Acta Cryst. (1978). B**34**, 2923–2925

2-Methoxymethoxycyclopentene-1-carboxylic Acid

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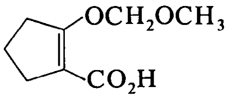
(*Received* 13 *April* 1978; *accepted* 12 *May* 1978)

Abstract. $C_8H_{12}O_4$, $M_r = 172{\cdot}18$, triclinic, $P\bar{1}$, $a = 5{\cdot}379\,(3)$, $b = 8{\cdot}393\,(6)$, $c = 9{\cdot}618\,(7)$ Å, $\alpha = 87{\cdot}78\,(5)$, $\beta = 75{\cdot}70\,(5)$, $\gamma = 85{\cdot}44\,(6)°$, $U = 419{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}363$ g cm^{-3}, μ(Mo $K\alpha$) = 0·7 cm^{-1}. The structure was refined to $R = 0{\cdot}059$ for 1960 reflexions. The molecules form centrosymmetric dimers by hydrogen bonding between carboxylic acid groups.

Introduction. An investigation of the dependence of reactivity on structure in intramolecular general acid catalysis (Kirby & Osborne, 1978) involved the synthesis of a series of acetals, formally derived by the *O*-methoxymethylation of β-ketoacids. No detailed structural information is available for compounds of this sort; we have therefore determined crystal structures in a few cases, to see how far differences in reactivity reflect differences in geometry. This paper deals with the structure of the enol acetal (I).



(I)

Large colourless crystals were grown from chloroform/hexane. Intensities in the range $0 < 2\theta < 60°$ were determined on an automated Syntex $P2_1$ diffractometer with monochromated Mo $K\alpha$ radiation. Crystals decomposed rapidly in the beam; when the intensities of two check reflexions fell below half their initial values, the crystal was discarded and a fresh one substituted. Intensities were scaled according to the check reflexion intensities. Three crystals were used (0·9 × 0·15 × 0·3 mm, 1133 reflexions; 0·8 × 0·25 × 0·15 mm, 1438 reflexions; 0·7 × 0·35 × 0·3 mm, 790 reflexions). Quoted cell dimensions are averages of those obtained for each crystal. Lp corrections were applied; averaging equivalent reflexions gave 1962 unique reflexions with $F > 4\sigma(F)$.

The structure was solved by multisolution $\sum_2$ sign expansion with 436 $E > 1{\cdot}2$, using the program *SHELX*; the best E map showed all non-hydrogen atoms. Least-squares refinement with anisotropic C and O atoms ($R = 0{\cdot}09$), was followed by a difference synthesis which showed all H atom positions. In the final stages of refinement a rigid methyl group (with C—H 1·08 Å and H—C—H 109·5°) was used; all other H atoms refined freely. Separate overall isotropic temperature factors were assigned to methyl and non-methyl H atoms. Convergence was achieved at $R = 0{\cdot}0591$, with a corresponding $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ of 0·0701. The weighting scheme was $w = 1/[\sigma(F) + 0{\cdot}0015F^2]$, which gave mean values of $w\Delta^2$ independent of $|F_o|$ or $\sin\theta$. A final difference map had no peaks $>0{\cdot}4$ e Å^{-3}. Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Tables 2 and 3.† Torsion angles are in Table 4. Diagrams of the structure are given in Figs. 1 and 2.

Table 1. *Atom coordinates* (×10^4)

The overall isotropic temperature factor for methyl H atoms [H(9),H(10),H(11)] refined to 0·122 (4) Å^2, the value for other H atoms was 0·056 (2) Å^2.

