Table 4. *Refined scattering lengths (10^{-12} cm)*

C1	0.646 (6)	S4	0.359 (5)
C2	0.644 (5)	S5	0.356 (5)
C3	0.647 (5)	S6	0.357 (5)
C4	0.640 (5)	S7	0.352 (5)
C5	0.648 (5)	S8	0.355 (5)
C6	0.653 (5)	D7A	0.620 (6)
C7	0.660 (6)	D7B	0.616 (7)
C8	0.651 (6)	D8A	0.621 (6)
C9	0.650 (6)	D8B	0.620 (6)
C10	0.661 (6)	D9A	0.620 (6)
S1	0.355 (5)	D9B	0.617 (6)
S2	0.354 (5)	D10A	0.624 (6)
S3	0.346 (5)	D10B	0.626 (6)

A detailed description of the IPNS SCD has been published and described elsewhere (Schultz, 1993). Since the IPNS is a pulsed neutron source, data are obtained by the time-of-flight (TOF) Laue technique utilizing an area position-sensitive ^{6}Li-glass scintillator detector with an active area of 30×30 cm^2 and a wavelength range of 0.7–4.2 Å. Each detected neutron is stored in a three-dimensional histogram with coordinates x, y, t corresponding to horizontal and vertical detector positions and the TOF, respectively. 32 histograms with different χ and φ crystal settings were required to cover a unique quadrant of reciprocal space. Counting time per histogram (*i.e.* per χ and φ setting) was approximately 6.5 h. Since all peaks were counted during each pulse no standards were required, only scaling between different crystal orientations.

The lattice parameters were refined from the observed positions and wavelengths of 1941 reflections. Bragg peaks were integrated in three dimensions (x, y, t) about calculated peak positions from an orientation matrix. Data were corrected for the Lorentz factor, absorption, the incident source spectrum and the detector efficiency. Linear absorption coefficients at each wavelength were calculated from the sum of the wavelength-dependent true absorption and the wavelength-independent total scattering: $\mu = 0.355 + 0.0052 \times \lambda$, with μ in units of cm^{-1} and λ in units of Å.

The programs used to analyze the data were as follows: *PEAKS*, to search the histogram for Bragg peaks (Jacobson, 1986); *BLIND*, an autoindexing program for time-of-flight data (Jacobson, 1986); *LSQRS*, to determine unit cell and orientation matrix least squares (Argonne program); *INTEGRATE*, which integrates Bragg peaks (Argonne program); *ANVRED*, for data reduction (Argonne program); *ANVLS*, for least-squares structure refinement with multiwavelength data (Argonne program), based on *ORFLS* (Busing, Martin & Levy, 1962); *ORTEP*III, for molecular graphics (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1170). Services for accessing these data are described at the back of the journal.

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A30, 129–147.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
Jacobson, R. A. (1986). *J. Appl. Cryst.* 19, 283–286.
Kini, A. M, Carlson, K. D., Wang, H. H., Schlueter, J. A., Dudek, J. D., Sirchio, S. A., Geiser, U., Lykke, K. R. & Williams, J. M. (1996). *Physica C*, 264, 81–94.

Kobayashi, H., Kobayashi, A., Yukiyoshi, S., Saito, G. & Inokuchi, H. (1986). *Bull. Chem. Soc. Jpn*, 59, 301–302.
Schultz, A. J. (1993). *Trans. Am. Crystallogr. Assoc.* 29, 29–41.
Schultz, A. J., Wang, H. H., Soderholm, L. C., Sifter, T. L., Williams, J. M., Bechgaard, K. & Whangbo, M.-H. (1987). *Inorg. Chem.* 26, 3757–3761.
Sears, V. F. (1986). *Methods of Experimental Physics*, Vol. 23, *Neutron Scattering*, Part A, edited by K. Skold & D. L. Price, pp. 521–550. Orlando: Academic Press.
Williams, J. M., Schultz, A. J., Geiser, U., Carlson, K. D., Kini, A. M., Wang, H. H., Kwok, W. K., Whangbo, M.-H. & Schirber, J. E. (1991). *Science*, 252, 1501–1508.

