Crystal data

$C_{18}H_{20}N_6O_2S_2 \cdot 2C_2H_6OS$
M_r = 572.78
Monoclinic
$C2/c$
a = 17.432 (4) Å
b = 17.339 (4) Å
c = 11.538 (4) Å
β = 124.49 (2)°
V = 2874.3 (13) Å^3
Z = 4
D_x = 1.324 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 4.76–12.61°
μ = 0.37 mm^{-1}
T = 293 (2) K
Block
0.42 × 0.36 × 0.32 mm
Yellow

Data collection

Siemens $P4$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3953 measured reflections
2420 independent reflections
1920 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

θ_{max} = 25.03°
$h = -14 \rightarrow 20$
$k = -15 \rightarrow 20$
$l = -13 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.111
S = 1.024
2417 reflections
182 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 1.7286P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C1	1.689 (2)	N3—C2	1.272 (3)
N2—C1	1.353 (3)	C1—N1	1.315 (3)
N2—N3	1.373 (2)	C3—C2	1.463 (3)
C1—N2—N3	118.3 (2)	N1—C1—S1	122.6 (2)
C2—N3—N2	119.0 (2)	N2—C1—S1	120.6 (2)
N1—C1—N2	116.8 (2)	N3—C2—C3	118.9 (2)

The H atoms of the main molecule were located from difference maps and their positions were refined isotropically, with $U_{iso} = 1.2U_{eq}$ of the parent atoms. Dimethyl sulfoxide H atoms were placed in calculated positions, with C—H = 0.96 Å and $U_{iso} = 1.5U_{eq}$ of the parent C atoms. The disorder of the dimethyl sulfoxide molecule was modelled with both S and O atoms occupying two sites having occupancy factors of 0.708 (2) and 0.292 (2). The methyl H atoms of dimethyl sulfoxide were likewise placed in two sets of sites with these occupancy factors.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1153). Services for accessing these data are described at the back of the journal.

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Hydrogen bonding and C—H···O interactions in 2,2′-dihydroxy-5,5′-dimethoxybiphenyl-3,3′-dicarbaldehyde

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Abstract

The title dialdehyde, $C_{16}H_{14}O_6$, crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule in the asymmetric unit. In this structure, one intermolecular and two intramolecular hydrogen bonds occur; the $O_D \cdots O_A$ distances are 3.030 (2), 2.626 (2) and 2.662 (2) Å. In addition, ten significant C—H···O interactions have C···O distances ranging from 3.342 (2) to 3.741 (3) Å and C—H···O angles ranging from 117 to 167°. The 11 intermolecular interactions link a molecule directly to eight neighbors and form a richly three-dimensional network. The dihedral angle between the best-fit planes of the benzene rings within a molecule (biphenyl twist angle) is 79.00 (8)°. The dihedral angles

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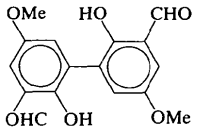
between the carboxaldehyde-group planes and the best-fit planes of the rings to which they are attached are 4.7 (10) and 2.6 (10)°.

Comment

This report on the title dialdehyde, (I), is one of a series on hydrogen bonding in organic solids. It follows



(I)

our reports on other biphenyls with hydrogen-bonding substituents, for example, 2-hydroxybiphenyl-3-carboxylic acid (Dobson & Gerkin, 1996), 6,6′-dimethylbiphenyl-2,2′-dicarboxylic acid (Gerkin, 1998) and 6,6′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl-2,2′-dimethanol (Dobson & Gerkin, 1999) [hereafter identified as (II), (III) and (IV), respectively]. Compound (I) crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule in the asymmetric unit. The refined molecule and the numbering scheme are shown in Fig. 1. Two intramolecular hydrogen bonds are formed in which the hydroxy groups are donors and the aldehyde O atoms are acceptors, and there is a single intermolecular O—H···O hydrogen bond in this structure. The H and O atoms involved in these bonds are ordered; geometric details are given in Table 2. As anticipated on the basis of the greater number of potential hydrogen-bond acceptors than of potential donors, C—H···O interactions are prominent. Ten C—H···O interactions have parameter values falling well within the criteria of Taylor & Kennard (1982) for significantly attractive interactions; geometric details for these are also given in Table 2. Altogether these interactions link a molecule directly to eight neighbors. The results of graph-set analysis (Bernstein *et al.*, 1995) of these 13 interactions, labeled *a–m* for this purpose in the order of their appearance in Table 2, are given in Table 3. Among these 91 patterns, 45 are rings and 42 are chains. The chains propagate variously along [100], [010], [001], [110], [1$\bar{1}$0], [011], [01$\bar{1}$], [10$\bar{1}$], [11$\bar{1}$] and [1$\bar{1}\bar{1}$], generating a richly three-dimensional network. Even if the inclusion of C—H···O interactions is restricted to those having H···O distances less than the sum of the corresponding Bondi (1964) van der Waals radii (eliminating entries *h–m* in Table 2), chains of only types [1$\bar{1}$0] and [1$\bar{1}\bar{1}$] no longer appear and the network remains strongly three-dimensional.

