$S = 1.39$
2018 reflections
149 parameters
All H atoms refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} < 0.01$
Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C4	1.308 (2)	C1—C4	1.463 (3)
O2—C4	1.217 (2)	C2—C3	1.462 (3)
C1—C2	1.529 (3)	C2—C5	1.487 (3)
C1—C3	1.488 (3)		
C2—C1—C3	58.0 (2)	O1—C4—O2	123.1 (2)
C1—C2—C3	59.6 (2)	O1—C4—C1	113.2 (2)
C1—C3—C2	62.4 (2)	O2—C4—C1	123.7 (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H4···O2^{i}	0.93 (2)	1.71 (3)	2.645 (2)	176 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

One quadrant of data was collected in the $P2_1/c$ setting. Scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences following a cell transformation and centrosymmetric intensity statistics then indicated space group $P2_1/n$. Since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. The extinction parameter was predicted to be negative and was not included in the refinement. The maximum positive residual peak was located ~1.0 Å from C7; the maximum negative peak was located ~1.0 Å from O1.

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*.

I 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: FR1081). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (1980). *Acta Cryst.* B**36**, 81–96.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bordner, J., Jones, L. A. & Johnson, R. L. (1972). *Cryst. Struct. Commun.* **1**, 389–391.
Creagh, D. C. & McAuley, W. J. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer Academic Publishers.
Gerkin, R. E. (1997). *Acta Cryst.* C**53**, 1280–1282.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELX*86. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

Acta Cryst. (1997). C**53**, 1991–1995

1,4,5,8-Naphthalenetetracarboxylic Acid Cyclic 1,8-Anhydride Bis(dimethyl sulfoxide) Solvate and 1,4,5,8-Naphthalenetetracarboxylic 1,8:4,5-Dianhydride

ANTHONY C. BLACKBURN, LAWRENCE J. FITZGERALD AND ROGER E. GERKIN

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

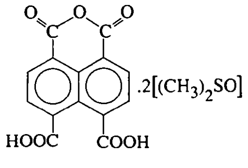
(Received 27 May 1997; accepted 2 September 1997)

Abstract

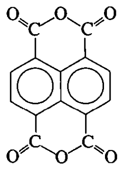
1,4,5,8-Naphthalenetetracarboxylic acid cyclic 1,8-anhydride crystallized from dimethyl sulfoxide (DMSO) as the solvate, $C_{14}H_6O_7.2C_2H_6OS$, in the centrosymmetric space group $P\bar{1}$. Two O—H···O hydrogen bonds with O···O distances of 2.592 (3) and 2.598 (3) Å are formed, with the two carboxylic acid OH groups as donors and the O atoms of the two inequivalent DMSO molecules as acceptors. The carboxylic H atoms are ordered, as are the carboxylic O atoms. In addition to the conventional hydrogen bonds, there are numerous C—H···O interactions consistent with the large number of potential CH donors and O-atom acceptors. 1,4,5,8-Naphthalenetetracarboxylic 1,8:4,5-dianhydride, $C_{14}H_4O_6$, crystallized in the centrosymmetric space group $P2_1/c$ with half the molecule as the asymmetric unit. Each molecule is involved in four significant C—H···O interactions as a donor and in an additional four as an acceptor. These eight interactions link each molecule to six neighboring molecules, forming a three-dimensional network. Geometric parameters of both substances are in general agreement with analogous parameters for naphthalic anhydride, monosodium 1,4,5,8-naphthalenetetracarboxylic acid cyclic 1,8-anhydride monohydrate and 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride, as reported previously.

