The Crystal and Molecular Structure of Methyl-2-acetonyl-3-ethyl-4-methoxy-5-oxo-dihydro-2*H*-furan-2-carboxylate, a But-2-enoic Acid γ-Lactone

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The title compound crystallizes in space group $P2_1/c$ with unit-cell constants $a = 16 \cdot 101$ (4), $b = 8 \cdot 805$ (4), $c = 9 \cdot 187$ (5) Å and $\beta = 98 \cdot 35$ (7)°. The structure was solved by the symbolic addition procedure; refinement was carried out by full-matrix least-squares to a final R_1 index of $0 \cdot 040$ based on 2050 observed X-ray reflexions. Significant planarity is found in the lactone group; the lactone ring is nearly planar and the C–O bonds in the ring exhibit the usual asymmetry of $\sim 0 \cdot 1$ Å. Comparison with the relevant normal bonds in an ester indicates that valence-bond resonance effects are small and contribute only little to this asymmetry; the *degree* of asymmetry is probably mainly determined by non-bonded interactions across the ring. The results from this and other X-ray analyses suggest that the normal C=O bond length in a lactone is $\sim 1 \cdot 215$ Å, this bond being shortened by $\sim 0 \cdot 015$ Å when the oxygen atom is not involved in hydrogen bonding. The final difference map shows excess density in C–C bonds, lower maxima or featureless regions in C–O bonds and rather broad maxima near the oxygen atoms on the opposite side of the C–O double bonds.

Introduction

The self-condensation of acetylpyruvic esters was first described 80 years ago by Claisen (1889). His own deduction of the structure of the condensation product was not correct, however, neither were later models put forward by other investigators from chemical experiments (Heikel, 1935, 1938; Berner & Laland, 1949). In a recent work by Berner & Kolsaker (1969) a new structure model also based on spectroscopic evidence was proposed. Their model may be characterized as a fully substituted but-2-enoic acid γ-lactone ring.

In order to establish the full configuration not only of the self-condensation product itself, but also of a hydrogenated derivative, an X-ray analysis was undertaken. The substance chosen for investigation was the methyl ether of the hydrogenated condensation product of methyl acetylpyruvate, hereafter called methyl ether of the hydrogenated methyl product (MHMP).

Experimental

Crystal data

Crystals of MHMP grown from ethanol–water were kindly supplied by Professor E. Berner, University of Oslo. The crystals are colourless, prismatic and elongated along a with well developed faces (010) and (001). Crystallographic data are summarized below:

Methyl-2-acetonyl-3-ethyl-4-methoxy-5-oxo-dihydro-2*H*-furan-2-carboxylate, $C_{12}H_{16}O_6$; F.W. $256 \cdot 26$; m.p. $67°C$; Monoclinic; $Z = 4$; $\lambda_{Cu\ K\alpha 1} = 1 \cdot 5405$ Å.

$$a = 16 \cdot 101 \pm 0 \cdot 004 \text{ Å}$$
$$b = \ 8 \cdot 805 \pm 0 \cdot 004$$
$$c = \ 9 \cdot 187 \pm 0 \cdot 005$$
$$\beta = 98 \cdot 35 \ \pm 0 \cdot 07° \ .$$

Volume of unit cell: $V = 1288 \cdot 6$ Å³.

Density, calculated with $Z = 4$: $D_x = 1 \cdot 321$ g.cm⁻³

Absorption coefficient for $\lambda_{Cu\ K\alpha}(= 1 \cdot 5418$ Å): $\mu = 9 \cdot 1$ cm⁻¹.

Systematic absences: $h0l$ when l odd and $0k0$ when k odd.

Space group: $P2_1/c$.

Two different crystals were used in the final diffractometer measurements, one with dimensions $0 \cdot 25 \times 0 \cdot 2 \times 0 \cdot 1$ mm, the other $0 \cdot 35 \times 0 \cdot 3 \times 0 \cdot 15$ mm.

Intensity measurements

Preliminary cell dimensions and intensity data were obtained from Weissenberg photographs collected from a crystal rotated about both the b and the c axes. Later the intensities were remeasured on a manually operated Siemens diffractometer with an Eulerian cradle. The crystal-to-detector distance was 170 mm. Fairly good monochromatization of the Cu radiation was achieved by means of a $K\beta$ filter and a pulse-height discriminator. The tube voltage and current were both stabilized with a Siemens KRISTALLOFLEX 4 unit, and a scintillation counter was used as a detector.

The intensities were measured by the 2θ-scan technique. Based on the equations derived by Alexander & Smith (1964) a scan of 2° was used for $2\theta < 80°$ and 4° for $2\theta > 80°$. Stationary background measurements were made at the start and the end of each scan. The detector aperture size was 4×4 mm. Out to $2\theta = 125°$ all reflexions were recorded with the full-circle goniostat in the symmetrical A setting (Arndt & Willis, 1966). Owing to geometrical limitations of the goniostat the fixed χ setting had to be used for $2\theta > 125°$. Only reflexions significantly above background were measured in the 2θ range 125–145°. In addition 13 reflexions with

$145° < 2\theta < 158°$ were recorded. Of the 2552 independent reflexions (not counting systematic absences) within $2\theta = 145°$ in the Cu $K\alpha$ sphere 2210 or 86·6% were measured, which gives a total of 2223 reflexions.

A reference reflexion was measured at regular intervals (after every 12–15 reflexions) to correct for variations in the intensities due to e.g. long-range instabilities in the X-ray intensity and detector system, temperature variations, and as a check on crystal alignment and stability. During a day the maximum variation in the reference intensity was ca. 1%, but there was hardly any systematic trend over a period of about one month when rather abruptly a significant decline took place. The drop in intensity appeared to be caused by radiation damage of the crystal and a second crystal (larger) was used for the rest of the data collection.

The net intensity is:

$$I = I' - B$$

where I' is the total number of counts recorded during the scan and B is the sum of the two background counts $(B = B_1 + B_2)$ each recorded at half the scan time. If the relative error in F based on counting statistics alone was greater than 50% the reflexion was considered unobserved. The relative error is:

$$\frac{\sigma(F)}{F} = \frac{1}{2} \frac{(I'+B)^{1/2}}{I'-B}.$$

Of the 2223 reflexions measured 170 were unobserved, but they were not removed from the data set until at a late stage of refinement.

During the collection of data from the smaller crystal 73 pairs of symmetry equivalent reflexions were measured and compared. The average deviation $\sum(||F_1| - |F_2||)/\frac{1}{2}\sum(|F_1|+|F_2|)$ between pairs of corresponding structure factors in this set was 1·35% with a maximum deviation of 30·1%. 88 equivalent reflexions in the 2θ region 65–125° were measured for both crystals and compared. Disregarding a trivial scale factor the average and maximum deviation between pairs of corresponding structure factors were 4·1 and 41·5% respectively. The larger deviations were in both cases found with reflexions of high $\sigma(F)$.

With a linear absorption coefficient of 9·1 cm⁻¹ one would expect a fairly uniform absorption error in the intensities. (For the larger crystal $(0·35 \times 0·3 \times 0·15$ mm) 86% of the measured reflexions had $2\theta \geq 90°$, only a few being $< 80°$.) Considering the generally good correlation in the data from the two crystals it was decided not to apply any absorption correction to the intensities and they were converted to structure factors in the ordinary way. During the initial stages of refinement separate scale factors were used for the two data sets.

