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Model porphyrin precursors: 1,2,4,5-tetrakis(cyanomethyl)benzene, methyl 3,4,5-triacetoxybenzoate and 2-(*N*-phthalimidomethyl)benzoic acid

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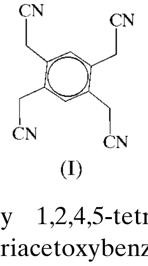
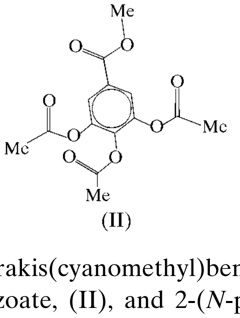
In the crystalline state, the centrosymmetric molecule 1,2,4,5-tetrakis(cyanomethyl)benzene, $C_{14}H_{10}N_4$, has one cyanomethyl group in the benzene plane and one cyanomethyl group rotated 67.2 (2)° out of the benzene plane. Molecules of methyl 3,4,5-triacetoxybenzoate, $C_{14}H_{14}O_8$, form chains with each molecule twisted ±89.6 (1)° from the preceding molecule. In this orientation, a close C—H···O contact is formed, with an H···O distance of 2.34 Å. The structure of 2-(*N*-phthalimidomethyl)benzoic acid, $C_{16}H_{11}NO_4$, reveals hydrogen-bonded dimers linked by the carboxyl groups of adjacent molecules. The O4···O3 distance is 2.636 (2) Å and the O4—H···O3 angle is 171 (2)°.

Comment

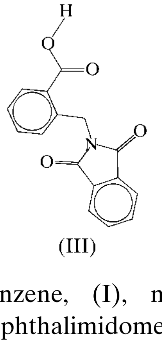
Derivatized porphyrins play useful roles as models for protein active sites. Particular effort has been paid to models for the heme active sites of myoglobin and hemoglobin (Momenteau & Reed, 1994). This laboratory has synthesized and characterized a number of four-atom-linked capped porphyrins (Johnson *et al.*, 1996), five-atom-linked capped porphyrins (Ma *et al.*, 1993), and five-plus-atom-linked capped porphyrins (Slebodnick *et al.*, 1996). We report herein the structures of three precursors characterized in the course of this research, namely 1,2,4,5-tetrakis(cyanomethyl)benzene, (I), methyl 3,4,5-triacetoxybenzoate, (II), and 2-(*N*-phthalimidomethyl)-benzoic acid, (III).



(I)



(II)



(III)

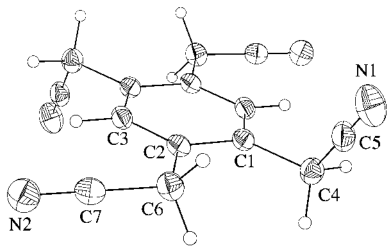


Figure 1
A view of the molecule of (I) showing 50% displacement ellipsoids. Only unique atoms are labeled. H atoms are drawn as spheres of arbitrary radii.

Compound (I) was prepared as a precursor for the synthesis of a three-atom-linked capped porphyrin. Fig. 1 is a displacement ellipsoid diagram of (I). The molecule sits on an inversion centre and its symmetry-generated ellipsoids are shown without labels. The benzene ring is planar by symmetry. Selected bond lengths and angles are listed in Table 1. One of the unique cyanomethyl groups remains nearly in the plane of the benzene ring, and this cyanomethyl group is linear, with a C6—C7—N2 angle of 179.8 (2) Å. The other unique cyanomethyl group is twisted 67.2 (2)° relative to the C1—C2 bond in the benzene ring (Table 1). This cyanomethyl group is also linear, with a bond angle of 179.67 (17) Å for C4—C5—N1. Viewed down the *c* axis, molecules of (I) form long straight columns aligned along the centroids of the benzene rings. The molecules in each column pack tilted at 72.8 (1)° relative to molecules in adjacent columns.

