Chemical and Theoretical Studies of Tautomerism in Meso-aza- and Meso-tetra-aza-porphyrins. Crystal Structure of 5-Aza-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrinatocobalt(II)

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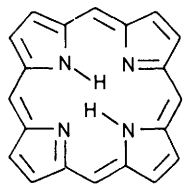
Meso-azoporhyrins exist in the meso-imino tautomeric form. Attempts to trap or generate the meso-amino tautomer were unsuccessful. STO-3G and CNDO/2 calculations indicate the meso-imino tautomer to lie > 22 kcal mol^{-1} below the meso-amino tautomer in both meso-monoaza- and meso-tetra-aza-porphyrins. The crystal structure of a meso-monoazaocta-alkylporphyrinatocobalt(II) complex is reported.

The porphyrins (**1**) contain vinylogous amidine moieties only, whilst the 5-aza- and 5,10,15,20-tetra-azaporphyrins (**2**) and (**3**) possess both amidine and vinylogous amidine moieties. Amidines may be classified as type III X=Y–ZH systems[1] and are potentially tautomeric.[2] Tautomerism in simple amidines has been studied by various techniques including i.r.[3] and n.m.r.[4] spectroscopy, although such studies are complicated by the potential for geometrical isomerism. In porphyrins and the meso-azaporphyrins the fixed geometry imposed by the macrocyclic skeleton precludes geometrical isomerism. However, in the aza- and tetra-azapoprhyrins (**2**) and (**3**) the meso-nitrogen atoms could potentially be involved in tautomeric equilibria, *i.e.* (**2**) ⇌ (**4a**) ⇌ (**5**) and (**3**) ⇌ (**6**) ⇌ (**7**). If the azaporphyrin is totally lacking in symmetry further NH tautomers are, of course, possible.

Tautomerism in porphyrins involves switching of the inner NH protons between the four nitrogen atoms. This process, which has been the subject of several n.m.r. studies,[5–7] does not interfere with the aromaticity of the macrocycle. In meso-tetraarylporphyrins the process is intramolecular, has an activation energy of *ca.* 12 kcal mol^{-1} which is independent of the nature of the meso-aryl substituent,[6] and occurs by tunnelling between two quantised NH stretching states.[7]

Our interest in tautomerism in meso-aza- and -tetra-azaporphyrins stems from our general interest in prototropy[1,8] and an interest in trying to trap the meso-NH tautomers (**4a**) or (**5**). Tautomerism involving meso-nitrogen atoms does not interfere with the aromaticity of either aza- or tetra-azaporphyrins since the presence of a lone pair on the meso-nitrogen atom in (**4a**)—(**7**) ensures both cyclic delocalisation and an unchanged total number of π-electrons. Meso-monoazaporphyrins have been known for nearly 50 years[9] but their chemistry has been largely neglected. A good synthetic method is available[10] involving the cyclisation of a 1,19-dibromo-1,19-dideoxybiladiene-*ac* dihydrobromide (**8**) with sodium azide in methanol [*e.g.* (**8**) → (**2**)].

Attempts to synthesize the meso-*N*-methylated azaporphyrin tautomer (**4b**) by reaction of (**8**; R^1 = R^2 = Me, R^3 = CH_2CO_2Et) with excess of methylamine in pyridine (104 °C; 8 h) or (**8**; R^2 = Me, R^1 = R^3 = Et) with excess of methylamine in ethanol (90 °C; sealed tube; 48 h) failed to produce products with a Soret band. Heating a solution of (**8**; R^2 = Me, R^1 = R^3 = Et) in boiling methanol containing hydroxylamine hydrochloride and potassium carbonate gives multiple products but no meso-*N*-hydroxyazaporphyrin (**4c**) or its nitrone tautomer. Several unsuccessful attempts were made to oxidise the palladium complex of (**2**; R^2 = Me, R^1 = R^3 = Et) to the meso-*N*-oxide, *e.g.* both hydrogen peroxide in acetic acid at 65—70 °C and *m*-chloroperbenzoic acid in boiling chloroform failed to effect oxidation whilst hydrogen peroxide in tri-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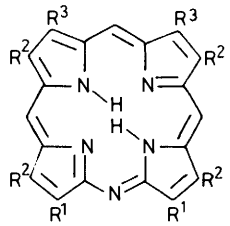
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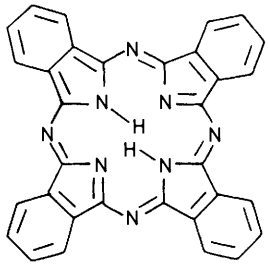
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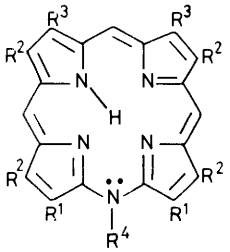
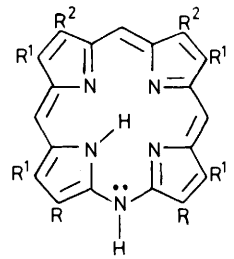

(4) a; R^4 = H
b; R^4 = Me
c; R^4 = OH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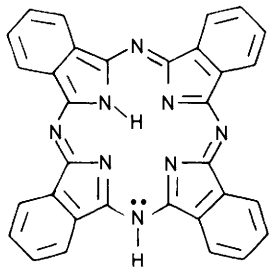
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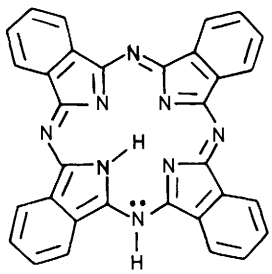

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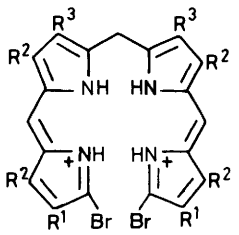

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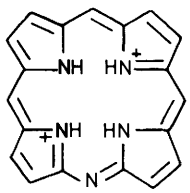

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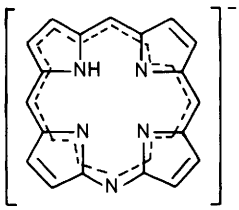