	x	*y*	*z*
C(1)	5559 (3)	2800 (2)	8552 (2)
C(2)	6885 (3)	2727 (2)	7165 (2)
C(3)	9358 (3)	1696 (2)	6974 (2)
C(4)	9090 (3)	847 (2)	8428 (2)
C(5)	6992 (3)	1835 (2)	9502 (2)
C(6)	3189 (3)	3770 (2)	9133 (2)
C(7)	7794 (4)	3360 (3)	4650 (2)
C(8)	5334 (5)	1788 (4)	3614 (3)
O(1)	2450 (2)	3705 (2)	10545 (1)
O(2)	1953 (2)	4579 (2)	8393 (1)
O(3)	6163 (2)	3544 (2)	6082 (1)
O(4)	7633 (3)	1911 (2)	4080 (2)
H(1)	10784 (34)	2472 (26)	6779 (22)
H(2)	9593 (35)	931 (26)	6178 (22)
H(3)	10846 (37)	761 (27)	8685 (21)
H(4)	8656 (36)	−221 (26)	8391 (22)
H(5)	7774 (33)	2550 (25)	10069 (21)
H(6)	5877 (34)	1095 (25)	10199 (21)
H(7)	9593 (35)	3434 (26)	4699 (22)
H(8)	7240 (34)	4198 (26)	4136 (23)
H(9)	5335	640	3143
H(10)	5246	2724	2822
H(11)	3684	1947	4514
H(12)	927 (34)	4332 (26)	10838 (22)

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33619 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·349 (3)	C(1)–C(5)	1·509 (3)
C(1)–C(6)	1·456 (3)	C(2)–C(3)	1·503 (3)
C(3)–C(4)	1·524 (3)	C(4)–C(5)	1·540 (3)
C(2)–O(3)	1·345 (3)	C(6)–O(1)	1·318 (3)
C(6)–O(2)	1·238 (3)	C(7)–O(3)	1·445 (3)
C(7)–O(4)	1·371 (4)	C(8)–O(4)	1·428 (4)
C(3)–H(1)	1·023 (21)	C(3)–H(2)	0·996 (23)
C(4)–H(3)	1·030 (22)	C(4)–H(4)	0·949 (23)
C(5)–H(5)	1·006 (23)	C(5)–H(6)	1·012 (20)
C(7)–H(7)	0·987 (21)	C(7)–H(8)	0·917 (23)
O(1)–H(12)	0·925 (19)		

Table 3. *Bond angles* (°)

C(1)–C(2)–C(3)	112·2 (2)	C(1)–C(2)–O(3)	124·3 (2)
C(3)–C(2)–O(3)	123·4 (2)	C(2)–C(1)–C(5)	110·8 (2)
C(2)–C(1)–C(6)	126·8 (2)	C(5)–C(1)–C(6)	122·2 (2)
C(1)–C(5)–C(4)	103·3 (2)	C(5)–C(4)–C(3)	106·3 (2)
C(2)–C(3)–C(4)	103·3 (2)	O(3)–C(7)–O(4)	112·6 (3)
C(1)–C(6)–O(2)	124·3 (2)	C(1)–C(6)–O(1)	113·4 (2)
O(2)–C(6)–O(1)	122·4 (2)	C(2)–O(3)–C(7)	118·2 (2)
C(7)–O(4)–C(8)	114·1 (3)	C(1)–C(5)–H(5)	111·2 (13)
C(4)–C(5)–H(5)	111·1 (11)	C(1)–C(5)–H(6)	113·3 (13)
C(4)–C(5)–H(6)	109·8 (12)	H(5)–C(5)–H(6)	108·2 (18)
C(5)–C(4)–H(3)	113·2 (12)	C(3)–C(4)–H(3)	109·1 (12)
C(5)–C(4)–H(4)	111·7 (11)	C(3)–C(4)–H(4)	111·0 (14)
H(3)–C(4)–H(4)	105·5 (19)	C(2)–C(3)–H(1)	105·6 (12)
C(4)–C(3)–H(1)	111·6 (14)	C(2)–C(3)–H(2)	112·0 (12)
C(4)–C(3)–H(2)	112·2 (13)	H(1)–C(3)–H(2)	111·6 (17)
O(3)–C(7)–H(7)	108·2 (13)	O(4)–C(7)–H(7)	107·9 (14)
O(3)–C(7)–H(8)	104·1 (12)	O(4)–C(7)–H(8)	112·2 (15)
H(7)–C(7)–H(8)	111·9 (18)	C(6)–O(1)–H(12)	108·8 (14)

Table 4. *Torsion angles* (°)

Sign convention as defined by Klyne & Prelog (1960).

