Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.330 (2)	O5—C11	1.207 (2)
O1—C1	1.448 (2)	C11—C12	1.477 (2)
O2—C2	1.193 (2)	C3—C2	1.515 (3)
O3—C11	1.352 (2)	C3—C4	1.537 (3)
O3—C3	1.424 (2)	C4—C5	1.492 (2)
O4—C4	1.215 (2)		
C2—O1—C1	116.54 (15)	O4—C4—C3	118.3 (2)
C11—O3—C3	114.62 (14)	C5—C4—C3	119.8 (2)
O5—C11—O3	122.2 (2)	C10—C5—C4	118.5 (2)
O5—C11—C12	125.6 (2)	C6—C5—C4	122.4 (2)
O3—C11—C12	112.2 (2)	C17—C12—C11	118.4 (2)
O3—C3—C2	106.60 (14)	C13—C12—C11	121.9 (2)
O3—C3—C4	111.26 (15)	O2—C2—O1	125.9 (2)
C2—C3—C4	109.51 (14)	O2—C2—C3	125.8 (2)
O4—C4—C5	121.9 (2)	O1—C2—C3	108.4 (2)

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Butyne-1,4-diol

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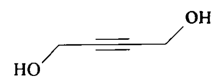
Abstract

A crystallographic twofold axis passes through the central C≡C triple bond of the title molecule, $C_4H_6O_2$. The conformation is markedly non-planar with the two O—C1—C2 planes almost perpendicular to one another. The hydroxyl groups form infinite cooperative hydrogen-bond chains.

Comment

Several crystal structures have been published where 2-butyne-1,4-diol, (1), is complexed by organic hosts or is used as a ligand in organometallic compounds (see below). The crystal structure of (1) itself has not been reported as yet and is therefore presented here.



(1)

The conformation of (1) is non-planar with an O—C1···C1′—O1′ torsion angle of −94.7 (3)°, *i.e.* the two O—C1—C2 planes are roughly perpendicular to one another. The OH group is *gauche* with respect to the C1—C2 bond [C2—C1—O—H −77 (2)°] (Fig. 1).

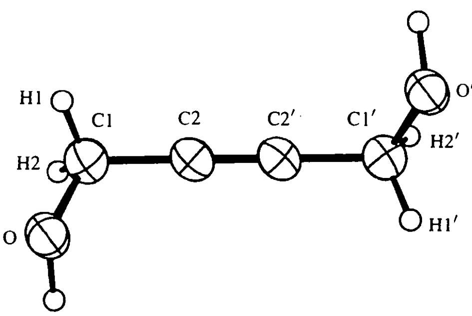


Fig. 1. The molecular structure and atom labelling of the title compound. Projection is along the twofold axis intersecting the C≡C triple bond. Displacement ellipsoids are drawn at the 30% probability level.

The hydroxyl groups form infinite chains of cooperative O—H···O—H···O hydrogen bonds, with O···O($x-\frac{1}{2}$, $y-\frac{1}{4}$, $-z+\frac{1}{4}$) separations of 2.681 (2) Å (Fig. 2). Based on a normalized H-atom position (O—H 0.98 Å), the H···O separation is 1.70 Å, the O—H···O angle 174° and the H···O—C angle 117° [experimental values: O—H 1.04 (3), H···O 1.65 (3) Å, O—H···O 174 (3) and H···O—C 116.6 (9)°]. The hydrogen bond chains at $z/c = \frac{1}{8}$ and $z/c = \frac{3}{8}$ run in the [$1\bar{1}0$] and [$\bar{1}10$] directions, respectively, *i.e.* in the directions of the different diagonals of the *ab* plane. The apparently cyclic motifs in Fig. 2 are, therefore, in fact, screw axes; this is indicated by broken hydrogen bonds in the chain at $z/c = \frac{3}{8}$. Note that the projection of Fig. 2 is along the polar axis of the crystal structure; in this projection, all O-atom lone pairs point away from the viewer, whereas all C—H2 bonds point towards the viewer. On the macroscopic level, this must lead to different polarities and growth characteristics of the (100) and ($\bar{1}00$)

crystal faces (compare with Weissbuch, Popovitz-Biro, Lahav & Leiserowitz, 1995).

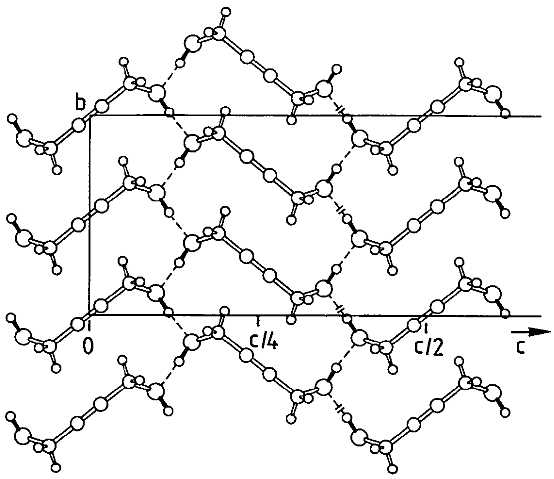


Fig. 2. Crystal-packing scheme and hydrogen-bonding pattern. The hydrogen-bond chains at $z/c = \frac{1}{8}$ and $z/c = \frac{3}{8}$ are not parallel, but run along the [$\bar{1}\bar{1}0$] and [$\bar{1}10$] directions, respectively; this is indicated by broken bonds in the chain at $z/c = \frac{3}{8}$ (see text).

