.47	+1.02(×2) +1.49(×2)	f
				2.61	4.46							
[[Tmc]H ₂][Sb ₂ OCl ₆]	<i>endo</i>	(<i>R</i> , <i>R</i> , <i>S</i> , <i>S</i>)- [<i>trans</i> (III)]	0.92	2.22	4.28	1.50	1.45	1.50	1.49	1.47	±1.20 ±1.31	f
				2.75	4.33							

* Mean values.

References:

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(e) This work.

(f) Reference [4].

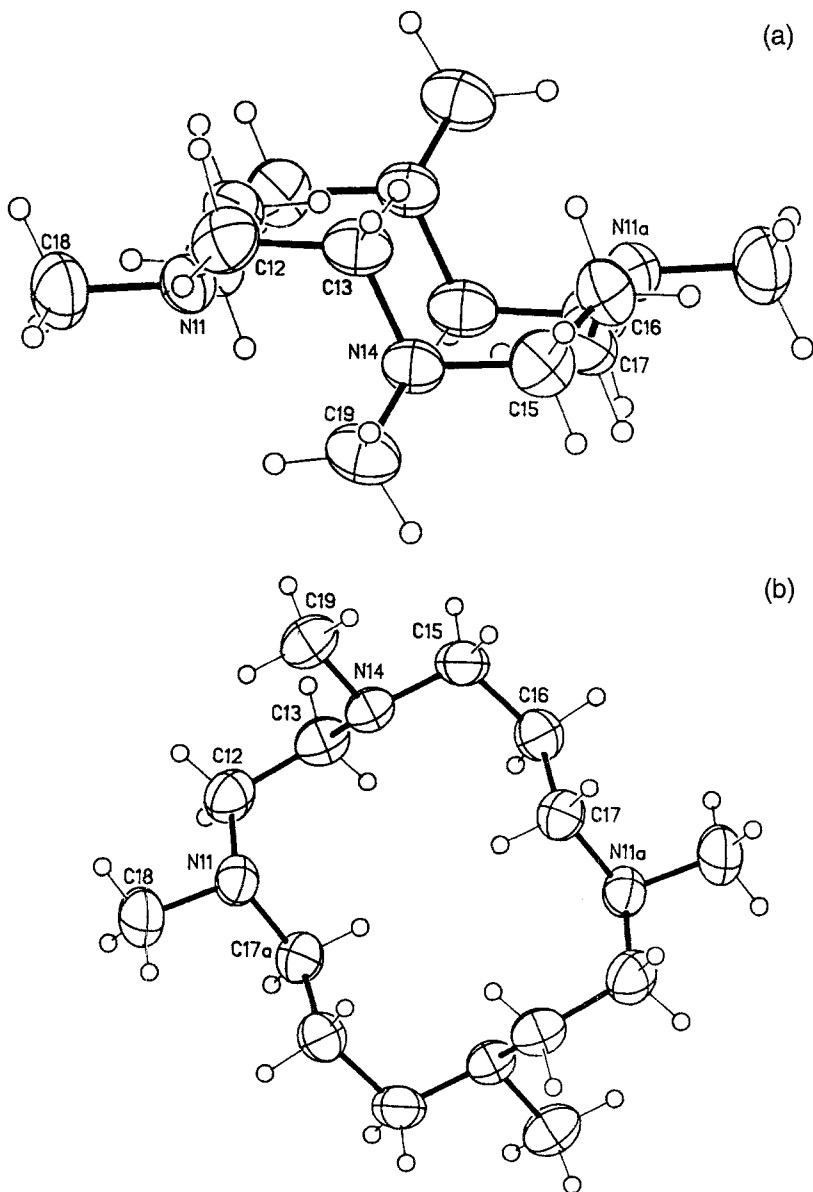


Fig. 1a-b. Views of Tmc molecule (1) with atomic numbering.

3.1. TRENDS

- (i) In all cases bar one the four nitrogen atoms are coplanar. The exception, $[(\text{Tmc})\text{H}_2][\text{As}_4\text{O}_2\text{Cl}_{10}]$, shows deviations from the mean N_4 plane of $\pm 0.19 \text{ \AA} (\times 2)$.
- (ii) The ring C-C bond distances are invariant (1.51–1.52 \AA).