Two Related Benzylcamphor Dimers

Il-Hwan Suh,[a] Sungjo Choi,[b] David E. Lewis[b] and William P. Jensen[b]

[a]*Department of Physics, Chungnam National University, Taejon 305-764, Korea, and* [b]*Chemistry Department, South Dakota State University, Brookings, SD 57007, USA. E-mail: jensenb@mg.sdstate.edu*
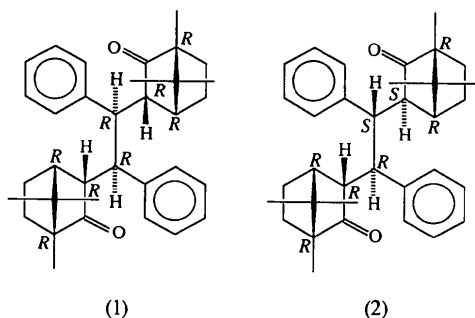
Abstract

The crystal structures of two related dimeric 3-benzyl-camphors, namely, (1R,3R,4R,1'R,3'R,4'R)-3,3'-[(1R,2R)-1,2-diphenylethylene]bis(1,7,7-trimethylbicyclo[2.2.1]-heptan-2-one), (1), and (1R,3R,4R,1'R,3'R,4'R)-3,3'-[(1R,2S)-1,2-diphenylethylene]bis(1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one), (2), both $C_{34}H_{42}O_2$, are reported. Compound (1) possesses C_2 molecular symmetry; it adopts a conformation in the crystal in which the two phenyl rings are *gauche* with respect to one another and *anti* to the C3—C4 bond (terpene numbering) of the camphor ring system. Compound (2) lacks a molecular C_2 axis of symmetry; it adopts a conformation in the crystal where the two phenyl rings are *anti* with respect to one another, and in which one phenyl ring is partially in the *endo* cavity of the camphor ring system. In both compounds, C3 of both camphor ring systems (terpene numbering) is distorted to trigonal pyramidal from tetrahedral; the C—C—C bond angles about C3 in both camphor rings are considerably expanded from idealized tetrahedral values and the dihedral angle between the benzyl C atom and the carbonyl O atom is reduced from the idealized value of 60° to less than 48°.

Comment

The ^{13}C NMR spectrum of the minor isomer (1) exhibits only ten resonances typical of sp^3-hybridized C atoms

and only one carbonyl resonance, and the ¹H NMR spectrum exhibits only three singlet methyl resonances. These spectroscopic data indicate that this molecule has twofold molecular symmetry; since the starting material is optically active (thus precluding reflection or inversion symmetry in the molecule), the molecular point group must be C_2. The ¹³C NMR spectrum of the major isomer (2) contains 18 resonances typical of sp^3-hybridized C atoms and two carbonyl resonances. These data are inconsistent with any simple axis of rotation in this molecule, and reflection or inversion symmetry is precluded in this compound for these reasons. The ¹H NMR spectrum confirmed the lack of C_2 rotation symmetry by exhibiting six singlet methyl resonances. The ¹H and ¹³C NMR spectra of either compound did not permit the unambiguous assignment of the stereochemistry of the new chiral centers, although the chemical shifts of the proton at C3 in compound (1) were consistent with the C3 substituent being in the endo position. In order to evaluate their potential as chiral auxiliaries themselves and their potential for use as precursors to chiral alcohols that might serve as useful chiral auxiliaries, it was imperative that the stereochemistry of these compounds be elucidated. Accordingly, we undertook the single-crystal X-ray structure analysis of these two isomeric compounds.