For complexes with organic host molecules, different conformations of (1) have been observed. In the crystal structure of the inclusion complex (1)–β-cyclodextrin, compound (1) adopts an almost planar shape, with an O—C1···C4—O torsion angle of 163° (Steiner & Saenger, 1995), and in the complex with diaza-18-crown-6, it is found to be exactly planar, with an O—C1···C4—O torsion angle of 180° (Watson, Vögtle & Müller, 1988). In the inclusion complex (1)–α-cyclodextrin, a similar conformation as that shown in Fig. 1 is observed, with an O—C1···C4—O torsion angle of −83° (Steiner & Saenger, 1996). When acting as a ligand in organometallic compounds, with the metal···C≡C interaction, the covalent geometry of (1) becomes heavily distorted with an elongated triple bond and bent C—C—C angles (see, for example, Baert, Guelzim & Coppens, 1984; Rosenthal *et al.*, 1991).

Experimental

The title compound, (1), is commercially available (Sigma). It was recrystallized by slow evaporation of MeOH solutions. Crystals tend to exhibit extremely high mosaicity, so that several specimens had to be tested until a suitable one was found.

Crystal data

$C_4H_6O_2$
$M_r = 86.09$
Orthorhombic
F2dd
$a = 4.3326 (12)$ Å
$b = 7.966 (3)$ Å
$c = 26.889 (17)$ Å
$V = 928.0 (7)$ Å^3
$Z = 8$
$D_x = 1.232$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54176$ Å
Cell parameters from 25 reflections
$\theta = 11.6–26.1°$
$\mu = 0.838$ mm^{-1}
$T = 293 (2)$ K
Plate
0.65 × 0.55 × 0.04 mm
Pale yellow

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.938$, $T_{max} = 0.998$
394 measured reflections
343 independent reflections

325 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0206$
$\theta_{max} = 59.99°$
$h = -4 \rightarrow 4$
$k = -8 \rightarrow 0$
$l = -30 \rightarrow 4$
3 standard reflections
frequency: 30 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0321$
$wR(F^2) = 0.1019$
$S = 1.074$
337 reflections
40 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.2401P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.082$ e Å^{-3}
$\Delta\rho_{min} = -0.089$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.1 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	0.6953 (4)	0.1127 (2)	0.09839 (5)	0.0692 (6)
C1	0.4905 (5)	0.1620 (3)	0.05943 (7)	0.0678 (6)
C2	0.4997 (4)	0.0474 (2)	0.01733 (5)	0.0594 (5)

Table 2. *Selected geometric parameters (Å, °)*

O—C1	1.428 (3)	C2—C2^i	1.200 (4)
C1—C2	1.454 (3)		
O—C1—C2	112.4 (2)	C2^i—C2—C1	178.41 (12)
O^i—C1^i···C1—O	−94.7 (3)	C2—C1—O—H(O)	−77 (2)

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

Due to broad reflection profiles, an ω-scan mode was used with a 1.5° scan range.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octakis(3,5-dimethylphenylthio)-naphthalene

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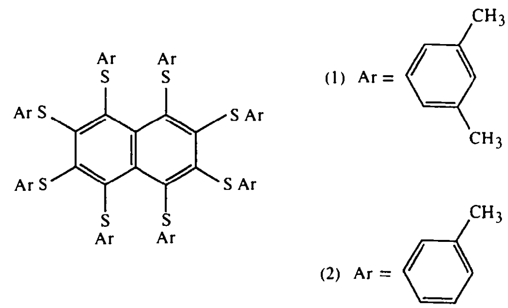
Abstract

The title compound, $C_{74}H_{72}S_8$, possesses a conformation which is unique for a per(arylthio)naphthalene in that the side chains at one of the *peri* positions adopt a *syn* arrangement, whereas all molecules of this class studied previously uniformly exhibit *anti* arrangements at the *peri* positions. This asymmetric conformation is of the previously uncategorized *abbaabab* type, where *a* and *b* denote side chains projecting, respectively, above and below the mean plane of the naphthalene core. A significant non-planarity of the naphthalene core is imparted by a substantial twist around its central carbon–carbon bond characterized by the symmetry-independent intra-ring torsion angles.

Comment

In the course of a study of spider hosts (Downing & MacNicol, 1996), a conformationally mobile class of molecule (Barbour, Freer & MacNicol, 1983; MacNicol, 1984; MacNicol, Mallinson & Robertson, 1985; Freer, MacNicol, Mallinson & Robertson, 1989), we prepared octakis(3,5-dimethylphenylthio)naphthalene, (1), which corresponds to the formal introduction of a second *meta*-methyl substituent to the side chain of octakis(*m*-tolylthio)naphthalene, (2). The introduction of this second methyl group precludes adoption of a conformation directly analogous to that of (2), owing to prohibitive transannular interactions.



In contrast to the exactly D_2-symmetric conformation of compound (2) (MacNicol, Mallinson & Robertson, 1985), the molecule of (1), which occupies a general position in the unsolvated triclinic crystal, possesses a highly asymmetric conformation (Fig. 1). A conformational feature of compound (1), unique for a per(arylthio)-substituted naphthalene, is that two per related side chains, linked to the naphthalene core by S4 and S5, possess a *syn* relationship. As a consequence, the *abbaabab* conformation observed, where *a* and *b* denote side chains projecting, respectively, above and below the mean plane of the naphthalene core, corresponds to none of the 14 previously identified side-chain orientational distributions for spider host molecules (MacNicol, Mallinson & Robertson, 1985). The naphthalene core of compound (1) is markedly non-planar, the largest displacements from its mean plane being −0.29 (1), 0.25 (1), −0.30 (1) and 0.23 (1) Å for atoms C1, C3, C5 and C8, respectively. Although the naphthalene core lacks symmetry, one of the six-membered rings (but not the substituent arrangement) is approximately C_s symmetric, with the approximate mirror plane passing