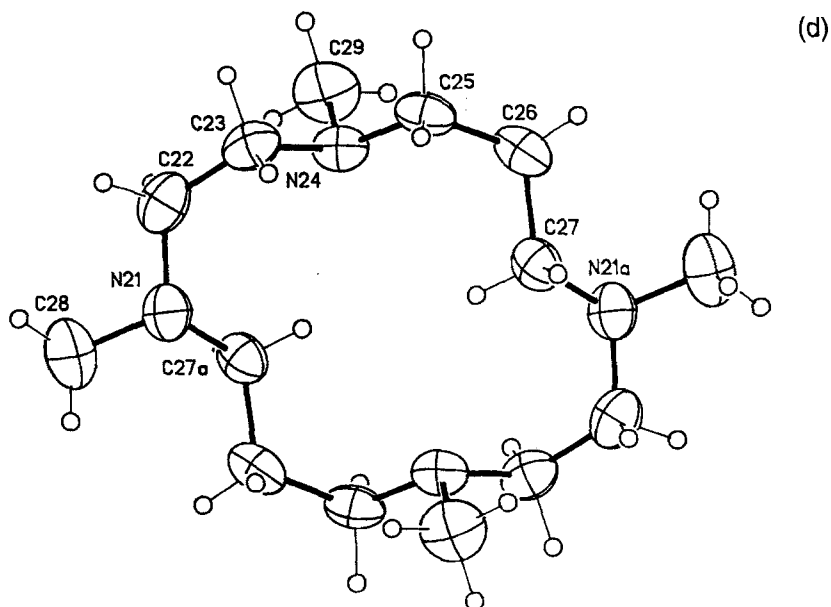
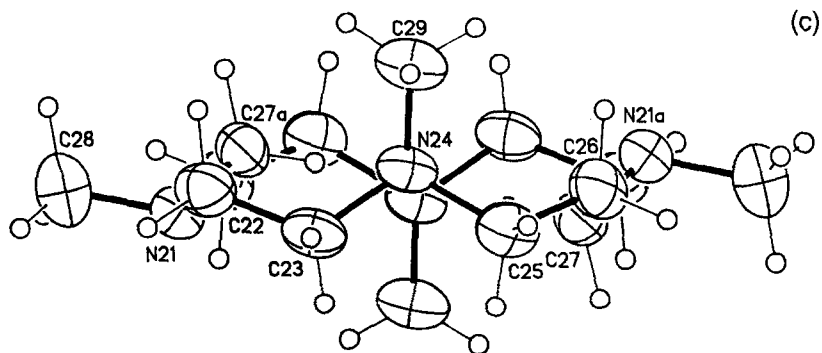


Fig. 1c–d. Views of Tmc molecule (2) with atomic numbering.

- (iii) There is a small variation in the ring C–N bond distances depending on the identity of the nitrogen atoms involved. Those bonds associated with protonated (four coordinate) nitrogen centres are marginally longer than those linked with basic (three coordinate) amine centres i.e., for [(cyclam) H_2] $^{2+}$ Δ (mean difference) ~ 0.03 Å and for [(Tmc) H_2] $^{2+}$ $\Delta \sim 0.02$ Å. Individual C–N bond distances lie within the range 1.46–1.52 Å.
- (iv) For cationic [(Tmc) H_2] $^{2+}$ a similar trend is discernible with respect to N–CH₃ bond distances *viz.*, CH₃ – N_(protonated) > CH₃ – N_(basic), $\Delta \sim 0.05$ Å.

TABLE IV

Intra-ring torsion angles ($^{\circ}$) (esds 0.2°).