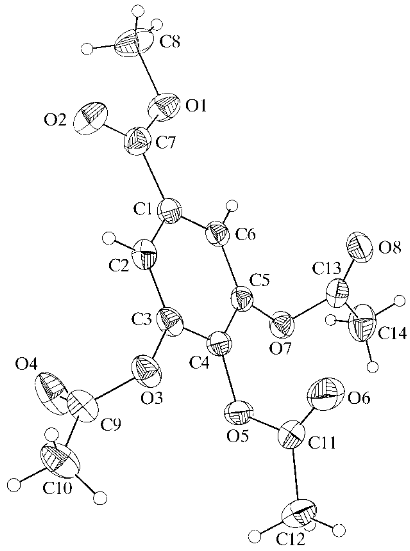


Figure 2
A view of the molecule of (II) showing 50% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

The structure of durene (1,2,4,5-tetramethylbenzene) has been examined both as a donor in charge-transfer complexes (Lefebvre, 1989) and to understand equilibrium conformations of the molecule (Prince *et al.*, 1973, and references therein). There has been interest in 1,2,4,5-tetracyanobenzene (TCNB) as an acceptor in charge-transfer complexes (Lefebvre, 1989, and references therein). In the series durene,

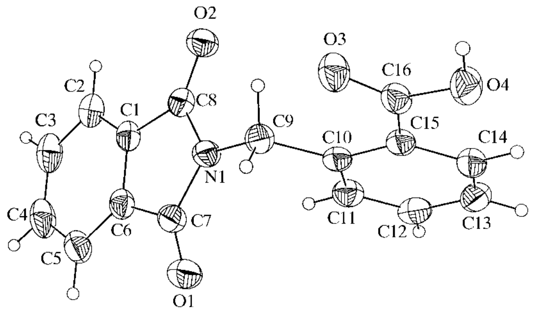


Figure 3
A view of the molecule of (III) showing 50% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

(I) and TCNB, there is a shift from mildly electron-donating methyl substituents to strongly electron-withdrawing cyano substituents. The changes in electron donation and conjugation have no significant effect on the C$\cdots$C bond lengths in the benzene ring. However, durene structures and (I) exhibit geometric distortion of the benzene ring, presumably resulting from the bulky substituents. In durene structures, the angle formed by the unsubstituted C atoms with their nearest C neighbours is approximately 122–123°, with a corresponding reduction of other ring angles. For (I), this angle is 122.14 (14)°.

Compound (II) (Fig. 2) was prepared as a precursor for a capped porphyrin with asymmetric linkages between the benzene 'cap' and the porphyrin. In (II), the central benzene ring is planar, with a maximum deviation from the mean plane of 0.007 (1) Å for atom C5. Selected bond lengths and angles are listed in Table 2. The three acetoxy groups are rotated out of the benzene plane by 83.22 (17), −84.37 (17) and −133.03 (14)° (as measured by torsion angles). In contrast, the carbomethoxy group remains nearly in the plane, with a torsion angle of −3.2 (2)°.

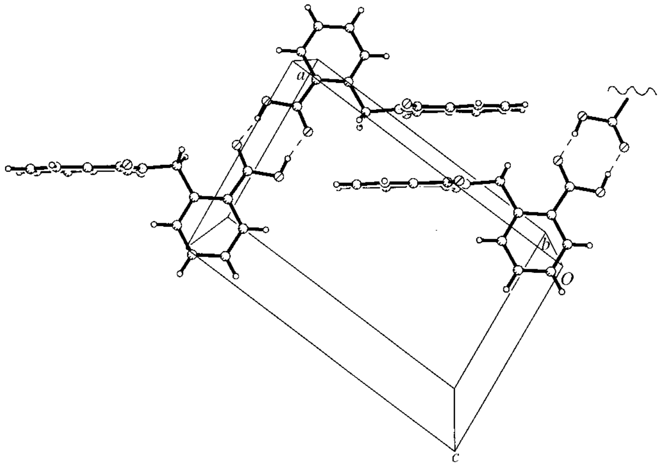


Figure 4
Part of the unit cell of (III) showing the hydrogen-bonded dimers and the stacking of the phthalimide rings.

