

skew, *cis*, skew' conformation). It becomes impossible for molecules taking this twisted structure in the  $\gamma_1$  phase to form a highly symmetric subcell structure such as  $O'$ .

The thermal factors of the C atoms increase gradually from the *cis*-olefin group towards the methyl terminal, whereas those of the carboxyl-terminal chain (positions 2–11) are almost identical. This shows that the introduction of the *cis*-double bond increases the mobility of the methyl-terminal chains. It is concluded that this dynamical behavior of the acyl chains in the  $\gamma_1$  phase is an important factor for the reversible order–disorder phase transition accompanied by conformational disordering in the methyl-terminal chain.

The carboxyl group is somewhat twisted with respect to the skeletal plane of the carboxyl-terminal chain (Table 2). The O...O hydrogen-bond distance is 2.652 (3) Å. The carbonyl group and the C(2)—C(3) bond take *cis* geometry.

## References

- ABRAHAMSSON, S., DAHLÉN, B., LÖFGREN, H. & PASCHER, I. (1978). *Prog. Chem. Fats Other Lipids*, **16**, 125–143.
- ABRAHAMSSON, S. & RYDERSTEDT-NAHRINGBAUER, I. (1962). *Acta Cryst.* **15**, 1261–1268.
- ASHIDA, T. (1979). *HBL5-V and FMLS. The Universal Crystallographic Computing System – Osaka*, pp. 53–60. The Computation Center, Osaka Univ., Japan.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- KOBAYASHI, M. (1988). *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. GARTI & K. SATO, pp. 139–187. New York: Marcel Dekker.
- KOBAYASHI, M., KANEKO, F., SATO, K. & SUZUKI, M. (1986). *J. Phys. Chem.* **90**, 6371–6378.
- SMALL, D. (1986). *The Physical Chemistry of Lipids*, edited by D. SMALL, pp. 43–87. New York: Plenum Press.
- SUZUKI, M., OGAKI, T. & SATO, K. (1985). *J. Am. Oil Chem. Soc.* **62**, 1600–1604.
- SUZUKI, M., SATO, K., YOSHIMOTO, N., TANAKA, S. & KOBAYASHI, M. (1988). *J. Am. Oil Chem. Soc.* **65**, 1942–1947.
- TANAKA, N. & YASUOKA, N. (1979). *MFP A. The Universal Crystallographic Computing System – Osaka*, pp. 16–18. The Computation Center, Osaka Univ., Japan.

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## Structure of (4*Z*,6*Z*)-6-Acetyl-7-hydroxy-2,4,6-octatriene-4-olide

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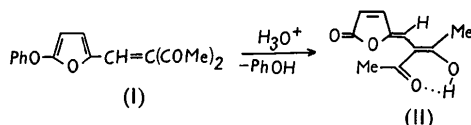
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**Abstract.**  $C_{10}H_{10}O_4$ ,  $M_r = 194.2$ , monoclinic,  $P2_1/c$ ,  $a = 9.266$  (7),  $b = 14.570$  (10),  $c = 7.404$  (5) Å,  $\beta = 108.60$  (6)°,  $V = 947$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.35$  (1),  $D_x = 1.362$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.66$  mm<sup>-1</sup>,  $F(000) = 408$ ,  $T = 293$  K, final  $R = 0.050$  for 869 unique observed reflections. The molecule exists as the enolic tautomer and consists of two planar fragments oriented at an angle of 61.4 (2)° to

one another. The main stabilizing factor of the enol form appears to be a strong intramolecular O—H...O hydrogen bond of 2.422 (3) Å. The structural results are compared with those of other similar analogues reported previously.

**Introduction.** The title compound (II) was prepared by acid hydrolysis of the 2-(5-phenoxy-2-

furylmethylene)-1,3-diketone (I) at ambient temperature (Marchalin, Ilavsky & Mlynarik, 1992). Spectroscopic and analytical data were consistent with the structure (II), *i.e.* the product appears to exist as the enol tautomer. To confirm this and, at the same time, to determine the detailed stereochemistry of this compound, an X-ray structural study of (II) was undertaken.