(1)   (2)

The most surprising result is that afforded by the crystal structure of compound (2), in which one of the two camphor ring systems carries a substituent α to the carbonyl group in the exo position. Since the equilibrium for simple benzylcamphor derivatives favors endo orientation of alkyl groups in this position by a ratio of approximately 13:1 (Richer & Rossi, 1972; Wall, 1990), this result was completely unexpected. Moreover, it does not appear that this orientation is required by packing constraints within the crystal. We hypothesize that the exo orientation of this alkyl group may reflect its formation by a kinetic protonation of the enolate during the work-up step of the reaction.

The aromatic rings and carbonyl C atoms are all planar in both structures with maximum deviations from planarity of less than 0.03 Å. The crystal conformation about the central bond in both molecules is similar to the extent that it is staggered in both with the
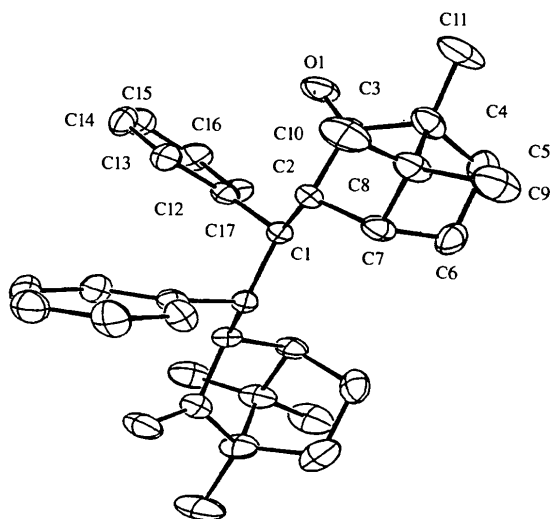
two camphor rings anti with respect to one another. This leads to the two aromatic rings being anti with respect to one another in compound (2), which results in the molecule having a pseudo-center of symmetry (an actual center of symmetry is precluded by the chirality of the two camphor ring systems). The two aromatic rings are gauche with respect to one another in compound (1), which possesses both a molecular C_2 axis of symmetry and a crystal C_2 axis of symmetry. The crystal conformation of compound (1) is similar to that of 3-endo-(p-methoxybenzyl)isobornyl p-nitro-benzoate (Suh, Seo, Lewis, Jensen & Jacobson, 1993), with the aromatic ring anti to C4 (terpene numbering) of the camphor ring system. The α-carbon of each camphor ring is distorted from its ideal tetrahedral shape to trigonal pyramidal, with the benzyl C atom in each instance being displaced outward from the camphor ring system. This distortion is evidenced by the dihedral angles involving the bond between the benzyl C atom and the camphor ring system. Idealized tetrahedral geometry at this position would result in a dihedral angle of 60° between the benzyl C atom and the carbonyl O atom. In compound (1), this angle is 47.6 (4)°. In compound (2), both α-C atoms are also pyramidalized by a distortion that moves the benzyl C atom away from the camphor ring system. As might have been anticipated due to the buttressing effects of the bridgehead methyl group, the introduction of the benzyl group into the exo position of the camphor ring system induces a more severe pyramidalization of the camphor C3 atom compared to a dihedral angle of 42.5 (7)° between the corresponding bonds in the endo-substituted ring system. The bond angles at the α-C atoms of the camphor moieties corroborate the distortions revealed by the torsion angles and the C—

Fig. 1. ORTEP (Johnson, 1976) drawing of compound (1) with a molecular C_2 axis. Displacement ellipsoids are drawn at the 30% probability level.