The benzene rings in (I) are nearly planar, the maximum deviation of any of their atoms from the best-fit planes describing them being 0.014 (2) and 0.007 (2) Å, while the average deviations are 0.008 (2)

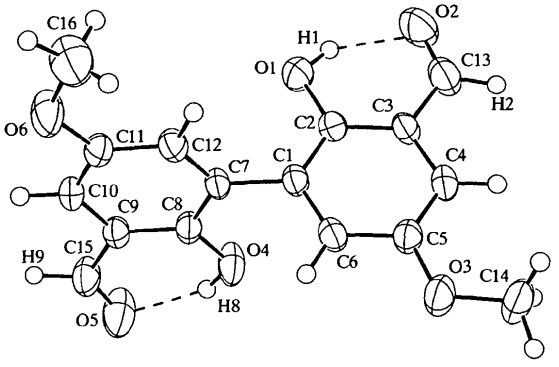


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) showing the numbering scheme. Displacement ellipsoids are drawn for 50% probability for non-H atoms; spheres of arbitrary small radii depict H atoms. The two intramolecular hydrogen bonds are depicted by dashed lines.

and 0.005 (2) Å. These values are quite similar to the corresponding maximum and average deviations found in a comparably extensively substituted biphenyl, (IV) above: 0.011 (2) and 0.014 (2) Å, and 0.007 (3) and 0.008 (4) Å, respectively. The dihedral angle between the benzene-ring planes within a molecule (biphenyl twist angle) in (I) is 79.00 (8)°. This value may be compared with the corresponding values for the 2,2′,6,6′-substituted biphenyls cited above: 84.9 (1)° in (III) and 87.3 (1)° in (IV). In contrast, in (II), which has only a single 2-substituent, this angle is 40.52 (8)°. Twist angles in biphenyls unsubstituted at the positions *ortho* to the ring–ring bond have been discussed by Brock & Minton (1989). In (I), the dihedral angles between the planes of the carboxaldehyde groups and the planes of the rings to which they are attached are 4.7 (10) and 2.6 (10)°.

The nearly planar arrangement of all the non-H atoms in each half of the title molecule is apparent in the packing diagram (Fig. 2). The diagram also makes clear that the principal difference in the two halves of the molecule is in the relative orientations of the C—O bonds in the methoxyl groups.

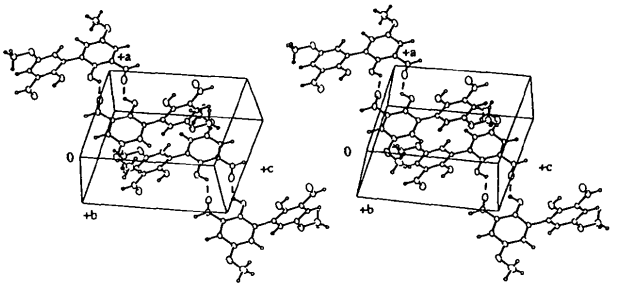


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 20% probability for non-H atoms; spheres of arbitrary small radii depict H atoms. Single dashes depict the sole conventional intermolecular hydrogen bond. The $R_2^2(12)$ pattern is apparent.

Distances and angles of special interest are given in Table 1. 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 C2 and H14C^{ii} [symmetry code: (ii) $-x$, $1-y$, $1-z$], and are 0.11 Å less than the corresponding Bondi radius sums.

Experimental

The title dialdehyde, whose synthesis is described by Hart & Mannino (1996), was obtained from a sample in Dr D. J. Hart's chemical collection as a yellow powder. From an ether solution of the powder, clear pale-golden plates were formed upon slow evaporation at room temperature. One of these plates was cut to provide the experimental sample.

