

## 2-(1,3-Dithian-2-yl)benzaldehyde and N-[2-[2-(1,3-dioxan-2-yl)phenoxy]- ethyl]phthalimide

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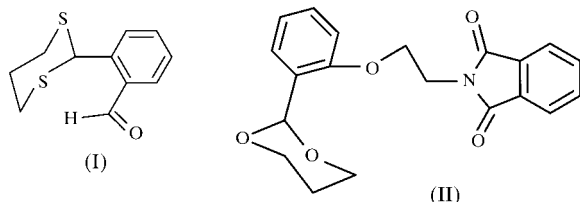
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The crystal structures of two elaborated-porphyrin precursors have been determined. In the crystalline state, 2-(1,3-dithian-2-yl)benzaldehyde,  $C_{11}H_{12}OS_2$ , has its dithiane ring in a slightly distorted chair conformation. The molecules pack in anti-parallel chains. *N*-[2-[2-(1,3-dioxan-2-yl)phenoxy]ethyl]-phthalimide,  $C_{20}H_{19}NO_5$ , is in a folded conformation. The dihedral angle between the phthalimide and phenyl planes is  $80.07(3)^\circ$ . In the crystalline states, molecules stack on top of one another.

### Comment

Linked porphyrins have been used to model the photo-synthetic reaction centers of *Rhodospseudomonas viridis* and *Rhodobactersphaeroides* (Clement *et al.*, 1998; Kadish *et al.*, 1998, and references therein). This laboratory has previously reported the structures of precursors for linked porphyrins, as well as their syntheses (Jene & Ibers, 1999, and references therein). Capped porphyrins play important roles as models for protein active sites. There has been particular interest in porphyrin-based models of the heme active site (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), five-plus-atom-linked capped porphyrins (Sleboznick *et al.*, 1996), and their precursors (Jene *et al.*, 1999). We report here the structures of two further related precursors, namely 2-(1,3-dithian-2-yl)benzaldehyde, (I), and *N*-[2-[2-(1,3-dioxan-2-yl)phenoxy]ethyl]phthalimide, (II).



Compound (I) (Fig. 1 and Table 1) is a precursor for a rigidly connected *o*-diporphyrinbenzene system with different

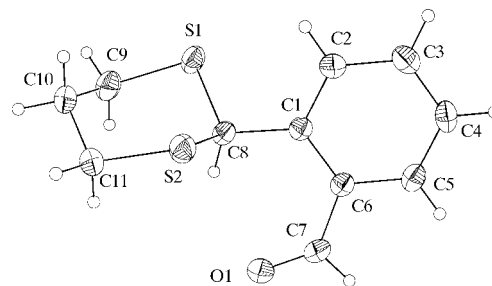


Figure 1

The structure of (I) showing 50% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

porphyrins attached. The benzene ring is planar with a maximum deviation of  $0.0126(9)$  Å for atom C1. The dithiane ring is in the chair conformation with the benzaldehyde moiety in the equatorial position. The C—C and C—S bond lengths are normal. The  $C9-C10-C11$  angle of  $114.16(14)^\circ$  is larger than both the tetrahedral value of  $109.5^\circ$  and the  $111.3^\circ$  angle in cyclohexane, but is in agreement with larger than expected values in similar systems (Kalf & Romers, 1966). Torsion angles for the dithiane ring are listed in Table 1.

In the solid state, molecules of (I) pack in anti-parallel sheets. Each sheet is formed of parallel chains with a closest contact for  $O1 \cdots H10B(x, 1 + y, z)$  of  $2.74$  Å between molecules in a chain. The closest S-contact,  $S1 \cdots H5A$  at  $3.10$  Å, occurs between anti-parallel sheets. The relation between anti-parallel chains involved in the contact is  $1 - x, 2 - y, 1 - z$ . There is a  $3.28(1)$  Å separation between benzene rings in opposite chains, and they are in a suitable position for  $\pi$  overlap.

Compound (II) (Fig. 2 and Table 2) is used in the synthesis of capped porphyrins containing N and O atoms at intermediate positions on the 'arms' linking the benzene 'cap' to the porphyrin. Compound (II) is a primary amine of the form  $RNH_2$ , protected with phthalimide. The phthalimide group is