Structure determination

The symbolic addition procedure was used for the structure determination (Karle & Karle, 1963). Normalized structure factor amplitudes, $|E_\mathbf{h}|$'s, were calculated from the properly scaled set of $|F_\mathbf{h}|$'s corrected for thermal motion. The values of $\langle|E_\mathbf{h}|\rangle = 0·808$ and $\langle|E_\mathbf{h}^2 - 1|\rangle = 0·935$ compare well with the theoretical distributions for the centric case, 0·798 and 0·968, respectively. A listing of $\sum_2$ relations

$$sE_\mathbf{h} \sim s \sum_k E_\mathbf{k} \cdot E_{\mathbf{h-k}}$$

(where s means 'sign of') between the 305 reflexions with $|E_\mathbf{h}| \geq 1·50$ was produced in which the product $\sigma_3 \cdot \sigma_2^{-3/2} \cdot |E_\mathbf{h}|$ and all possible $|E_\mathbf{k}|$, $|E_\mathbf{h} \cdot E_\mathbf{k}|$, and $|E_{\mathbf{h-k}}|$ appeared for every $|E_\mathbf{h}|$. $\sigma_n = \sum_{j=1}^{N} Z_j^n$, Z_j is the atomic number of the jth atom in a cell containing N atoms.

Three suitable linearly independent reflexions were chosen and arbitrarily given signs in order to define the origin. The signs of two more reflexions and at a later stage also a third were specified with symbols. This basic set for the application of the $\sum_2$ formula is shown in Table 1. The propagation of new signs was made manually in a stepwise manner. In the first step only reflexions with $|E_\mathbf{h}| \geq 1·90$ were considered and 10 new signs and 84 symbols were established. The $|E_\mathbf{h}|$ limit was successively lowered to 1·70 and 1·50. New signs were included based on the usual probability formula (Cochran & Woolfson, 1955) $P_+(h) \sim \frac{1}{2} + \frac{1}{2} \tanh (\sigma_3 \cdot \sigma_2^{-3/2} |E_\mathbf{h}| \sum_k E_\mathbf{k} \cdot E_{\mathbf{h-k}})$ and as a rule only for $P_+(h) > 0·98$. In a few cases, however, a lower limit of 0·97 had to be accepted. The total yield from this procedure was 28 signs and 229 symbols.

Table 1. *The basic set of normalized structure factor amplitudes for the application of the $\sum_2$ relationship*

h	k	l	$|E|$	Sign
3	2	1	2·98	+
10	4	$\bar{5}$	3·82	−
11	1	$\bar{7}$	3·38	+
3	3	10	2·97	b
6	6	3	2·76	c
10	3	$\bar{6}$	2·88	d

There were several strong indications between symbols and between symbols and signs. Of 81 relations between d and a sign 72 or 89% gave $d = -$. 48 relations were found between b and c of which 37 or 77% indicated $b = c$. Finally there was also a certain dominance of $b = -d$ and $b = +$. E maps for both possibilities $b(=c) = +$ or $-$ (with $d = -$) were calculated. From the map for $b = c = +$, 17 of the 18 heavier atoms (C and O) in the molecule were correctly located, only one of the selected positions being in error. All the 257 signs used in the calculation later proved to be correct.

The 18 heavier atoms were initially introduced as carbon atoms and the coordinates refined. Guided by the development of individual isotropic temperature factors in a subsequent refinement the one wrong atom

of the proposed model could be discarded and it appeared fairly obvious how to distinguish between carbon and oxygen atoms. The correct structure became evident from the relative heights of the maxima in a Fourier map.

Structure refinement

Structure refinement was carried out mainly by the least-squares method using a full-matrix program minimizing $\sum w(|F_o| - K|F_c|)^2$. Atomic form factors used were: carbon and oxygen (Doyle & Turner, 1968) and hydrogen (bonded) (Stewart, Davidson & Simpson, 1965).

From the beginning all 2223 F_o's given unit weight ($w = 1$) were used. With isotropic temperature factors the refinement converged rapidly at an R_1 index of 0·146. The R_1 index is the usual: $\sum ||F_o| - K|F_c||/\sum |F_o|$. Conversion to anisotropic temperature factors and further refinement effected only small coordinate shifts and R_1 was brought down to 0·119. Because of limited memory capacity in the computer only 150 parameters could be varied at a time, and the anisotropic refinement had to be carried out by systematic changing of the parameters to be refined within this maximum permissible number. From a difference map all the 16 hydrogen atoms could be located at peaks of density 0·40–0·77 e.Å^{-3}. The peaks around C(10) were somewhat blurred and selection of atomic positions had to be based also on stereochemical considerations. Refinement including isotropic B's for the hydrogen atoms converged after 3 cycles. R_1 was thereby reduced from the initial 0·091 to 0·052. At this stage intramolecular distances and angles were calculated. The values are given in square brackets in Tables 4 and 5.

The two data sets were then brought on to a common scale and the 170 unobserved reflexions (cf. Intensity measurements) omitted from the list. A correction for secondary extinction was made using the formula given by Zachariasen (1963):

$$(F_c) = F_{corr} = \frac{1}{K} F_o(1 + \beta_{2\theta} C I_o) .$$

Only very strong reflexions showed any systematic weakening that might be attributed to the effect of secondary extinction and from the 30 $|F_o|$'s $\geq 50 \, C$ was determined to be 4·0 × 10^{-8}. In view of the small value, only this group of reflexions was corrected for extinction. Absorption errors in large $|F_o|$'s will also be reduced to some extent by this procedure. One subsequent cycle of least-squares reduced R_1 to 0·043. The individual F_o's were finally given weights according to the following scheme:

$$1/w = [\sigma^2(F) + cF^2] .$$

$\sigma^2(F)$ is based on counting statistics alone and equals: $\frac{1}{4} \cdot \frac{I' + B}{I' - B} \cdot \frac{1}{K . \text{Lp}}$, Lp is the Lorentz–polarization factor.

The second term cF^2 was introduced to take account of random errors (Brown & Levy, 1964; Grant, Killean & Lawrence, 1968). c was determined to be 3·9 × 10^{-5} from a systematic analysis of the function $\frac{1}{N'} \sum w . (F_o - K . F_c)^2$ with groups of increasing F_o values. N' is the number of F's in a given group.

Inspection of the structure factor list revealed a few editing errors from the data processing and they were appropriately corrected. The net intensity of the strong 200 reflexion appeared to be in error owing to improper
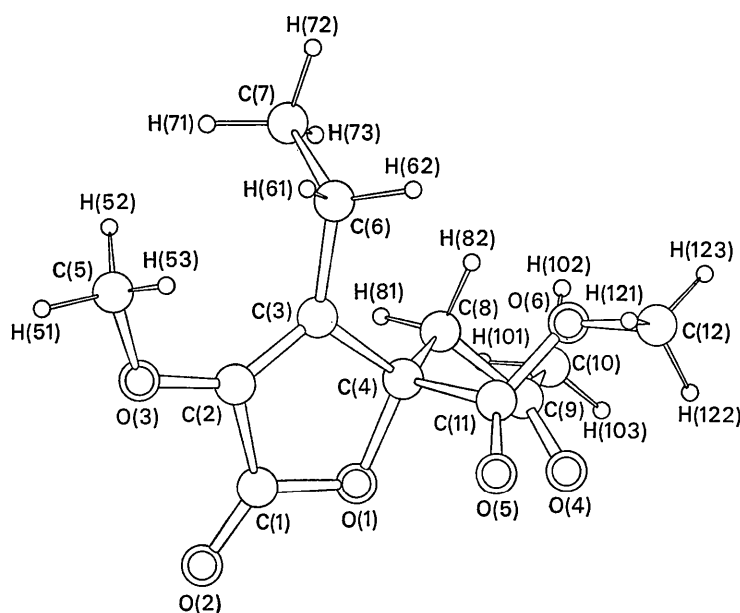

Fig. 1. Perspective view of the molecule as seen along the b axis,

Table 2. *Observed and calculated structure factors* (× 100)

The columns are k, l, $|F_o|$ and F_c, respectively. Unobserved reflexions are marked by a U.

k L |F₀| r_c

[Table of structure factors with section headers: H = 0, H = 1, H = 2, H = 3, H = 4, H = 5, H = 6, H = 7]

Table 2 (cont.)

