

Crystal Structures of $H_2[Me_2dibenzo[14]tetraene]N_4$ and $H_2[Me_2dixylyl[14]tetraene]N_4$: New Tetraaza Macrocycles

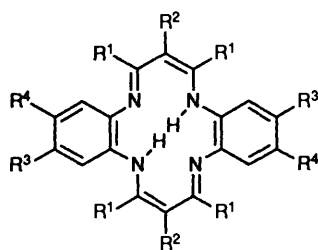
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Crystal structures are reported for $H_2[Me_2dibenzo[14]tetraene]N_4$ (I) and $H_2[Me_2dixylyl[14]tetraene]N_4$ (II), prepared by the condensation of *o*-phenylenediamine and dimethyl-*o*-phenylenediamine with 3-ethoxy-2-methylacrolein in dimethylformamide. The space groups are $P2_1/n$, with cell constants of $a = 9.940(4)$ Å, $b = 5.242(2)$ Å, $c = 15.329(5)$ Å, $B = 94.01(3)^\circ$, $Z = 2$ for I, ($C_{20}H_{20}N_4$), and $a = 7.309(1)$ Å, $b = 13.712(2)$ Å, $c = 10.010(3)$ Å, $B = 90.61(2)^\circ$, $Z = 2$ for II, ($C_2H_{28}N_4$). The macrocycles possess a near-planar structure with the largest deviation of any non-hydrogen atom from the least-squares molecular plane being 0.117 Å for macrocycle I. The N-to-centre distance (R_H) of 1.92 Å found in both I and II is smaller than that found in porphyrins and non-conjugated N_4 14-membered macrocyclic rings such as cyclam, but very similar to the value found in phthalocyanines.

While the number of macrocyclic ligands of known structure is ever increasing, the rules which determine the mode of coordination of these macrocycles with metal ions,¹ the size of the macrocyclic cavity² and the planarity³ of the ring itself are still being investigated. Macrocycles of the tetraaza[14]annulene (TAA) type have been shown to bind to metals largely as



- I $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$
 II $R^1 = H$, $R^2 = R^3 = R^4 = CH_3$
 III $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$

dianionic tetradentate ligands,⁴ but also as neutral bidentate ligands,⁵ depending on the size of the metal ion and the geometry of the ligand. To date, bis(TAA) metal complexes are unknown, though this type of binding is not uncommon amongst Pc (phthalocyanine) complexes of M^{III} and M^{IV} ions. The synthesis of macrocyclic compounds of large metal ions through the template reaction may also result in an expanded ring system containing unusual numbers of sub-units, as is the case in the synthesis of the so called uranyl superphthalocyanine⁶ which has an N_5 donor set coordinated around the central metal ion.

These ligands are of particular interest to coordination chemists as they form part of an unusual branch of macrocycles in which the degree of conjugation around the ring is high, but not aromatic, since they have insufficient electrons for a $(4n + 2)$ Hückel system. The two benzene rings and the two 1,3-propanediiminato segments in the dianionic or metal(II) complex form are each believed to be separate aromatic systems. Thus TAAs resemble porphyrins and phthalocyanines in being planar, but without the aromatic character and with a smaller 14-membered ring. The smaller ring size, limited π -bonding ability, and the inflexibility caused by the benzene rings are the main factors which limit the number of metals to which the ligand may bind.

A variety of ligand conformations is possible for these types of macrocycle. Largely due to the work of Goedken's group,⁴ there are several crystal structure reports of neutral TMTAA (tetramethyltetraazaannulene, $R^1 = Me$)^{4a} and the complexes of the dianionic ligand with M^{II} ($M = Fe$,^{4a,c} Mn ^{4b}) and M^{III} ($M = Fe$,^{4b} Co ^{4d}). These structures show that TMTAA usually has a saddle-shaped distortion in which the 2,4-pentadiiminato rings are bent back from the phenyl rings.⁷ This distortion is caused by the steric interaction of substituents in the R^1 position with the phenyl rings. The macrocycles we describe herein are substituted in the R^2 position and are thus not susceptible to distortion in the ring plane. Goedken has reported the structure of the Ni complex⁸ of a planar tetraazaannulene, TAA ($R^1 = R^2 = H$), and recently⁹ structural data on uncomplexed planar TAA has appeared. The way in which macrocycle planarity affects the redox properties,¹⁰ spectra and coordination chemistry of tetraazaannulene macrocycles is of interest to researchers in the seemingly diverse fields of bioinorganic chemistry, electrocatalysis and gas sensors.¹¹

