Structure of Methylene Oxalate

BY ÅKE KVICK AND RUNE LIMINGA

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Abstract. $C_3H_2O_4$, tetragonal, $P4_1$, $a = 6\cdot124$ (4), $c = 10\cdot381$ (8) Å, $V = 389\cdot3$ Å^3, $Z = 4$, $d_x = 1\cdot74$ Mg m^{-3}, $T = 153$ K, μ(Mo $K\alpha$) = $0\cdot16$ mm^{-1}. The high density and melting point indicate that the molecules are efficiently packed, although there are no strong intermolecular interactions. The closest contacts are between O and H atoms ($2\cdot4$–$2\cdot5$ Å) and between O and C atoms ($2\cdot73$–$2\cdot80$ Å). These weak interactions allow large rigid-body motion of the molecules even at 153 K.

Introduction. Methylene oxalate, the simplest carboxylic diester possible, is easily prepared from oxalic acid and paraformaldehyde in concentrated sulphuric acid (Serck-Hanssen, 1969). The colourless crystals sublime at 439 K, which is only about 20 K lower than for anhydrous oxalic acid. The density is about 1·6 Mg m^{-3} at room temperature (1·9 Mg m^{-3} for oxalic acid).

The melting point, as well as the density, is high. Strong hydrogen bonding in oxalic acid results in specific interactions between the molecules and may explain the observed physical properties. In methylene oxalate no interactions of this type can be expected, except for van der Waals forces. The determination of the crystal structure was of interest in order to determine whether trends in the packing of the molecules could explain the high density and melting point.

A preliminary film investigation indicated tetragonal symmetry and $P4_1$ (or $P4_3$) as possible space group. It was also observed from the films that the effect on the intensities of thermal motion was very large.

A preliminary set of intensities was collected at room temperature. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) and refined by least squares. Of the 580 independent reflexions measured for $\theta < 30°$, only about 20% had $I > 3\sigma(I)$ and were used in this preliminary refinement.

A second set of intensities was collected at 153 K. The crystal used was an octahedron with rounded corners and a maximum dimension of about 0·20 mm. The crystal was covered with a thin layer of polystyrene (dissolved in chloroform) to avoid sublimation. The cell dimensions were obtained by measuring the setting angles of 25 reflexions on the diffractometer and

refined by least squares. On cooling, a remained almost unchanged whereas c decreased by about 0·5 Å compared with the room-temperature values. The intensities were collected on a CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation and the $\omega/2\theta$ scan method. Cooling of the crystal was accomplished by a cold nitrogen gas stream obtained by a locally constructed low-temperature device. Background corrections were made by the profile-analysis method (Lehmann & Larsen, 1974). Four standard reflexions, monitored at regular intervals, indicated an average decrease in intensity of about 2·5% by the end of the experiment. A scaling function was derived as the average of the individual scaling functions for the different test reflexions. All intensities were corrected with this function. The intensities of all reflexions in the octant hkl and partly in $\bar{h}kl$ were measured out to $\sin \theta/\lambda = 0\cdot70$ Å^{-1}. After averaging of equivalent reflexions 596 independent reflexions remained. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Even at this lower temperature the decrease in intensity with scattering angle due to thermal effects was very pronounced. Only about 30% of the reflexions had $I > 3\sigma(I)$. As will be seen below this affects the refinement resulting in rather high final R values and e.s.d.'s of the parameters.

The structure was refined by minimizing $\sum w(|F_o| - |F_c|)^2$ with the program *UPALS*. The weights were $w = \sigma^2(F)^{-1}$. and $\sigma^2(F) = \sigma^2_{\text{count}}(F^2)/4F^2 + (0\cdot025F)^2$. The

Table 1. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s*

	x	y	z
O(1)	6562 (17)	3588 (21)	200 (19)
O(2)	9316 (15)	5868 (16)	450*
O(3)	8524 (21)	1583 (17)	2434 (19)
O(4)	10843 (16)	4367 (15)	2178 (6)
C(1)	8161 (19)	4130 (19)	720 (17)
C(2)	9121 (17)	3145 (21)	1899 (19)
C(3)	11063 (21)	6043 (23)	1306 (22)
H(1)	1104 (13)	745 (17)	164 (9)
H(2)	1291 (17)	635 (12)	96 (7)

* Fixed to define the origin.

refinement was started with the preliminary parameters derived earlier, and was based on the 393 reflexions having positive intensities. The 71 parameters refined comprised one scale factor, positional parameters for the nine atoms, anisotropic thermal parameters for the non-hydrogen and isotropic for the H atoms. The shifts in the final cycle were all $<0\cdot1\sigma$. The final weighted R_w was $0\cdot094$ and $R = 0\cdot173$. R for the 194 reflexions with $F \geq 3\sigma(F)$ was $0\cdot073$.