Comment

This is one of a series of reports on hydrogen bonding in aromatic polycarboxylic acids and follows a report on the monohydrated monosodium salt of 1,4,5,8-naphthalenetetracarboxylic acid cyclic 1,8-anhydride (Fitzgerald, Gallucci & Gerkin, 1992, in which the alternative naming as the 4,5-anhydride was used). In 1,4,5,8-naphthalenetetracarboxylic acid cyclic 1,8-anhydride solvated with two DMSO molecules, (I), two strong hydrogen bonds are formed with the two carboxylic OH groups as donors and the O atoms of the two inequivalent DMSO molecules as acceptors, as shown in Fig. 1(*a*), which also shows the atom-numbering scheme. (It should be noted that although one of the DMSO molecules is disordered, the disorder does not involve its O atom, O9, the acceptor of one of the two strong hydrogen bonds.) As is apparent from the figure, chains or rings involving one or both of the hydrogen-bond types cannot be formed. In terms of graph set analysis (Bernstein *et al.*, 1995), the first-level graph set is *DD* and the second-level graph set is $D^2_2(11)$. Since potential acceptor O atoms O1–O4 and O6 remain available after the two hydrogen bonds are accommodated, and since there are many potential C—H donors, the occurrence of numerous C—H···O interactions is to be expected. The geometric parameters of the two hydrogen bonds and of those C—H···O interactions for which the H···O distance is equal to or less than the corresponding Bondi (1964) van der Waals radius sum are given in Table 2. It is noteworthy that among the O atoms only O2 is not involved in any of these interactions. From the data in Tables 1 and 2, it is clear that both the carboxylic O atoms and the carboxylic H atoms are ordered. As expected for ordered carboxylic O atoms, the principal axes of their displacement tensors are almost normal to the carboxyl group plane as evident in Fig. 1.



(I)



(II)

Apart from the carboxyl groups, the acid molecule exhibits a pseudo-twofold axis along the C9—C10 bond direction: the r.m.s. difference within the eight pairs of distances which would be identical under such symmetry is 0.005 Å, and thus is less than twice the variance of the individual distances. This result duplicates the corresponding result found for the monosodium salt of the acid cited above. The angular geometry at the C atoms bearing the carboxyl groups in the title acid and in its monosodium salt are also in excellent agreement: the r.m.s. difference taken within the five pairs of corresponding angles is 0.5°, about twice the variance of the individual angles (whose values range over ~8°).

The naphthopyran core of the title acid is roughly planar, the maximum deviation of a core atom from