Molecules of (II) are associated in two ways. The first involves the close contact O2$A^{\rm i}\cdots$H10A—C10 [symmetry code: (i) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$]. The C10—H10$A$ distance is 0.98 Å (fixed with a riding model, see refinement details below) and the O2$A^{\rm i}\cdots$H10A distance is 2.34 Å, whereas the O2$A^{\rm i}\cdots$H10A—C10 bond angle is 170°. Molecules of (II) form chains oriented along these contacts and molecules in the chain tilt back and forth 89.6 (1)° relative to each other. The second association is dimeric: molecules generated by (x, y, z) and ($-x$, $2 - y$, $1 - z$) form offset dimers. The benzene rings are parallel, but the molecules are rotated 180° with respect to each other and the benzene centroids are slightly offset. The separation between the benzene planes is 3.29 (1) Å.

Compound (III) (Fig. 3) was prepared as a precursor for capped porphyrins containing N atoms at an intermediate position on the 'arms' linking the benzene 'cap' to the porphyrin. Compound (III) is a primary amine of the form RNH$_2$, protected with phthalimide. The phthalimide group is planar, with a maximum deviation from the 11-atom mean plane of 0.013 (1) Å for atom C6. The benzene of the benzyl group is also planar, with a maximum deviation of 0.007 (1) Å for atom C12. The dihedral angle between these planes is 80.86 (4)°. Selected bond lengths and angles are listed in Table 3. The twist in the molecule occurs at atom C9; the C10—C9—N1—C7 torsion angle is 86.6 (2)°. Molecules of (III) form hydrogen-bonded dimers through their carboxyl groups. The O4—H4B distance is 0.95 (2) Å and the H4$B\cdots$O3$A^{\rm ii}$ distance is 1.69 (2) Å [symmetry code: (ii) $-x$, $-y + 2$, $-z - 1$]. The O4$\cdots$O3$A^{\rm ii}$ distance is 2.636 (2) Å and the O4—H4$B\cdots$O3$A^{\rm ii}$ bond angle is 171 (2)°. This short distance is normal for strongly hydrogen-bonded carboxylic acid dimers in the crystalline state (Speakman, 1972). Molecules of (III) pack with alternating layers of hydrogen-bonded carboxylbenzyl groups and stacked phthalimide groups (Fig. 4).

Experimental

Crystals of (I) were prepared according to the method of Buckland *et al.* (1983) and recrystallized from acetonitrile (m.p. 484–487 K, literature m.p. 486–488 K). Compound (II) can be prepared by acylation of the alcohol functions of gallic acid, followed by esterification of the carboxyl group (m.p. 404.0–405.5 K). Crystals of (III) were prepared using the method of Sasaki *et al.* (1978) to protect 2-methylaminobenzoic acid with phthalimide (m.p. 535.0–537.0 K). Melting points were measured on a Mel-Temp melting point apparatus from Laboratory Instruments, Holliston, Massachusetts, USA.

Compound (I)

Crystal data

$C_{14}H_{10}N_4$
$M_r = 234.26$
Monoclinic, $P2_1/c$
$a = 8.818$ (1) Å
$b = 8.377$ (1) Å
$c = 8.174$ (1) Å
$\beta = 108.51$ (1)°
$V = 572.48$ (15) Å^3
$Z = 2$

$D_x = 1.359$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 853 reflections
$\theta = 2.44$–28.20°
$\mu = 0.086$ mm^{-1}
$T = 153$ (2) K
Square plate, colourless
0.12 × 0.11 × 0.06 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*/*PC*; Sheldrick, 1997)
$T_{\rm min}$ = 0.985, $T_{\rm max}$ = 0.995
3540 measured reflections

1335 independent reflections
836 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035
$\theta_{\rm max}$ = 28.20°
$h = -6 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 6$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.098$
$S = 1.00$
1335 reflections

82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.397 (2)	C4—C5	1.464 (2)
C2—C3	1.396 (2)	C6—C7	1.459 (2)
C3—C1^{i}	1.390 (2)	C5—N1	1.149 (2)
C1—C4	1.518 (2)	C7—N2	1.1447 (19)
C2—C6	1.522 (2)		
C3^{i}—C1—C2	119.42 (13)	C3—C2—C6	121.05 (14)
C3—C2—C1	118.44 (14)	N1—C5—C4	179.67 (17)
C1^{i}—C3—C2	122.14 (14)	N2—C7—C6	179.8 (2)
C2—C1—C4—C5	−67.20 (19)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

Compound (II)