(10)

fluoroacetic acid (25 °C; 15 min) caused decomposition. After the experimental phase of our work was completed Bonnett *et al.*[11] reported the preparation of a porphyrin *N*-oxide using hypofluorous acid as the oxidising agent. We have previously reported *N*-alkylation studies on meso-monoazaporphyrins.[12] Mono-, di-, and tri-*N*-methylated derivatives can be prepared depending on the conditions. However, all these alkylations are restricted to the central porphyrin core and do not involve the meso-nitrogen atom. Meso-monoazaporphyrins react in an analogous way to porphyrins with di-μ-chlorobisdicarbonylrhodium giving out-of-plane bisdicarbonylrhodium complexes involving only the core nitrogen atoms.[13] Such complexation has been shown to require one imino- and one amino-nitrogen atom for the complexation of each $Rh(CO)_2$ moiety.[13]

We have also studied the protonation of meso-monoazaporphyrin and shown that it readily forms a dicationic salt in acidic media like the porphyrins. However, unlike porphyrins, the meso-monoazaporphyrin undergoes a third protonation in sulphuric acid–acetic acid mixtures at high sulphuric acid concentration.[14] The addition of the third proton presumably involves the meso-nitrogen atom giving a tricationic species, whose first dissociation constant in water is pK_3 *ca.* −3.3.[14] The similarity of the visible spectra of the meso-monoazaporphyrin dication and dianion[15] support the core-protonated formulation (**9**) of the dication.

Chemical studies on meso-monoazaporphyrins suggest a reluctance of the macrocycle to react in the tautomeric form (**4a**) or (**5**). It was of interest therefore to determine the *X*-ray structure of a representative member of this class of macrocycle and to carry out molecular orbital calculations to gauge the magnitude of the energy differences between the imino (**2**) and amino (**4a**), (**5**) tautomers.

The structure of 5-aza-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrinatocobalt(II) was therefore determined by an *X*-ray crystal structure analysis. The azaporphyrin (**2**; $R^1 = R^2 = Me$, $R^3 = Et$) was prepared by cyclisation of the biladiene (**8**; $R^1 = R^2 = Me$, $R^3 = Et$) in 66% yield. Insertion of cobalt(II) was achieved using cobalt(II) acetate in chloroform–methanol. The molecule, shown in Figure 1, shows no remarkable departure from expected bond lengths and angles and, apart from the terminal methyls of the two ethyl groups, is planar (within experimental error). There has been no previous report of a full crystal structure analysis involving the monoazaporphin unit. The structure of tetrabenzomonoazaporphin, obtained from two-dimensional projections, has been reported[16] but the meso-nitrogen atom was indistinguishable from the meso-CH groups, either because of structural disorder or because the electron density differences were not resolvable. In the present study the poorly diffracting crystal led to a low data:parameter ratio which is reflected in the high standard deviations of the results (Tables 1—3). However, bond lengths and angles averaged over chemically equivalent bonds are in agreement with those of cobalt complexes of porphyrins[17] and phthalocyanines.[18] Averages are Co–N = 1.962(10), N–C(1) = 1.380(11), C(1)–C(2) = 1.446(11), C(2)–C(3) = 1.383(15), C(meso)–C = 1.382(12), and N(meso)–C = 1.321(20) Å compared with the high-resolution 100 K values for meso-tetraphenylporphyrinatocobalt(II)[17] of Co–N = 1.949(1), N–C(1) = 1.378(1), C(1)–C(2) = 1.441(1), C(2)–C(3) = 1.362(1), C(meso)–C = 1.391(1) Å, and the average value N(meso)–C = 1.317(2) for phthalocyaninatocobalt(II).[18]

The molecules pack in columns with their mean planes

Table 1. (*a*) Fractional co-ordinates, with standard deviations in parentheses

Atom	*X/A*	*Y/B*	*Z/C*
Co(1)	0.373 9(4)	0.114 59(7)	0.312 6(2)
N(1)	0.233(2)	0.155 3(4)	0.312(1)
N(2)	0.376(3)	0.115 5(6)	0.446(1)
N(3)	0.514(2)	0.074 0(4)	0.312(2)
N(4)	0.382(3)	0.112 6(5)	0.180(1)
C(1)	0.178(4)	0.170 0(8)	0.234(2)
C(2)	0.078(3)	0.201 8(6)	0.264(2)
C(3)	0.077(3)	0.202 3(7)	0.354(2)
C(4)	0.169(3)	0.175 0(8)	0.382(2)
C(5)	0.199(4)	0.164 3(6)	0.472(2)
C(6)	0.296(3)	0.138 9(6)	0.503(1)
C(7)	0.321(3)	0.126 9(7)	0.593(1)
C(8)	0.422(3)	0.098 1(6)	0.595(2)
C(9)	0.455(2)	0.092 2(7)	0.497(2)
C(10)	0.545(4)	0.064 7(7)	0.472(2)
C(11)	0.579(4)	0.055 1(7)	0.385(2)
C(12)	0.670(3)	0.027 5(6)	0.352(2)
C(13)	0.669(3)	0.027 2(7)	0.261(2)
C(14)	0.581(3)	0.058 0(8)	0.237(2)
N(15)	0.543(3)	0.064 0(6)	0.150(1)
C(16)	0.458(4)	0.089 9(7)	0.121(2)
C(17)	0.442(4)	0.099 8(8)	0.031(1)
C(18)	0.326(4)	0.127 8(7)	0.024(2)
C(19)	0.294(3)	0.133 8(7)	0.125(2)
C(20)	0.200(5)	0.164 0(8)	0.146(2)
C(21)	−0.002(3)	0.226 3(6)	0.203(2)
C(22)	0.001(3)	0.228 1(7)	0.419(2)
C(23)	0.105(4)	0.259 4(6)	0.441(2)
C(24)	0.257(3)	0.146 3(6)	0.679(2)
C(25)	0.346(4)	0.180 3(6)	0.698(2)
C(26)	0.482(3)	0.078 3(6)	0.672(1)
C(27)	0.759(4)	0.002 5(7)	0.418(2)
C(28)	0.748(3)	0.003 7(6)	0.199(2)
C(29)	0.496(3)	0.078 1(7)	−0.046(2)
C(30)	0.266(4)	0.146 4(7)	−0.051(2)

Table 1 (*continued*)

(*b*) Hydrogen atoms designated according to the atom to which they are attached.