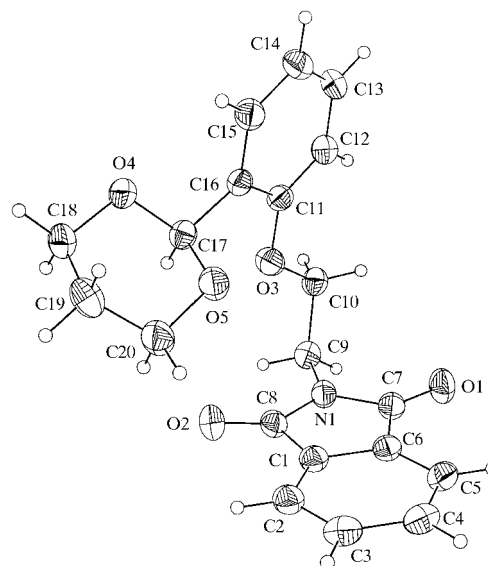
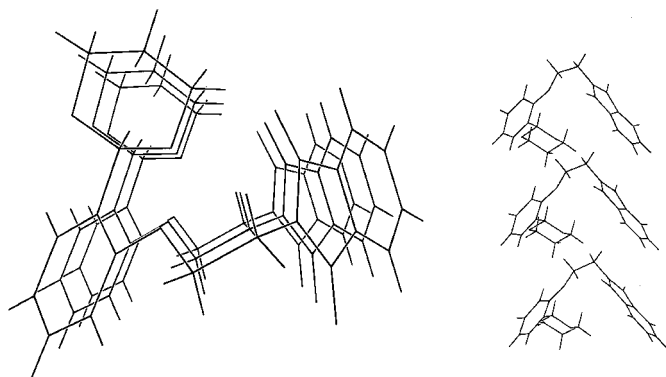


Figure 2

The structure of (II) showing 50% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

planar with a maximum deviation from the 11-atom mean plane of 0.020 (1) Å for atom O2. The phenoxy group is planar with a maximum deviation of 0.016 (1) Å for atom C11. The dihedral angle between the planes is 80.07 (3)°. The twist in the molecule occurs along atoms C9, C10, and O3 that link the two moieties. The acetal C—O bond lengths in (II), C17—O4 and C17—O5, are equal within experimental error [average 1.411 (3) Å]. This is consistent with the lack of hydrogen bonds to the acetal O atoms (Gandour *et al.*, 1986). These C—O bonds average 1.407 (10) Å in other reported unsubstituted (2,6-dioxahexyl)arenes (Gandour *et al.*, 1986; De & Kitagawa, 1991). Both in these compounds and in the present study, the 2,6-dioxahexyl rings have the chair conformation (see torsion angles in Table 2).

Molecules of (II) stack along the *a* axis (Fig. 3). Each molecule is shifted 6.020 (4) Å from the molecule below it. The closest contact between molecules in the stack is H9A...O5 at 2.34 Å. The closest contact between columns is H18A...H10A( $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ) at 2.55 Å.



**Figure 3**  
Packing views of compound (II) down the *a*\* axis (left-hand side) and the *b*\* axis (right-hand side).

## Experimental

1,3-Dithiane derivatives can be synthesized following the literature method of Marshall & Belletire (1971). The melting point of compound (I) is 361.0–362.0 K. Crystals of compound (II) were prepared according to the literature method of Sasaki *et al.* (1978) to protect the amino starting material with phthalimide. The melting point for compound (II) is 438.0–439.0 K. Melting points were measured on a Mel-Temp melting point apparatus from Laboratory Instruments, Holliston, Massachusetts, USA.

### Compound (I)

#### Crystal data

$C_{11}H_{12}OS_2$	$Z = 2$
$M_r = 224.33$	$D_x = 1.407 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.6363 (13) \text{ \AA}$	Cell parameters from 2850 reflections
$b = 8.1836 (16) \text{ \AA}$	$\theta = 2.67\text{--}28.00^\circ$
$c = 10.468 (2) \text{ \AA}$	$\mu = 0.465 \text{ mm}^{-1}$
$\alpha = 70.68 (3)^\circ$	$T = 153 (2) \text{ K}$
$\beta = 88.01 (3)^\circ$	Block, colorless
$\gamma = 80.77 (3)^\circ$	$0.46 \times 0.37 \times 0.30 \text{ mm}$
$V = 529.45 (18) \text{ \AA}^3$	

#### Data collection

Bruker SMART 1000 CCD diffractometer	2363 independent reflections
$\omega$ scans	2201 reflections with $I > 2\sigma(I)$
Absorption correction: numerical face-indexed (SHELXTL/PC; Sheldrick, 1997)	$R_{\text{int}} = 0.014$
$T_{\text{min}} = 0.845, T_{\text{max}} = 0.896$	$\theta_{\text{max}} = 28^\circ$
3410 measured reflections	$h = -7 \rightarrow 8$
	$k = -9 \rightarrow 10$
	$l = -13 \rightarrow 14$
	Intensity decay: <2%

#### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$wR(F^2) = 0.112$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 2.07$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
2363 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
127 parameters	

