L-Thr^3					
φ	C-2	N-3	Cα-3	C-3	−125.7 (8)
ψ	N-3	Cα-3	C-3	N-4	64.6 (7)
ω	N-3	Cα-3	Cβ-3	Cγ-3	−171.7 (7)
βAla^4					
φ	C-3	N-4	Cα-4	Cβ-4	98.6 (9)
ψ	N-4	Cα-4	Cβ-4	C-4	−74.1 (7)
ψ†	Cα-4	Cβ-4	C-4	N-5	99.6 (8)
ω	Cβ-4	C-4	N-5	Cα-5	174.9 (8)
D-Leu^5					
φ	C-4	N-5	Cα-5	C-5	122.7 (8)
ψ	N-5	Cα-5	C-5	N-6	−158.5 (7)
ω	Cα-5	C-5	N-6	Cα-6	−179.0 (7)
N-Me-L-Ile^6					
φ	C-5	N-6	Cα-6	C-6	−106.3 (7)
ψ	N-6	Cα-6	C-6	N-7	100.2 (8)
ω	Cα-6	C-6	N-7	Cα-7	−165.9 (9)
βAla^7					
φ	C-6	N-7	Cα-7	Cβ-7	−131.5 (9)
ψ	N-7	Cα-7	Cβ-7	C-7	78.0 (8)
ψ†	Cα-7	Cβ-7	C-7	N-8	−137.3 (9)
ω	Cβ-7	C-7	N-8	Cα-8	−173.7 (9)
D-*a*Ile^8					
φ	C-7	N-8	Cα-8	C-8	126.0 (9)
ψ	N-8	Cα-8	C-8	N-9	−161.6 (8)
ω	Cα-8	C-8	N-9	Cα-9	−171.3 (8)
N-Me-L-Val^9					
φ	C-8	N-9	Cα-9	C-9	−112.7 (8)
ψ	N-9	Cα-9	C-9	N-10	100.2 (9)
ω	Cα-9	C-9	N-10	Cα-10	0.7 (9)
N-Me-L-Ala^{10}					
φ	C-9	N-10	Cα-10	C-10	−109.4 (9)
ψ	N-10	Cα-10	C-10	N-11	−164.6 (8)
ω	Cα-10	C-10	N-11	Cα-11	−171.2 (8)
βAla^{11}					
φ	C-10	N-11	Cα-11	Cβ-11	72.3 (7)
ψ	N-11	Cα-11	Cβ-11	C-11	68.5 (6)
ψ†	N-12	C-11	Cβ-11	Cα-11	−93.3 (7)
ω	Cβ-11	C-11	N-12	Cα-12	−173.3 (8)
D-Leu^{12}					
φ	C-11	N-12	Cα-12	C-12	87.0 (7)
ψ	N-12	Cα-12	C-12	N-13	−158.1 (8)
ω	Cα-12	C-12	N-13	Cα-13	−177.2 (8)
N-Me-D-*a*Ile^{13}					
φ	C-12	N-13	Cα-13	C-13	−56.3 (7)
ψ‡	N-13	Cα-13	C-13	Oγ-3	−50.1 (6)
ω‡	Cβ-3	Oγ-3	C-13	Cα-13	172.2 (8)

† The β-alanine has two torsion angles corresponding to ψ. ‡ The angle is for the ester linkage between C-13(*N*-Me-D-*a*Ile^{13}) and the hydroxy Oγ-3(L-Thr^3) atom.

Intensities were measured to a maximum 2θ value of 120°, because reflections are only detected poorly beyond this limit. Direct-methods trials were extensively carried out using *SHELXS*86 (Sheldrick, 1985), but no clear solution was obtained. The structure was solved by the Shake-and-Bake method using the program *SnB* (Miller *et al.*, 1994; Chang *et al.*, 1996); a single running of the program gave a solution with a default setting and 700 trial structures. The absolute stereochemistry was assigned from chemical methods (Kobayashi, Kanzaki *et al.*, 1994). Successful refinement of the Flack (1983) parameter was not possible because intensities from Friedel pairs were not measured. The difference Fourier map showed 12 peaks, which were interpreted as solvent molecules. At the *N*-Me-Ile^6 residue, the Cδ1 atom was disordered into two parts, with probabilities of 0.78 and 0.22.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SnB*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1064). Services for accessing these data are described at the back of the journal.