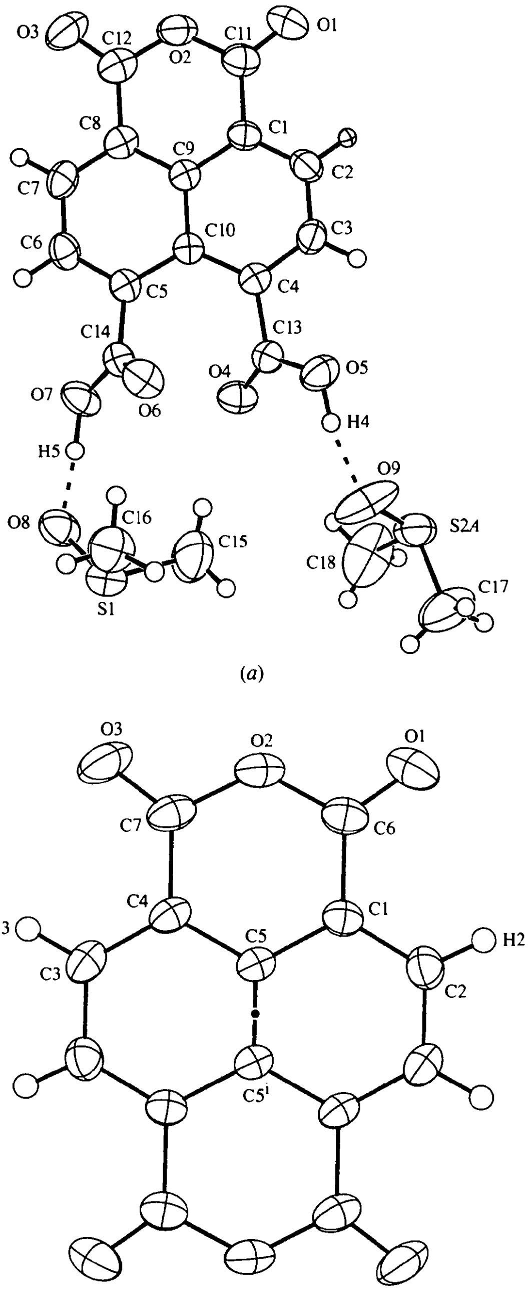


Fig. 1. *ORTEP*II (Johnson, 1976) drawings of (*a*) compound (I) and (*b*) compound (II) showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H for which they have been set artificially small. In (*a*), for clarity, only one set of the disordered atoms of the second DMSO molecule is shown; the hydrogen bonds are drawn as dashed lines. In (*b*), the center of symmetry through which the second half of the molecule is generated is depicted as a solid sphere.

the best-fit plane describing them being 0.088 (3) Å, while the average deviation is 0.026 (3) Å. The carboxyl group planes make dihedral angles of 42.7 (1) and 56.4 (1)° with the best-fit core plane and of 32.4 (4)° with each other. The carboxyl group C atoms, C13 and C14, lie on opposite sides of the core plane, 0.150 (3) and 0.375 (3) Å from it, respectively. Similarly, the 'anhydride' O atoms O1 and O3 lie on opposite sides of the core plane, 0.080 (3) and 0.260 (3) Å from it. In comparison, the dihedral angles in the monosodium salt between the best-fit core plane and the carboxylic and carboxylate group planes are 62.6 (1) and 61.2 (1)°, respectively, and the carboxyl group C atoms lie on opposite sides of the core plane, 0.102 (3) and 0.286 (3) Å from it. Further, in the monosodium salt the 'anhydride' O atoms also lie on opposite sides of the core plane, 0.054 (3) and 0.137 (3) Å from it. Thus, overall, the geometries are very similar.

Intramolecular distances and angles of special interest in the title substance are given in Table 1. It may be noted that the geometric parameters of the *A* and *B* components of the disordered DMSO molecule are in reasonably close agreement with those of the other (ordered) DMSO molecule. The closest intermolecular approaches, excluding pairs of atoms within directly hydrogen-bonded groups or in C—H···O interactions listed in Table 2, are between O4 and $C12^{vi}$, and O4 and $C8^{vi}$ [symmetry code: (vi) $2-x$, $3-y$, $2-z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.37 and 0.18 Å, respectively.

For 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride, (II), conventional hydrogen bonds are not possible but, as in the title acid, there are potential O-atom acceptors, O1–O3, and potential H-atom donors, C2 and C3, in the asymmetric unit, as shown in Fig. 1(*b*), which also shows the atom-numbering scheme. Two intermolecular C—H···O interactions having H···O distances equal to or less than the sum of the corresponding Bondi (1964) van der Waals radii do occur and involve O1 and O3, and H2 and H3; the geometric details are given in Table 4. Altogether, each dianhydride molecule is thus involved in four such interactions as a donor and in four as an acceptor. This set of interactions links a molecule to six neighboring molecules in a three-dimensional array. As in the title acid, O2 is not involved in such interactions.

The 16 atoms constituting the four-ring core of the dianhydride molecule lie nearly in a plane: the maximum deviation of any of these atoms from the best-fit core plane is 0.045 (2) Å while the average deviation is 0.018 (2) Å. This core, though larger, is thus more nearly planar than the naphthopyran core of the title acid. As in the title acid, the 'anhydride' O atoms, O1 and O3, lie on opposite sides of this plane 0.068 (2) and 0.096 (2) Å from it. The dihedral angle between the core planes of the two translationally inequivalent sets of molecules is 81.7 (1)°.