**Table 1**

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

S1—C8	1.8198 (15)	C10—C11	1.525 (2)
S2—C8	1.8233 (15)	C1—C8	1.5118 (19)
S1—C9	1.8113 (17)	C6—C7	1.479 (2)
S2—C11	1.8161 (16)	C7—O1	1.2080 (18)
C9—C10	1.523 (3)		
C9—S1—C8	97.89 (8)	C1—C8—S1	110.48 (10)
C11—S2—C8	97.73 (8)	C1—C8—S2	108.61 (10)
C2—C1—C8	119.79 (13)	S1—C8—S2	113.06 (8)
C6—C1—C8	121.80 (13)	C10—C9—S1	114.74 (12)
C5—C6—C7	115.14 (12)	C9—C10—C11	114.16 (14)
C1—C6—C7	125.22 (13)	C10—C11—S2	114.07 (12)
O1—C7—C6	128.29 (13)		
C8—C1—C9—C10	41.9 (2)	C10—C11—S2—C8	−59.84 (14)
C1—C9—C10—C11	−36.58 (15)	C6—C1—C7—O1	177.00 (19)
C9—C10—C11—S2	64.50 (18)	C2—C1—C7—O1	172.00 (18)

### Compound (II)

#### Crystal data

$C_{20}H_{19}NO_5$	$D_x = 1.373 \text{ Mg m}^{-3}$
$M_r = 353.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2806 reflections
$a = 6.0200 (4) \text{ \AA}$	$\theta = 2.55\text{--}27.74^\circ$
$b = 15.0289 (11) \text{ \AA}$	$\mu = 0.099 \text{ mm}^{-1}$
$c = 18.9660 (13) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 94.841 (1)^\circ$	Square prism, colorless
$V = 1709.8 (2) \text{ \AA}^3$	$0.47 \times 0.12 \times 0.06 \text{ mm}$
$Z = 4$	

#### Data collection

Bruker SMART 1000 CCD diffractometer	4034 independent reflections
$\omega$ scans	2314 reflections with $I > 2\sigma(I)$
Absorption correction: numerical face-indexed (SHELXTL/PC; Sheldrick, 1997)	$R_{\text{int}} = 0.041$
$T_{\text{min}} = 0.967, T_{\text{max}} = 0.994$	$\theta_{\text{max}} = 28^\circ$
11 075 measured reflections	$h = -7 \rightarrow 8$
	$k = -19 \rightarrow 18$
	$l = -24 \rightarrow 24$
	Intensity decay: <2%

#### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.03F_o^2)^2]$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
4034 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
235 parameters	

**Table 2**

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

O1—C7	1.209 (2)	O3—C11	1.3632 (19)
O2—C8	1.2070 (19)	C16—C17	1.498 (2)
N1—C7	1.388 (2)	O4—C17	1.4085 (19)
C6—C7	1.491 (2)	O4—C18	1.4297 (19)
C1—C8	1.484 (2)	C18—C19	1.503 (2)
N1—C8	1.397 (2)	C19—C20	1.506 (3)
N1—C9	1.454 (2)	O5—C20	1.438 (2)
C9—C10	1.505 (2)	O5—C17	1.4132 (19)
O3—C10	1.432 (2)		
C11—O3—C10	117.74 (14)	N1—C9—C10	111.57 (14)
C7—N1—C9	123.90 (15)	O3—C10—C9	106.81 (14)
C8—N1—C9	123.69 (14)	O3—C11—C12	123.90 (17)
C2—C1—C8	129.82 (17)	O3—C11—C16	115.33 (16)
C5—C6—C7	130.61 (16)	C15—C16—C17	120.71 (16)
C1—C6—C7	107.74 (15)	C11—C16—C17	120.92 (16)
N1—C7—C6	105.81 (15)	O4—C17—O5	111.13 (14)
C7—N1—C8	112.37 (15)	O4—C17—C16	107.72 (14)
N1—C8—C1	105.26 (15)	O5—C17—C16	109.06 (14)
C6—C1—C8	108.79 (15)	C17—O4—C18	111.48 (13)
O1—C7—N1	125.12 (17)	O4—C18—C19	109.80 (15)
O1—C7—C6	129.06 (16)	C18—C19—C20	108.99 (16)
O2—C8—N1	125.56 (17)	O5—C20—C19	110.32 (15)
O2—C8—C1	129.18 (17)	C17—O5—C20	110.82 (13)
C7—N1—C9—C10	−75.2 (2)	C17—O4—C18—C19	58.16 (19)
N1—C9—C10—O3	−58.87 (18)	O4—C18—C19—C20	−53.9 (2)
C9—C10—O3—C11	162.18 (14)	C18—C19—C20—O5	53.8 (2)
C10—O3—C11—C16	−169.17 (15)	C19—C20—O5—C17	−57.2 (2)

H atoms were placed at calculated positions and refined with a riding model (methylene C—H = 0.99 Å, methine C—H = 1.00 Å and aromatic C—H = 0.95 Å). The  $U_{iso}$  value for a given H atom was assigned as 1.2 times  $U_{iso}$  of the atom to which it is attached.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (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: BK1516). Services for accessing these data are described at the back of the journal.

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