C(3)–C(2)–C(1)–C(5)	0·9 (3)
C(3)–C(2)–C(1)–C(6)	175·4 (3)
O(3)–C(2)–C(1)–C(5)	−175·9 (3)
O(3)–C(2)–C(1)–C(6)	−1·3 (4)
C(1)–C(2)–C(3)–C(4)	11·7 (3)
O(3)–C(2)–C(3)–C(4)	−171·5 (3)
C(1)–C(2)–O(3)–C(7)	179·3 (3)
C(3)–C(2)–O(3)–C(7)	2·9 (3)
C(2)–C(1)–C(5)–C(4)	−12·9 (3)
C(6)–C(1)–C(5)–C(4)	172·2 (2)
C(2)–C(1)–C(6)–O(2)	6·0 (4)
C(2)–C(1)–C(6)–O(1)	−174·4 (3)
C(5)–C(1)–C(6)–O(2)	−180·0 (3)
C(5)–C(1)–C(6)–O(1)	−0·3 (3)
C(1)–C(5)–C(4)–C(3)	19·6 (3)
C(5)–C(4)–C(3)–C(2)	−19·1 (3)
O(4)–C(7)–O(3)–C(2)	73·7 (3)
O(3)–C(7)–O(4)–C(8)	75·5 (3)

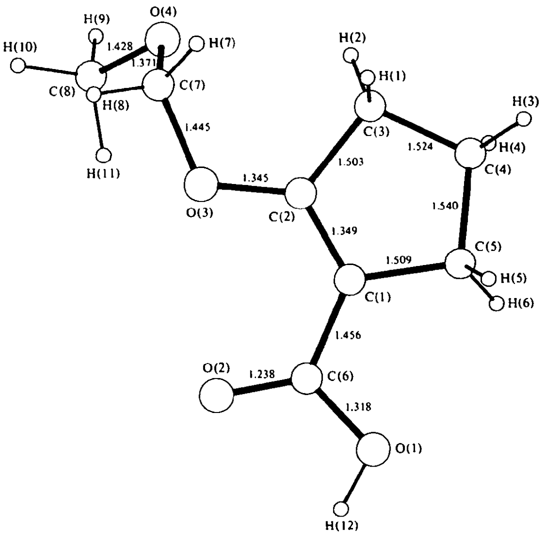

Fig. 1. The title compound, with bond lengths in Å, showing the atomic numbering scheme.

Discussion. Unsymmetrical acetals with good leaving groups O*R'* are hydrolysed by a mechanism (1) which involves the cleavage of the bond to the leaving group and an increase in the order of the *R*O–C bond (Fife, 1975):

$$RO{-}CH_2{-}OR' \rightarrow R\overset{+}{O}{=}CH_2 + \overset{-}{O}R'. \qquad (1)$$

Changes in this direction are already apparent in the ground-state structure of (1) (Fig. 1). The bond to the leaving-group oxygen [C(7)–O(3)] is 1·445 (3) Å, though it might have been expected to be shorter than the typical C–O single-bond length of 1·43 Å (Kennard *et al.*, 1972) because O(3) is sp^2 hybridized [C(2)–O(3)–C(7) = 118·2°]. On the other hand C(7)–O(4), which increases in bond order in the transition state, has shortened to 1·371 (4) Å. A detailed discussion of structure and reactivity in this and similar systems will be given elsewhere (Jones, Kennard, Kirby & Osborne, 1978).

The molecules are linked by the usual carboxylic acid H bonding (Fig. 2) into centrosymmetric dimers. Associated non-bonded distances are: H(12)···O(2′) 1·75, O(1)···O(2′) 2·67 Å (primed atoms at $-x$, $1-y$, $2-z$).

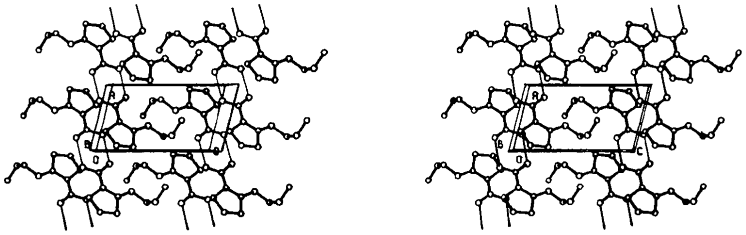

Fig. 2. Stereo packing diagram showing hydrogen bonding (narrow lines). H atoms are omitted.