Atom	*X/A*	*Y/B*	*Z/C*
H(5)	0.150	0.1791	0.521
H(10)	0.596	0.0503	0.522
H(20)	0.125	0.1786	0.098
H(21a)	−0.077	0.2380	0.230
H(21b)	0.071	0.2453	0.177
H(21c)	−0.051	0.2142	0.148
H(22a)	−0.030	0.2153	0.476
H(22b)	−0.099	0.2370	0.389
H(23a)	0.049	0.2757	0.484
H(23b)	0.201	0.2503	0.472
H(23c)	0.132	0.2721	0.385
H(24a)	0.257	0.1308	0.734
H(24b)	0.142	0.1528	0.666
H(25a)	0.300	0.1931	0.751
H(25b)	0.456	0.1741	0.710
H(25c)	0.341	0.1960	0.643
H(26a)	0.597	0.0878	0.697
H(26b)	0.400	0.0901	0.709
H(26c)	0.478	0.0520	0.683
H(27a)	0.861	−0.0058	0.401
H(27b)	0.774	0.0133	0.476
H(27c)	0.701	−0.0208	0.423
H(28a)	0.679	−0.0167	0.181
H(28b)	0.845	−0.0056	0.234
H(28c)	0.771	0.0168	0.140
H(29a)	0.572	0.0917	−0.086
H(29b)	0.542	0.0554	−0.027
H(29c)	0.402	0.0720	−0.087
H(30a)	0.132	0.1451	−0.040
H(30b)	0.301	0.1726	−0.049
H(30c)	0.298	0.1365	−0.110

Table 2. Lengths of bonds not involving hydrogen, with standard deviations in parentheses, in Å

C(1)–C(2)	1.55(4)	C(12)–C(13)	1.34(3)
C(1)–N(1)	1.36(3)	C(12)–C(27)	1.56(3)
C(1)–C(20)	1.35(3)	C(13)–C(14)	1.43(3)
C(2)–C(3)	1.33(3)	C(13)–C(28)	1.45(3)
C(2)–C(21)	1.46(3)	C(14)–N(15)	1.35(3)
C(3)–C(4)	1.36(3)	C(14)–N(3)	1.39(3)
C(3)–C(22)	1.52(3)	N(15)–C(16)	1.30(3)
C(4)–C(5)	1.42(3)	C(16)–C(17)	1.39(4)
C(4)–N(1)	1.38(3)	C(16)–N(4)	1.38(3)
C(5)–C(6)	1.36(3)	C(17)–C(18)	1.46(4)
C(6)–C(7)	1.42(3)	C(17)–C(29)	1.47(3)
C(6)–N(2)	1.41(3)	C(18)–C(19)	1.53(3)
C(7)–C(8)	1.40(3)	C(18)–C(30)	1.41(3)
C(7)–C(24)	1.56(3)	C(19)–C(20)	1.44(4)
C(8)–C(9)	1.50(3)	C(19)–N(4)	1.37(3)
C(8)–C(26)	1.45(3)	C(22)–C(23)	1.52(3)
C(9)–C(10)	1.35(3)	C(24)–C(25)	1.52(3)
C(9)–N(2)	1.35(3)	Co(1)–N(1)	1.96(2)
C(10)–C(11)	1.37(3)	Co(1)–N(2)	1.97(2)
C(11)–C(12)	1.39(4)	Co(1)–N(3)	1.95(2)
C(11)–N(3)	1.40(3)	Co(1)–N(4)	1.97(2)

parallel to *c* and inclined to *b* by 38° (and hence to *a* by 52°). In the columns adjacent molecules are rotated with respect to each other, through an axis perpendicular to the ring, by 90°. These features are clearly seen by reference to Figures 2 and 3.

Theoretical Studies.—The relative stability of tautomeric forms of the parent azaporphin (**2**; $R^1 = R^2 = R^3 = H$) has been investigated by molecular orbital theory in an endeavour to ascertain whether meso-amino tautomers such as (**4a**) or (**5**)

Table 3. Angles, not involving hydrogen, in degrees, with standard deviations in parentheses

C(20)–C(1)–C(2)	119(3)	C(11)–C(12)–C(27)	121(2)
C(20)–C(1)–N(1)	135(4)	C(13)–C(12)–C(27)	128(3)
N(1)–C(1)–C(2)	106(2)	C(12)–C(13)–C(14)	104(3)
C(1)–C(2)–C(3)	107(2)	C(12)–C(13)–C(28)	130(3)
C(1)–C(2)–C(21)	125(2)	C(14)–C(13)–C(28)	126(2)
C(3)–C(2)–C(21)	127(3)	C(13)–C(14)–N(15)	120(3)
C(2)–C(3)–C(4)	106(3)	C(13)–C(14)–N(3)	112(2)
C(2)–C(3)–C(22)	130(3)	N(3)–C(14)–N(15)	126(3)
C(4)–C(3)–C(22)	123(2)	C(11)–N(3)–C(14)	103(2)
C(3)–C(4)–C(5)	127(2)	C(11)–N(3)–Co(1)	130(2)
C(3)–C(4)–N(1)	115(2)	C(14)–N(3)–Co(1)	127(2)
C(5)–C(4)–N(1)	118(3)	C(14)–N(15)–C(16)	126(2)
C(1)–N(1)–C(4)	106(2)	N(15)–C(16)–C(17)	125(3)
C(1)–N(1)–Co(1)	122(2)	N(15)–C(16)–N(4)	122(3)
C(4)–N(1)–Co(1)	132(2)	C(17)–C(16)–N(4)	113(3)
C(4)–C(5)–C(6)	130(2)	C(16)–C(17)–C(18)	109(3)
C(5)–C(6)–C(7)	130(2)	C(16)–C(17)–C(29)	124(3)
C(5)–C(6)–N(2)	123(2)	C(18)–C(17)–C(29)	125(3)
N(2)–C(6)–C(7)	107(2)	C(17)–C(18)–C(19)	100(2)
C(6)–C(7)–C(8)	111(2)	C(17)–C(18)–C(30)	131(2)
C(6)–C(7)–C(24)	124(2)	C(19)–C(18)–C(30)	129(3)
C(8)–C(7)–C(24)	125(2)	C(18)–C(19)–C(20)	115(2)
C(7)–C(8)–C(9)	102(2)	C(18)–C(19)–N(4)	113(2)
C(7)–C(8)–C(26)	130(2)	N(4)–C(19)–C(20)	131(2)
C(9)–C(8)–C(26)	128(2)	C(16)–N(4)–C(19)	104(2)
C(8)–C(9)–C(10)	119(2)	C(16)–N(4)–Co(1)	132(1)
C(8)–C(9)–N(2)	110(2)	C(19)–N(4)–Co(1)	123(2)
N(2)–C(9)–C(10)	130(2)	C(19)–C(20)–C(1)	115(3)
C(6)–N(2)–C(9)	109(2)	C(3)–C(22)–C(23)	112(2)
C(6)–N(2)–Co(1)	128(2)	C(7)–C(24)–C(25)	112(2)
C(9)–N(2)–Co(1)	124(2)	N(1)–Co(1)–N(2)	90(1)
C(9)–C(10)–C(11)	126(3)	N(1)–Co(1)–N(3)	180(1)
C(10)–C(11)–C(12)	130(3)	N(1)–Co(1)–N(4)	93(1)
C(10)–C(11)–N(3)	120(3)	N(2)–Co(1)–N(3)	91(1)
N(3)–C(11)–C(12)	110(2)	N(2)–Co(1)–N(4)	178(1)
C(11)–C(12)–C(13)	110(2)	N(3)–Co(1)–N(4)	87(1)

