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Interwoven Hydrogen-Bonding Networks in Benzene-1,3,5-triacetic Acid

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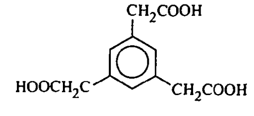
(*Received 2 December 1996; accepted 18 February 1997*)

Abstract

The title compound, $C_{12}H_{12}O_6$, crystallized in the centrosymmetric space group $P2_1/n$. Each molecule is hydrogen bonded to four others by ten hydrogen bonds forming a three-dimensional network. Two sets of such networks, which are not linked, comprise the structure. The carboxyl O atoms are ordered, as are the carboxyl H atoms. The best-fit acetic acid group planes make dihedral angles of 84.3 (1), 89.8 (2) and 58.0 (2)° with the best-fit benzene core plane.

Comment

This structural study of benzene-1,3,5-triacetic acid, (I), was conducted as one of a series on hydrogen bonding in aromatic carboxylic acids. The refined molecule together with our numbering scheme is shown in Fig. 1. In this structure each molecule is hydrogen bonded to four others by ten hydrogen bonds. Each participates in three (eight-membered) cyclic dimer hydrogen bonds, one of which involves a center of symmetry and, in addition, in four weaker hydrogen bonds involving atoms in the carboxyl groups at C1 and C5 which form two four-membered rings, as shown in Fig. 2. Geometric details of the hydrogen bonds are given in Table 2. Although the hydrogen bonds involve each molecule in a three-dimensional network, it is interesting to note that there are sets of two types of such networks which are not linked. Molecules related by the identity and inversion operations (and translations) form one type, those related by ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) and its inversion (and translations) form the other. In terms of graph-set analysis (Bernstein, Davis, Shimoni & Chang, 1995), the first-level graph set is $C(10)$, $C(10)$, $R_2^2(8)$, D, D: the first of these involves the first entry of Table 2 in a chain propagating along the *a* axis; the second involves the third entry also in a chain propagating along **a**; and the third involves the fourth entry in an eight-membered ring about a center of symmetry. Among the second-level graphs are $R_2^2(8)$, $R_2^2(4)$, $C_2^2(14)$ and $C_2^2(20)$: the first of these involves the first and third entries of Table 2 in an eight-membered ring; the second involves the second and fifth entries in a four-membered ring.



(I)

The data in Tables 1 and 2 establish that the three carboxyl H atoms are ordered as also are the carboxyl O atoms, which are at clear-cut single- and double-bond distances from the carboxyl C atoms. As in previous studies (Fitzgerald & Gerkin, 1993, 1996), and as is apparent in Fig. 1 (except for O5), the principal displacement tensor axes of the O atoms are nearly perpendicular to the carboxyl group planes, as expected for ordered carboxyl O atoms.

The benzene core is characterized by C—C distances with no significant variation, ranging from 1.382 (3) to 1.389 (3) Å with an average value of 1.386 (2) Å. In contrast, the interior C—C—C angles alternate systematically, the mean value at the substituted C atoms being 3.4° less than that at the unsubstituted C atoms. These results are in very good accord with those for the structurally similar molecule benzene-1,3,5-trimethanol

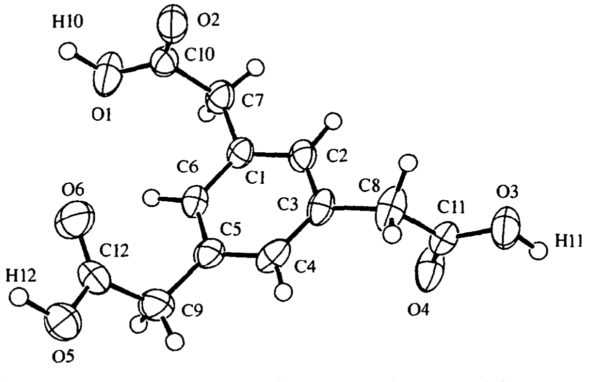


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of benzene-1,3,5-triacetic acid showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. Displacement ellipsoids for H atoms have been drawn artificially small.