Experimental

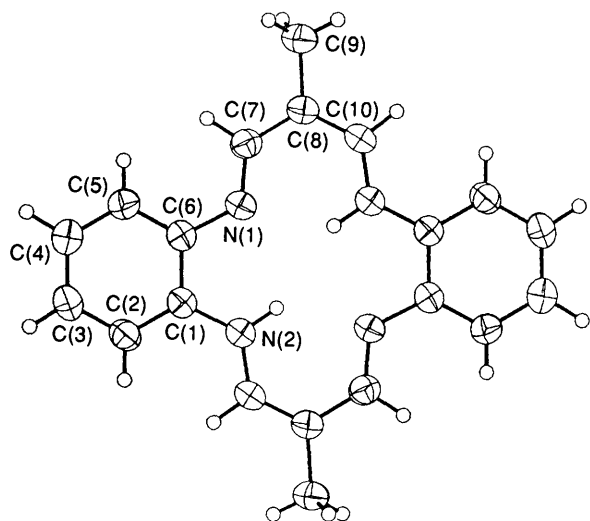
Synthesis and Characterisation of $H_2[Me_2dibenzo[14]tetraene]N_4$ and $H_2[Me_2dixylyl[14]tetraene]N_4$.—The compounds $H_2Me_2dibenzo[14]tetraene]N_4$ and $H_2[Me_2dixylyl[14]tetraene]N_4$ were prepared by the condensation of *o*-phenylenediamine or its 2,3-dimethyl derivative with 3-ethoxy-2-methylacrolein in dimethylformamide as we have reported.^{10a,12} Crystals for X-ray analysis were obtained by recrystallisation of the reaction product from boiling dimethylsulphoxide, which yields needle-like crystals of the intensely coloured purple product.

Crystallographic Studies.—Crystal data for the two compounds are listed in Table 1. In each case, considerable difficulty was met in obtaining suitable single crystals—both materials tended to give intergrowing clusters, and the specimens used were smaller than would be preferred. Data for compound I were collected on a CAD4 diffractometer, using monochromated Mo-K α radiation. The data for compound II were collected on an Enraf-Nonius Fast area detector diffractometer positioned at the window of a rotating anode generator, equipped

Table 1 Crystal data, data collection and structure refinement for compounds I and II

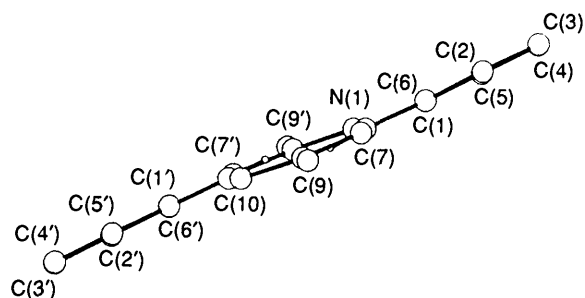
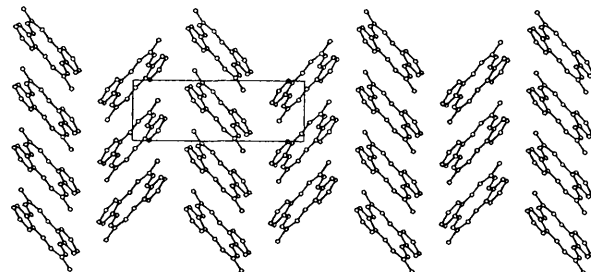
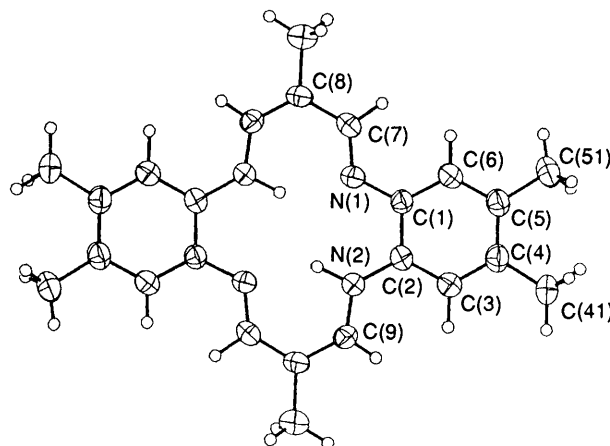
	I	II
<i>Crystal data</i>		
Stoichiometry	C ₂₀ H ₂₀ N ₄	C ₂₄ H ₂₈ N ₄
Formula wt.	316.40	372.51
Crystal system	Monoclinic	Monoclinic
a/Å	9.940(4)	7.309(1)
b/Å	5.242(2)	13.712(2)
c/Å	15.329(5)	10.010(3)
B/deg	94.01(3) ^o	90.61(2) ^o
V/Å ³	796.77	1003.16
Space group	P2 ₁ /n	P2 ₁ /n
Z	2 ^a	2 ^a
D _c /g cm ⁻³	1.32	1.23
μ/cm ⁻¹	0.44	0.69
F(000)	332	400
<i>Data collection</i>		
Temperature/K	291	291
Theta min./max.	1.5/25	3.0/25
Total data measured	2902	6049
Total data unique	1404	1769
Total observed	1080	1067
Significance test	F _o > 3σ(F _o)	F _o > 6σ(F _o)
<i>Refinement</i>		
No. of parameters	140	183
Weighting scheme		
Parameter g ^b	0.000 86	0.0025
Max shift/esd	0.7	0.8
Max residual electron density e/Å ³	0.16	0.28
Final R	0.048	0.066
Final R _w	0.056	0.087

