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

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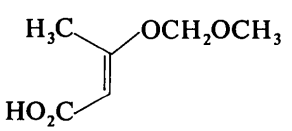
Abstract. $C_6H_{10}O_4$, $M_r = 146{\cdot}14$, triclinic, $P\bar{1}$, $a = 4{\cdot}818$ (2), $b = 8{\cdot}241$ (3), $c = 9{\cdot}712$ (3) Å, $\alpha = 87{\cdot}68$ (3), $\beta = 83{\cdot}92$ (3), $\gamma = 79{\cdot}08$ (3)°, $U = 376{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}289$ g cm^{-3}, μ(Mo $K\alpha$) = 0·7 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 $K\alpha$ radiation and a crystal 0·7 × 0·4 × 0·2 mm. 1951 reflexions were measured; the 2θ 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 $F > 4\sigma(F)$.

* External Staff, Medical Research Council.

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)

Table 2. *Bond angles* (°)

C(3)–C(2)–C(1)	124·2 (3)	C(3)–O(4)–C(5)	118·9 (3)
C(7)–O(6)–C(5)	114·9 (3)	O(6)–C(5)–O(4)	112·6 (3)
C(2)–C(1)–O(1)	125·8 (3)	O(2)–C(1)–O(1)	122·0 (3)
O(2)–C(1)–C(2)	112·3 (3)	O(4)–C(3)–C(2)	122·8 (3)
C(8)–C(3)–C(2)	127·6 (3)	C(8)–C(3)–O(4)	109·6 (3)
C(1)–O(2)–H(10)	103·7 (18)		

Table 3. *Torsion angles* (°)

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

C(3)–C(2)–C(1)–O(1)	1·1 (4)
C(3)–C(2)–C(1)–O(2)	−178·0 (4)
C(1)–C(2)–C(3)–O(4)	−178·7 (4)
C(1)–C(2)–C(3)–C(8)	0·8 (4)
C(3)–O(4)–C(5)–O(6)	−74·8 (4)
C(5)–O(4)–C(3)–C(2)	4·7 (4)
C(5)–O(4)–C(3)–C(8)	−175·0 (4)
C(7)–O(6)–C(5)–O(4)	−62·5 (4)

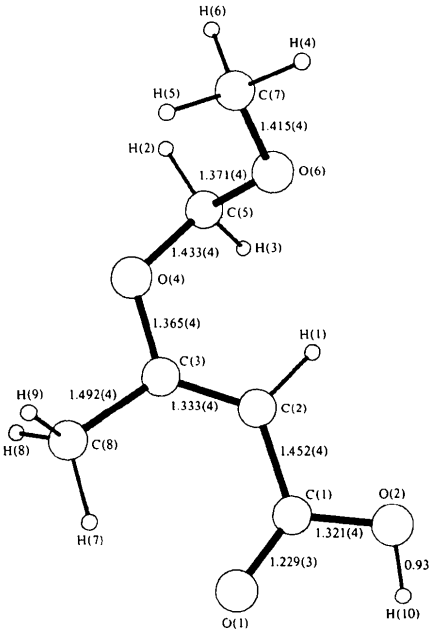


Fig. 1. The title compound showing the atomic numbering scheme (bond lengths in Å).

The structure was solved by multisolution $\sum_2$ sign expansion with 324 $E > 1{\cdot}2$. Isotropic least-squares refinement proceeded to $R = 0{\cdot}23$ and anisotropic to $R = 0{\cdot}13$, when a difference synthesis showed all H except H(10); extra peaks associated with the methyl groups suggested rotational disorder of these groups. When H atoms were included in the refinement, a model of twofold disorder (Jones & Kennard, 1977) proved successful in refining the methyl groups;* all C–H distances were fixed at 1·08 Å and methylene H–C–H angles at 109·5°. The R factor, however, remained high (0·10) and the final H atom could not be located. In view of the large mosaic spread of reflexions on preliminary photographs, an anisotropic scaling correction was then made to the data (Shakked & Rabinovich, 1977). R fell to 0·07 and the final H atom appeared on a difference map. In the final stages of refinement the O(2)–H(10) distance was constrained to be 0·93 Å within an e.s.d. of 0·01 Å and separate overall isotropic temperature factors were allocated to methyl and non-methyl H atoms. The final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·0758, with a corresponding R of 0·0657; the weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}002F^2]$, which gave mean $w\Delta^2$ almost independent of $\sin\theta$ or $|F_o|$. Final site occupation factors were: H(4), H(5), H(6) 0·56; H(4*A*), H(5*A*), H(6*A*) 0·44; H(7), H(8), H(9) 0·44; H(7*A*), H(8*A*), H(9*A*) 0·56 (all e.s.d.'s 0·02). Final values of components of the symmetric scaling tensor were 1·04, 1·00, 0·97, 0·02, 0·13 and −0·28 (all e.s.d.'s 0·02) (*cf.* the values for pure isotropic scaling: 1, 1, 1, −0·02, −0·10, −0·19). Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Fig. 1 and Table 2.† Torsion angles are given in Table 3. Diagrams of the structure are given in Figs. 1 and 2.

