Table 3. *Results of energy minimization*

$\vec{r}_c$: molecular centre of mass, θ: molecular rotation.

Cell constants	
Δa	0·4%
Δb	0·1
Δc	0·5
Molecular parameters	
$\lvert\Delta\vec{r}_c\rvert$	0·02 Å
θ	2·6°
Subrotations ($\Delta\tau$)	
C1—C4—O41—C41	1·1°
C4—C5—O51—C51	−2·3
C5—C6—O61—C61	−1·8
C6—C7—O71—C71	−0·6
C7—C8—O81—C81	−2·7
C3—C2—C21—C22	−1·3

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Structure of 2-Methyl-1,3-cyclopentanedione

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Abstract. $C_6H_8O_2$, $M_r = 112{\cdot}13$, monoclinic, $C2/m$, $a = 12{\cdot}766\,(2)$, $b = 6{\cdot}807\,(2)$, $c = 6{\cdot}4814\,(8)$ Å, $\beta = 93{\cdot}94\,(1)°$, $V = 561{\cdot}9\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, m.p. = 486–488 K, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 1{\cdot}07$ cm^{-1}, $F(000) = 240$, $T = 292$ K, final $R = 0{\cdot}040$ for 541 observed reflections. The structure consists of chains along z of hydrogen-bonded enol molecules [O···O distance 2·598 (2) Å]. The molecules lie on a mirror plane and the chains, in turn, are arranged in layers perpendicular to y. The positions of the H atoms of the methyl group are well defined and consistent with the constraints of the mirror plane, the H atom in the plane being on the side of the hydroxyl group; a metastable position of the methyl H atoms, corresponding to a 180° rotation of the methyl group, has also been detected.

Introduction. This study of 2-methyl-1,3-cyclopentanedione (MCPD) (enol form) was undertaken primarily to establish the arrangement of the MCPD molecules in the crystal and their intermolecular interactions. In the structures of cyclic β-diketomethanes investigated so far the molecules are interconnected by strong —O—H···O= hydrogen bonds shorter than 2·6 Å, which form chains – as has been observed in 1,3-cyclohexanedione (CHD) (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986), 1,3-cyclopentanedione (Katrusiak, 1989) and dimedone (5,5-dimethyl-1,3-cyclohexanedione) (Semmingsen, 1974; Singh & Calvo, 1975). It was demonstrated by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986) that, in the presence of suitable guest molecules, cyclomers can be formed from the hydrogen-bonded CHD molecules. We also wanted to investigate the intermolecular hydrogen bond and to compare it with those in similar structures, and look at the molecular dimensions of the MCPD molecule, the twofold symmetry of which is broken by the alternating HO—C=C—C=O π-bond system.

Experimental. Crystals of MCPD were recrystallized from ethanol. Colourless, elongated plates with y along the long and z along the short edges of the plates, dimensions 0·27 × 0·27 × 0·15 mm. The inten-

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sity data were collected using a CAD-4 diffractometer and graphite-monochromated Mo $K\alpha$ radiation. The Bragg angles of 16 automatically centred reflections used in the least-squares fit to refine the crystal-orientation matrix had $6{\cdot}0 \leq \theta \leq 15{\cdot}0°$. Stationary background, θ–2θ scan mode with a variable scan speed (0·5–20·0° min^{-1}) depending on reflection intensity. 627 reflections collected to $2\theta_{\max} = 52°$, 599 independent ($R_{\rm merge} = 0{\cdot}011$), range of indices: h 0→15, k 0→8, l −7→7. Two standard reflections monitored every 3 h did not show any systematic variation in intensity throughout the data collection. The data were corrected for Lp effects only.