The scattering factors for neutral H, C, and O were taken from *International Tables for X-ray Crystallography* (1974). All calculations, except solution of the structure, were made on the IBM 1800 and NORD 10 computers with programs described by Lundgren (1976). Atomic coordinates are given in Table 1.*

Discussion. The molecule is illustrated in Fig. 1, which also defines the atomic notation. The distances from the plane defined by the three C atoms indicate that the heavy atoms deviate slightly from planarity (Table 2). The C—O bonds to the methylene C atom are considerably longer than those to the remaining two C atoms (Fig. 1). The exocyclic O atoms show typical

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34887 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
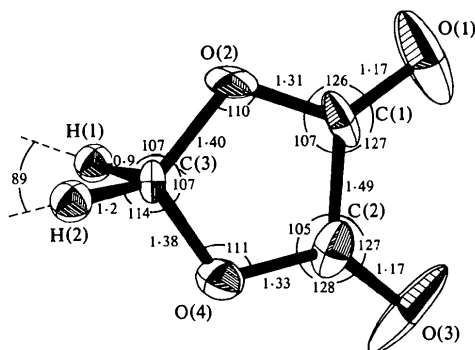
carbonyl C=O bond distances. Because of the high thermal motion of the atoms even at 153 K, the observed bond distances are somewhat shorter than the equilibrium bond distances. The C—H distances were determined with low precision and a more realistic value is $1\cdot10$ Å. This estimation is based on the comparable C—H bonds of $1\cdot099$ Å determined in the low-temperature neutron diffraction study of α-glycylglycine (Kvick, Al-Karaghouli & Koetzle, 1977).

The present molecular dimensions may be compared with the results from the structure determination of the two crystalline modifications of oxalic acid, where the rigid-body motion is considerably smaller than in the present case. The C=O and C—C distances in oxalic acid are $1\cdot207$ (1), $1\cdot222$ (1) Å and $1\cdot537$ (1), $1\cdot537$ (1) Å for the α and β modifications, respectively (Derissen & Smit, 1974).

The packing of the molecules is illustrated in Fig. 2. Intermolecular distances < 3 Å are given in Table 3, and are also illustrated in Fig. 3. The methylene H atoms are involved in short contacts with the endocyclic O atoms. If the H atom positions are adjusted in the C—H bond directions to give the expected C—H distances of $1\cdot10$ Å, the $O(2)\cdots H(1)$ and $O(4)\cdots H(2)$ distances are $2\cdot50$ and $2\cdot42$ Å, respectively. The sum of the van der Waals radii for O and H is $2\cdot4$ Å. Other intermolecular contacts of importance for the stabili-

Fig. 1. Bond distances (Å) and angles (°) in methylene oxalate. The e.s.d.'s are 0·02 Å for distances and 1° for angles. The distances and angles involving H atoms have e.s.d.'s of 0·1 Å and 4–6° respectively.
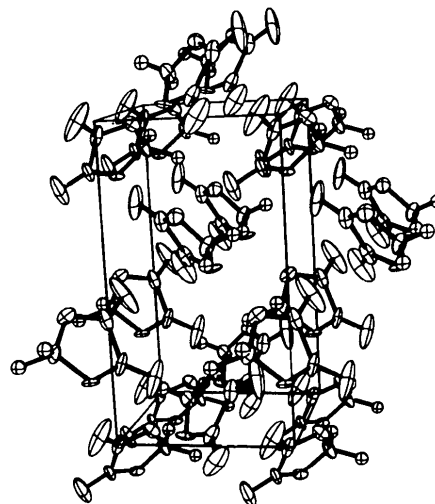

Fig. 2. Illustration of the crystal structure of methylene oxalate. The crystallographic c axis is vertical and b is in the plane of the paper. The thermal ellipsoids are scaled to enclose 20% probability.