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3-[2-(1,3-Dioxolan-2-yl)ethyl]-2-methylbenzoic acid

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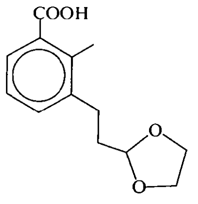
Abstract

The title acid, $C_{13}H_{16}O_4$, crystallized in the centrosymmetric space group *Pbca* with one molecule in the asymmetric unit. In the single type of hydrogen bond, which forms cyclic dimers about centers of symmetry, the carboxylic-H and O atoms are ordered. The $O_{donor}\cdots O_{acceptor}$ distance is 2.639 (3) Å. Each molecule is also linked to two additional molecules by significant C—H···O interactions. The dihedral angle between the best-fit planes of the benzene ring and the carboxyl group is 4.6 (3)°. The dioxolane ring adopts an envelope conformation.

Comment

This report on the title acid, (I), is one of a series on hydrogen bonding in carboxylic acids. Compound (I) crystallized in the centrosymmetric space group *Pbca* with one molecule in the asymmetric unit. The refined molecule and the numbering scheme are shown in Fig. 1. A single hydrogen bond occurs in this structure, and it forms cyclic dimers about centers of symmetry. The carboxyl group H and O atoms are ordered. Geometric details are given in Table 2. Hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) gives the first-level descriptor as $R_2^2(8)$; there are, of course, no higher-level graphs. In addition, there are two significant intermolecular C—H···O interactions for which the H···O distances are less than, or only slightly larger than, the sum of the corresponding Bondi (1964) van der Waals radii; geometrical details for these are given in Table 2. These latter interactions link a central molecule to two additional neighbors. Examples of these interactions are apparent in the packing diagram (Fig. 2).



(I)

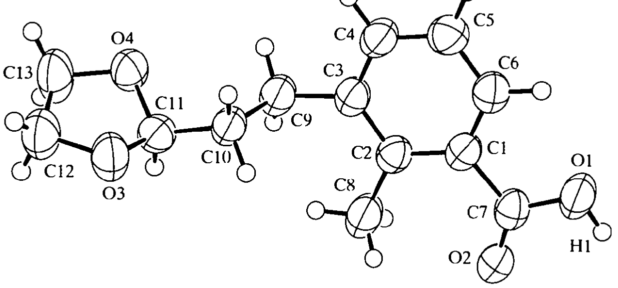


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn for 50% probability for non-H atoms. Spheres of arbitrary small radius depict H atoms.

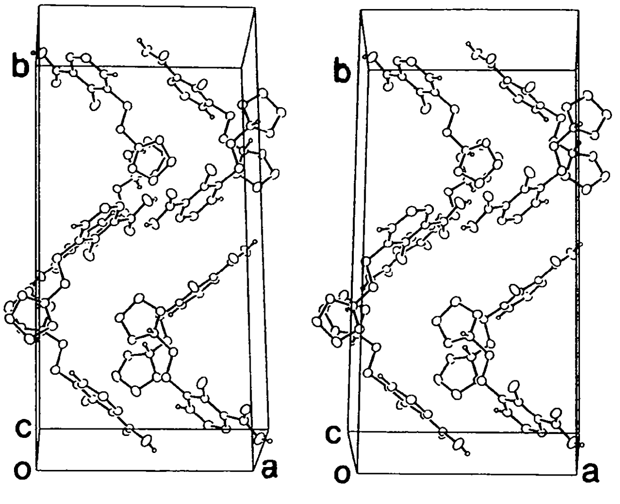


Fig. 2. *ORTEP*II (Johnson, 1976) stereopacking diagram of (I). Displacement ellipsoids are drawn for 20% probability for non-H atoms. Spheres of arbitrary small radius depict H atoms. For clarity, all H atoms, except those cited in Table 2, have been omitted.

The benzene ring in (I) is nearly planar, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.008 (2) Å, while the average deviation is 0.005 (2) Å. The dihedral angle between the benzene plane and that of the carboxyl group is 4.6 (3)°. The dioxolane ring adopts an envelope conformation with C11 as the flap atom. The maximum deviation of any of the envelope body atoms (O3/O4/C12/C13) from the best-fit plane describing them is 0.005 (2) Å, while the dihedral angle between the envelope body and flap (C11/O3/O4) planes is 33.9 (3)°.