**Experimental.** Single crystals were grown from an ethanol solution and a light-yellow crystal of dimensions 0.20 × 0.25 × 0.55 mm was selected.  $D_m$  was determined by flotation in *n*-octane/CCl<sub>4</sub>. Systematic absences  $0k0$  for  $k$  odd and  $h0l$  for  $l$  odd were determined from Weissenberg photographs. A Syntex P2<sub>1</sub> diffractometer with graphite-monochromated Mo  $K\alpha$  radiation was used for collection of the intensity data ( $h = 0$  to 12,  $k = 0$  to 16,  $l = -9$  to 9). The unit-cell parameters and their *e.s.d.*'s were determined by a least-squares refinement of 25 reflections with  $7 < 2\theta < 25^\circ$ . The  $\theta$ - $2\theta$  scan mode was used with the scan rate ranging from 2.0 to 29.3° min<sup>-1</sup>, depending on intensity. The background time to scan time used was 1.0, and the scan range from -1.0 to 1.0 ( $2\theta$ ) about the  $K\alpha$  doublet. Two check reflections were measured after every 98 reflections and no significant fluctuation was observed. The intensities were corrected for Lorentz-polarization effects but not for absorption. Of the 2183 unique ( $R_{int} = 0.031$ ) reflections measured ( $2\theta_{max} = 55^\circ$ ), 869 with  $I > 2\sigma(I)$  were considered observed. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined by block-diagonal least-squares methods with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms (all H atoms were located from a  $\Delta\rho$  map). 167 parameters refined. The final error indices were  $R = 0.050$ ,  $wR = 0.050$  and  $S = 1.45$ . The largest shift/*e.s.d.* ratio in the final cycle of refinement was 0.03. The function minimized was  $\sum w(\Delta F)^2$ , where  $w = 1$  was found to be the most appropriate weighting scheme [ $w(\Delta F)^2$  approximately independent of  $|F_o|$  and  $\sin\theta/\lambda$ ]. The maximum and minimum heights in the final  $\Delta\rho$  synthesis were 0.18 and  $-0.20 e \text{ \AA}^{-3}$ , respectively. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations except those using *SHELXS86* were performed with a local version of *NRC* (Ahmed, Hall, Pippy & Huber, 1973).

Table 1. *Final atomic coordinates* ( $\times 10^4$ ) *and equivalent isotropic thermal parameters* ( $\text{\AA}^2$ ) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$
C(1)	5289 (3)	7181 (2)	1762 (4)	4.82 (8)
C(2)	6513 (3)	7813 (2)	1958 (4)	5.16 (9)
C(3)	5964 (3)	8646 (2)	1846 (3)	4.20 (7)
C(4)	4362 (2)	8599 (2)	1576 (3)	3.52 (6)
C(5)	3339 (2)	9241 (1)	1464 (3)	3.49 (7)
C(6)	1730 (2)	9086 (1)	1217 (3)	3.23 (7)
C(7)	790 (3)	8632 (2)	-364 (3)	3.89 (7)
C(8)	1261 (3)	8290 (2)	-1970 (4)	5.16 (9)
C(9)	1112 (3)	9429 (2)	2573 (3)	3.83 (8)
C(10)	2054 (3)	9955 (2)	4234 (4)	4.93 (10)
O(1)	5240 (2)	6365 (1)	1813 (3)	6.60 (7)
O(2)	3977 (2)	7681 (1)	1506 (2)	4.04 (5)
O(3)	-636 (2)	8486 (1)	-538 (2)	5.09 (6)
O(4)	-272 (2)	9296 (1)	2431 (3)	5.24 (6)

Table 2. *Bond lengths* ( $\text{\AA}$ ) *and angles* ( $^\circ$ ) *with e.s.d.'s in parentheses*

C(1)–C(2)	1.431 (4)	C(5)–C(6)	1.460 (4)
C(1)–O(1)	1.191 (3)	C(6)–C(7)	1.384 (3)
C(1)–O(2)	1.378 (3)	C(7)–O(3)	1.304 (3)
C(2)–C(3)	1.308 (4)	C(7)–C(8)	1.478 (4)
C(3)–C(4)	1.434 (3)	C(6)–C(9)	1.399 (4)
C(4)–O(2)	1.381 (3)	C(9)–O(4)	1.267 (3)
C(4)–C(5)	1.315 (3)	C(9)–C(10)	1.474 (4)
O(1)–C(1)–C(2)	132.5 (3)	C(5)–C(6)–C(7)	121.4 (2)
O(1)–C(1)–O(2)	119.5 (3)	C(5)–C(6)–C(9)	119.4 (2)
O(2)–C(1)–C(2)	108.0 (2)	C(7)–C(6)–C(9)	119.2 (2)
C(1)–C(2)–C(3)	108.1 (3)	C(6)–C(7)–O(3)	120.4 (2)
C(2)–C(3)–C(4)	109.2 (2)	C(6)–C(7)–C(8)	125.1 (2)
C(3)–C(4)–O(2)	107.1 (2)	C(8)–C(7)–O(3)	114.5 (2)
C(3)–C(4)–C(5)	132.0 (2)	C(6)–C(9)–O(4)	121.3 (2)
C(5)–C(4)–O(2)	120.9 (2)	C(6)–C(9)–C(10)	121.0 (2)
C(4)–O(2)–C(1)	107.5 (2)	C(10)–C(9)–O(4)	117.7 (2)
C(4)–C(5)–C(6)	125.8 (2)		

**Discussion.** Final atomic coordinates of non-H atoms and equivalent isotropic  $B$  values are listed in Table 1,\* bond distances and angles in Table 2. A view of the molecule with the atom numbering is shown in Fig. 1. As seen in Fig. 1, the crystal structure determination has confirmed the indication from the spectroscopic data that the molecule solely exists in the enol form.