Table 2. *Deviations* (Å) *from the plane defined by* C(1), C(2) *and* C(3)

The equation of the plane is $3\cdot549657x - 3\cdot583534y - 5\cdot887166z - 0\cdot992746 = 0$ (x,y,z are the fractional coordinates of a point in the coordinate system defined by the cell).

C(1)	0·0	O(3)	0·033 (15)
C(2)	0·0	O(4)	0·009 (6)
C(3)	0·0	H(1)	−0·71 (9)
O(1)	−0·067 (15)	H(2)	0·75 (9)
O(2)	−0·054 (8)		

Table 3. *Intermolecular distances* (Å) $<3\cdot0$ Å

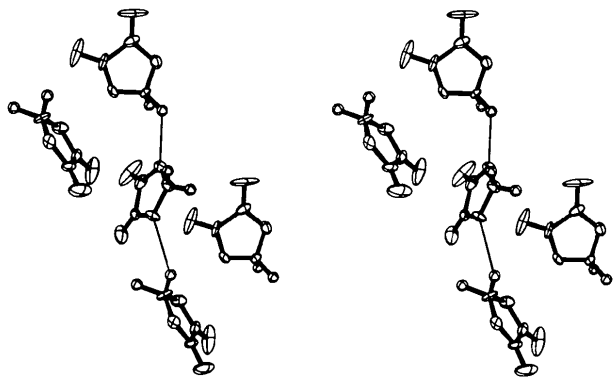|			
C(1)···O(1)	2·75 (2)	O(1)···H(2)	2·81 (9)
C(1)···O(3)	2·78 (2)	O(1)···O(2)	2·97 (2)
C(2)···O(1)	2·80 (2)	O(2)···H(1)	2·59 (9)
C(2)···O(3)	2·73 (2)	O(2)···H(2)	2·85 (8)
		O(4)···H(2)	2·35 (8)
		O(3)···O(4)	2·96 (2)

Fig. 3. Stereoscopic illustration of the crystal packing. The thermal ellipsoids are scaled to enclose 20% probability.

which explains the large thermal motion of the rigid molecule in the crystal, even at 153 K. The packing is, however, rather efficient, a fact which is borne out by the surprisingly high density (1.74 Mg m^{-3}) and melting point (439 K).

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zation of the crystal structure are the contacts made by O(1) and O(3) with C(1) and C(2). The two C=O groups approach other molecules almost perpendicular to the plane of the ring from opposite sides. The negative parts of the C=O dipoles evidently are directed towards the more positive C(1)–C(2) fragments of adjacent molecules. These contacts are all very similar in length, ranging from 2.73 (2) to 2.80 (2) Å. The crystal-packing forces are obviously rather weak,

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2,3-Dihydro-5-methyl-1,4-dithiin 1,1,4,4-Tetroxide

BY ROBERT B. BATES AND GEORGE R. KRIEK

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA

AND ARTHUR D. BREWER

Research Laboratories, Uniroyal Ltd, 120 Huron Street, Guelph, Ontario, Canada N1H 6N3

Abstract. $C_5H_8O_4S_2$, $M_r = 196.24$, monoclinic, $P2_1/a$ (systematic absences $h0l$, h odd; $0k0$, k odd), $a = 10.613$ (8), $b = 6.067$ (5), $c = 12.732$ (7) Å, $\beta = 103.61$ (5)°, $Z = 4$, $D_c = D_m = 1.64$ Mg m^{-3} (flotation in aqueous KI). The structure was refined to a final R of 0.068 for 1081 reflections. Structural comparisons to the 5,6-dimethyl compound are made.

Introduction. Certain 2,3-dihydro-1,4-dithiin 1,1,4,4-tetroxides (I) have biological activity: (I*a*) is a very effective plant-growth regulator and defoliant (Neidermyer, Brewer & Judge, 1974; McIntyre, Lambert & Brewer, 1977; Murphy, 1975), while (I*b*) has micro-

biocidal activity (Brewer & Davis, 1977). The X-ray study of a crystal of (I*a*) has been reported (Arora, Bates, Kriek & Brewer, 1978) and showed unexpectedly long vinyl-to-sulfone bonds, presumably for steric reasons. We now report the structure of (I*b*), which provides a test of the idea that the bonds are long for steric reasons, as it contains one methyl group on the double bond to provide hindrance and one hydrogen to exemplify an unhindered situation.

(I*a*) R = Me

(I*b*) R = H