C—C bond angles involving the benzyl-carbon–ring-carbon bond are expanded from the tetrahedral angle by as much as 10°.
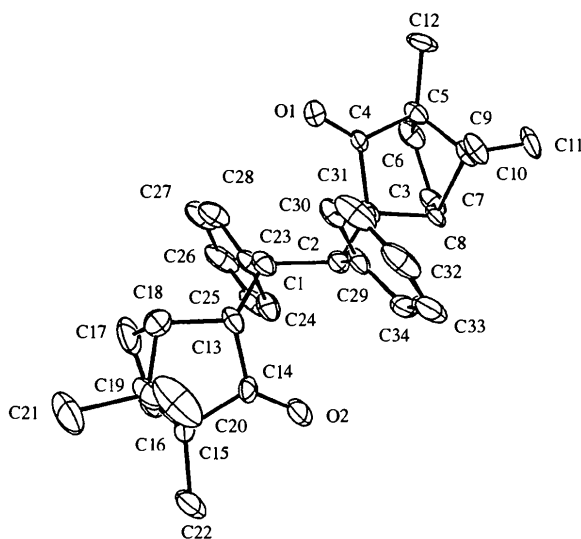

Fig. 2. *ORTEP* (Johnson, 1976) drawing of compound (2) with no molecular C_2 axis. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

As part of a program to develop new reagents for asymmetric synthesis based on the (1R)-3-benzylcamphor skeleton, we have undertaken the reduction of (1R)-3-benzylidenecamphor under acyloin conditions in an effort to prepare C_2-symmetric dimeric 3-*endo*-benzylcamphor derivatives. The title compounds were prepared by reduction of (1R)-3-benzylidenecamphor with sodium metal and chlorotrimethylsilane in refluxing toluene, followed by methanolysis to afford the two title compounds as major components of the product mixture. The two compounds were separated by flash chromatography and crystallized from ethanol.

Compound (1)

Crystal data

$C_{34}H_{42}O_2$
$M_r = 482.70$
Tetragonal
$P4_12_12$
$a = 10.6524 (12)$ Å
$c = 25.548 (4)$ Å
$V = 2899.0 (6)$ Å^3
$Z = 4$
$D_x = 1.106$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 25 reflections
$\theta = 5.68$–$7.00°$
$\mu = 0.06$ mm^{-1}
$T = 293$ K
Prism
$0.46 \times 0.30 \times 0.23$ mm
Colorless

Data collection

Nonius CAD-4 diffractometer
ω scans
Absorption correction: none

$\theta_{max} = 23.90°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 29$

1152 measured reflections
1152 independent reflections
758 reflections with
$I_{net} > 3\sigma(I_{net})$

3 standard reflections
frequency: 180 min
intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.027$
$S = 2.18$
759 reflections
185 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.04$

$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction:
Larson (1970)
Extinction coefficient:
$3.0 (2) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

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

	x	y	z	U_{eq}
O1	0.9291 (4)	0.5977 (4)	0.11135 (14)	0.070 (3)
C1	0.8233 (5)	0.7784 (5)	0.02817 (18)	0.037 (4)
C2	0.9299 (6)	0.6834 (5)	0.0223 (2)	0.040 (4)
C3	0.9871 (6)	0.6351 (6)	0.0738 (2)	0.044 (4)
C4	1.1297 (6)	0.6386 (7)	0.0694 (2)	0.061 (6)
C5	1.1570 (7)	0.7831 (8)	0.0752 (3)	0.083 (6)
C6	1.1062 (6)	0.8380 (7)	0.0231 (3)	0.069 (5)
C7	1.0513 (6)	0.7242 (6)	−0.0060 (2)	0.049 (4)
C8	1.1465 (6)	0.6197 (7)	0.0099 (2)	0.057 (5)
C9	1.2822 (6)	0.6435 (8)	−0.0095 (3)	0.089 (7)
C10	1.1094 (8)	0.4872 (7)	−0.0081 (3)	0.075 (6)
C11	1.2002 (7)	0.5547 (9)	0.1075 (3)	0.092 (7)
C12	0.7184 (5)	0.7289 (6)	0.0626 (2)	0.040 (4)
C13	0.6723 (6)	0.6078 (6)	0.0592 (2)	0.051 (4)
C14	0.5796 (6)	0.5656 (7)	0.0933 (2)	0.059 (5)
C15	0.5328 (6)	0.6434 (8)	0.1314 (3)	0.067 (6)
C16	0.5759 (7)	0.7651 (7)	0.1353 (2)	0.067 (6)
C17	0.6683 (6)	0.8058 (5)	0.1012 (2)	0.050 (4)