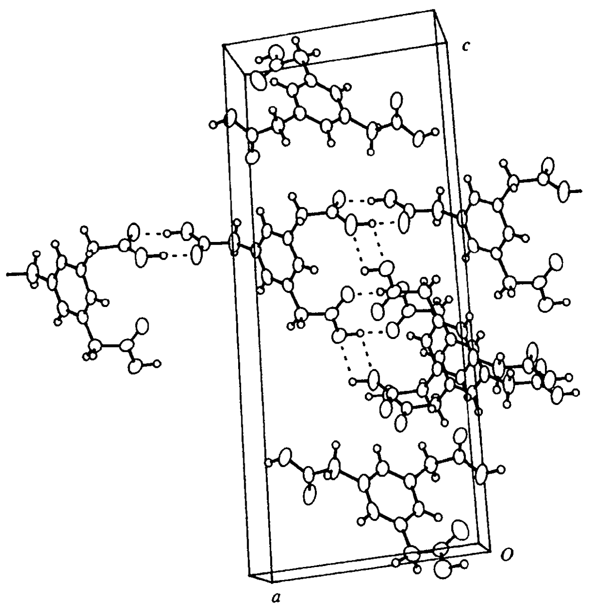


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of benzene-1,3,5-triacetic acid. Dashed lines delineate the ten hydrogen bonds in which the central molecule participates. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. Displacement ellipsoids for H atoms have been drawn artificially small. Note that the cell origin lies at its lower right rear corner.

(hereafter, BTM) (Bell, Coupar, Ferguson & Glidewell, 1996), in which no significant differences in benzene core distances were found and in which the interior C—C—C angles alternate in the same sense as in the title molecule, the mean difference in BTM being 2.7°. These angular results are not, however, in agreement with those for the structurally similar molecule benzene-1,3,5-tricarboxylic acid (hereafter, TA) (Duchamp & Marsh, 1967) for which, for the six nonequivalent benzene cores in that structure, the C—C—C angles are stated to range nonsystematically from 119.2 to 121.0°.

The benzene core in (I) is almost planar. The maximum deviation of a core atom from the best-fit core plane is 0.010 (3) Å, while the average deviation is 0.005 (3) Å. For comparison, in BTM the corresponding average deviation is 0.002 Å (our calculation) and in TA, 0.004, 0.003, 0.006, 0.007, 0.012 and 0.011 Å for the six nonequivalent cores.

In each of the acetic acid groups in (I), the four non-H atoms lie very nearly in a plane. The dihedral angles between the best-fit acetic acid group planes and the best-fit core plane are 84.3 (1), 89.8 (2) and 58.0 (2)°, respectively. This disposition of the acetic acid groups precludes any potential pseudo-threefold symmetry. For comparison, in BTM the dihedral angles with the best-fit core plane made by planes describing the relevant ring-C atom and the non-H atoms of the methanol groups are 6.1, 68.5 and 69.8° (our calculation), respectively. Again, pseudo-threefold symmetry is precluded, as noted also by those authors on the basis of similar considerations. In TA, the carboxyl group planes make smaller dihedral angles with the core planes, the maximum being ~27° as stated by Duchamp & Marsh (1967), but again pseudo-threefold symmetry is not observed.

The molecular packing is shown in Fig. 2. The dihedral angle between the two orientations of the best-fit benzene core planes is 87.4 (1)°. Excepting pairs of atoms in directly hydrogen-bonded carboxyl groups, the closest intermolecular approaches are between O2 and an H atom on C7^{v} [(v) = $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$] and fall short of the corresponding sum of Bondi (1964) van der Waals radii by 0.10 Å.

Refined C—H distances ranged from 0.91 (2) to 0.99 (2) Å with a mean value of 0.97 (3) Å. Refined O—H distances appear in Table 2.