* It has recently been shown (Fitzgerald & Jensen, 1978) that apparent H-atom positions might be sensitive to crystal deterioration. This might serve to cast doubt on the validity of the model of twofold disorder. However, the final difference map showed no significant peaks in the methyl regions.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33620 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

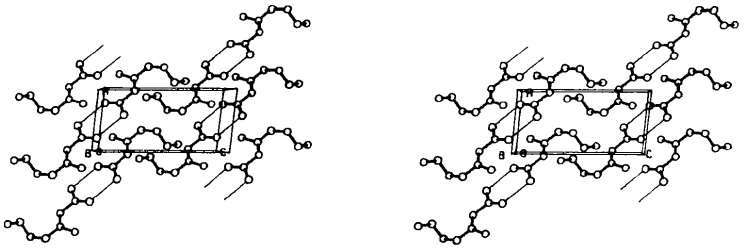


Fig. 2. Stereo packing diagram showing H bonding (narrow lines). H atoms are omitted.

Discussion. Bond lengths and angles in the acetal group of (I) are closely similar to those of the acetal enol ether described in the preceding paper (Jones *et al.*, 1978), and thus confirm the significance of the deviations from normal C—O bond lengths.

The molecules are linked to form centrosymmetric dimers by typical carboxylic acid H bonding, with non-bonded distances (Å) as follows: O(1)···O(2′) 2·64, O(1)···H(10′) 1·75 (primed atoms at $1-x$, $-y$, $2-z$).

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3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one

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Abstract. $C_3Cl_2N_2OS$, monoclinic, $P2_1/c$, a = 7·9504 (5), b = 13·2827 (12), c = 6·3390 (4) Å, β = 106·350 (5)°, Z = 4, D_c = 1·89 g cm^{-3}. The crystal structure has been solved by direct methods and refined by least-squares techniques to R_w = 5·7%. The thiadiazine ring is nearly planar.

Introduction. A number of compounds related to the title compound, whose structure is given in Fig. 1, have been studied in the Organic Chemistry Laboratory of this University (Geevers & Trompen, 1974). In order to establish the accurate geometry of these compounds an X-ray structure analysis of $C_3Cl_2N_2OS$ has been carried out.

A crystal suitable for X-ray diffraction experiments (maximum dimension 0·5 mm) was supplied by Dr W. P. Trompen. Cell constants were determined by a least-squares fit of diffraction angles of 41 reflexions, determined accurately on a Philips PW1100 four-circle diffractometer. Intensities were measured using an ω–2θ scan (Mo $K\alpha$ radiation, λ = 0·71069 Å, graphite monochromator, θ_{max} = 30°). The space group was determined as $P2_1/c$ from the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The number of reflexions measured was 2004. 1444 reflexions had $I > 2\sigma(I)$ and were considered to be observed. No systematic change in the intensities of the standard reflexions (measured at intervals of one hour) could be detected. No absorption correction was applied.

The structure was solved by the program *MULTAN* (Germain, Main & Woolfson, 1971). Positions and anisotropic thermal parameters were refined with the *ORFLS* program (Busing, Martin & Levy, 1962). The scattering factors for C, N and O were calculated from Clementi's (1965) wavefunctions (Harkema, 1971).

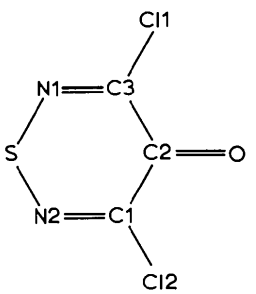

Fig. 1. Atomic arrangement of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one.

Table 1. *Positional parameters* (×10^4)

	x	*y*	*z*
C(1)	94 (4)	1141 (2)	3747 (5)
C(2)	1454 (4)	1504 (2)	5693 (5)
C(3)	3252 (4)	1311 (2)	5563 (6)
N(1)	3699 (3)	915 (2)	3967 (5)
N(2)	323 (3)	710 (2)	2057 (4)
O	1131 (3)	1920 (2)	7231 (4)
Cl(1)	4891 (1)	3342 (1)	2857 (2)
Cl(2)	7965 (1)	1299 (1)	3844 (2)
S	7739 (1)	5515 (1)	3213 (2)