* * * * H = 8 * * * *

* * * * H = 9 * * * *

* * * * H = 10 * * * *

* * * * H = 11 * * * *

* * * * H = 12 * * * *

* * * * H = 13 * * * *

* * * * H = 14 * * * *

* * * * H = 15 * * * *

* * * * H = 16 * * * *

* * * * H = 17 * * * *

* * * * H = 18 * * * *

* * * * H = 19 * * * *

correction for a high and very asymmetric background and it was excluded from the data. Two weak reflexions, 222 and 651, in error probably because of missetting during the intensity measurements, were also excluded. Refinement was terminated after a few more least-squares cycles. The final values of R_1 and the weighted discrepancy index, R_2, defined as: $R_2 = [\sum w(|F_o| - K|F_c|)^2 / \sum w \cdot F_o^2]^{1/2}$ and based on 2050 observed reflexions were: $R_1 = 0.040$ and $R_2 = 0.044$. Including the 170 unobserved reflexions R_1 was 0.044. Although only ca. 4.5% of all the observed F's were compared from the two crystals, the correlation value of $4 \cdot 1\%$ should give a good indication of the quality of the data. The final R_1 index is seen to compare closely with this value. The average and maximum values of the last coordinate shifts were 0.06σ and 0.32σ, respectively. The average and maximum values of the final shifts of thermal parameters were 0.03σ and 0.24σ for the heavier atoms and 0.11σ and 0.25σ for the hydrogen atoms, respectively. Averaged estimated standard deviations (e.s.d.'s) of atomic coordinates are:

	x	y	z
C	0.0019 Å	0.0021 Å	0.0020 Å
O	0.0012	0.0014	0.0013
H	0.0252	0.0271	0.0253

Observed and calculated structure factors are reproduced in Table 2. Final positional and thermal parameters are given in Table 3.

Results and discussion

Molecular configuration

Fig. 1 shows the molecule as viewed down the b axis. The molecular configuration is in agreement with the findings of Berner & Kolsaker (1969).

Equations of mean planes through various parts of the molecule have been calculated according to Blow (1960). The equations are referred to a new orthogonal coordinate system, in which the coordinates, $x'y'z'$ in Å, are related to the monoclinic coordinates, xyz, as follows: $x' = x + z \cos \beta$, $y' = y$, $z' = z \sin \beta$.

Table 3. *Final atomic parameters of* MHMP

Thermal parameters, $U_{ij}(\times 10^{-4})$, as given here are defined by:

$$\exp\left[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\right].$$

For explanation of B', see text. E.s.d.'s of the parameters appear in parentheses. The H atoms are identified by the number of the attached C or O atom.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B'
C(1)	0.1567 (1)	0.4873 (2)	0.7434 (2)	479 (8)	364 (10)	326 (8)	30 (7)	96 (6)	8 (7)	3.03 Å²
C(2)	0.1265 (1)	0.5647 (2)	0.6036 (2)	350 (7)	335 (10)	352 (8)	8 (7)	46 (6)	6 (7)	2.73
C(3)	0.1817 (1)	0.5449 (2)	0.5093 (2)	353 (7)	306 (9)	310 (7)	−11 (6)	23 (5)	27 (6)	2.57
C(4)	0.2563 (1)	0.4608 (2)	0.5925 (2)	369 (6)	373 (10)	259 (7)	31 (6)	41 (6)	9 (6)	2.64
C(5)	0.0206 (1)	0.7283 (3)	0.4793 (3)	451 (9)	487 (13)	623 (12)	110 (9)	36 (9)	100 (10)	4.14
C(6)	0.1806 (1)	0.5887 (2)	0.3511 (2)	439 (9)	562 (13)	353 (8)	53 (8)	80 (6)	136 (9)	3.54
C(7)	0.1347 (2)	0.4726 (3)	0.2444 (2)	731 (14)	804 (18)	319 (8)	112 (12)	−12 (9)	−41 (11)	4.95
C(8)	0.2781 (1)	0.3115 (2)	0.5246 (2)	419 (7)	363 (10)	340 (8)	23 (7)	61 (7)	−21 (7)	2.95
C(9)	0.3507 (1)	0.2294 (2)	0.6151 (2)	540 (9)	436 (11)	383 (9)	95 (8)	99 (7)	39 (8)	3.56
C(10)	0.3665 (2)	0.0702 (3)	0.5718 (4)	1100 (19)	517 (16)	720 (17)	356 (14)	2 (15)	−36 (14)	6.25
C(11)	0.3299 (1)	0.5730 (2)	0.6201 (2)	397 (8)	403 (11)	437 (9)	44 (7)	−2 (7)	−44 (8)	3.31
C(12)	0.4437 (1)	0.6757 (3)	0.5166 (3)	427 (10)	559 (16)	970 (19)	−102 (10)	108 (11)	31 (13)	5.15
O(1)	0.2324 (1)	0.4258 (1)	0.7341 (1)	466 (6)	473 (8)	275 (5)	109 (5)	64 (4)	54 (5)	3.19
O(2)	0.1232 (1)	0.4731 (2)	0.8512 (1)	730 (7)	651 (10)	403 (6)	145 (7)	266 (5)	82 (7)	4.55
O(3)	0.0515 (1)	0.6323 (2)	0.6006 (1)	410 (6)	541 (8)	515 (7)	129 (6)	138 (5)	115 (6)	3.81
O(4)	0.3931 (1)	0.2906 (2)	0.7167 (2)	579 (7)	672 (10)	550 (8)	196 (7)	−104 (6)	−57 (7)	4.88
O(5)	0.3394 (1)	0.6613 (2)	0.7200 (2)	665 (8)	668 (10)	674 (9)	−107 (8)	64 (7)	−342 (8)	5.31
O(6)	0.3762 (1)	0.5658 (1)	0.5120 (1)	387 (6)	454 (8)	552 (7)	−54 (5)	108 (5)	−33 (6)	3.64

	x	y	z	B
H(51)	−0.035 (1)	0.766 (3)	0.502 (2)	5.1 (0.5) Å²
H(52)	0.011 (1)	0.662 (3)	0.389 (3)	6.2 (0.6)
H(53)	0.060 (1)	0.805 (3)	0.471 (2)	5.0 (0.5)
H(61)	0.155 (1)	0.689 (2)	0.335 (2)	3.6 (0.4)
H(62)	0.239 (1)	0.600 (2)	0.330 (2)	4.1 (0.4)
H(71)	0.074 (2)	0.469 (3)	0.253 (3)	6.7 (0.6)
H(72)	0.146 (1)	0.507 (3)	0.145 (3)	6.4 (0.6)
H(73)	0.160 (2)	0.370 (3)	0.263 (3)	8.2 (0.7)
H(81)	0.230 (1)	0.249 (2)	0.512 (2)	4.1 (0.4)
H(82)	0.293 (1)	0.331 (2)	0.432 (2)	3.5 (0.4)
H(101)	0.316 (2)	0.011 (4)	0.579 (4)	10.6 (1.0)
H(102)	0.371 (2)	0.055 (4)	0.471 (5)	11.6 (1.1)
H(103)	0.413 (2)	0.028 (4)	0.629 (3)	8.8 (0.8)
H(121)	0.422 (2)	0.779 (5)	0.505 (3)	10.7 (1.0)
H(122)	0.480 (2)	0.659 (3)	0.603 (3)	7.6 (0.7)
H(123)	0.475 (2)	0.649 (4)	0.443 (3)	9.2 (0.8)