Central bond	Molecule 1	Molecule 2
N(1)–C(2)	-64.7	-70.0
C(2)–C(3)	-52.9	78.5
C(3)–N(4)	175.2	-165.9
N(4)–C(5)	-69.1	157.3
C(5)–C(6)	-60.7	-71.0
C(6)–C(7)	171.8	163.2
C(7)–N(1a)	-170.1	-174.0

Intrinsic differences between the cyclam and Tmc ligands emerge, however, when we consider the effects of protonation *vis à vis* hydrogen bonding. The parent cyclam molecule adopts an endodentate geometry and has two hydrogen atoms within the ring cavity involved in weak N–H \cdots N hydrogen bonding to adjacent nitrogen atoms. The remaining two hydrogen atoms form weak bonding interactions with neighbouring molecules giving rise to a loosely-associated chain-type structure. On adding two protons to alternate nitrogen atoms to give [(cyclam)H₂]²⁺ both the endodentate ring geometry and the intracavity hydrogen bonding are retained; the intermolecular hydrogen bonding now involves N–H \cdots O interactions with perchlorate counter anions. Addition of two further protons leads to the cation [(cyclam)H₄]⁴⁺ with two significant changes: the endodentate ring geometry ‘flips’ to exodentate and, coincident with the NH₂⁺ centres now pointing away from the centre of the ring, there can be no intracavity hydrogen bonding.

As discussed above, the neutral Tmc ligand exists in two isomeric forms. The ring conformation is neither exo- nor endodentate but mesodentate. Thus, as depicted in Figure 2, in molecule (1) the angles between the assumed N-lone pair direction and the N-ring centroid direction are 69.4° (N(11)) and 40.1° (N(14)); the corresponding angles in molecule (2) are 85.5° (N(21)) and 17.0° (N(24)).

Protonation of Tmc affords the [(Tmc)H₂]²⁺ cation (endodentate) with the two hydrogen atoms attached to alternate nitrogen centres. The presence of strong N–H \cdots N (2.1–2.2 Å) and weaker N–H \cdots N (2.6–2.7 Å) bifurcated hydrogen bonding within the ring cavity evidently stabilises the resulting geometry. It should be pointed out that these chelating H-bonds are incorporated into six-membered rings and that a similar network of internal hydrogen bonds (N–H \cdots N 2.06 and 2.61 Å) is observed for [(cyclam)H₂]²⁺. As a further ramification of such endodentate/intracavity hydrogen bonding enhancement, we might expect the four nitrogen atoms to be drawn together as closely as possible. The fact that both [(cyclam)H₂]²⁺ and [(Tmc)H₂]²⁺ have a similar cavity size, as gauged by the respective *trans*-

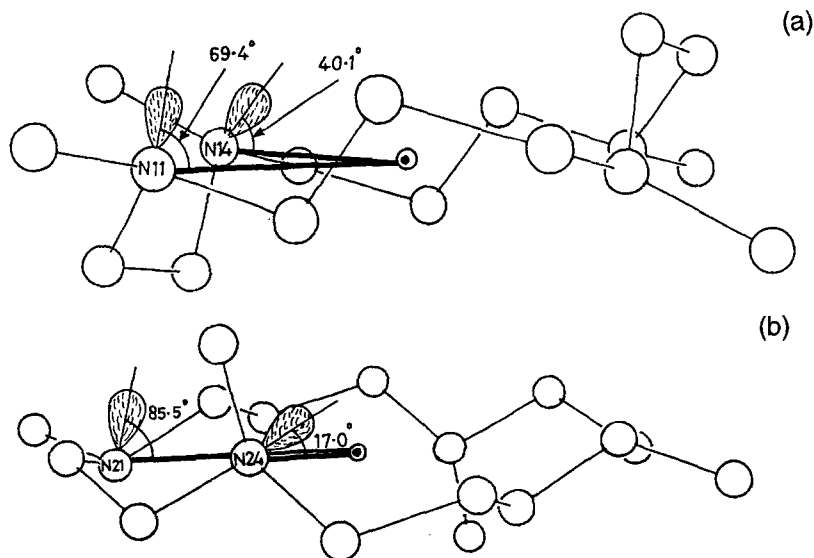


Fig. 2. Directionality of nitrogen lone pairs in the mesodentate conformations of molecules (1) (Fig. 2a) and (2) (Fig. 2b) of Tmc.

$N \cdots N$ separation distances (*ca.* 4 Å), is in accord with this model. By way of contrast, neutral Tmc has *trans*- $N \cdots N$ separation distances in the range 4.53–6.09 Å (mean 5.28 Å). Thus on going from Tmc \rightarrow [(Tmc) H_2] $^{2+}$ there is a cavity constriction of \sim 1 Å as a direct result of internal hydrogen bonding. Interestingly the dication [(Tmc) H_2] $^{2+}$ has been isolated in two isomeric forms, i.e. (*R, S, R, S*)-[*trans* (I)] and (*R, R, S, S*)-[*trans* (III)]. In each the CH_3 groups are symmetrically displaced from the N_4 plane at distances within the range 1.02–1.48 Å.