Table 2. *Selected geometric parameters (Å, °) for (1)*

O1—C3	1.209 (7)	C4—C5	1.573 (11)
C1—C1^i	1.591 (9)	C4—C8	1.545 (9)
C1—C2	1.528 (8)	C5—C6	1.551 (10)
C2—C3	1.538 (8)	C6—C7	1.538 (10)
C2—C7	1.545 (9)	C7—C8	1.560 (9)
C3—C4	1.523 (9)		
C1^i—C1—C2	109.5 (4)	C3—C4—C8	100.7 (5)
C1^i—C1—C12	114.1 (4)	C5—C4—C8	101.5 (5)
C1—C2—C3	115.6 (4)	C4—C5—C6	102.9 (6)
C1—C2—C7	118.8 (5)	C5—C6—C7	104.5 (5)
C3—C2—C7	99.4 (5)	C2—C7—C6	108.2 (5)
O1—C3—C2	125.9 (6)	C2—C7—C8	102.8 (5)
O1—C3—C4	125.2 (5)	C6—C7—C8	100.9 (5)
C2—C3—C4	108.9 (5)	C4—C8—C7	95.0 (5)
C3—C4—C5	101.7 (5)		

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

Compound (2)

Crystal data

$C_{34}H_{42}O_2$
$M_r = 482.70$

Cu $K\alpha$ radiation
$\lambda = 1.54056$ Å

Monoclinic
$P2_1$
$a = 13.453 (3)$ Å
$b = 10.1847 (16)$ Å
$c = 10.2639 (18)$ Å
$\beta = 101.012 (17)°$
$V = 1380.4 (4)$ Å^3
$Z = 2$
$D_x = 1.161$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 25.0-29.5°$
$\mu = 0.50$ mm^{-1}
$T = 293$ K
Prism
$0.26 \times 0.20 \times 0.20$ mm
Colorless

Data collection

Nonius CAD-4 diffractom-
eter
ω scans
Absorption correction: none
2040 measured reflections
2040 independent reflections
1808 reflections with
$I_{net} > 3\sigma(I_{net})$

$\theta_{max} = 59.88°$
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 180 min
intensity decay: 2.2%

Refinement

Refinement on F
$R = 0.080$
$wR = 0.067$
$S = 7.32$
1808 reflections
325 parameters
H atoms not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.125$