(A) Lactone ring: O(1), C(1), O(2), C(2), C(3), C(4)
$-0.38442x' - 0.85282y' - 0.35343z' - 6.62553 = 0$

(B) Lactone group: C(4), O(1), C(1), O(2), C(2)
$-0.38751x' - 0.84453y' - 0.36960z' - 6.70693 = 0$

(C) Acetonyl group: C(8), C(9), C(10), O(4)
$+0.71382x' + 0.33214y' - 0.61656z' + 0.66839 = 0$

(D) Ester group: C(11), O(5), O(6), C(12)
$-0.55043x' + 0.63905y' - 0.53726z' - 2.27352 = 0$

The deviations of the atoms from the calculated planes are given in Table 6.

The lactone ring (A) is roughly planar, the carbon atoms involved in the double bond exhibiting the largest deviations from planarity with C(2) lying 0.027 Å below and C(3) 0.035 Å above the plane. The lactone group (B) is significantly planar having a greatest deviation from the plane of 0.007 Å.

The conformation about the bonds C(6)–C(7) and C(4)–C(8) is staggered as can be seen from Fig. 2. C(3) lies between H(71) and H(73) viewed along C(6)–C(7) and between H(81) and H(82) viewed along C(4)–C(8). The deviation from an ideal staggered arrangement about C(6)–C(7) is probably significant. The favourable
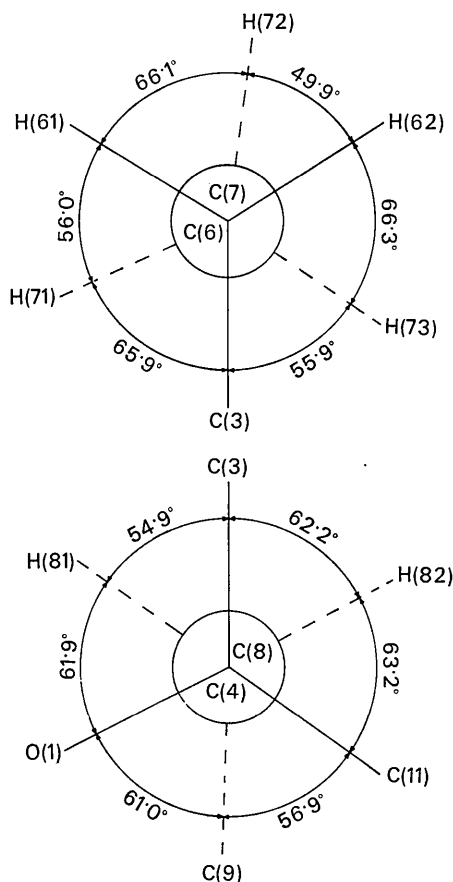

Fig. 2. Newman projections showing conformation about C(6)–C(7) and C(4)–C(8) bonds.

conformation, with C(2) anti to H(51), is adopted about the O(3)–C(5) bond. The dihedral angle between planes defined by C(2), O(3), C(5) and O(3), C(5), H(51) is 179.0°.

The acetonyl group (C) is significantly planar and the bond C(4)–C(8) is bent about 11° out of this plane. The ester group (D) is also significantly planar with the alcohol carbon C(12) cis to the C=O group. The bond C(4)–C(11) is bent 5.5° out of the plane. This bending may be explained in terms of short intramolecular contacts (cf. Bond lengths and angles). In agreement with a general statement put forward by Mathieson (1965) on the preferred conformation of esters involving primary alcohols the hydrogen atoms H(121) and H(122) are staggered in relation to the double-bonded oxygen O(5). The relevant dihedral angles deviate by no more than 5.0 and 1.4° from the 'ideal' value of 60°.

Bond lengths and angles

Bond lengths and angles in MHMP are presented in Fig. 3 and in Tables 4 and 5. In the lactone ring the two C–O bonds are unequal, the one adjacent to the carbonyl group being 0.095 Å shorter than the other. This asymmetry, by now a well established feature of lactones (see e.g. Mathieson & Taylor, 1961; Karle & Karle, 1966; Jeffrey, Rosenstein & Vlasse, 1967; Hvoslef, 1968), has often been explained in terms of a contribution from the valence-bond resonance form C–C=O⁺–C. However, the rather short C(1)–O(2) car-

$$O^-$$

bonyl bond in MHMP, 1.201 ± 0.003 Å, does not indicate that resonance effects are important (see also Kalyani & Vijayan, 1969). At the refined positions for O(2), C(1) and O(1) the residual electron density was found to be $+0.05$, -0.06 and ~ 0 e.Å^{-3}, respectively, with a $\sigma(\Delta\varrho) = 0.03$ e.Å^{-3}. Even if the figures (cf. Table 10) may not contradict the resonance explanation they do not seem to give substantial support to it either. The C(1)–O(1) bond can be compared with the carbonyl

C–O single bond in the ester grouping —C(=O)(–O—) for
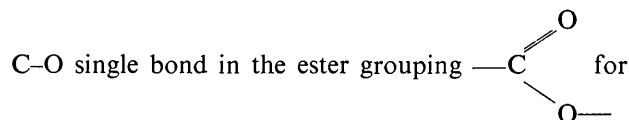
which Curl (1959) found 1.334 ± 0.01 Å in methyl formate. Baird, Dewar & Sustman (1969) give 1.315 Å for this type of bond. The slight extension of the C(1)–O(1) bond may be explained in terms of a higher degree of single bond character, i.e. less resonance contribution, in the γ-lactone than in an ester group. The C(4)–O(1) bond does not differ significantly from the normal C(sp³)–O bond.

Table 4. Bond lengths

E.s.d.'s of bonds between heavier atoms appear in parentheses. The bond lengths at $R_1 = 0.052$ are given in square brackets.

C(1)—C(2)	1.473 (3) Å	[1.475 Å]
C(2)—C(3)	1.339 (3)	[1.335]

Table 4 (cont.)