^a Both molecules lie on centres of symmetry. ^b Weights $-\left[\sigma^2(F) + gF_o^2\right]^{-1}$.

**Fig. 1** ORTEP diagram (50% probability ellipsoids) of macrocycle I with labelling scheme

with a molybdenum target and graphite monochromator. Full details of the data collection procedures used will be published elsewhere, but the main features are as follows: the detector swing angle was 18° and the crystal-to-detector distance was 40 mm. Using steps of 0.15° in ω , reciprocal space was scanned to the extent of 190° with the crystal set at $\Psi = 0^\circ$, and 140° with the crystal set at $\Psi = 90^\circ$, giving measurement of all reflections in slightly more than one-half of the hemisphere with the 2 θ max. of at least 51°.

For both data sets L_p corrections were applied, as well as

**Fig. 2** A view of I along the N(1)-N(2) axis showing the slight deviations of atoms from the plane**Fig. 3** A view along the A₀ axis of I showing the herringbone pattern typical of the solid state structure of macrocyclic ligands**Fig. 4** ORTEP diagram of macrocycle II with the key to the labelling scheme

detector specific corrections for II, but no absorption corrections were made. The structures were solved *via* direct methods and refined by full matrix least squares. Hydrogen and non-hydrogen atoms were refined with isotropic and anisotropic displacement factor coefficients respectively.

Results and Discussion

Both macrocycles crystallise in the P2₁/n space group with two molecules per unit cell, each on a centre of symmetry. Figs. 1-3 depict views of the structure of macrocycle I, and Fig. 4 shows the structure of macrocycle II. Experimental details of the crystal structure determination are given in Table 1, while atomic fractional coordinates are given in Table 2. The main features of the structures are discussed below.

The Macrocyclic Hole Size.—The hole size is a parameter which is frequently discussed and is of much interest, particularly when it can be compared in a group of structurally related macrocycles.^{2,4} The size of the macrocyclic cavity is determined by the ring size, the degree of conjugation or π -bonding around the ring, the type of donor atom, and, in the case of metal complexes the extent, if any, of the π -bonding