For molecular structural comparisons, portions of the structure of 2,3-dimethylbenzoic acid (Smith *et al.*, 1971) and of 2-(di-*p*-anisylmethyl)-1,3-dioxolane (van den Hark *et al.*, 1974) are well suited, respectively, for the substituted benzoic acid portion and the dioxolane ring portion of (I). For the substituted benzoic acid moiety, the r.m.s. deviation within pairs of 11 corresponding distances from Smith *et al.* and this study is 0.017 Å; within pairs of 15 corresponding angles, the r.m.s. deviation is 0.9°. For the dioxolane ring, the r.m.s. deviation within pairs of five corresponding distances from van den Hark *et al.* and this study is 0.013 Å; within pairs of five corresponding angles the r.m.s. deviation is 1.7°. The poorer angular agreement for the dioxolane ring may be related to the fact that, while van den Hark *et al.* find an envelope conformation with a dihedral angle [35.7 (4)°; our calculation] very similar to that in (I), the flap atom is not the same.

Distances and angles of special interest are given in Table 2. All distances and angles fall within normal ranges. Excluding pairs of atoms in hydrogen-bonded groups or involved in C—H···O interactions, the closest intermolecular approaches are between C5 and $C7^{iv}$, and between C13 and H11^{iii}, and are 0.04 Å less than the corresponding Bondi (1964) radius sums [symmetry codes: (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$].

Experimental

The title acid, whose synthesis is described by Chuang (1984), was obtained as a colorless plate from a crystalline sample in Dr D. J. Hart's chemical collection. This was cut to provide the experimental sample.

Crystal data

$C_{13}H_{16}O_4$
$M_r = 236.27$
Orthorhombic
Pbca
$a = 12.148$ (2) Å
$b = 24.682$ (2) Å
$c = 8.021$ (2) Å
$V = 2405.0$ (8) Å^3
$Z = 8$
$D_x = 1.305$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.5$–$16.9°$
$\mu = 0.10$ mm^{-1}
$T = 296$ K
Cut plate
0.42 × 0.27 × 0.15 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
2776 measured reflections
2776 independent reflections
1169 reflections with $I > 2\sigma_I$
$\theta_{max} = 27.55°$

$h = 0 \rightarrow 15$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 10$
6 standard reflections every 150 reflections intensity variation: ±1.8% (average maximum relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.077$
$S = 1.42$
2776 reflections
178 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/\sigma^2(F^2)$, where $\sigma^2 = \sigma^2_{cs} + (0.006I)^2$
$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.322 (3)	O3—C12	1.428 (4)
O2—C7	1.213 (3)	O4—C11	1.406 (3)
O3—C11	1.413 (3)	O4—C13	1.432 (4)
C11—O3—C12	106.4 (2)	O2—C7—C1	125.3 (3)
C11—O4—C13	105.9 (2)	O3—C11—O4	105.4 (2)
C2—C1—C7	122.0 (3)	O3—C11—C10	109.9 (2)
C6—C1—C7	117.4 (3)	O4—C11—C10	112.0 (2)
O1—C7—O2	121.2 (3)	O3—C12—C13	104.7 (3)
O1—C7—C1	113.5 (3)	O4—C13—C12	105.6 (3)
C11—O3—C12—C13	21.0 (4)	C13—O4—C11—O3	33.8 (3)
O3—C12—C13—O4	−0.6 (4)	C12—O3—C11—O4	−34.4 (3)
C11—O4—C13—C12	−20.2 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

No s.u.'s are given for quantities involving H4 since it was fixed.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^i	0.89 (3)	1.76 (3)	2.639 (3)	172 (3)
C11—H11···O4^{ii}	1.07 (2)	2.44 (2)	3.451 (4)	157 (2)
C4—H4···O3^{iii}	0.98	2.77	3.656 (3)	150

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Scan widths were (1.50 + 0.30tanθ)° in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated uniquely space group *Pbca* (No. 61). Since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate initial H-atom positions, and the H atoms were then refined isotropically. Refined C—H distances ranged from 0.88 (3) to 1.07 (2) Å, with a mean value of 0.97 (5) Å. Subsequently, the benzene ring, the methyl group and the methylene group H atoms were made canonical with C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom. The dioxolane-ring and carboxylic-H atoms were refined; the O—H distance is given in Table 2. The extinction coefficient was predicted to be negative in the late stages of refinement, and was thus not included in the model. The maximum positive residual peak is located ~1.4 Å from O2, while the maximum negative peak is located ~1.1 and 1.4 Å from C8 and C2, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1181). Services for accessing these data are described at the back of the journal.