Crystal data

$C_{14}H_{14}O_8$
M_r = 310.25
Monoclinic, $P2_1/n$
a = 9.2233 (7) Å
b = 11.747 (1) Å
c = 13.936 (1) Å
β = 90.451 (1)°
V = 1509.9 (2) Å^3
Z = 4

D_x = 1.365 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4507 reflections
θ = 2.27–25.5°
μ = 0.114 mm^{-1}
T = 153 (2) K
Truncated block, colourless
0.41 × 0.30 × 0.27 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*/*PC*; Sheldrick, 1997)
$T_{\rm min}$ = 0.959, $T_{\rm max}$ = 0.976
8088 measured reflections

2789 independent reflections
2320 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 25.50°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 10$
$l = -16 \rightarrow 16$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.116$
$S = 1.84$
2789 reflections

203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

C1—C2	1.395 (2)	C11—O6	1.186 (2)
C2—C3	1.370 (2)	C13—O8	1.1918 (19)
C3—C4	1.387 (2)	C3—O3	1.4006 (17)
C4—C5	1.383 (2)	C4—O5	1.3939 (17)
C5—C6	1.386 (2)	C5—O7	1.3937 (17)
C1—C6	1.390 (2)	C9—O3	1.3751 (18)
C1—C7	1.492 (2)	C11—O5	1.3646 (18)
C7—O2	1.2061 (18)	C13—O7	1.3719 (19)
C9—O4	1.1910 (19)		
O2—C7—O1	123.63 (14)	C7—O1—C8	115.96 (13)
O4—C9—C10	127.43 (15)	C9—O3—C3	115.95 (11)
O6—C11—C12	127.67 (15)	C11—O5—C4	116.60 (11)
O8—C13—C14	126.61 (15)	C13—O7—C5	119.24 (12)
C2—C3—O3—C9	83.22 (17)	C4—C5—O7—C13	−133.03 (14)
C3—C4—O5—C11	−84.37 (17)	C6—C1—C7—O1	−3.2 (2)

Compound (III)

Crystal data

$C_{16}H_{11}NO_4$
M_r = 281.26
Monoclinic, $P2_1/c$
a = 12.125 (1) Å
b = 13.720 (1) Å
c = 7.725 (1) Å
β = 96.72 (1)°
V = 1276.2 (2) Å^3
Z = 4

D_x = 1.464 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2323 reflections
θ = 1.69–25.5°
μ = 0.107 mm^{-1}
T = 153 (2) K
Prism, colourless
0.33 × 0.17 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*/*PC*; Sheldrick, 1997)
$T_{\rm min}$ = 0.974, $T_{\rm max}$ = 0.992
6929 measured reflections

2365 independent reflections
1722 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026
$\theta_{\rm max}$ = 25.50°
$h = -14 \rightarrow 11$
$k = -16 \rightarrow 15$
$l = -9 \rightarrow 9$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.089$
$S = 1.10$
2365 reflections

194 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

O1—C7	1.210 (2)	N1—C7	1.398 (2)
O2—C8	1.215 (2)	C6—C7	1.492 (2)
O3—C16	1.228 (2)	C6—C1	1.385 (2)
O4—C16	1.322 (2)	C1—C8	1.483 (2)
C9—C10	1.524 (2)	C8—N1	1.397 (2)
N1—C9	1.454 (2)		
C8—N1—C7	111.97 (12)	N1—C8—C1	106.01 (13)
N1—C7—C6	105.52 (13)	N1—C9—C10	114.30 (13)
C1—C6—C7	108.25 (12)	O3—C16—O4	121.61 (15)
C6—C1—C8	108.24 (13)		
C10—C9—N1—C7	86.6 (2)		

H atoms were placed at calculated positions and refined with a riding model ($C_{methyl}—H = 0.98$ Å, $C_{methylene}—H = 0.99$ Å and $C_{aromatic}—H = 0.95$ Å). The U_{iso} value for a given H atom was assigned as 1.2 times the U_{iso} of the atom to which it is attached (1.5 for methyl). The methyl groups in (II) were constrained to ideal tetrahedral geometries. The acidic proton H4*B* in (III) was refined isotropically.

For all compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART* (Bruker, 1999); data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL*/*PC* (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1493). Services for accessing these data are described at the back of the journal.

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