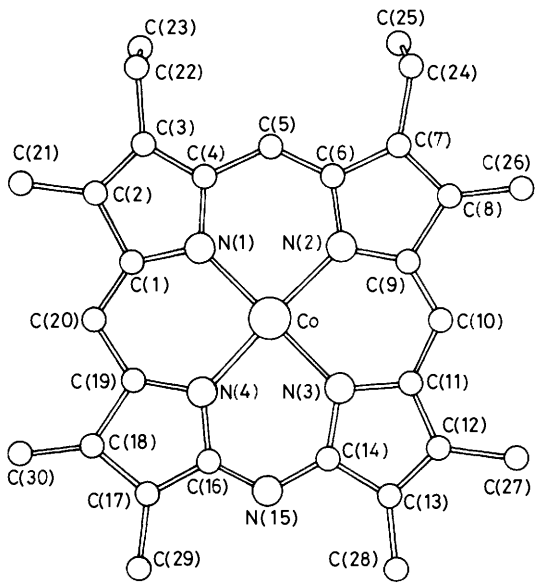

Figure 1.

can exist. Calculations were carried out at both the semi-empirical CNDO/2[19] and *ab initio* STO-3G[20] levels. The geometries selected for calculation were taken from the *X*-ray co-ordinates of Table 1 with removal of the metal atom and appropriate alkyl substituents. The inner coplanar hydrogen

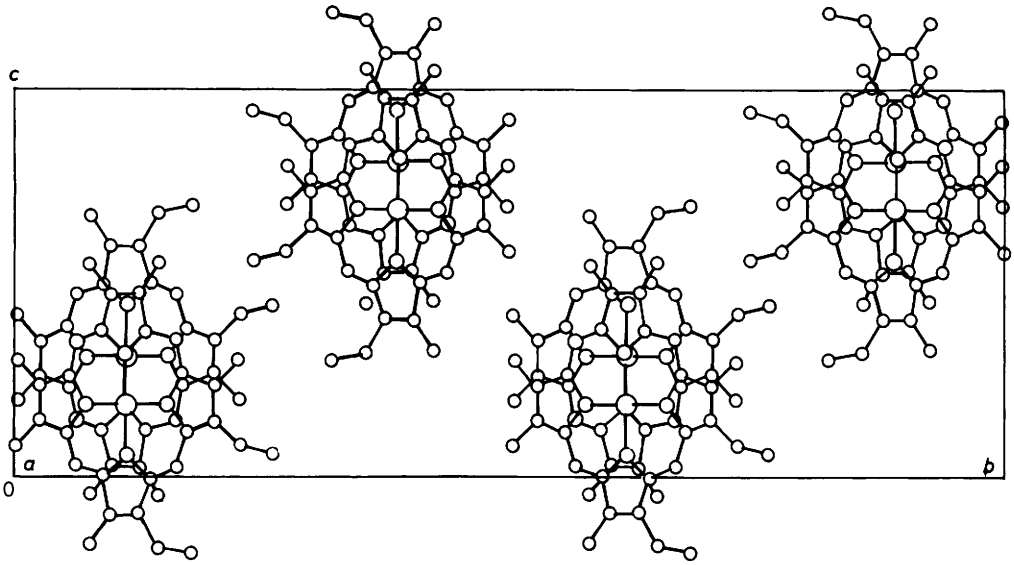

Figure 2.

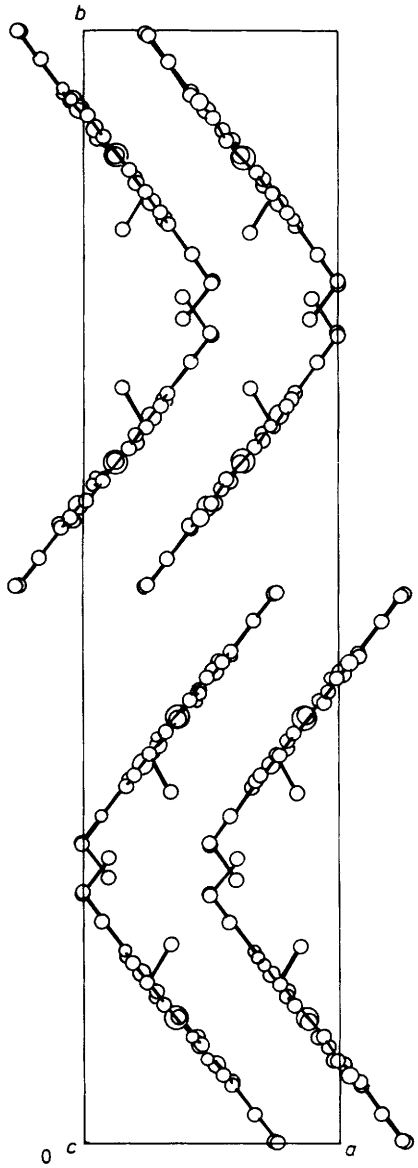

Figure 3.

