Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6403 measured reflections
5766 independent reflections (including Friedel pairs)
5468 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 68.0°$
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.161$
$S = 0.990$
5745 reflections
391 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.136P)^2 + 0.142P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.284$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.270$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (2)

The methyl C24 atom of the ethoxy group attached to C8 of (2) had only partial site occupancy which refined to a value of 0.35 (2). The H atoms were included at geometrically idealized positions, with C—H and O—H distances of 0.95 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1415). Services for accessing these data are described at the back of the journal.

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Hydrogen-Bonding Patterns in a Centrosymmetric Structure with $Z' = 2$: α,α',α''-Trimethyl-1,3,5-benzenetrimethanol

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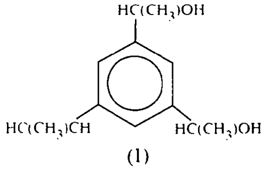
Abstract

The title molecule, $C_{12}H_{18}O_3$, crystallized in the centrosymmetric space group $P2_1/c$ with two molecules in the asymmetric unit. Each molecule donates three, and accepts three, hydrogen bonds. The $O_d\cdots O_a$ distances in these bonds range from 2.687 (3) to 2.787 (2) Å. The hydroxyl H atoms are ordered. A three-dimensional network of hydrogen-bond chains is formed which is 'decorated' with sets of cyclic hydrogen bonds and numerous finite hydrogen-bond patterns. This structure shows both similarities and differences with respect to the structures of the related molecules benzene-1,3,5-triacetic acid and benzene-1,3,5-trimethanol.

Comment

This report on α,α',α''-trimethyl-1,3,5-benzenetrimethanol, (I), is one of a series on hydrogen bonding in aromatic organic solids and follows a study of the related substance benzene-1,3,5-triacetic acid (hereafter BTA) which was shown to have extensive interwoven hydrogen-bonding networks (Fitzgerald & Gerkin, 1997). Structural comparisons with the closely related substance benzene-1,3,5-trimethanol (hereafter BTM) (Bell *et al.*, 1996) are of particular interest.



(I)

The title substance crystallized in the centrosymmetric space group $P2_1/c$ with two molecules in the asymmetric unit. The refined molecules, designated *A* and *B*, and the numbering scheme are shown in Fig. 1. Each of the molecules contains three chiral groups: the groups at C7*A* and C7*B* have the *R* configuration, while those at C9*A*, C11*A*, C9*B* and C11*B* have the *S* configuration in the molecules specified by the atom list.

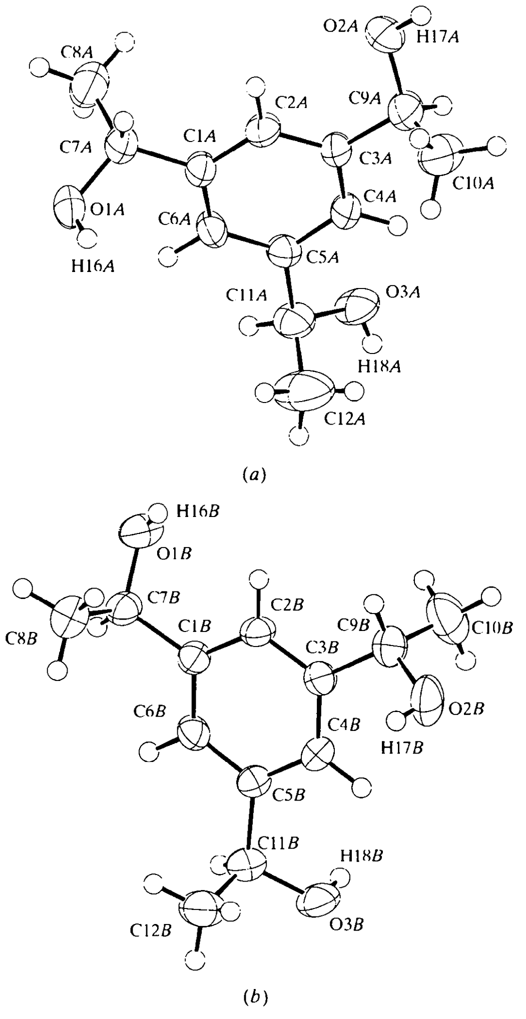


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of α,α′,α″-trimethyl-1,3,5-benzenetrimethanol: (*a*) the *A* molecule; (*b*) the *B* molecule, showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for non-H atoms and H atoms are shown as small spheres. The disordered methyl C atom, C51*A*, has been omitted for clarity.