The structure was solved routinely by direct phase determination (Sheldrick, 1986). All non-H atoms were found in the first E map, all H atoms were located from the subsequent difference Fourier maps after anisotropic refinement of the non-H atoms. The H atoms were included in the refinement with isotropic temperature factors. 541 reflections with $F_o \geq 3{\cdot}92\sigma(F_o)$ were used in the least-squares refinement; final $R = 0{\cdot}040$, $wR = 0{\cdot}042$ and $S = 1{\cdot}08$, $w = \sigma^{-2}(F_o)$. The final atomic positions and equivalent, or isotropic, vibrational parameters are listed in Table 1.* The highest and the lowest peaks in the final ΔF map were 0·22 and −0·14 e Å^{-3}, respectively; $(\Delta/\sigma)_{\max} = 0{\cdot}2$ for non-H atoms. Of the eight highest peaks in the final ΔF map, five were located between the C atoms in the ring with a slight displacement towards the outside of the ring and one was between C(2) and C(6) – these peaks may correspond to the bonding electrons. The other two peaks were in the positions corresponding to the opposite [*i.e.* rotated by 180° about C(2)—C(6)] position of the methyl group. These eight peaks were followed by the noise signals, the highest of which was 0·13 e Å^{-3}. Most of the calculations were performed with program *SHELX*76 (Sheldrick, 1976) on a NAS-80 computer, atomic scattering factors were those incorporated in *SHELX*76.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (*isotropic for* H *atoms*)

All atoms with y=0 lie on the mirror plane; their y coordinate was fixed in the refinement

$$U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$ (Å^2)
O(1)	0·19671 (14)	0·0	−0·0692 (2)	0·054
O(2)	0·32011 (13)	0·0	0·6284 (2)	0·042
C(1)	0·19896 (18)	0·0	0·1216 (3)	0·037
C(2)	0·28977 (17)	0·0	0·2634 (3)	0·032
C(3)	0·25630 (17)	0·0	0·4577 (3)	0·031
C(4)	0·13894 (18)	0·0	0·4651 (3)	0·045
C(5)	0·10044 (19)	0·0	0·2372 (4)	0·045
C(6)	0·39981 (21)	0·0	0·1998 (5)	0·049
H(2)	0·275 (2)	0·0	0·757 (4)	0·070 (9)
H(41)	0·1161 (12)	0·118 (2)	0·543 (2)	0·055 (5)
H(51)	0·0629 (15)	0·121 (3)	0·201 (3)	0·078 (7)
H(61)	0·444 (2)	0·0	0·314 (4)	0·082 (11)
H(62)	0·4124 (17)	0·111 (3)	0·114 (3)	0·110 (9)

Table 2. *Bond distances* (Å) *and valency angles* (°)

O(1)—C(1)	1·235 (2)	O(2)—C(3)	1·328 (2)
C(1)—C(2)	1·429 (3)	C(2)—C(3)	1·358 (3)
C(1)—C(5)	1·508 (3)	C(3)—C(4)	1·502 (3)
C(2)—C(6)	1·491 (3)		
C(4)—C(5)	1·525 (3)		
O(2)—H(2)	1·05 (2)		
C(4)—H(41)	1·003 (15)	C(5)—H(51)	0·974 (19)
C(6)—H(61)	0·90 (2)	C(6)—H(62)	0·96 (2)
O(1)—C(1)—C(2)	127·30 (17)	C(1)—C(2)—C(6)	124·10 (16)
O(2)—C(3)—C(2)	123·96 (15)	C(1)—C(2)—C(3)	107·67 (15)
O(1)—C(1)—C(5)	122·34 (16)	C(3)—C(2)—C(6)	128·23 (17)
O(2)—C(3)—C(4)	121·96 (15)	C(1)—C(5)—C(4)	104·90 (15)
C(2)—C(1)—C(5)	110·37 (15)	C(3)—C(4)—C(5)	102·99 (14)
C(2)—C(3)—C(4)	114·07 (15)	H(2)—O(2)—C(3)	108·6 (14)

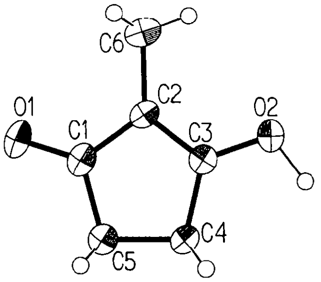

Fig. 1. *ORTEP* (Johnson, 1965) view of the MCPD molecule perpendicular to its plane – the vibrational ellipsoids correspond to 50% probability contours of mean atomic displacements, the H atoms are represented as small circles. Atoms H(41) and H(42), H(51) and H(52), and H(62) and H(63) are superimposed in this drawing.