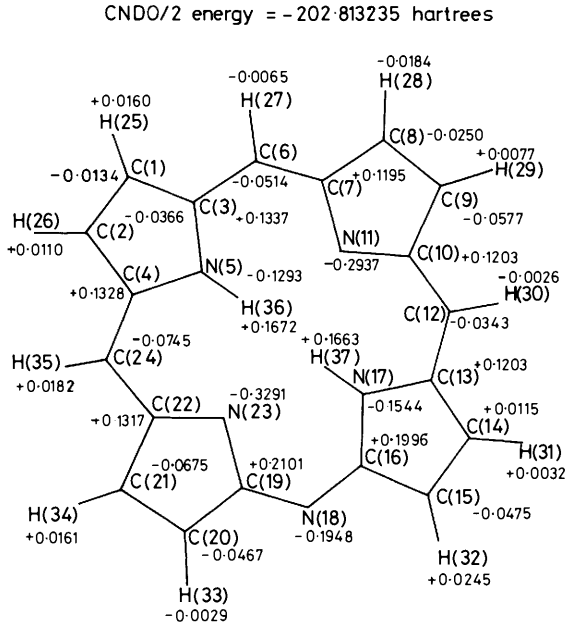

Figure 4. Charge distribution in azaporphin (**2**; $R^1 = R^2 = R^3 = H$)

atoms of the azaporphin (**2**; $R^1 = R^2 = R^3 = H$) were added at angles which bisect the C–N–C axis of each pyrrole unit, in line with crystallographic data for the related phthalocyanine[21] and porphyrin structures.[22,23] Each inner hydrogen atom therefore was joined to one nitrogen atom only as in phthalocyanine itself[21] with no hydrogen bonding to adjacent nitrogen centres. Tautomers (**4a**) and (**5**) in which one hydrogen atom is joined to the meso-nitrogen atom were constructed in a similar way. A standard N–H bond length of 0.95 Å was used throughout.

The results of these calculations are summarised in Table 4 and illustrated in Figures 4—9. The calculated molecular energies show that tautomers (**4a**) and (**5**) are relatively unstable by comparison with (**2**; $R^1 = R^2 = R^3 = H$) by at least 22 kcal mol^{-1}. Remarkably both theoretical methods show the same trend even though *inter alia* the core approximation and neglect of differential overlap reduces the CNDO/2 calculated energy by a large amount relative to the more accurate STO-3G

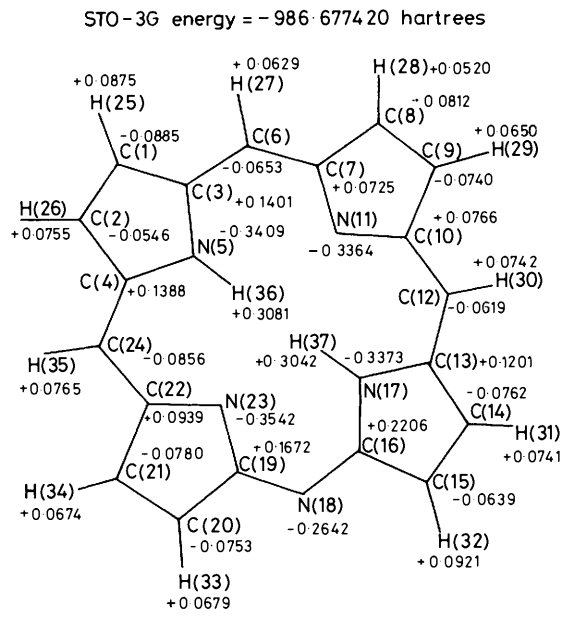

Figure 5. Charge distribution in azaporphin (**2**)

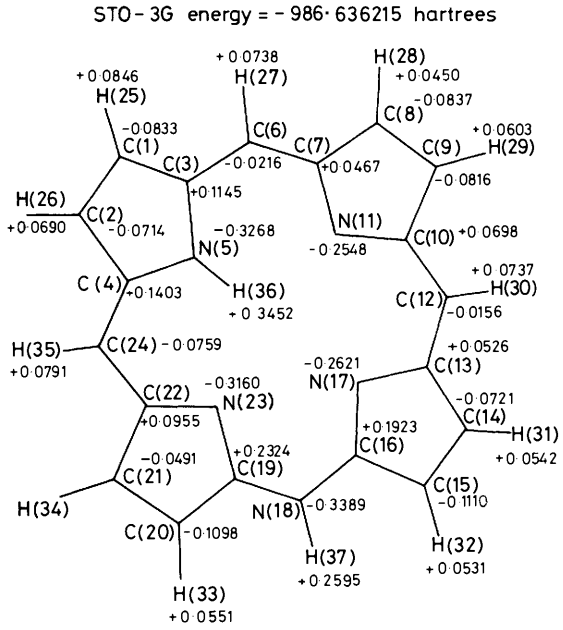

Figure 7. Charge distribution in azaporphin (**4a**)