C(3)—C(4)	1·520 (3)	[1·519]
C(3)—C(6)	1·501 (3)	[1·505]
C(6)—C(7)	1·531 (4)	[1·541]
C(4)—C(8)	1·517 (3)	[1·519]
C(8)—C(9)	1·515 (3)	[1·513]
C(9)—C(10)	1·489 (4)	[1·496]
C(4)—C(11)	1·536 (3)	[1·534]
C(1)—O(1)	1·348 (2)	[1·350]
C(1)—O(2)	1·201 (3)	[1·202]
C(2)—O(3)	1·343 (2)	[1·343]
C(5)—O(3)	1·430 (3)	[1·433]
C(4)—O(1)	1·443 (2)	[1·444]
C(9)—O(4)	1·201 (3)	[1·204]
C(11)—O(5)	1·196 (3)	[1·200]
C(11)—O(6)	1·326 (3)	[1·331]
C(12)—O(6)	1·452 (3)	[1·455]

C(5)–H(51)	1·00 Å	C(8)—H(81)	0·95 Å
–H(52)	1·01	—H(82)	0·93
–H(53)	0·94	C(10)–H(101)	0·98
C(6)–H(61)	0·98	–H(102)	0·95
–H(62)	0·99	–H(103)	0·93
C(7)–H(71)	0·99	C(12)–H(121)	0·98
–H(72)	1·00	–(H122)	0·93
–H(73)	0·99	–H(123)	0·93

The internal angles of the lactone ring are in the range 105·2–109·8° ($\sigma \simeq 0.16°$) with the smallest angle at C(4). The average value is 108·0°. It is noticed that bond lengths and angles in the ring are such as to make the five second-neighbour contacts across the ring fairly equal as they range from 2·279 [C(1)···C(4)] to 2·354 Å [O(1)···C(3)] with an average of 2·304 Å. The two external angles at C(1) exhibit the characteristic asymmetry found in many other γ-lactones, the angle nearer to O(1) being 7·6° less than the other.
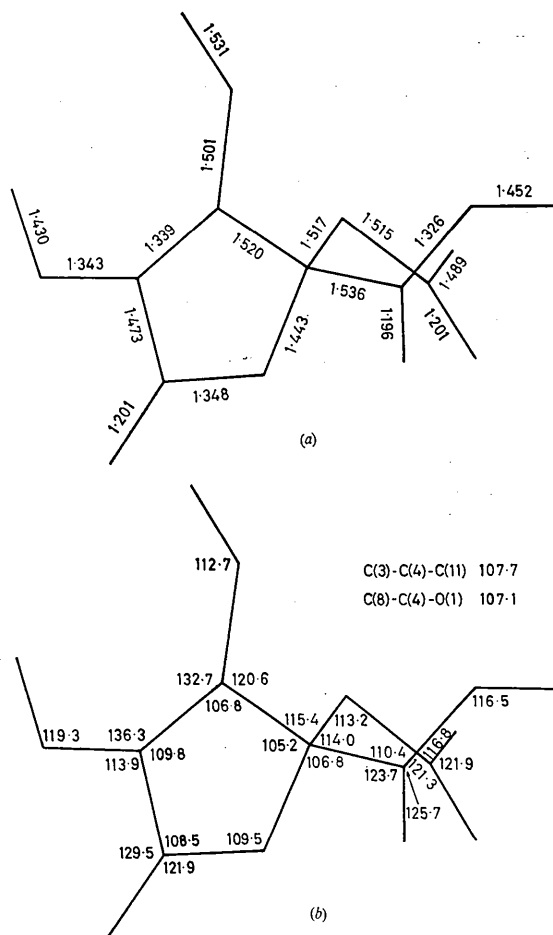

Fig. 3. Bond lengths (Å) and bond angles (°) in MHMP

Table 5. Bond angles

E.s.d.'s of the angles appear in parentheses. The bond angles at $R_1 = 0.052$ are given in square brackets.

O(1)-C(1)-C(2)	108·50 (16)°	[108·34]°	C(8)—C(4)—C(11)	113·96 (16)°	[114·02]°
–O(2)	121·94 (20)	[122·20]	C(11)-C(4)—O(1)	106·83 (15)	[106·67]
O(2)-C(1)-C(2)	129·54 (19)	[129·45]	C(4)—O(1)—C(1)	109·49 (15)	[109·39]
C(1)-C(2)-C(3)	109·77 (17)	[109·90]	C(2)—O(3)—C(5)	119·28 (17)	[119·20]
–O(3)	113·86 (16)	[113·60]	C(3)—C(6)—C(7)	112·66 (21)	[112·25]
O(3)-C(2)-C(3)	136·34 (19)	[136·46]	C(4)—C(8)—C(9)	113·18 (17)	[113·02]
C(2)-C(3)-C(4)	106·78 (16)	[106·87]	C(8)—C(9)—C(10)	116·83 (23)	[116·83]
–C(6)	132·65 (18)	[132·56]	—O(4)	121·26 (22)	[121·60]
C(6)-C(3)-C(4)	120·56 (16)	[120·57]	C(10)-C(9)—O(4)	121·92 (25)	[121·56]
C(3)-C(4)-O(1)	105·19 (14)	[105·26]	C(4)—C(11)—O(5)	123·68 (19)	[124·07]
–C(8)	115·37 (16)	[115·59]	—O(6)	110·44 (18)	[110·46]
–C(11)	107·71 (17)	[107·67]	O(5)—C(11)—O(6)	125·66 (21)	[125·25]
C(8)-C(4)-O(1)	107·09 (16)	[106·92]	C(11)-O(6)—C(12)	116·49 (20)	[116·43]

O(3)-C(5)-H(51)	104·8 (1·5)°	C(4)—C(8)—H(81)	108·8 (1·5)°
–H(52)	107·3 (1·5)	–H(82)	108·5 (1·6)
–H(53)	109·3 (1·7)	C(9)—C(8)—H(81)	110·2 (1·5)
C(3)-C(6)-H(61)	108·7 (1·2)	–H(82)	108·2 (1·4)
–H(62)	109·7 (1·7)	C(9)—C(10)-H(101)	107·8 (2·2)
C(7)-C(6)-H(61)	110·6 (1·2)	–H(102)	115·5 (2·1)
–H(62)	109·1 (1·7)	–H(103)	112·3 (2·7)
C(6)-C(7)-H(71)	111·1 (1·6)	O(6)—C(12)-H(121)	111·3 (2·4)
–H(72)	104·4 (1·8)	–H(122)	107·3 (2·0)
–H(73)	110·6 (1·7)	–H(123)	107·1 (2·5)

Table 6. *Deviations of atoms from calculated mean planes in the molecule*

	(A)	(B)	(C)	(D)
C(1)	−0·010 Å	−0·007 Å	—	—
C(2)	−0·027	0·003	—	—
C(3)	0·035	—	—	—
C(4)	−0·020	−0·002	—	—
C(6)	—	—	—	—
C(8)	—	—	0·000 Å	—
C(9)	—	—	−0·000	—
C(10)	—	—	0·000	—
C(11)	—	—	—	0·001 Å
C(12)	—	—	—	0·000
O(1)	0·009	0·005	—	—
O(2)	0·013	0·001	—	—
O(3)	—	—	—	—
O(4)	—	—	0·000	—
O(5)	—	—	—	−0·001
O(6)	—	—	—	−0·001

Table 7. *Comparison of some bond lengths and angles found in αβ-unsaturated γ-lactone rings*

The atomic numbering of MHMP is used for the L-ascorbic acid; however, both *enediol* C–O bonds in the latter are included.