Crystal data

$C_{16}H_{14}O_6$
M_r = 302.28
Triclinic
$P\overline{1}$
a = 7.691 (1) Å
b = 9.1327 (8) Å
c = 10.982 (1) Å
α = 75.815 (8)°
β = 71.109 (8)°
γ = 89.304 (10)°
V = 705.7 (1) Å^3
Z = 2
D_x = 1.422 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 16.9–17.5°
μ = 0.110 mm^{-1}
T = 296 K
Cut plate
0.38 × 0.27 × 0.15 mm
Clear, pale-golden

Data collection

AFC-5S diffractometer
ω scans
Absorption correction: none
3499 measured reflections
3255 independent reflections
2209 reflections with $I > 2\sigma I$
R_{int} = 0.013

θ_{max} = 27.56°
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 14$
6 standard reflections every 150 reflections intensity decay: 1.1%

Refinement

Refinement on F^2
$R(F)$ = 0.047
$wR(F^2)$ = 0.080
S = 1.98
3255 reflections
216 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2_{cs} + (0.010I)^2]$
$(\Delta/\sigma)_{max}$ = 0.0003

$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 2.5 (3) × 10^{-6}
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C2	1.360 (2)	O4—C8	1.357 (2)
O2—C13	1.224 (2)	O5—C15	1.218 (2)
O3—C5	1.369 (2)	O6—C11	1.374 (2)
O3—C14	1.423 (2)	O6—C16	1.395 (2)
C5—O3—C14	117.7 (1)	O4—C8—C7	118.5 (1)
C11—O6—C16	119.0 (1)	O4—C8—C9	121.6 (1)
O1—C2—C1	119.3 (1)	O6—C11—C10	115.9 (1)
O1—C2—C3	121.0 (1)	O6—C11—C12	124.5 (2)
O3—C5—C4	125.3 (1)	O2—C13—C3	125.4 (2)
O3—C5—C6	115.3 (1)	O5—C15—C9	125.0 (2)
C2—C1—C7—C8	−101.3 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.88 (2)	1.82 (2)	2.626 (2)	153 (2)
O4—H8···O5	0.90 (2)	1.88 (2)	2.662 (2)	144 (2)
O4—H8···O5^{i}	0.90 (2)	2.43 (2)	3.030 (2)	124 (2)
C4—H4···O4^{ii}	0.98	2.51	3.426 (2)	155
C6—H6···O3^{iii}	0.98	2.49	3.454 (2)	167
C15—H9···O1^{iv}	1.01 (2)	2.46 (2)	3.342 (2)	146 (1)
C12—H12···O2^{v}	0.98	2.57	3.478 (2)	154
C10—H10···O1^{iv}	0.98	2.75	3.530 (2)	138
C14—H14C···O4^{ii}	0.98	2.78	3.536 (2)	134
C14—H14C···O1^{ii}	0.98	2.81	3.556 (2)	133
C13—H2···O5^{vi}	1.00 (2)	2.89 (2)	3.615 (2)	130 (1)
C16—H16A···O5^{iv}	0.98	2.91	3.741 (3)	144
C16—H16C···O3^{vii}	0.98	2.96	3.519 (2)	117

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $-1-x, 1-y, 1-z$; (iv) $-x, 2-y, -z$; (v) $-x, 2-y, 1-z$; (vi) $x, y, 1+z$; (vii) $-1-x, 2-y, 1-z$.

Table 3. *Basic first- and second-level graph-set descriptors involving interactions designated a–m in the order given in Table 2*