Table 2 Fractional atomic coordinates ($\times 10^4$) and relevant bond lengths and angles for **I** and **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fractional atomic coordinates ($\times 10^4$)			
Compound I			
C(1)	7 582(2)	5 279(4)	5 722(1)
C(2)	8 957(2)	5 004(4)	5 929(1)
C(3)	9 644(2)	6 670(4)	6 493(1)
C(4)	8 967(2)	8 641(4)	6 863(1)
C(5)	7 604(2)	8 926(4)	6 672(1)
C(6)	6 882(2)	7 268(3)	6 104(1)
C(7)	4 745(2)	9 183(4)	6 194(1)
C(8)	3 353(2)	9 572(4)	5 970(1)
C(9)	2 641(2)	11 623(5)	6 444(2)
C(10)	2 647(2)	8 182(4)	5 336(1)
N(1)	5 494(2)	7 456(3)	5 860(1)
N(2)	6 843(2)	3 684(3)	5 134(1)
Compound II			
C(1)	2 224(4)	1 303(2)	4 882(3)
C(2)	3 564(4)	1 686(2)	4 034(3)
N(2)	5 175(4)	1 148(2)	3 869(3)
C(3)	3 250(4)	2 579(3)	3 411(3)
C(4)	1 637(4)	3 096(3)	3 583(4)
C(41)	1 383(5)	4 054(3)	2 874(5)
C(5)	276(4)	2 710(3)	4 395(3)
C(51)	-1 508(5)	3 230(3)	4 606(4)
C(6)	601(4)	1 825(3)	5 021(3)
N(1)	2 635(3)	417(2)	5 522(3)
C(7)	1 691(4)	114(3)	6 528(3)
C(8)	2 084(4)	-729(3)	7 303(3)
C(81)	788(5)	-1 000(3)	8 387(4)
C(9)	6 391(4)	1 292(3)	2 908(3)
Bond lengths/Å for compound I			
C(2)–C(1)	1.389(3)	C(6)–C(1)	1.405(3)
N(2)–C(1)	1.399(3)	C(3)–C(2)	1.375(4)
C(4)–C(3)	1.377(4)	C(5)–C(4)	1.374(4)
C(6)–C(5)	1.393(4)	N(1)–C(6)	1.407(3)
C(8)–C(7)	1.417(3)	N(1)–C(7)	1.300(3)
C(9)–C(8)	1.502(5)	C(10)–C(8)	1.368(4)
N(2)–C(10')	1.343(4)	H[N(2)]–N(2)	0.928(24)
Bond lengths/Å for compound II			
C(2)–C(1)	1.405(5)	C(6)–C(1)	1.394(5)
N(1)–C(1)	1.405(5)	N(2)–C(2)	1.401(5)
C(3)–C(2)	1.392(6)	C(9)–N(2)	1.331(5)
C(4)–C(3)	1.388(5)	C(41)–C(4)	1.504(7)
C(5)–C(4)	1.395(5)	C(51)–C(5)	1.503(6)
C(6)–C(5)	1.386(6)	C(7)–N(1)	1.295(5)
C(8)–C(7)	1.420(5)	C(81)–C(8)	1.495(5)
C(9)–C(8)	1.372(5)	H[N(2)]–N(2)	0.987(19)
Bond angles/° for compound I			
C(6)–C(1)–C(2)	119.4(3)	N(2)–C(1)–C(2)	123.4(3)
N(2)–C(1)–C(6)	117.3(2)	C(3)–C(2)–C(1)	121.0(3)
C(4)–C(3)–C(2)	120.0(3)	C(5)–C(4)–C(3)	119.8(3)
C(6)–C(5)–C(4)	121.5(3)	C(5)–C(6)–C(1)	118.3(3)
N(1)–C(6)–C(1)	116.5(3)	N(1)–C(6)–C(5)	125.1(3)
N(1)–C(7)–C(8)	125.5(3)	C(9)–C(8)–C(7)	118.1(3)
C(10)–C(8)–C(7)	122.7(3)	C(10)–C(8)–C(9)	119.3(3)
C(7)–N(1)–C(6)	121.5(3)	C(8)–C(10)–N(2')	124.6(3)
C(1)–N(1)–C(10')	124.5(4)		
Bond angles/° for compound II			
C(6)–C(1)–C(2)	117.9(4)	N(1)–C(1)–C(2)	116.9(4)
N(1)–C(1)–C(6)	125.2(4)	N(2)–C(2)–C(1)	117.8(4)
C(3)–C(2)–C(1)	119.1(4)	C(3)–C(2)–N(2)	123.1(4)
C(9)–N(2)–C(2)	125.2(4)	C(4)–C(3)–C(2)	122.0(4)
C(41)–C(4)–C(3)	119.3(4)	C(5)–C(4)–C(3)	119.3(4)
C(5)–C(4)–C(41)	121.4(4)	C(51)–C(5)–C(4)	121.8(4)
C(6)–C(5)–C(4)	118.4(4)	C(6)–C(5)–C(51)	119.8(4)
C(5)–C(6)–C(1)	123.1(4)	C(7)–N(1)–C(1)	121.3(4)
C(8)–C(7)–N(1)	125.5(4)	C(7)–C(8)–C(9)	122.3(4)
C(81)–C(8)–C(7)	118.2(4)	C(81)–C(8)–C(9')	119.5(4)
N(2)–C(9)–C(8')	125.1(4)		