3.2. MOLECULAR MODELLING

3.2.1. Neutral Tmc

As described above, the two crystallographically independent molecules differ not only in conformation but also in the configurations at nitrogen. Molecule (1) shows a distortion energy of only 12.97 kJ and an RMS atomic deviation from the lowest energy minimum of only 0.04 Å. This implies close agreement between the experimental and calculated geometries; similar calculations for molecule (2) also give good agreement with values of 22.05 kJ and 0.14 Å. At the experimental geometry and at the unconstrained minima, molecule (2) is the higher energy form by 24.14 and 15.06 kJ, respectively. This is consistent with the failure to observe an (*R, S, S, R*)-isomer of a metal–Tmc compound. Extensive studies using as starting structures the diprotonated species and results from an independent study of metal–Tmc complexes [13] and also using the global minimum facilities in PCMODEL, failed to discover any minima lower than those derived by minimising the two

independent molecules. We thus take molecule (1) to be the global minimum and attribute this to a favourable orientation of the nitrogen-lone pair axes. In structures derived from metal complexes by deletion of the metal these axes are all pointing inwards; in those derived from the diprotonated species, the nitrogen-lone pair axes are pointing at one another in pairs. Both crystallographically independent molecules in this study have the nitrogen-lone pair axes nearly orthogonal to one another, leading to less electrostatic repulsion; we have described this conformation as mesodentate.

3.2.2. Diprotonated Tmc Species

The two independent molecules with the $[\text{Sb}_2\text{OCl}_6]^{2-}$ counterion have the same configurations at nitrogen and very similar conformations (RMS deviation 0.10 Å). Both show significant distortion energies (39.79 and 40.46 kJ) relative to their energy-minimised structures and larger RMS deviations (0.42 and 0.45 Å). Even these, however, are considered to be good fits [14].

The N–H···N distances are longer than those reported for the hydrogen diquinuclidinone cation ($[\text{B} \cdot \text{H} \cdot \text{B}]^+$ where $\text{B} = \text{C}_7\text{H}_{11}\text{NO}$, N–H 1.32 Å, N···N 2.64 Å) [15] and in 9-ethylguanine ($\text{C}_7\text{H}_9\text{N}_5\text{O}$, N–H 0.97 Å, N···N 2.78 Å) [16] and found in calculations for a monocyclic model $[\text{Me}_2\text{NH}(\text{CH}_2)_3\text{NMe}_2]^+$, and an acyclic one, $[\text{Me}_3\text{N} \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{NMe}_3]^+$, which both show minima at N···N distances of about 2.5 Å using the MMX force field. The energy of diprotonated Tmc shows only a weak dependence on this N···N distance between 2.6 and 3.2 Å, so we consider that the long distance arises because of competition between the strengthening of the hydrogen bond and the distortion of the conformation of the macrocycle. All the structures except for the arsenic compound have the nitrogen atoms coplanar. In that latter case, constraining the nitrogens to coplanarity imposes a penalty of 54.22 kJ.

We noted above that diprotonation of Tmc contracts the cavity, as measured by the *trans*-N···N distance, by about 1 Å. The modelling gives a quantitative assessment of the energy penalty involved in distorting the macrocycle conformation to accommodate the intramolecular hydrogen bonds. Starting at the geometry of molecule 1, for which the *trans*-N···N distances are 5.10 and 5.38 Å, and fixing these distances at 4.28 and 4.33 Å, as in the antimony version of $[(\text{Tmc})\text{H}_2]^{2+}$ led to a very high distortion energy (> 167 kJ). Clearly this particular conformation of Tmc is not sufficiently flexible to take up a smaller cavity. However, reversing the process by starting at the geometry of the antimony version of $[(\text{Tmc})\text{H}_2]^{2+}$ and fixing the *trans*-N···N distances at 5.10 and 5.38 Å led to a distortion energy of only 3.60 kJ. Clearly this conformation is highly flexible and can accommodate a wide range of hole sizes.

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