The bond distances within the butenolide moiety [atoms C(1)–C(5), O(1), O(2)] show typical features of similar structures reported in the literature (*e.g.* Thackeray & Gafner, 1975; Murray-Rust & Murray-Rust, 1978; Brassy, Bachet, Molho & Molho, 1985), *i.e.* they are consistent with integer bond orders. The five-membered butenolide ring is approximately planar with no atom displaced more than 0.006 (2)  $\text{\AA}$

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54821 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA0011]

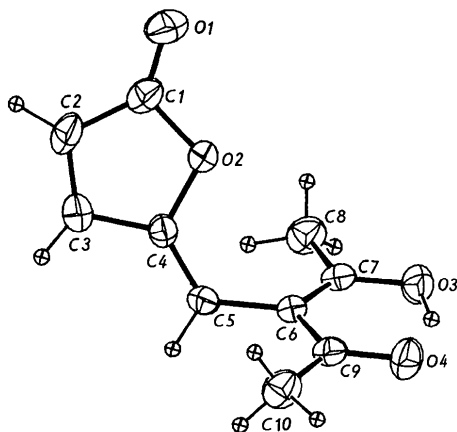


Fig. 1. A perspective view of molecule (II) showing the numbering of the atoms. The thermal ellipsoids are drawn at the 50% probability level.

out of the plane; on the other hand, the O(1) and C(5) atoms are displaced by 0.039 (2) and 0.063 (2) Å, respectively, on the same side of the five-atom plane.

On the other end of the molecule there is a strong intramolecular hydrogen bond between O(3)—H and O(4) (obviously, the main factor stabilizing the enol

form), thus effectively forming a six-membered ring; the details of this H bond are: O(3)⋯O(4) = 2.422 (3), O(3)—H = 1.09 (3), H⋯O(4) = 1.41 (3) Å, O(3)—H⋯O(4) = 151 (3)°. The effects of the strong hydrogen bond are reflected in the overall geometry of the hydrogen-bonded ring, which exhibits a shortening and a lengthening of the formal single and double bonds, respectively; the ring is also planar to within  $\pm 0.014$  (2) Å. Thus, the molecule can be regarded as consisting of two planar fragments, with a twist angle of 61.4 (2)° about the central C(5)—C(6) single bond.

#### References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). *NRC Crystallographic Programs for the IBM360 System*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.
- BRASSY, C., BACHET, B., MOLHO, L. & MOLHO, D. (1985). *Acta Cryst.* **41**, 781–783.
- MARCHALIN, S., ILAVSKY, D. & MLYNARIK, V. (1992). *Collect. Czech. Chem. Commun.* Submitted.
- MURRAY-RUST, P. & MURRAY-RUST, J. (1978). *Acta Cryst.* **B34**, 2065–2066.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- THACKERAY, M. M. & GAFNER, G. (1975). *Acta Cryst.* **B31**, 335–338.

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## Structure of 2,3-Di-*tert*-butyl-5,6,7,8-*endo*-tetrakis(hydroxymethyl)bicyclo[2.2.2]oct-2-ene

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**Abstract.** C<sub>20</sub>H<sub>36</sub>O<sub>4</sub>,  $M_r = 340.50$ , orthorhombic, *Pbca*,  $a = 29.056$  (9),  $b = 13.127$  (3),  $c = 10.068$  (2) Å,  $V = 3840$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.178$ ,  $D_m = 1.174$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.075$  mm<sup>-1</sup>,  $F(000) = 1504$ ,  $T = 293.7$  K,  $R = 0.083$  for 2435 observed reflections. Owing to the bulky *ortho* substituents, *tert*-butyl groups and *endo*-hydroxymethyl groups, large deviations from the torsion angles of an eclipsed conformation and large

C—C—R ( $R = \textit{tert}-butyl or hydroxymethyl) angles were observed. The crystal packing is constructed from double layered networks formed by O⋯O hydrogen bonds. These double layers are stacked along the  $a$  axis and interactions between double layers are of a van der Waals type involving *tert*-butyl groups.$

**Introduction.** Two isomers were obtained from Diels–Alder reaction of 3,4-di-*tert*-butylthiophene 1,1-dioxide and maleic anhydride. The conformation of

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