Table 3 M–N bond lengths for complexes of first row transition metals with macrocyclic ligands

Complex	Bond length/Å	Ref.
Mn ^{II} TMTAA	2.12	4b
Fe ^{III} TMTAA	2.00	4b
Fe ^{II} TMTAA	1.92	4a
Co ^{III} TMTAA	1.90	4b
Ni ^{II} TAA	1.87	8
Ni ^{II} Pc	1.83	13
Cu ^{II} Pc	1.93	13
Zn ^{II} Pc	1.98	13

between the metal and the ring. The planarity of the ligand also has an effect on the overall size of the cavity.

In the case of a planar ligand such as **I** or **II** the N–N distance ($2R_H$) of the diametrically opposed nitrogen atoms gives a reliable measure of the ligand hole size.² This hole size, $2R_H$, does not take into account the van der Waals radii of the donor atoms. For **I** and **II** an average N–N value of 3.84 Å is obtained [$N(2)–N(2') = 3.91$ Å, $N(1)–N(1') = 3.77$ Å in **I**, 3.799 Å and 3.888 Å in **II**]. The slight variation of the individual N–N distances reflects the slight rhombic distortion in the N_4 plane caused by the two types of N atom. The $N(1)–N(2')$ and $N(2)–N(1')$ distances are 2.674 Å and 2.753 Å respectively. The R_H of 1.92 Å is identical to that found in the larger macrocycle phthalocyanine¹³ and compares with values found in TAA (2.15 Å),⁹ cyclam (2.07 Å), tetraphenyl porphyrin (2.06 Å), and tetramethyltetraazaannulene (**III**) (1.90 Å). Comparison of the R_H distance of **I** with cyclam, which also has a 14-membered ring, shows the effect of planarity and conjugation in enforcing a small contraction in the macrocyclic cavity.

The R_H distance of a metal ligand complex can be expected to be significantly smaller than the R_H value of the free ligand due to the increased conjugation present in the dianionic form of the ligand. Thus the smaller transition metal ions are most likely to form planar complexes, and this reflects itself in the ease of synthesis of Co^{II} and Ni^{II} derivatives of the ligand by template methods. Table 3 lists some of the M–N bond lengths of the first row transition metal complexes with some representative macrocyclic ligands. Complexes of the larger metal cations demand that the metal atom lies above the N_4 plane. While macrocycles capable of extensive π -bonding are able to accommodate this, it appears that the smaller tetraazaannulene macrocycle is more limited in its ability to bind larger metal ions.

The Conjugation around the Macrocyclic Ring.—The delocalisation about the 1,3-propanediiminato linkages is apparent from a comparison of the bond lengths about the bridging moiety and those of other C–C and N–C linkages. Thus the average *o*-phenylenediamine N–C [*e.g.* $N(2)–C(6)$] bond length is 1.407 Å which is substantially longer than both of the N–C bonds of the diiminato linkage the values here being 1.30 Å for the $N(1)–C(7)$ and 1.34 Å for the $N(2')–C(10)$. The delocalisation which takes place is a consequence of the hydrogen bonding between the iminato nitrogen and the inner proton, and the contribution of the nitrogen lone pair permitting delocalisation through the five atom ring $N(1)–C(7)–C(8)–C(10)–N(2')$. The hydrogen bonds between the bridge nitrogen atoms $N(1)$ and $N(2')$ have a bond length of *ca.* 1.9–2.0 Å, which may be compared to the non-bonding N–H distance $N(1)$ to $N(2)–H$ between the *o*-phenylenediamine subunits of 2.2–2.4 Å.