In the title structure, each hydroxyl group H atom is ordered and each participates in one hydrogen bond. Each hydroxyl O atom participates in two hydrogen bonds, once as a donor and once as an acceptor. The geometric details of these bonds are given in Table 2. Each *A* molecule is linked by its six hydrogen bonds to two neighboring *A* molecules and to four neighboring *B* molecules; each *B* molecule is linked by its six hydrogen bonds to four neighboring *A* molecules but to only one neighboring *B* molecule (with which it forms a cyclic dimer). The hydrogen-bonding neighbors of an *A* and a *B* molecule are shown in Figs. 2(*a*) and 2(*b*), respectively; hydrogen bonds are designated (*a*)–(*f*) in the order given in Table 2. The relative simplicity of this description belies the extensive and varied hydrogen-bonding patterns which develop, which are compactly described in terms of hydrogen-bond graph sets (Bernstein *et al.*, 1995). The graph-set descriptors for the first-level and basic second-level graphs are given in Table 3, which makes apparent the

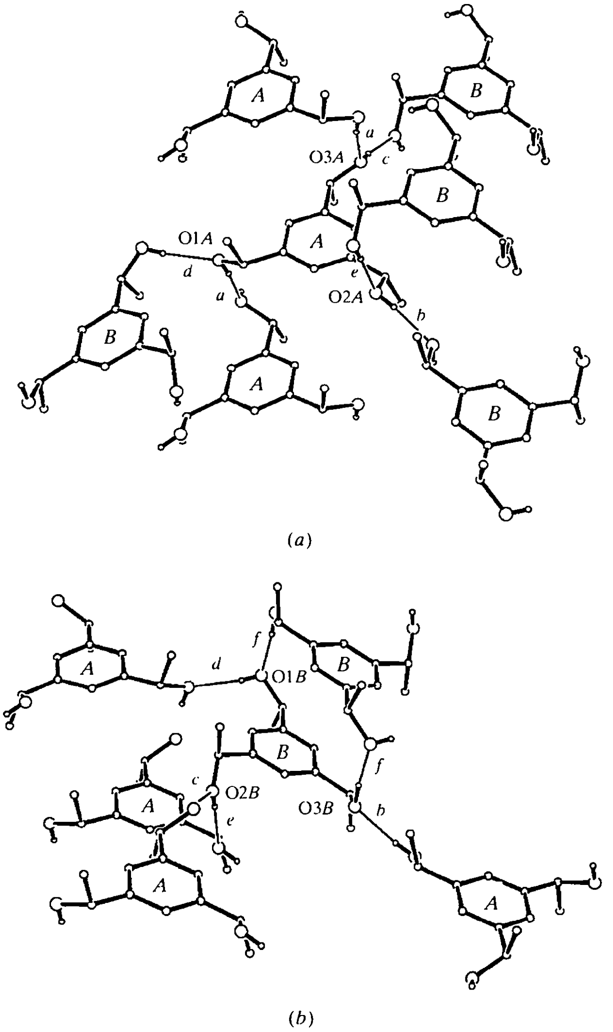


Fig. 2. *ORTEP*II (Johnson, 1976) drawings of (*a*) a central *A* molecule and its six hydrogen-bonded neighbors, and (*b*) a central *B* molecule and its five hydrogen-bonded neighbors. The hydrogen bonds are depicted by the lighter lines and are labeled (*a*)–(*f*) in the order in which they appear in Table 2. For clarity, all H atoms except those involved in hydrogen bonding have been omitted and all atoms are arbitrarily small but with O atoms drawn larger for emphasis. Both views are from nearly along the *a* axis with the *b* axis horizontal.

rich variety of chains, rings and finite patterns formed by these hydrogen bonds. The hydrogen-bond chains, in their order of appearance in Table 3, propagate in the following directions: **c**, **b**, $[20\bar{1}]$, **a** and **c**. Clearly these chains constitute a three-dimensional network which is 'decorated' with the three types of hydrogen-bonding rings and the numerous finite patterns. The abundance of $D[R]$ second-level graph-set descriptors is as anticipated for centrosymmetric structures with $Z' > 1$ (Bernstein *et al.*, 1995; p. 1568).

The benzene core C—C distances show no significant variation, ranging from 1.383 (3) to 1.395 (3) Å for molecule *A* and from 1.378 (3) to 1.393 (3) Å for *B*, with an average value of 1.387 (4) Å for *A* and 1.388 (5) Å for *B*; these values are in good agreement with corresponding values for BTA and BTM. The core interior angles alternate systematically, the mean value at the substituted C atoms being 2.4° less than that at the unsubstituted C atoms; this result is in very good agreement with results for BTA and BTM, for which the corresponding values are 3.4 and 2.7°, respectively. However, whereas for BTM, the C—O bond lengths are stated by those authors to vary widely (a range of 43×10^{-3} Å), they are quite uniform in the present structure, the six values lying in the interval from 1.416 (3) to 1.426 (3) Å, with a mean value of 1.421 (3) Å.