Intramolecular distances and angles of special interest in the dianhydride are given in Table 3. The r.m.s. difference within the six pairs of corresponding distances involving C6 and C7 in the dianhydride and C11 and C12 in the title acid is 0.009 Å, only two to three times the variances of the title acid distances. Similar to the acid, the dianhydride exhibits a pseudo-twofold axis along the C5—$C5^{i}$ [symmetry code: (i) $1-x$, $1-y$, $1-z$] bond direction: the r.m.s. difference within the five pairs of distances which would be identical under twofold symmetry (and that are not related by the center of symmetry) is 0.006 Å, three times the variance of the individual values. Excluding the pairs of atoms within a C—H···O interaction listed in Table 4, the closest intermolecular approach is between O1 and $C7^{iv}$ [symmetry code: (iv) $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$] and falls short of the corresponding Bondi (1964) van der Waals radius sum by 0.26 Å.

The relevant geometric results for both title substances are in general agreement with somewhat less precise results for naphthalic anhydride (Grigor'eva & Chetkina, 1975).

During review of this paper, we were first made aware of an earlier paper on the dianhydride (Born & Heywang, 1990). While overall, the two sets of metric results are in good agreement, the present analysis is based on more extensive data, the e.s.d.'s are generally smaller and there are some small but statistically significant differences of which two examples are (using the present numbering system): (*a*) bond lengths for C4—C5 and C5—$C5^{i}$ differ by 0.001 (2) Å in this study, but by 0.041 (3) Å in that of Born & Heywang; (*b*) atoms C6 and C7 are found on opposite sides of the best-fit plane describing the naphthalene core in both studies, disposed almost symmetrically in the present study [0.048 (2) *versus* 0.035 (2) Å] but quite asymmetrically in the previous study [0.01 *versus* 0.07 Å], as stated by Born & Heywang.

Experimental

Compound (I): hydrated 1,4,5,8-naphthalenetetracarboxylic acid, obtained from the Aldrich Chemical Company as a tan fine powder, was dissolved in hot DMSO. Slow evaporation of the solvent at 313 K produced colorless predominantly rod-shaped crystals, one of which was cut to provide the experimental sample. Compound (II): in an attempt to produce crystals of a trivalent salt of 1,4,5,8-naphthalenetetracarboxylic acid, the hydrated acid cited above and $Tl(NO_3)_3$ were dissolved in DMSO. Upon slow evaporation of the solution to dryness at 313 K, large golden crystals with morphology similar to that of a knife blade were formed. One of these was cut to provide the experimental sample, which subsequent analysis of the X-ray data showed to be the tetraacid dianhydride. The production of anhydrides in the two crystal growths described above was not desired, but is consistent with the known sensitivity of 1,4,5,8-naphthalenetetracarboxylic acid to anhydride formation, as discussed by Kofman *et al.* (1988).

Compound (I)

Crystal data

$C_{14}H_6O_7.2C_2H_6OS$
$M_r = 442.47$
Triclinic
$P\bar{1}$
$a = 8.584\ (2)$ Å
$b = 8.893\ (2)$ Å
$c = 13.851\ (3)$ Å
$\alpha = 106.94\ (2)°$
$\beta = 101.90\ (2)°$
$\gamma = 96.50\ (2)°$
$V = 972.6\ (4)$ Å^3
$Z = 2$
$D_x = 1.511$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 25 reflections
$\theta = 13.2–17.2°$
$\mu = 0.309$ mm^{-1}
$T = 296$ K
Cut rod
0.34 × 0.34 × 0.23 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
4796 measured reflections
4495 independent reflections
2959 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 17$
6 standard reflections every 150 reflections intensity decay: 2.8%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.040$
$S = 2.09$
2959 reflections
281 parameters
H atoms: see below
$w = 1/\sigma(F^2)$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $12\ (1) \times 10^{-7}$
Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Cromer & Waber (1974) (C, O)