$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction:
Larson (1970)
Extinction coefficient:
$1.32 (7) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (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}
O1	0.1687 (5)	0.75770	0.2636 (6)	0.059 (5)
O2	0.3309 (6)	0.6787 (9)	−0.2628 (6)	0.068 (5)
C1	0.1915 (8)	0.6782 (14)	−0.0440 (8)	0.046 (6)
C2	0.2938 (7)	0.7434 (13)	0.0314 (8)	0.038 (6)
C3	0.2749 (7)	0.8583 (13)	0.1195 (9)	0.043 (6)
C4	0.2274 (8)	0.8419 (14)	0.2441 (9)	0.041 (6)
C5	0.2683 (7)	0.9554 (13)	0.3336 (8)	0.043 (6)
C6	0.2263 (8)	1.0809 (15)	0.2544 (10)	0.055 (7)
C7	0.2984 (8)	1.0914 (13)	0.1507 (9)	0.053 (7)
C8	0.3543 (7)	0.9644 (15)	0.1657 (8)	0.045 (6)
C9	0.3796 (7)	0.9495 (14)	0.3233 (8)	0.043 (6)
C10	0.4345 (8)	0.8227 (14)	0.3745 (9)	0.053 (7)
C11	0.4440 (8)	1.0636 (15)	0.3906 (9)	0.063 (7)
C12	0.2428 (8)	0.9473 (16)	0.4748 (8)	0.060 (8)
C13	0.2141 (7)	0.5721 (14)	−0.1423 (9)	0.044 (6)
C14	0.2615 (7)	0.6048 (14)	−0.2592 (9)	0.039 (6)
C15	0.2097 (7)	0.5186 (13)	−0.3736 (9)	0.044 (6)
C16	0.1071 (8)	0.5916 (15)	−0.4130 (9)	0.061 (8)
C17	0.0474 (8)	0.5549 (18)	−0.3055 (12)	0.090 (9)
C18	0.1284 (9)	0.4770 (16)	−0.2044 (11)	0.061 (8)
C19	0.1825 (10)	0.4011 (14)	−0.3029 (11)	0.066 (8)
C20	0.2719 (14)	0.3223 (17)	−0.2348 (14)	0.124 (14)
C21	0.1022 (11)	0.3066 (16)	−0.3936 (12)	0.098 (11)
C22	0.2658 (9)	0.5031 (15)	−0.4870 (9)	0.074 (8)
C23	0.1188 (7)	0.7847 (14)	−0.1037 (9)	0.044 (6)
C24	0.1411 (8)	0.8741 (14)	−0.1985 (10)	0.056 (7)
C25	0.0754 (10)	0.9715 (16)	−0.2506 (9)	0.070 (8)
C26	−0.0192 (10)	0.9760 (18)	−0.2140 (10)	0.080 (10)
C27	−0.0425 (9)	0.8883 (19)	−0.1214 (11)	0.083 (10)
C28	0.0240 (9)	0.7928 (15)	−0.0652 (9)	0.065 (8)
C29	0.3672 (8)	0.6376 (14)	0.0968 (9)	0.045 (6)
C30	0.3382 (8)	0.5414 (15)	0.1806 (9)	0.049 (6)
C31	0.4098 (11)	0.4487 (16)	0.2378 (10)	0.073 (9)
C32	0.5031 (10)	0.4442 (18)	0.2137 (10)	0.073 (9)
C33	0.5359 (9)	0.5412 (19)	0.1335 (10)	0.075 (9)
C34	0.4635 (8)	0.6355 (15)	0.0741 (9)	0.053 (7)

Table 4. *Selected geometric parameters (Å, °) for (2)*

O1—C4	1.208 (12)	C7—C8	1.489 (19)
O2—C14	1.206 (14)	C8—C9	1.596 (12)
C1—C2	1.590 (14)	C13—C14	1.500 (14)
C1—C13	1.547 (17)	C13—C18	1.547 (17)
C2—C3	1.530 (17)	C14—C15	1.524 (15)
C3—C4	1.543 (14)	C15—C16	1.552 (16)
C3—C8	1.531 (17)	C15—C19	1.480 (18)
C4—C5	1.514 (16)	C16—C17	1.530 (18)
C5—C6	1.561 (18)	C17—C18	1.570 (19)
C5—C9	1.522 (13)	C18—C19	1.559 (18)
C6—C7	1.575 (16)		
C2—C1—C13	110.5 (8)	C5—C9—C8	92.6 (7)
C2—C1—C23	109.3 (10)	C1—C13—C14	122.2 (11)
C1—C2—C3	112.4 (8)	C1—C13—C18	118.9 (9)
C2—C3—C4	123.3 (11)	C14—C13—C18	101.9 (8)
C2—C3—C8	122.5 (9)	O2—C14—C13	127.8 (10)
C4—C3—C8	101.2 (8)	O2—C14—C15	125.4 (9)
O1—C4—C3	127.0 (10)	C13—C14—C15	106.7 (9)
O1—C4—C5	127.9 (9)	C14—C15—C16	100.2 (9)
C3—C4—C5	105.1 (9)	C14—C15—C19	102.0 (8)
C4—C5—C6	104.8 (8)	C16—C15—C19	103.0 (9)
C4—C5—C9	100.1 (9)	C15—C16—C17	104.9 (10)
C6—C5—C9	105.1 (9)	C16—C17—C18	101.9 (9)
C5—C6—C7	101.5 (9)	C13—C18—C17	109.0 (12)
C6—C7—C8	103.6 (9)	C13—C18—C19	100.1 (9)
C3—C8—C7	105.8 (8)	C17—C18—C19	99.9 (9)
C3—C8—C9	104.3 (9)	C15—C19—C18	96.1 (10)
C7—C8—C9	101.1 (9)		