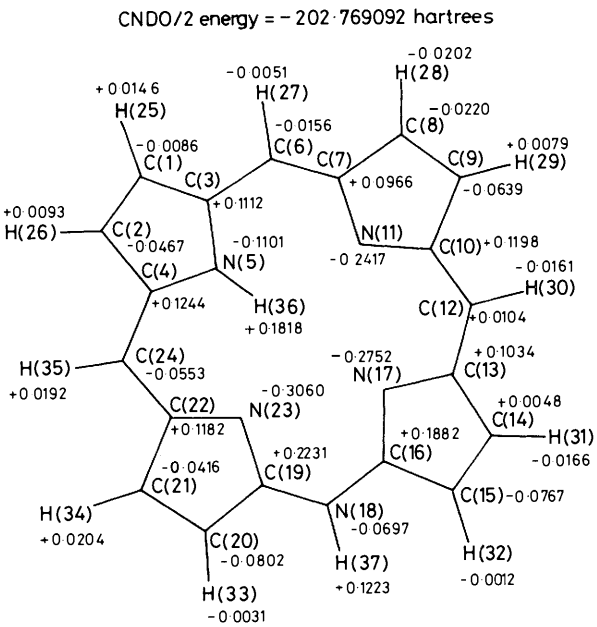

Figure 6. Charge distribution in azaporphin (**4a**)

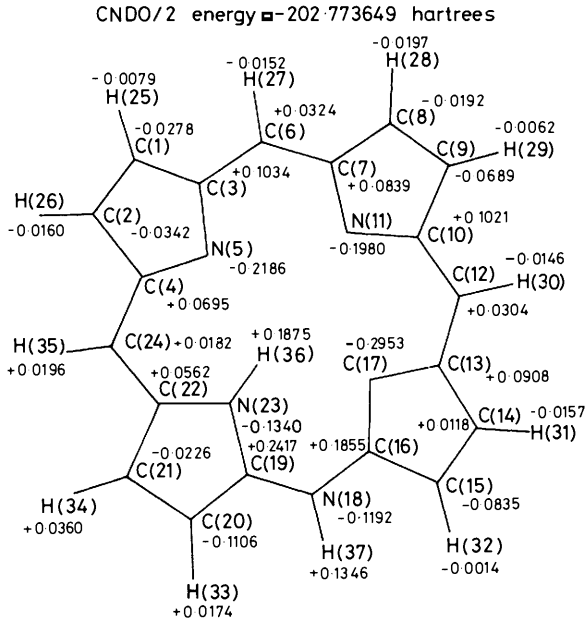

Figure 8. Charge distribution in azaporphin (**5**; $R^1 = R^2 = R^3 = H$)

method. The charge distributions also are generally similar except at the bridgehead C–H bonds and at the N–H bonds which are calculated to be more polarised at the STO-3G level.

The relative stability of phthalocyanine tautomers such as (**3**) and (**6**) has also been calculated by both methods in order to assess the energy differences between the known tautomer (**3**) and the unknown tautomer (**6**). A comparison between the phthalocyanine energy differences on the one hand and those of the azaporphins on the other should indicate whether tautomerism is possible in the latter.

Phthalocyanine calculations were carried out using the almost symmetrical structure of iron(II) phthalocyanine[24] (which is better resolved than that of phthalocyanine itself) by removal of the metal atom and addition of hydrogen atoms in the same way as before. The results obtained are shown in Table 4 and Figures 10—13. The calculations at both levels clearly show that the known tautomer (**3**) is considerably more stable than the unknown tautomer (**6**) by > 28 kcal mol^{-1}. It is clear that the magnitude of this barrier is comparable to the azaporphin case, and it follows that tautomers of the type (**4a**), (**5**), and (**6**) are unlikely to exist. Because 'isolated molecule' calculations of this type do not consider solvation, it is possible that azaporphins (**4a**) and (**5**) might be additionally stabilised by selective solvation at the peripheral N–H bond. However, this is unlikely to be a major factor since the same argument applies to the phthalocyanine tautomer (**6**) which is unknown

Table 4. Calculated energies of tautomers of azaporphin and phthalocyanine

Tautomer	MO Method	Total energy (a.u.)	Relative energy (a.u.)	Relative energy (kcal mol^{-1})
(**2**; $R^1 = R^2 = R^3 = H$)	CNDO/2	−202.813 235		
(**4a**)	CNDO/2	−202.769 092	+0.044 143	+27.70
(**5**; $R^1 = R^2 = R^3 = H$)	CNDO/2	−202.773 649	+0.039 586	+24.84
(**2**; $R^1 = R^2 = R^3 = H$)	STO-3G	−986.677 420		
(**4a**)	STO-3G	−986.636 215	+0.041 205	+25.85
(**5**; $R^1 = R^2 = R^3 = H$)	STO-3G	−986.640 851	+0.036 569	+22.95
(**3**)	CNDO/2	−334.352 705		
(**6**)	CNDO/2	−334.305 320	+0.047 385	+29.73
(**3**)	STO-3G	−1 637.252 184		
(**6**)	STO-3G	−1 637.207 269	+0.044 915	+28.18

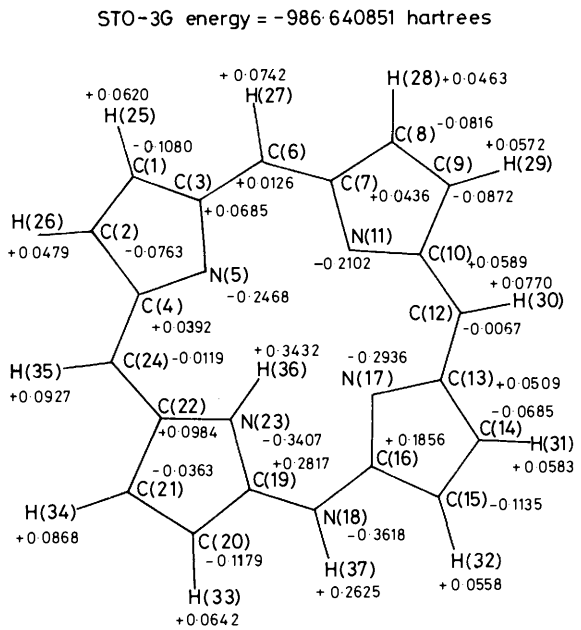

Figure 9. Charge distribution in azaporphin (**5**; $R^1 = R^2 = R^3 = H$)