	MHMP (present study)	L-ascorbic acid Hvoslef (1968)
C(1)–O(1)	1·348 (2) Å	1·355 (2) Å
C(1)–O(2)	1·201 (3)	1·216 (2)
C(1)–C(2)	1·473 (3)	1·452 (3)
C(2)–C(3)	1·339 (3)	1·338 (2)
C(2)–O(3)	1·343 (2)	1·361 (2)
		1·326 (3)
C(3)–C(4)	1·520 (3)	1·493 (3)
C(4)–O(1)	1·443 (2)	1·444 (2)
O(1)–C(1)–C(2)	108·50 (16)°	109·5 (2)°
−O(2)	121·95 (20)	121·4 (3)
O(2)–C(1)–C(2)	129·54 (19)	129·1 (2)
C(1)–C(2)–C(3)	109·77 (17)	107·8 (2)
C(2)–C(3)–C(4)	106·78 (16)	109·5 (2)
C(3)–C(4)–O(1)	105·19 (14)	104·0 (2)
C(4)–O(1)–C(1)	109·49 (15)	109·1 (2)

With but a few exceptions all bond lengths in the molecule compare well with the relevant normal values, some of which have been listed below:

C(sp³)–C(sp³)		1·534 Å	BT
C(sp³)–C(sp²)		1·510	S
C(sp²)–C(sp²)	single	1·474	BT
	double	1·335	S
C(sp³)–O		1·426	S
		1·437	C
		(in ester)	
C(sp²)–O		1·380	BDS

BDS: Baird, Dewar & Sustman (1969)
BT: Bastiansen & Trætteberg (1962)
C: Curl (1959)
S: Sutton (1965)

The C(2)–O(3) bond (1·343 Å) is rather short compared with the standard C(sp²)–O bond. Hvoslef (1968)

found 1·361 and 1·326 Å for the C(sp²)–O bonds from the αβ-unsaturated γ-lactone ring in L-ascorbic acid. As a consequence of the planar arrangement of atoms O(3)–C(2)–C(3)–C(6) in MHMP the external angles at C(2) and C(3) near to the double bond have been considerably increased over the trigonal value. The exocyclic angular asymmetry is greater at C(2) and the main reason for this appears to be that some important intramolecular contacts involving C(6) (*cf.* Table 8) effectively prevent further opening at C(3). The shorter C(sp²)–O bond in L-ascorbic acid was also found at the carbon with the greater exocyclic angular asymmetry. A comparison of some bond lengths and angles found in the αβ-unsaturated γ-lactone rings of MHMP and L-ascorbic acid is shown in Table 7. For reasons pointed out above the internal angle at C(2) in MHMP should rather be compared with that at C(3) in L-ascorbic acid and *vice versa*. With a possible exception for bonds C(1)–C(2) and C(3)–C(4) good agreement is found between the two parameter sets.

Table 8. *Important intramolecular contact distances*

i	j	D_{ij}	i	j	D_{ij}
C(1)	C(11)	3·25 Å	C(3)	H(81)	2·72 Å
C(2)	C(11)	3·26	C(3)	H(82)	2·76
C(3)	C(5)	3·03	C(4)	H(62)	2·68
C(5)	C(6)	3·23	C(5)	H(61)	2·71
C(6)	C(8)	3·20	C(8)	H(101)	2·74
C(6)	C(11)	3·19	C(8)	H(102)	2·78
C(9)	C(11)	3·05	C(10)	H(81)	2·70
C(4)	O(4)	2·77	C(11)	H(82)	2·75
C(8)	O(6)	2·75	C(11)	H(121)	2·66
C(9)	O(1)	2·90	C(11)	H(122)	2·56
C(11)	O(4)	2·78	O(1)	O(5)	2·71
C(12)	O(5)	2·69	O(6)	H(82)	2·51
C(2)	H(52)	2·65	O(4)	H(103)	2·48
C(2)	H(53)	2·60	H(53)	G(61)	2·34
C(2)	H(61)	2·79	H(61)	H(71)	2·40
C(3)	H(71)	2·79	H(61)	H(72)	2·36
C(3)	H(73)	2·72	H(62)	H(72)	2·25

The bond C(4)–C(11) is long compared with the expected value $1·506 \pm 0·005$ Å (Sutton, 1965). From Fig. 1 and Table 8 it is seen that extension of this bond will effect lengthening notably of some short intramolecular C···C contacts involving C(11). Short contacts also appear to be mainly responsible for the larger bond angles at C(4).

The three carbonyl bonds in MHMP are equal within 2σ with a mean value of 1·199 Å. Generally accepted values for the carbonyl bond length in ketones and in esters are $1·215 \pm 0·005$ Å (Sutton, 1965) and 1·245 Å (Baird *et al.*, 1969) respectively. A survey of the published results from 10 X-ray investigations on different lactones seems to indicate that the C=O bond length (uncorrected) is close to 1·215 Å, and that it is shortened by about 0·015 Å in structures where the oxygen atom does not participate in hydrogen bonding. The carbonyl bonds in MHMP are probably not significantly shorter than their normal values; however, they exhibit a consistent tendency towards shortening which

we feel can be largely attributed to the lack of hydrogen bonding. The C=O stretching frequencies in the infrared, measured in KBr, for the three carbonyl groups with the normally accepted (Bellamy, 1958) ranges (solution) in parentheses are as follows: αβ-unsaturated γ-lactone 1772 cm^{-1} (1760–1740 cm^{-1}); normal saturated ester 1753 cm^{-1} (1750–1735 cm^{-1}); open-chain saturated ketone 1713 cm^{-1} (1725–1705 cm^{-1}).

The 16 C(sp^3)–H bond lengths are all in the range 0·93–1·01 Å.

E.s.d.'s have not been calculated but the error is assumed to be 0·04–0·05 Å. The average value, 0·97 Å, is about 0·12 Å shorter than the spectroscopic value. The nature and magnitude of this shortening has been discussed in detail by Stewart et al. (1965).

In Tables 4 and 5, the bond lengths and angles at $R_1 = 0·052$ are given in square brackets. Before continued refinement 170 unobserved reflexions were removed and the remaining data were: (a) brought onto a common scale, (b) corrected for secondary extinction and (c) given individual weights. The fit between the two parameter sets is very good, the average and maxi-

mum shifts in bond lengths being 1·0σ and 2·5σ, and 0·9σ and 2·1σ in bond angles, respectively. Table 4 indicates a slight tendency for shifts in the final cycles of refinement to give shortening of bonds. However, the conclusion must be that the corrections and amendments mentioned above did not significantly alter the observed geometry of the molecule. As expected larger shifts were introduced in the temperature factors. The average and maximum shifts in the carbon and oxygen U_{ij}'s were as follows: C: 1·6σ; 5·3σ and O: 2·5σ; 6·0σ. Moreover, these shifts showed a systematic trend as ΔU_{22} and ΔU_{33} were in general larger than the others, and almost 80% of the shifts were in the same direction. The final temperature factors are presumedly physically more reliable, the main residual errors being caused by inadequate atomic models and absorption effects.