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Capped-porphyrin precursors

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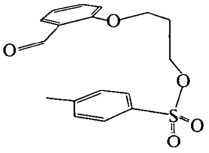
Abstract

In the crystalline state, 2-[3-(tosyloxy)propoxy]benzaldehyde [(I), $C_{17}H_{18}O_5S$] exists in a U-shaped conformation. The benzaldehyde and toluene rings are nearly parallel. Crystals of 2-[2-(tosyloxy)ethoxy]-benzaldehyde occur with two habits. The X-ray structure determinations of these habits reveal an anhydrous form [(II), $C_{16}H_{16}O_5S$] and a hemihydrated form [(III), $C_{16}H_{16}O_5S\cdot0.5H_2O$]. In (III), a water molecule bridges two carbonyl functions [O6···O1 2.87 (1) Å]. 1,2,4,5-Tetrakis{2-[2-(1,3-dioxolan-2-yl)-phenoxy]ethoxy}benzene [(IV), $C_{50}H_{54}O_{16}$] was prepared by protecting the aldehyde function of (II) or (III) with ethylene glycol and reacting the resulting compound with 1,2,4,5-tetrahydroxybenzene. Compound (IV) has $\bar{1}$ symmetry.

Comment

There is considerable interest in sterically hindered porphyrins as models for heme active sites (Momenteau & Reed, 1994). In particular, a great deal of interest has been paid to model complexes with a high degree of discrimination between O_2 and CO binding (Slebodnick & Ibers, 1997). New models continue to be introduced (Jaquinod *et al.*, 1998; Collman *et al.*, 1997). In the course of our work in this area, three different capped-porphyrin precursors have been structurally characterized. One of these precursors occurs in both anhydrous and hemihydrated crystal forms.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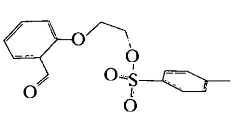
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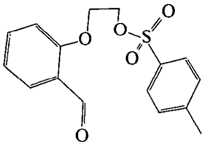
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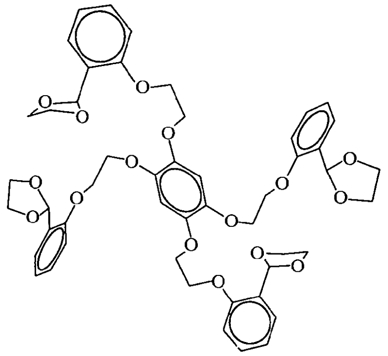
(IV)

Compound (I), 2-[3-(tosyloxy)propoxy]benzaldehyde, is an intermediate in the synthesis of the sterically hindered five-atom-linked capped porphyrin 5,10,15,20-{benzene-1,2,4,5-tetrakis[(2-phenyloxy)propoxy]-2′,2″,2‴,2⁗-tetrayl}porphyrin (Ma *et al.*, 1993). The synthesis involves a condensation proposed by Almog *et al.* (1975), which was more generally elaborated later (Almog *et al.*, 1981). Compound (I) (Fig. 1) contains two symmetry-independent molecules, referred to hereafter as *A* and *B*, related by a pseudo-symmetry center at $x = 0.13$, $y = 0$. For structures with more than one molecule in the asymmetric unit of $Pna2_1$, such symmetry centers are common and they occur predominantly at about $x = \frac{1}{8}$, $y = 0$ (Marsh *et al.*, 1998). In both *A* and *B*, the distance between the two benzene planes is 3.49 (1) Å (measured from the centroid of the toluene to the mean plane of the benzaldehyde), with a dihedral angle of 2.0 (1)° between the planes. The dihedral angle between the two molecules in the asymmetric unit is 3.4 (2)° (measured as the angle between the mean plane of C2–C7 in *A* and the mean plane of C19–C24 in *B*). Equivalent bond lengths between *A* and *B* are nearly identical. Table 1 lists equivalent bond lengths and angles one after another. This appears to be a genuine instance of two nearly identical molecules in the asymmetric unit. The *MISSYM* algorithm (Le Page, 1987, 1988) in the *PLATON* suite of programs (Spek, 1990) revealed no extra symmetry; ex-

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