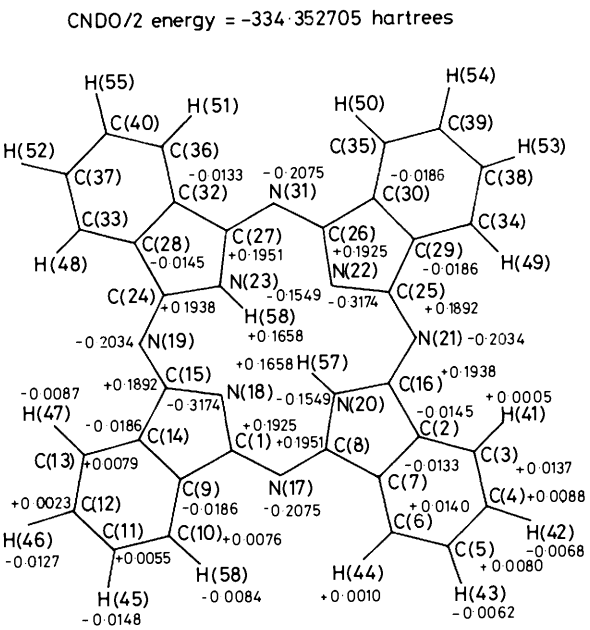

Figure 10. Charge distribution in phthalocyanine (**3**)

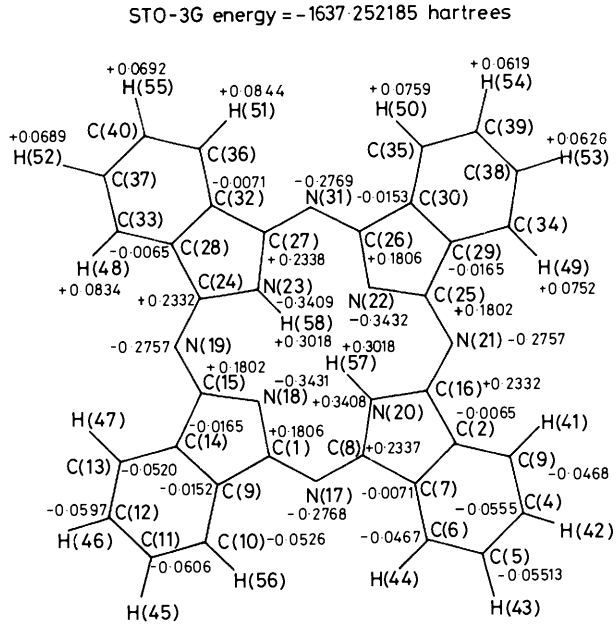

Figure 11. Charge distribution in phthalocyanine (**3**)

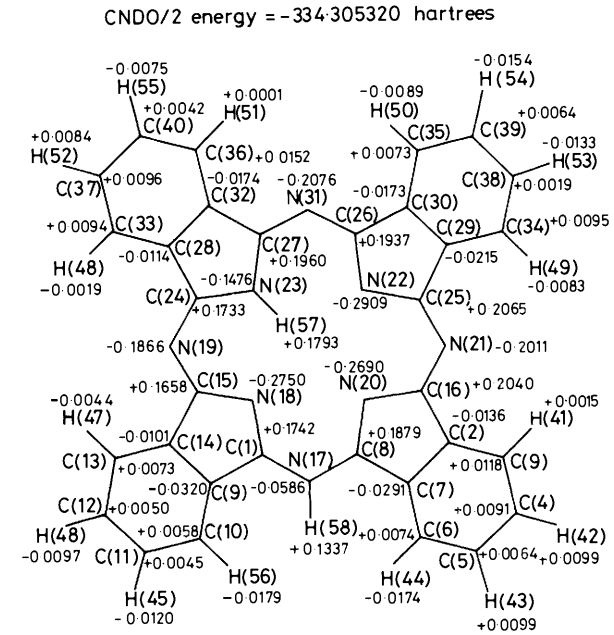

Figure 12. Charge distribution in phthalocyanine (**6**)

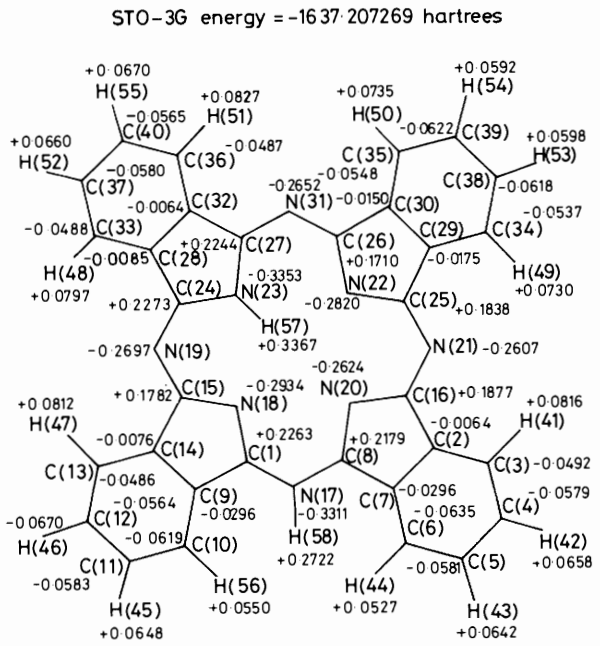

Figure 13. Charge distribution in phthalocyanine (**6**)

even in protic solvents. The possibility that the calculated energy differences observed between the sets of tautomers results from the selection of inaccurate geometries for the azaporphin tautomers (**4a**) and (**5**) and the phthalocyanine tautomer (**6**) cannot be discounted since these structures are unknown. However, this error is unlikely to be serious in view of the use of crystal data and the correlation between experimental and theoretical stability for the phthalocyanine structures.