Thermal motion

The thermal parameters in Table 3 were used to calculate the root-mean-square amplitudes of vibration $\langle u^2 \rangle^{1/2}$, along the principal axes of the thermal ellipsoids
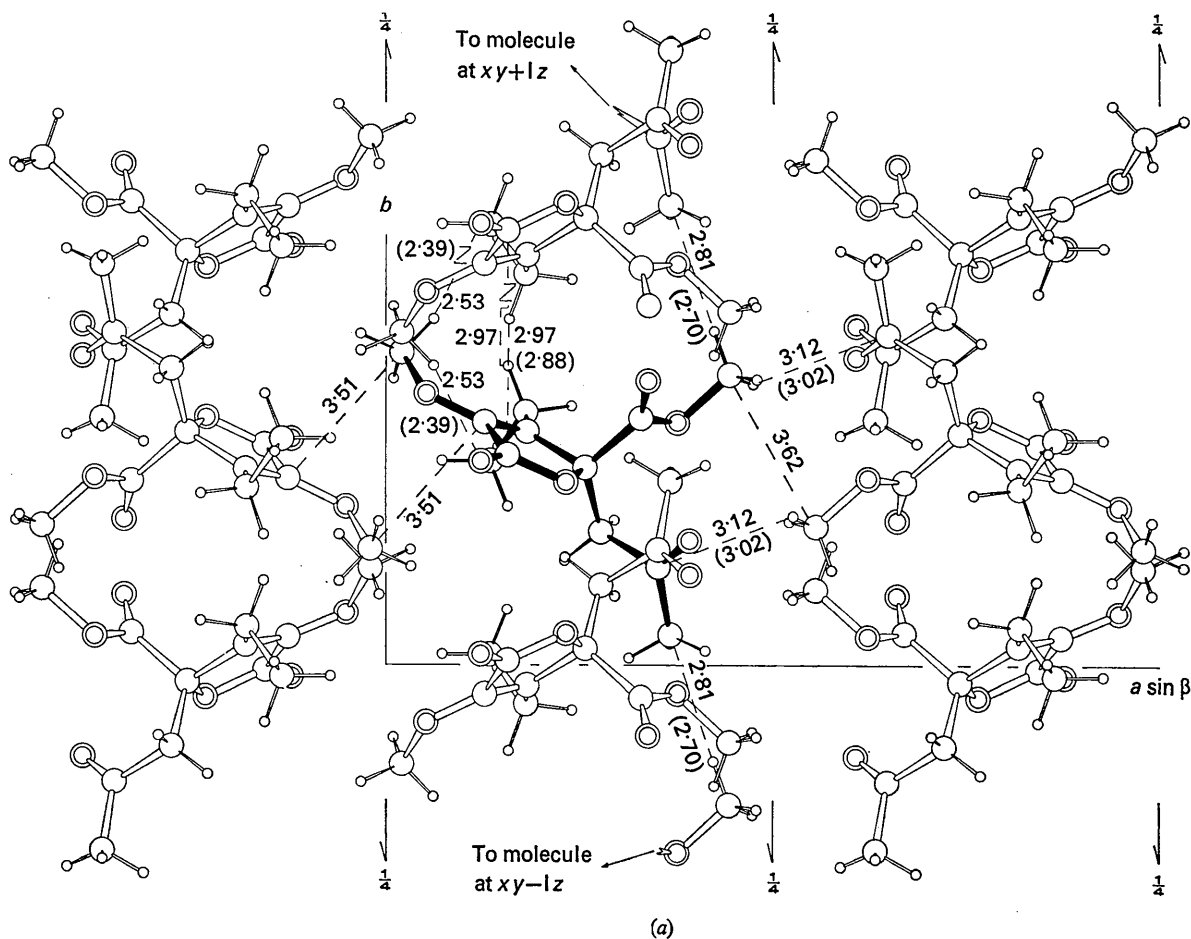

Fig. 4. (a) Packing of molecules as viewed down the c axis. Double circles are oxygen atoms, large and small open circles are carbon and hydrogen atoms, respectively. Some of the shortest intermolecular contacts are shown, with corrected values in parentheses. Contacts marked with a Z lead to the molecule one unit below (z − 1), that shown in the Figure.
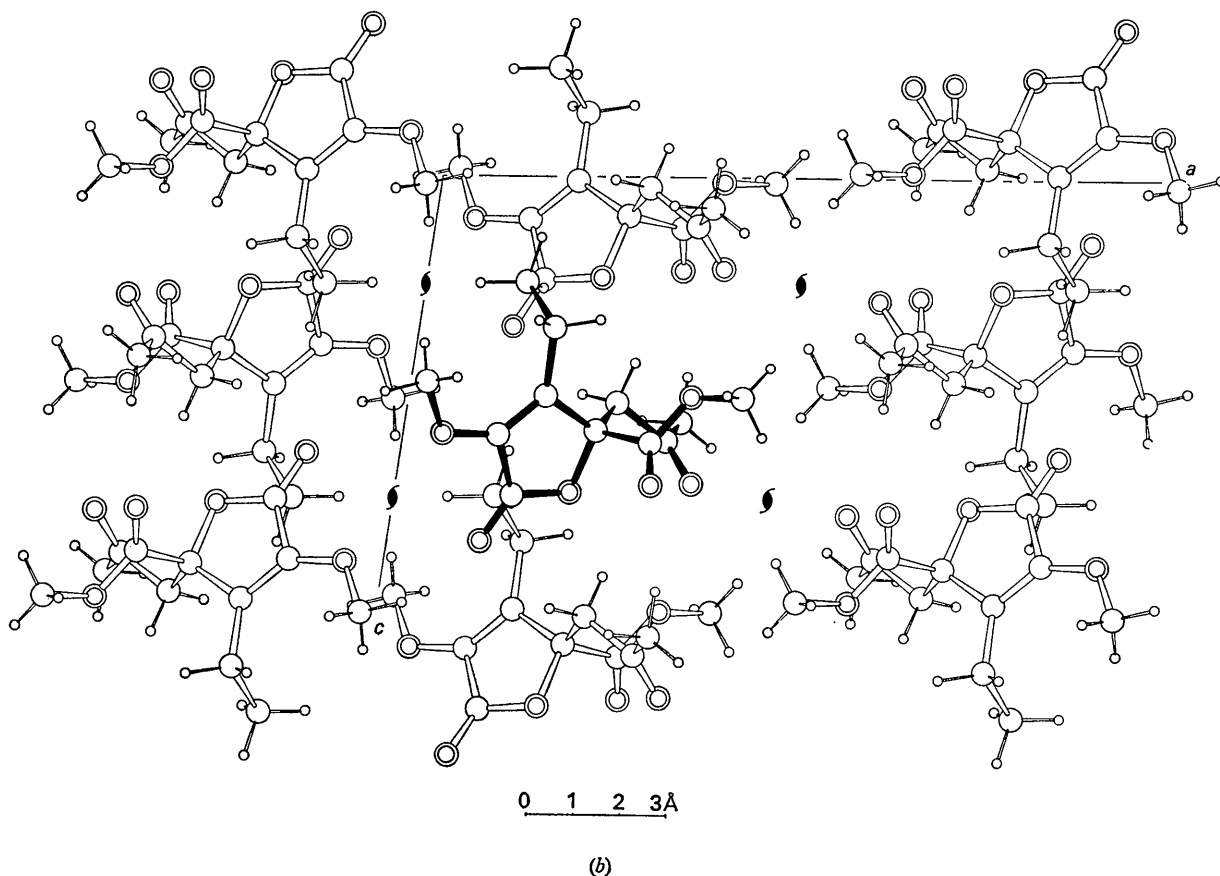
0   1   2   3Å

(b)

Fig. 4 (cont.). (b) Packing of molecules as viewed down the b axis. Symbols as in Fig. 4(a).

and their orientation relative to crystal axes a, b and c*. In the last column of this Table are given the average B's defined as $B'=\frac{1}{3}(B_1+B_2+B_3)$. The subscripts refer to the three principal axes of vibration and $B'=8\pi^2\langle u^2\rangle$.