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

S1—O8	1.504 (2)	O2—C12	1.380 (3)
S1—C15	1.772 (4)	O3—C12	1.196 (3)
S1—C16	1.770 (3)	O4—C13	1.204 (3)
S2*A*—O9	1.437 (3)	O5—C13	1.306 (3)
S2*A*—C17	1.681 (4)	O6—C14	1.206 (3)
S2*A*—C18	1.752 (4)	O7—C14	1.324 (3)
S2*B*—O9	1.445 (3)	C1—C11	1.470 (4)
S2*B*—C17	1.654 (4)	C4—C13	1.508 (3)
S2*B*—C18	1.755 (4)	C5—C14	1.495 (3)
O1—C11	1.193 (3)	C8—C12	1.472 (4)
O2—C11	1.388 (3)		
O8 S1—C15	106.5 (2)	C4—C10—C5	125.9 (2)
O8—S1—C16	106.5 (1)	O1—C11—O2	116.6 (3)
C15—S1—C16	97.7 (2)	O1—C11—C1	125.9 (3)
O9—S2*A*—C17	110.8 (2)	O2—C11—C1	117.5 (3)
O9—S2*A*—C18	107.5 (2)	O2—C12—O3	116.2 (3)
C17—S2*A*—C18	99.9 (2)	O2—C12—C8	117.9 (3)
O9—S2*B*—C17	111.9 (2)	O3—C12—C8	125.8 (3)
O9—S2*B*—C18	107.0 (2)	O4—C13—O5	125.0 (2)
C17—S2*B*—C18	100.9 (2)	O4—C13—C4	123.2 (2)
C11—O2—C12	124.0 (2)	O5—C13—C4	111.6 (2)
C3—C4—C13	116.2 (2)	O6—C14—O7	124.6 (3)
C10—C4—C13	123.6 (2)	O6—C14—C5	122.2 (2)
C6—C5—C14	115.8 (2)	O7—C14—C5	113.0 (2)
C10—C5—C14	123.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H4···O9	0.95 (3)	1.66 (3)	2.592 (3)	167 (3)
O7—H5···O8	1.09 (4)	1.53 (4)	2.598 (2)	166 (3)
C6—H6···O7$^{\rm i}$	0.98	2.69	3.559 (3)	148
C7—H7···O8$^{\rm i}$	0.98	2.50	3.318 (3)	140
C15—H10···O4	0.98	2.63	3.397 (4)	135
C16—H11···O6	0.98	2.48	3.386 (4)	153
C16—H12···O1$^{\rm ii}$	0.98	2.67	3.565 (4)	151
C16—H13···O5$^{\rm iii}$	0.98	2.61	3.451 (4)	144
C17—H14*A*···O1$^{\rm iv}$	0.98	2.44	3.212 (4)	135
C17—H14*B*···O1$^{\rm iv}$	0.98	2.28	3.212 (4)	161
C18—H17*B*···O3$^{\rm v}$	0.98	2.65	3.566 (5)	156

Symmetry codes: (i) $1 - x, 3 - y, 2 - z$; (ii) $2 - x, 2 - y, 2 - z$; (iii) $x - 1, y, z$; (iv) $x - 1, y - 1, z - 1$; (v) $x, y - 1, z - 1$.

Compound (II)

Crystal data

$C_{14}H_4O_6$
$M_r = 268.18$
Monoclinic
$P2_1/c$
$a = 7.880\ (2)$ Å
$b = 5.322\ (1)$ Å
$c = 12.6012\ (9)$ Å
$\beta = 107.257\ (9)°$
$V = 504.7\ (1)$ Å^3
$Z = 2$
$D_x = 1.765$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.9–17.5°$
$\mu = 0.133$ mm^{-1}
$T = 296$ K
Cut plate
0.29 × 0.29 × 0.15 mm
Golden