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*
a	$S(6)$	$D^2_2(10)$	$R^4_4(36)[S(6)]$	$R^4_4(24)[S(6)]$	$R^4_4(28)[S(6)]$	$R^4_4(24)[S(6)]$	$R^2_4(16)$	$R^4_4(24)[S(6)]$	$R^4_4(30)[S(6)]$	$R^4_4(20)[S(6)]$	$C^2_2(12)$	$R^4_4(40)[S(6)]$	$R^4_4(32)[S(6)]$
b		$S(6)$	$R^2_2(4)$	$R^4_4(24)[S(6)]$	$D^3_3(17)[S(6)R^2_2(8)]$	$R^4_4(20)$	$R^4_4(32)[S(6)]$	$R^4_4(24)[S(6)]$	$R^4_4(26)[S(6)]$	$R^4_4(36)[S(6)]$	$C^1_2(10)$	$R^4_4(20)$	$R^4_4(32)[S(6)]$
c			$R^2_2(12)$	$C^2_2(12)$	$C^2_2(16)$	$C^2_2(10)$	$C^2_2(16)$	$C^2_2(12)$	$C^2_2(13)[C(6)]$	$C^2_2(18)$	$R^4_4(20)$	$C^1_2(10)$	$C^2_2(16)$
d				$R^2_2(16)$	$C^2_2(10)$	$C^2_2(10)$	$C^2_2(10)$	$C^2_2(10)$	$R^1_2(7)$	$R^2_2(12)$	$R^4_4(20)$	$C^3_2(16)$	$C^2_2(12)$
e					$R^2_2(8)$	$C^2_2(14)$	$C^2_2(12)$	$C^2_2(14)$	$C^2_2(9)$	$C^2_2(8)$	$R^4_4(28)$	$C^2_2(18)$	$C^1_2(10)$
f						$R^2_2(16)$	$C^2_2(12)$	$R^1_2(6)$	$C^2_2(13)$	$C^1_2(12)$	$R^4_4(16)$	$R^3_2(12)$	$C^2_2(14)$
g							$R^2_2(16)$	$C^2_2(10)$	$C^2_2(13)$	$C^2_2(14)$	$R^4_4(20)$	$C^2_2(16)$	$C^2_2(12)$
h								$R^2_2(16)$	$C^2_2(13)$	$C^1_2(12)$	$R^4_4(20)$	$R^3_2(14)$	$C^2_2(13)$
i									$R^2_2(18)$	$R^1_1(7)$	$R^4_4(26)$	$C^2_2(17)$	$C^2_2(11)$
j										$R^2_2(16)$	$R^4_4(32)$	$C^2_2(18)$	$C^2_2(12)$
k											$C(10)$	$R^4_4(24)$	$R^4_4(28)$
l												$R^2_2(16)$	$C^2_2(12)$
m													$R^2_2(20)$

Scan widths were (1.60 + 0.35tanθ)° in ω, with a background/scan time-ratio of 0.5. A linear decay correction was applied. The data were corrected for Lorentz and polarization effects. The Laue group assignment and centrosymmetric intensity statistics indicated space group $P\bar{1}$ (No. 2). 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 ring and methyl C—H distances ranged from 0.94 (2) to 0.99 (2) Å, with a mean value of 0.97 (2) Å. Subsequently, the ring and methyl-group H atoms were made canonical with C—H = 0.98 Å and U_{iso} = 1.2U_{eq} of the attached C atom. The refined hydroxyl group O—H distances and aldehyde group C—H distances are given in Table 2. An extinction coefficient was introduced in the late stages of refinement; the maximum effect of extinction is 5.44% of F_o for 211. The maximum positive residual peak is located ~0.8 Å from C4 and C5, and the maximum negative peak is located ~0.8 Å from C4.

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: FR1197). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1179–1181

1,2:3,4:5,6-Tri-*O*-isopropylidene-D-mannitol

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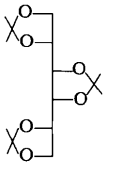
(Received 11 August 1998; accepted 15 February 1999)

Abstract

In the title compound, $C_{15}H_{26}O_6$, the three five-membered rings adopt envelope conformations, with the three C atoms in the flap positions at distances of 0.500 (3), −0.424 (2) and −0.490 (3) Å from the least-squares plane of the remaining four atoms in the five-membered rings.

Comment

The title compound, triacetone mannitol, (I), is one of a series of acetone derivates of mannitol, namely, monoacetone mannitol, diacetone mannitol and triacetone mannitol (Wiggins, 1946; Schmid *et al.*, 1991). Its crystal structure has not previously been reported.



(I)

The molecule has three five-membered rings, each of which has two O atoms and two ether bonds. The C13/C12/O1/C11/O2 and C32/C33/O6/C31/O5 rings are on one side of the C13—C12—C22—C23—C32—C33 backbone, and the C23/C22/O3/C21/O4 ring is on the other side.

Selected bond distances and angles are given in Table 1. The O—C bond distances are within a narrow range [1.417 (4)–1.429 (3) Å], averaging 1.423 (4) Å. The three five-membered rings adopt envelope conformations, with C13, C23 and C33 occupying the flap positions at distances of 0.500 (3), −0.424 (2) and