Experimental

Benzene-1,3,5-triacetic acid was obtained from a sample in the chemical collection of Dr M. S. Newman as a tan powder. The powder was dissolved in dimethoxyethane and the solution filtered. Slow evaporation of the solvent at room temperature produced usable crystals.

Crystal data

$C_{12}H_{12}O_6$
M_r = 252.22
Monoclinic
$P2_1/n$
a = 9.994 (2) Å
b = 4.798 (2) Å
c = 24.160 (3) Å
β = 92.94 (2)°
V = 1156.8 (4) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13.4–14.9°
μ = 0.110 mm^{-1}
T = 296 K
Clear plate
0.58 × 0.31 × 0.08 mm
Colorless

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.970, T_{max} = 1.000
3141 measured reflections
2976 independent reflections
2132 reflections with $I > 0.01\sigma(I)$

R_{int} = 0.023
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 6$
$l = -31 \rightarrow 31$
6 standard reflections every 150 reflections intensity variation: ±2.4% (average maximum relative intensity)

Refinement

Refinement on F^2
R = 0.057
wR = 0.093
S = 1.11

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 8.2 (23) × 10^{-7}

2132 reflections
212 parameters
All H atoms refined
$w = 1/(\sigma_F^2)^2$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Scattering factors from Stewart, Davidson & Simpson (1965) for H and Cromer & Waber (1974) for C and O atoms

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

O1—C10	1.282 (3)	C1—C7	1.513 (3)
O2—C10	1.228 (3)	C3—C8	1.502 (3)
O3—C11	1.296 (2)	C5—C9	1.507 (3)
O4—C11	1.222 (3)	C7—C10	1.499 (3)
O5—C12	1.298 (3)	C8—C11	1.502 (3)
O6—C12	1.216 (3)	C9—C12	1.506 (3)
C10—O1—H10	114 (2)	O2—C10—C7	121.8 (2)
C11—O3—H11	111 (2)	O3—C11—O4	123.8 (2)
C12—O5—H12	108 (2)	O3—C11—C8	113.3 (2)
C1—C7—C10	108.6 (2)	O4—C11—C8	123.0 (2)
C3—C8—C11	115.3 (2)	O5—C12—O6	123.1 (2)
C5—C9—C12	113.6 (2)	O5—C12—C9	114.0 (2)
O1—C10—O2	122.7 (2)	O6—C12—C9	122.9 (2)
O1—C10—C7	115.5 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H10···O4^{i}	1.06 (4)	1.61 (4)	2.670 (2)	178 (3)
O1—H10···O5^{ii}	1.06 (4)	2.88 (3)	3.020 (2)	87 (2)
O3—H11···O2^{iii}	1.02 (3)	1.64 (3)	2.650 (2)	172 (3)
O5—H12···O6^{iv}	1.05 (4)	1.64 (4)	2.692 (2)	178 (3)
O5—H12···O1^{ii}	1.05 (4)	2.88 (3)	3.020 (2)	87 (2)

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

The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $P2_1/n$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). 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*.

Support provided to LJF by PPG Industries is gratefully acknowledged. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1266). Services for accessing these data are described at the back of the journal.

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Intermediates in the Synthesis of Forskolin. I

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(*Received 17 December 1996; accepted 19 February 1997*)

Abstract

In 4-acetyl-3,4-epoxy-3,6,6,8b-tetramethyl-2a,3,4,6,-7,8,8a,8b-octahydro-2*H*-naphtho[1,8a,8-*bc*]furan-2-one, $C_{17}H_{22}O_4$, the saturated ring (*A*) adopts a chair conformation, the cyclohexene ring (*B*) a distorted half-chair conformation and the furan ring an envelope conformation. The lactone and the epoxy moieties are *trans* to each other.

Comment

Forskolin, (3), is a polyoxygenated labdanyl diterpenoid isolated from the root of *Coleus forskohlii* Briq. (Bhat, Bajwa, Dornauer & de Souza, 1977). This natural