Discussion. The bond lengths and valency angles for the MCPD molecule are listed in Table 2; the atom labelling is shown in Fig. 1. The double bonds are well defined in the conjugated alternating π-electron bond system (O═C—C═C—OH). According to Allmann (1977), these bonds have bond orders of 1·87, 1·32, 1·82 and 1·30, respectively. Very similar bond-length and bond-order values were observed for CHD and for dimedone – apparently these values in MCPD have been only slightly affected by the strain in its five-membered ring; the valency angles inside and outside the ring are strongly deformed from their ideal values as a result of the strain. The molecule is planar due to the symmetry requirements of the mirror plane. The methyl group also assumes the position required by the crystal symmetry, with one H atom, H(61), lying in the mirror plane and

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* Lists of anisotropic thermal parameters and structure factors, and a veiw of the MCPD molecules perpendicular to the *bc* plane have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52010 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

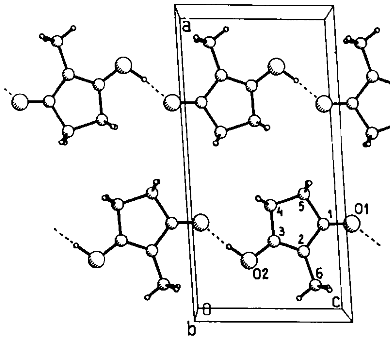

Fig. 2. Arrangement of the MCPD molecules (*PLUTO*, Motherwell, 1976) in the crystal lattice: the chains of MCPD molecules are viewed perpendicular to the *ac* plane and to the plane of the molecules. Hydrogen bonds are represented as dashed lines and only half of the unit-cell contents are included in the direction perpendicular to the drawing to avoid overlaying of the molecules.

pointing towards the O(2)H hydroxyl group. As already mentioned above, the final Fourier map showed a number of peaks, the strongest of which could be assigned to the bonding electrons of each of the C—C bonds and to the disordered H atoms with opposite methyl-group orientation [rotated by 180° about C(2)—C(6)]. These peaks were relatively low, both about 0·16 e Å^{-3}, which was about 0·25 of the electron density corresponding to H(61) or H(62); the distances of these peaks to C(6) were 1·02 and 1·04 Å. One explanation for the appearance of these peaks is that the methyl group is not stable in the structure but can rotate and the opposite orientation is its metastable position which could be detected in this X-ray study due to the relatively high precision of the collected data.

The arrangement of the MCPD molecules in the crystal lattice is presented in Fig 2. The molecules are interconnected into chains along the *z* axis of the crystal by short hydrogen bonds between the enol hydroxyl H(2) atoms and the carbonyl O(1) atoms. The hydrogen-bond configuration is *anti–syn* [O(1)···O(2) 2·5980 (18), O(1)···H(2) 1·555 (21) Å] and nearly linear [∠O(1)···H(2)—O(2) 174·0 (19)°]. A similar *syn–syn* hydrogen bond of 2·595 (2) Å was observed in dimedone (Semmingsen, 1974), while significantly shorter hydrogen bonds were found in the two forms of CHD: 2·561 (4) Å for the *anti–anti* hydrogen bond in CHD and 2·579 (1) Å for the *syn–anti* hydrogen bond in the 6:1 CHD:benzene inclusion compound (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986). Two even shorter independent hydrogen bonds have been observed in the crystals of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione): 2·553 (1) and 2·554 (1) Å (Semmingsen, Hollander & Koetzle, 1977).

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Structure of Thiamin Hydrochloride Hemisulfate Monohydrate

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Abstract. $C_{12}H_{18}N_4OS^{2+}.Cl^-.\frac{1}{2}SO_4^{2-}.H_2O$, M_r = 367·9, monoclinic, $C2/c$, a = 20·766 (6), b = 11·825 (2), c = 13·367 (2) Å, β = 101·15 (2)°, V = 3220 (1) Å^3, Z = 8, D_x = 1·52 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 4·45 cm^{-1}, $F(000)$ = 1544, room temperature, R = 0·0405 for 2075 observed reflections for which $I > 3\sigma(I)$. The thiamin cation is found in the usual F conformation. The extensive network of

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