The benzene cores in (I) are almost planar: the maximum deviation of a core atom from the best-fit plane describing the *A* core is 0.004 (2) Å, while for the *B* core, it is 0.009 (2) Å; the average deviation is 0.002 (1) Å for the *A* core and 0.005 (3) Å for the *B* core. These values are quite similar to the corresponding values for BTA and BTM. Choosing the ring C atom to which a substituent is attached, the central C atom of that substituent and the O atom of that substituent to define a substituent plane, we find the dihedral angles between these substituent planes and the benzene core planes to be 30.9 (2), 26.8 (3) and 35.9 (2)° for the *A* molecules, and 34.7 (2), 35.8 (3) and 22.6 (2)° for the *B* molecules in the title structure. Clearly, pseudo-threefold symmetry is precluded by these values which are, however, much more nearly uniform than those for the corresponding planes in BTA [84.3 (1), 89.8 (2) and 58.0 (2)°] or in BTM [6.1, 68.5, and 69.8° (our calculation)]. The dihedral angle between the core planes of the two non-parallel sets of *A* molecules is 10.5 (1)°, while for the *B* molecules, it is 29.0 (1)°. The dihedral angles between the core planes of the *A* molecules and the core planes of the *B* molecules are 9.2 (1) and 19.8 (1)°.

Distances and angles of special interest in the title molecule are given in Table 1.

The closest intermolecular approaches, excluding pairs of atoms within directly hydrogen-bonded groups, are between C11*A* and H16*A*$^{\text{iv}}$ [symmetry code: (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$], and are 0.08 Å less than the corresponding Bondi (1964) van der Waals radius sum.

Experimental

α,α',α''-Trimethyl-1,3,5-benzenetrimethanol was obtained as small colorless crystals from the chemical collection of Dr M. S. Newman. These crystals were dissolved in ethanol and the resulting solution evaporated at room temperature to produce X-ray quality crystals, one of which was cut to provide the experimental sample. A preparation of the title compound is described by Wallace *et al.* (1992).

Crystal data

$C_{12}H_{18}O_3$
$M_r = 210.27$
Monoclinic
$P2_1/c$
$a = 9.386\ (2)$ Å
$b = 27.500\ (1)$ Å
$c = 10.316\ (2)$ Å
$\beta = 115.51\ (2)°$
$V = 2403.2\ (9)$ Å^3
$Z = 8$
$D_x = 1.162$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.6$–$17.1°$
$\mu = 0.082$ mm^{-1}
$T = 296$ K
Cut plate
0.35 × 0.35 × 0.19 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
6027 measured reflections
5697 independent reflections
3119 reflections with $I > 2\sigma_I$
$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.56°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 35$
$l = -13 \rightarrow 12$
6 standard reflections every 150 reflections intensity variation: ±2.2% (average maximum relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.071$
$wR(F^2) = 0.083$
$S = 2.11$
5563 reflections
300 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ 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*A*—C7*A*	1.419 (3)	O1*B*—C7*B*	1.426 (3)
O2*A*—C9*A*	1.423 (3)	O2*B*—C9*B*	1.416 (3)
O3*A*—C11*A*	1.420 (3)	O3*B*—C11*B*	1.422 (3)
C7*A*—C8*A*	1.508 (3)	C7*B*—C8*B*	1.505 (3)
C9*A*—C10*A*	1.447 (4)	C9*B*—C10*B*	1.493 (4)
C11*A*—C12*A*	1.478 (4)	C11*B*—C12*B*	1.466 (3)
C2*A*—C1*A*—C6*A*	118.8 (2)	C2*B*—C1*B*—C6*B*	118.8 (2)
C1*A*—C2*A*—C3*A*	121.4 (2)	C1*B*—C2*B*—C3*B*	120.8 (2)
C2*A*—C3*A*—C4*A*	118.6 (2)	C2*B*—C3*B*—C4*B*	119.1 (2)
C3*A*—C4*A*—C5*A*	121.0 (2)	C3*B*—C4*B*—C5*B*	120.6 (2)
C4*A*—C5*A*—C6*A*	119.0 (2)	C4*B*—C5*B*—C6*B*	119.2 (2)
C1*A*—C6*A*—C5*A*	121.3 (2)	C1*B*—C6*B*—C5*B*	121.4 (2)
O1*A*—C7*A*—C1*A*	112.2 (2)	O1*B*—C7*B*—C1*B*	113.1 (2)
O1*A*—C7*A*—C8*A*	107.5 (2)	O1*B*—C7*B*—C8*B*	110.9 (2)
O2*A*—C9*A*—C3*A*	108.8 (2)	O2*B*—C9*B*—C3*B*	112.8 (2)
O2*A*—C9*A*—C10*A*	114.1 (3)	O2*B*—C9*B*—C10*B*	107.4 (2)
O3*A*—C11*A*—C5*A*	108.2 (2)	O3*B*—C11*B*—C5*B*	112.6 (2)
O3*A*—C11*A*—C12*A*	113.0 (2)	O3*B*—C11*B*—C12*B*	108.5 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H16*A*···O3*A*^{i}	0.86 (3)	1.87 (3)	2.726 (3)	171 (3)
O2*A*—H17*A*···O3*B*^{ii}	0.83 (2)	1.96 (2)	2.787 (2)	173 (3)
O3*A*—H18*A*···O2*B*^{iii}	0.74 (2)	1.96 (2)	2.697 (3)	170 (3)
O1*B*—H16*B*···O1*A*^{iv}	0.77 (2)	2.00 (2)	2.764 (3)	171 (3)
O2*B*—H17*B*···O2*A*	0.80 (2)	1.94 (2)	2.737 (3)	175 (3)
O3*B*—H18*B*···O1*B*^{v}	0.89 (2)	1.80 (2)	2.687 (3)	175 (3)