Data collection

Rigaku *AFC-5S* diffractometer
ω scans
Absorption correction: none
1730 measured reflections
1626 independent reflections
1059 reflections with $I > 0.75\sigma(I)$
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 30.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 7$
$l = -17 \rightarrow 16$
6 standard reflections every 150 reflections intensity variation: ±1.4% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.051$
$wR = 0.053$
$S = 1.79$
1059 reflections
100 parameters
All H atoms refined
$w = 1/\sigma(F^2)$
$(\Delta/\sigma)_{\rm max} = < 0.01$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $6\ (1) \times 10^{-6}$
Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Cromer & Waber (1974) (C, O)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C6	1.188 (2)	C1—C6	1.480 (2)
O2—C6	1.385 (2)	C3—C4	1.375 (2)
O2—C7	1.396 (2)	C4—C7	1.475 (2)
O3—C7	1.185 (2)	C5—C5$^{\rm i}$	1.415 (3)
C6—O2—C7	125.7 (1)	O2—C7—O3	116.9 (2)
O1—C6—O2	117.0 (2)	O2—C7—C4	116.9 (1)
O1—C6—C1	125.9 (2)	O3—C7—C4	126.2 (2)
O2—C6—C1	117.1 (1)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{ii}	0.92 (2)	2.60 (2)	3.358 (2)	139 (1)
C3—H3···O3^{iii}	0.96 (2)	2.44 (2)	3.337 (2)	155 (1)

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

In compound (I), scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment and intensity statistics were consistent with centrosymmetry and indicated space group $P\overline{1}$ (No. 2); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. In later stages of refinement, all H atoms except the carboxylic H atoms (H4 and H5) were made canonical with C—H = 0.98 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached C atom. The carboxylic H atoms were refined isotropically. H atoms of the (disordered) methyl groups of the disordered DMSO molecule were assigned fixed occupancies of 0.5 consistent with the refined S-atom populations of the two disorder components; canonical methyl-group geometries were generated using not less than two experimentally determined H-atom locations per methyl group. The maximum effect of extinction was 5.7% of F_o for $02\overline{2}$. The maximum positive residual peak was located near the midpoint of the S2*A*—C18 bond; the maximum negative peak was located ~0.6 Å from S1. In compound (II), scan widths were $(1.35 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry and indicated space group $P2_1/c$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions; both H atoms were refined isotropically. The maximum effect of extinction was 14.9% of F_o for $11\overline{3}$. The maximum positive residual peak was located very near the center of symmetry between C5 and C5^{i} [symmetry code: (i) $1-x, 1-y, 1-z$]; the maximum negative peak was located near the center of the benzenoid ring.

For both compounds, 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 structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

We gratefully acknowledge support for LJF by PPG, Inc. We thank Dr Kurt Loening for his help with nomenclature and 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: FR1073). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Born, L. & Heywang, G. (1990). *Z. Kristallogr.* **190**, 147–152.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1992). *Acta Cryst.* C**48**, 460–465.

Grigor'eva, L. P. & Chetkina, L. A. (1975). *Kristallografiya*, **20**, 1289–1290.

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

Kofman, A. G., Chernysh, G. V., Shigalevskii, V. A. & Vorozhtsov, G. N. (1988). *Zh. Org. Khim.* **24**, 1973–1978.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1997). C**53**, 1995–1997

(5a*S*,7*S*)-7-Isopropenyl-3-methyl-5a,6,8,9-tetrahydro-1*H*,7*H*-pyrano[4,3-*b*][1]benzopyran-1-one

Duy H. Hua,[a] Yi Chen,[a] Paul D. Robinson[b] and Cal Y. Meyers[c]

[a]*Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA,* [b]*Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA, and* [c]*Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA. E-mail: robinson@geo.siu.edu*

(Received 23 May 1997; accepted 19 August 1997)

Abstract

A remarkable asymmetric induction was observed in the one-pot condensation reaction of (*S*)-(−)-perillaldehyde with 4-hydroxy-6-methyl-2-pyrone in the presence of L-proline which provided the title compound, $C_{16}H_{18}O_3$, a tricyclic pyrone, as a single diastereomer in 78% yield. As the configuration of the cyclohexane C atom holding the isopropenyl group is the same as that in the (*S*)-aldehyde substrate, the total absolute stereochemistry