Crystals of compound (II) were difficult to obtain. Numerous crystallization attempts yielded only a few crystals that had smooth faces and no re-entrant angles. The best of these crystals were examined with a Weissenberg camera and one was chosen for data collection with Mo $K\alpha$ radiation (sealed tube). The data obtained were not satisfactory so new data were measured with the more intense Cu $K\alpha$ radiation from a rotating-anode source. Even so, the agreement factors are still high, the precision of the bond lengths is low and the shapes of some of the atomic ellipsoids (Fig. 2) are odd. Compound (II) is included in this paper because of its close relationship to compound (I) and because of its unusual stereochemistry. The atomic ellipsoids for compound (I) (Fig. 1) appear to be elongated in the direction of the crystallographic twofold axis. The relatively low resolution of the data ($\theta_{max} = 23°$) may be a factor. The structures were solved by direct methods using *NRCVAX* software (Gabe, Le Page, Charland, Lee & White, 1989). All non-H atoms were refined anisotropically. H atoms were either located from difference maps or placed in calculated positions. Only isotropic refinement was carried out on these atoms.

For both compounds, data reduction: *NRCVAX DATRD2*; program(s) used to solve structures: *NRCVAX SOLVER*; program(s) used to refine structures: *NRCVAX LSTSQ*; molecular graphics: *NRCVAX*; software used to prepare material for publication: *NRCVAX TABLES* (version of January 1994).

References

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Richer, J.-C. & Rossi, A. (1972). *Can. J. Chem.* **50**, 1376.

Suh, I.-H., Seo, B.-I., Lewis, D. E., Jensen, W. P. & Jacobson, R. A. (1993). *Acta Cryst.* C49, 562–565.

Wall, L. K. (1990). MS thesis, Baylor University, Waco, TX, USA.

Acta Cryst. (1997). C53, 967–969

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

Lawrence J. Fitzgerald and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

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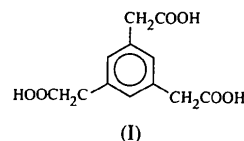
The data in Tables 1 and 2 establish that the three carboxyl H atoms are ordered as also are the carboxyl O atoms, which are at clear-cut single- and double-bond distances from the carboxyl C atoms. As in previous studies (Fitzgerald & Gerkin, 1993, 1996), and as is apparent in Fig. 1 (except for O5),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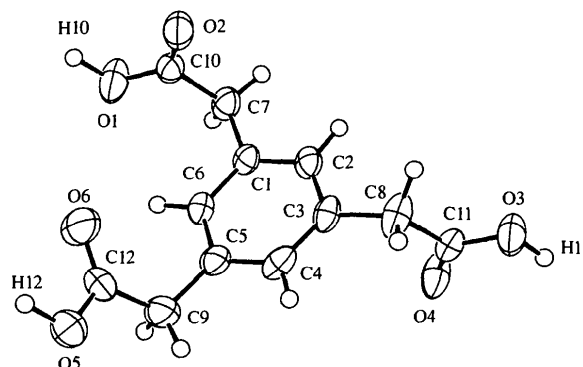

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of benzene-1,3,5-triacetic acid showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. Displacement ellipsoids for H atoms have been drawn artificially small.