Underlying reasons for the predicted substantial differences in stability of the core NH tautomer (**2**) and meso-NH (**4a**), (**5**) tautomers may be appreciated by consideration of the preferred site of protonation of the corresponding monoanion of (**2**; $R^1 = R^2 = R^3 = H$). Clearly in such a monoanion (**10**) the concentration of negative charge, nitrogen lone pairs and core geometry will exert a proton-sponge-like effect[25] and greatly favour core nitrogen atom protonation over meso-nitrogen atom protonation. Steric effects are also more easily minimised in the core by tilting of pyrrole rings as shown by *N*-methylation studies.[12]

Experimental

General details were as described previously.[13]

1,19-*Dideoxy*-8,12-*diethyl*-2,3,7,13,17,18-*hexamethyl*-1,19-*dibromobiladiene*-ac *Dihydrobromide* (**8**; $R^1 = R^2 = Me$, $R^3 = Et$).—2-Bromo-3,4-dimethylpyrrole-5-carbaldehyde (1.62 g, 7.5 mmol) and 5,5′-dicarboxy-4,4′-dimethyl-3,3′-diethyl-2,2′-dipyrromethane were stirred in hot methanol (40 ml) and 48% hydrobromic acid (10 ml) added. The mixture was allowed to cool to room temperature and then kept at 0 °C for 16 h. The precipitate was filtered off, washed with methanolic hydrobromic acid, and dried *in vacuo* to give the product as a brown powder (2.83 g, 98%), m.p. > 300 °C (Found: C, 46.05; H, 4.85; N, 7.3. $C_{29}H_{36}Br_4N_4$ requires C, 45.8; H, 4.75; N, 7.35%), $\lambda_{max.}$ ($CHCl_3$) 289, 384, 408, 449infl., 467, 515infl., and 542 nm (ε 6 050, 16 070, 18 110, 12 090, 24 550, 48 880, and 160 920 dm^3 mol^{-1} cm^{-1}). The compound was too insoluble for an n.m.r. spectrum to be measured.

5-*Aza*-13,17-*diethyl*-2,3,7,8,12,18-*hexamethylporphyrin* (**2**; $R^1 = R^2 = Me$, $R^3 = Et$).—1,19-Dideoxy-8,12-diethyl-2,3,7,13,17,18-hexamethyl-1,19-dibromobiladiene-*ac* dihydrobromide (1.8 g) was added to solution of sodium azide (4 g) in dry methanol (250 ml) which had been purged with nitrogen. The mixture was boiled under reflux in a nitrogen atmosphere for 24 h and then allowed to cool to room temperature. The precipitate was filtered off, washed well with methanol, and crystallised from chloroform–methanol to afford the *product* (0.7 g, 66%) as purple prisms, m.p. > 300 °C (Found: C, 77.25; H, 7.4; N, 15.05. $C_{29}H_{33}N_5$ requires C, 77.15; H, 7.35; N, 15.5%), $\lambda_{max.}$($CHCl_3$) 276infl., 378, 483infl., 506, 535, 563, 616, and 654 nm (ε 7 140, 104 480, 3 760, 6 500, 19 690, 6 480, 19 430, and 9 960 dm^3 mol^{-1} cm^{-1}), δ(CF_3CO_2D) 10.7 (1 H, s, meso-H), 10.45 (2 H, s, 2 × meso-H), 4.05 (4 H, q, 2 × CH_2Me), 3.5, 3.4 (2 × 9 H, 2 × s, Me), and 1.7 (6 H, t, 2 × CH_2*Me*).

5-*Aza*-13,17-*diethyl*-2,3,7,8,12,18-*hexamethylporphyrinato-cobalt*(II).—5-Aza-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin (62 mg) was boiled under reflux for 2.5 h in a mixture of chloroform (350 ml) and methanol (200 ml) containing cobalt(II) acetate (500 mg). The solution was then concentrated to *ca.* 70 ml and allowed to cool and crystallise. The product was filtered off, washed with methanol, and crystallised from chloroform–methanol to afford the cobalt(II) complex (35 mg, 50%) as purple needles, m.p. > 300 °C (Found: C, 68.1; H, 6.05; N, 13.6. $C_{29}H_{31}CoN_5$ requires C, 68.45; H, 6.15; N, 13.75%).

Crystal Data.—$C_{29}H_{31}CoN_5$, $M = 508.5$. Orthorhombic, $a = 8.622(2)$, $b = 37.788(4)$, $c = 14.781(3)$ Å, $V = 4\,815.8$ Å^3 (by least-squares refinement on diffractometer angles for 16 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group *Pbca* (No. 61), $D_m = 1.40$ g cm^{-3}, $Z = 8$, $D_x = 1.402$ g cm^{-3}, $F(000) = 2\,136$, crystal dimensions: 0.2 × 0.02 × 0.02 mm, μ(Mo-K_α) = 7.72 cm^{-1}.

Data Collection and Processing.—Hilger and Watts four-circle diffractometer, ω–2θ mode scan, graphite-monochromated Mo-K_α radiation; the crystal was a weakly diffracting thin needle elongated along *a*, and only 966 reflections [$\theta \leqslant 23°$, $I > 2\sigma(I)$] were used in the analysis and refinement, after correcting for Lorentz and polarisation factors.

Structure Analysis and Refinement.—Patterson synthesis (for Co) followed by direct methods and Fourier methods (by SHELX[26]) gave all 35 non-hydrogen atoms. After least-squares refinement with anisotropic temperature factors the three meso-hydrogens and the ten ethyl hydrogens were included at calculated positions while the 18 methyl hydrogens were included at positions determined from a difference Fourier synthesis, and with a U of 0.05. In the final cycles of refinement hydrogen atom parameters were not allowed to vary. The weighting scheme was $\omega = 1.0/[A(0)\cdot T(0)\cdot X + A(1)\cdot T(1)\cdot X + A(2)\cdot T(2)\cdot X + A(3)\cdot T(3)\cdot X]$, where the A values are the coefficients of a Chebyshev series in $T(I)\cdot X$ with $X = F_0/F_0(\text{max.})$; the coefficients used were $A(0) = 18.9$, $A(1) = 13.6$, $A(2) = -10.4$, $A(3) = -9.4$. The final conventional R value was 0.069. Computer programs used were SHELX,[26] CRYSTALS,[27] and PLUTO.[28]

Table 1 gives the fractional co-ordinates of all atoms, Tables 2 and 3 the bond lengths and angles, respectively, not involving hydrogen atoms. Lists of parameters are available as Supplementary Publication No. SUP 56095 (8 pp.).* Figure 1 is a perspective drawing of the molecule, showing the crystallo-

* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

graphic atom numbering and Figures 2 and 3 are packing diagrams viewed down the *a* and *c* axes respectively.

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