We thank the MRC and SRC for financial support. The figures were drawn using the program *PLUTO* written by Dr W. D. S. Motherwell. All other crystallographic programs were written by Dr G. M. Sheldrick.

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Acta Cryst. (1978). B**34**, 2925–2927

(*E*)-3-Methoxymethoxybut-2-enoic Acid

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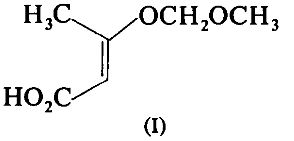
(*Received* 13 *April* 1978; *accepted* 12 *May* 1978)

Abstract. $C_6H_{10}O_4$, $M_r = 146{\cdot}14$, triclinic, $P\bar{1}$, $a = 4{\cdot}818\,(2)$, $b = 8{\cdot}241\,(3)$, $c = 9{\cdot}712\,(3)$ Å, $\alpha = 87{\cdot}68\,(3)$, $\beta = 83{\cdot}92\,(3)$, $\gamma = 79{\cdot}08\,(3)^\circ$, $U = 376{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}289$ g cm^{-3}, μ(Mo $K\alpha$) $= 0{\cdot}7$ cm^{-1}. The structure was refined to $R = 0{\cdot}066$ for 1272 unique reflexions. The molecules form centrosymmetric dimers by hydrogen bonding between the carboxyl groups.

Introduction. As part of the investigation referred to in the preceding paper (Jones, Kennard, Kirby & Osborne, 1978), the methoxymethoxy enol ether (I) of acetoacetic acid was prepared. The structure of (I) is of interest both in the context of acetal chemistry, and because of intriguing differences between the properties of the *cis* and *trans* enols of *β*-dicarbonyl compounds.



(I)

Large colourless crystals elongated along *a* were obtained from carbon tetrachloride/hexane. Intensities were measured on a Nonius CAD-4 diffractometer with monochromated Mo *Kα* radiation and a crystal 0·7 × 0·4 × 0·2 mm. 1951 reflexions were measured; the 2*θ* range was 0–60° initially but was reduced to 0–50° when rapid crystal decomposition became apparent. A repeatedly monitored check reflexion diminished steadily in intensity to 40% of its original value; other intensities were scaled accordingly. Lp corrections were applied; averaging equivalent reflexions gave 1272 unique reflexions with $F > 4\sigma(F)$.

Table 1. *Atom coordinates* (×10^4)

Overall temperature factors for H atoms refined to 0·075 (4) (non-methyl H) and 0·073 (5) Å^2 (methyl H). For occupation factors of disordered H atoms see text.

	x	*y*	*z*
C(1)	2302 (5)	763 (3)	8669 (2)
C(2)	380 (5)	1261 (3)	7610 (2)
C(3)	−1648 (5)	2611 (3)	7668 (2)
C(5)	−3327 (6)	1918 (3)	5556 (2)
C(7)	−1243 (10)	3314 (4)	3686 (3)
C(8)	−2342 (7)	3866 (3)	8777 (3)
O(1)	2291 (4)	1491 (2)	9750 (1)
O(2)	4170 (4)	−592 (2)	8341 (2)
O(4)	−3455 (4)	3032 (2)	6665 (2)
O(6)	−1010 (4)	1933 (2)	4609 (1)
H(1)	607	488	6718
H(2)	−5228	2268	5033
H(3)	−3225	681	5985
H(4)	676	3150	2982
H(4*A*)	448	3994	3743
H(5)	−1524	4487	4189
H(5*A*)	−3268	4136	3875
H(6)	−3041	3292	3115
H(6*A*)	−1068	2799	2669
H(7)	−1001	3502	9602
H(7*A*)	−3015	3271	9732
H(8)	−4538	3934	9177
H(8*A*)	−4047	4830	8491
H(9)	−2033	5061	8361
H(9*A*)	−510	4397	8917
H(10)	5052 (56)	−872 (31)	9144 (18)

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