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

Table 3. *First- and basic second-level graph-set descriptors involving hydrogen bonds designated (a) to (f) in the order given in Table 2*

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
(*a*)	$C(8)$	$D_2^2(10)$	$D_3^3(13)$	$D_2^2(4)$	$D_2^2(9)$	—
(*b*)		D	$R_4^4(32)$	$C_2^2(16)$	$R_4^4(20)$	$D_3^3(11)[R_2^2(16)]$
(*c*)			D	$C_2^2(16)$	$C_2^2(10)$	$D_3^3(17)[R_2^2(16)]$
(*d*)				D	$C_2^2(16)$	$D_3^3(13)[R_2^2(16)]$
(*e*)					D	$D_3^3(19)[R_2^2(16)]$
(*f*)						$R_2^2(16)$

Fourier difference methods were used to locate initial H-atom positions for all but one of the methyl H atoms; the H atoms were then refined isotropically. Subsequently, all H atoms except the hydroxyl H atoms were made canonical, with a C—H distance of 0.98 Å and isotropic displacement parameters fixed at 1.2 times those of the attached C atoms. The hydroxyl H atoms were refined isotropically. When the model with two molecules as the asymmetric unit converged, the maximum residual difference peak indicated methyl group disorder in the C10*A* group. The maximum residual peak was assigned as C51*A* and the populations of C10*A* and C51*A* were refined together with the six coordinates, anisotropic displacement components for C10*A* and an isotropic displacement factor for C51*A*. Taking into consideration the relatively small occupancy of C51*A*, 0.183, the geometry at the refined C51*A* atom is reasonable: C9*A*—C51*A* 1.35 (2) Å and C3*A*—C9*A*—C51*A* 122.3 (7)°. Due to the relatively small occupancy of C51*A*, no attempt was made to model its H atoms.

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: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Biphenyl-2-carboxylic Acid: a Layered Structure

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(Received 4 August 1997; accepted 5 December 1997)

Abstract

The title acid, $C_{13}H_{10}O_2$, crystallized in the centrosymmetric space group $P2_1/c$ with four molecules in the asymmetric unit. These four molecules form two pairs of cyclic hydrogen-bonded dimers of the usual sort, but these are not formed about centers of symmetry. The $O_{donor}\cdots O_{acceptor}$ distances in these hydrogen bonds are 2.660 (3), 2.638 (3), 2.676 (3) and 2.634 (3) Å. The carboxylic H atoms and the carboxylic O atoms are ordered. The biphenyl twist angles range from 46.5 (2) to 52.5 (2)°. The dihedral angles between the carboxyl group planes and the planes of the rings to which they are attached range from 43.6 (3) to 50.9 (3)°. In the two latter respects, this structure differs appreciably from the structures of the other two biphenyl monocarboxylic acids. The structure is layered parallel to the *ab* plane.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1397). Services for accessing these data are described at the back of the journal.