The Molecular Geometry.—The near planarity of this pair of macrocycles is expected in the absence of a coordinating metal atom; there is no steric constraint on the diiminato bridges, as is the case in **III**. The nitrogen atoms of the inner ring are

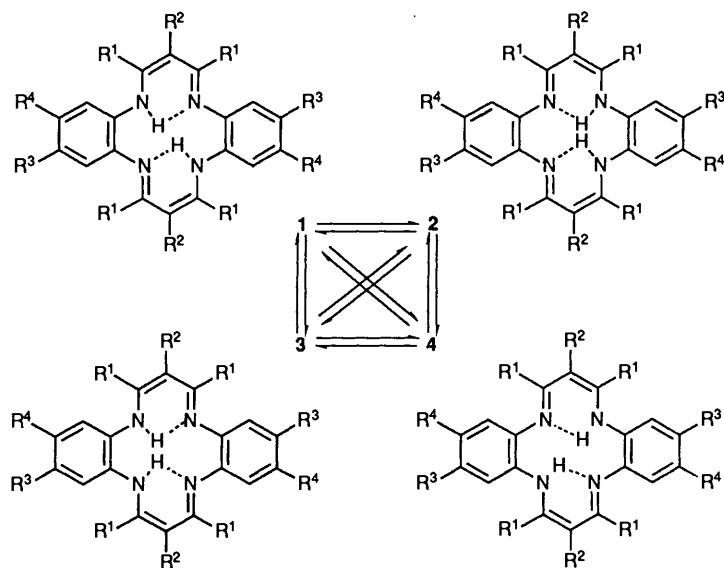


Fig. 5 Possible mechanisms of proton transfer in TAA macrocycles. $R^1R^3R^4 = H$, $R^2 = CH_3$ (I); $R^1 = H$, $R^2R^3R^4 = CH_3$ (II); $R^1 = CH_3$, $R^2R^3R^4 = H$ (III).

coplanar, but the benzene rings lie slightly outside of the N_4 plane and are orientated at an angle of 6.05° to the four nitrogen atoms. The small deviations can be seen in Fig. 2 which shows a view along the N(1)–N(2) axis of I. The largest deviation of any non-hydrogen atom from the N_4 plane and least-squares molecular plane, respectively. The latter figure compares with 0.06 \AA for TAA.⁹ The largest deviations are for the N(2) and N(2') atoms, suggesting steric repulsion between the N–H atoms.

Packing of the Molecules.—A diagram of the packing of I along the A_0 axis is shown in Fig. 3. The herringbone pattern observed is typical of the solid state structure of macrocyclic complexes of this type. Individual molecules stack along the b -axis inclined at 50.80° to the projected plane (010), with the perpendicular distance between individual stacks found to be 3.313 \AA .

The Position of the N–H Hydrogen Atoms.—The mechanism of proton transfer in macrocycles of the TAA family has been investigated by ^{15}N -CPMAS-NMR spectroscopy. Limbach *et al.*¹⁴ have found that while I exhibits only two peaks in its NMR spectrum (122–287 K), four peaks are observed in the spectrum of III¹⁵ at 288 K; at 100 K these coalesce into two peaks.

This data points to the existence of two different mechanisms of proton transfer in the macrocycles I and III. In III the four different states in Fig. 5 are populated at room temperature, while I clearly undergoes proton transfer *via* a concerted mechanism in which only states 1 and 4 are observed.^{14,16} ^{15}N -CPMAS-NMR spectroscopy also indicates that the two tautomeric states observed in I are non-degenerate, and exist in a 4:1 ratio in the solid state.¹⁴

A comparison of the crystal structures of III and I reveals above all the different conformations of the two molecules. While I is nearly planar, III exhibits a saddle-shape conformation due to the steric clash of the methyl groups with the benzene *ortho* protons. The difference in the two conformations provides the reason for the two different proton transfer mechanisms. The enhanced communication between the two halves of the molecule I resulting from its planarity and π -bonding dictates the concerted proton transfer which is observed. III on the other hand permits the non-concerted proton transfer because of the 'electronic isolation' of the two halves of

the molecule. This idea is supported by the energy difference of the π - π^* transitions in the electronic spectra of I and III. It is perhaps also noteworthy that Goedken detected disorder in the N–H proton positions in III,^{4a} whereas no such disorder is observed for I. In addition, the preservation of the inversion centre in I may demand a concerted proton transfer.

The cause of the uneven population of the two states 1 and 4 in I^{14,16} which is revealed by the NMR spectra is not apparent from the crystallographic data,^{4a} and we are therefore left to conclude, as have previous workers that the non-degeneracy of the two states arises from the rhombic distortion which is apparent in the N_4 plane.

Acknowledgements

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