Carbon atoms C(2), C(3) and C(4) in the lactone ring have the smallest vibration amplitudes, and for C(2) and C(3) the movement is fairly isotropic. A somewhat higher degree of anisotropy is exhibited by C(4), its largest amplitude lying mainly in the (001) plane. The anisotropy is augmented along the acetonyl carbon atoms and becomes more strongly directed along the a axis. The keto oxygen O(4) apparently has its largest amplitude approximately along [110]. O(1) and C(1) are more anisotropic than the other ring atoms, the carbonyl oxygen O(2) is even more so, and a vibration component along c*, also present in the motion of C(1), has become pronounced. The ethyl group atoms have their largest motion in the (100) plane but here the principal direction of vibration is more parallel with b.

In the ester group the anisotropy increases from C(11) over O(6) to C(12). The largest motions of O(6) and C(12) are roughly confined to the (100) plane and the maximum amplitude becomes more directed along c* going from O(6) to C(12). Carbonyl oxygen O(5) has a larger vibration component along a than the other atoms of the ester group.

In the methoxyl group O(3) has its largest vibration roughly along [111], whereas the maximum amplitude of the attached C(5) lies approximately in the (100) plane.

A qualitative evaluation of the relative orientations of the thermal ellipsoids strongly suggests that only parts of this irregular molecule may behave as a rigid body. However, a quantitative analysis of the molecular motion in terms of rigid-body modes of translation, libration and screw rotation (Schomaker & Trueblood, 1968) has not been made, and the bond lengths are not corrected for libration effects.

Molecular packing

The molecular packing is shown in Fig. 4. In Table 9 intermolecular contacts are listed within a limit of 0·2 Å greater than the sum of the relevant van der Waals (vdW) radii for which the values given by Kitaigorodskij (1961) has been used: $R_C=1·80$, $R_O=1·36$ and $R_H=1·17$ Å. Owing to symmetry, equivalent contacts occur in pairs, generally. Only one contact in each pair has been included. Distances involving hydrogen atoms have been recalculated assuming a value of 1·09 Å for the C–H bond length. The corrected distances, $D_{ij,corr}$, together with the corresponding C···H–C or O···H–C angles are also given in Table 9. Some of

the shorter intermolecular distances are shown in Fig. 4(*a*).

Only two distances (corrected) are significantly shorter than the sum of the van der Waals radii of the participants, *viz.* C(10)$\cdots$H(121) at $x, y-1, z$: 2·70 Å *vs.* 2·97 Å (vdW) and O(2)$\cdots$H(53) at $x, \frac{3}{2}-y, \frac{1}{2}+z$: 2·39 Å *vs.* 2·53 Å (vdW). Short intermolecular O$\cdots$H–C distances of similar magnitude have sometimes been interpreted as hydrogen bonds (*cf. e.g.* Gaultier & Hauw, 1966; Ammon, Sundaralingam & Stewart, 1969); however, the existence of such bonds has been much doubted by others (Donohue, 1967). The infrared stretching frequency of the C=O group in a γ-lactone is known (Bellamy, 1958) to be rather strongly influenced by hydrogen bonding, the occurrence of which may effect shifts of up to 15 cm^{-1}. The fact that this frequency in MHMP actually is found to be somewhat higher than the normal range (*cf. Bond lengths and angles*) does not lend weight to the hydrogen-bond interpretation in the present case. There are no short C$\cdots$O contacts between molecules indicating intermolecular carbonyl carbon–oxygen interactions of the types that have been discussed by Bolton (1964) and Klug (1965).

Within the limits given above there are 39 intermolecular contacts to atoms all around in a molecule. Contacts involving the substituent groups at C(2) and C(3) and the outermost part of the lactone ring as seen from

C(4) are particularly numerous. The molecular coordination number in three dimensions is 12, which is in agreement with the theory on close packing molecules (Kitaigorodskij, 1961).

Residual electron density

The maximum and minimum residual electron densities in the final difference map prepared after completion of the refinement are $+0\cdot19$ and $-0\cdot20$ e.Å^{-3}, respectively. The standard deviation, $\sigma(\Delta\varrho)$, calculated according to Cruickshank (1949) is 0·03 e.Å^{-3}. Consistent details of the difference map are as follows: maxima of peak densities 0·09–0·17 e.Å^{-3} in the C–C bonds (the peak position between C(6) and C(7) is shifted somewhat off the bond); featureless regions or small maxima of peak densities up to 0·07 e.Å^{-3} in the C–O bonds; broad maxima of peak densities 0·08$-$0·18 e.Å^{-3} located 0·7–1·0 Å away from the double-bonded oxygen atoms on the opposite side of the bond. Densities of peaks in bonds between the heavier atoms are listed in Table 10. The residual electron densities at the carbon and oxygen positions range from $-0\cdot06$ to $+0\cdot05$ e.Å^{-3} with an average value of $-0\cdot02$ e.Å^{-3} for carbon and 0·01 e.Å^{-3} for oxygen .The individual values appear in Table 10. In addition to the characteristic features described above there is a negative area near the ring centre with a minimum density of $-0\cdot20$ e.Å^{-3}.

Table 9. *Important intermolecular contact distances*

Distances are included within a limit of 0·2 Å greater than the sum of the van der Waals radii of the participants. $R_C = 1\cdot80$ Å, $R_O = 1\cdot36$ Å, $R_H = 1\cdot17$ Å. For explanation of $D_{ij \ corr}$ and contact angle (corr), see text.

Symmetry code

200	x	$-1+y$	z
2	x	$\frac{3}{2}-y$	$\frac{1}{2}+z$
202	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
402	x	$\frac{3}{2}-y$	$-\frac{1}{2}+z$
503	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
703	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
4	$1-x$	$1-y$	$1-z$
104	$-x$	$1-y$	$1-z$

i	j		D_{ij}	$D_{ij \ corr}$	Contact angle (corr)
C(1)	C(5)	104	3·77 Å	—	—
C(2)	C(5)	104	3·51	—	—
C(5)	C(7)	503	3·69	—	—
C(9)	C(12)	4	3·78	—	—
C(10)	C(12)	200	3·75	—	—
C(12)	C(12)	4	3·62	—	—
C(12)	O(5)	402	3·31	—	—
C(1)	H(73)	202	3·15	3·06 Å	152·9°
C(1)	H(61)	2	2·97	2·88	151·2
C(1)	H(52)	104	3·09	3·04	125·0
C(2)	H(61)	2	3·03	2·94	138·8
C(2)	H(52)	104	2·99	2·96	111·6
C(7)	H(51)	703	3·16	3·12	113·4
C(9)	H(123)	4	3·12	3·02	127·0
C(10)	H(121)	200	2·81	2·70	160·3
C(12)	H(123)	4	3·15	3·08	111·1
O(2)	H(53)	2	2·53	2·39	154·7
O(3)	H(71)	104	2·73	2·65	147·9
O(4)	H(122)	203	2·70	2·57	139·5
H(103)	H(121)	200	2·49	2·38	

Table 10. *Maximum residual electron densities in bonds between heavier atoms and at the final atomic positions*

$\sigma(\Delta\varrho) = 0.03$ e.Å^{-3} (Cruickshank, 1949)

Bond	$\Delta\varrho$ (e.Å^{-3})	Position	$\Delta\varrho$ (e.Å^{-3})
C(1)—C(2)	0·12	C(1)	−0·06
C(2)—C(3)	0·10	C(2)	−0·05
C(3)—C(4)	0·15	C(3)	−0·04
C(3)—C(6)	0·10	C(4)	−0·05
C(6)—C(7)	0·11	C(5)	−0·03
C(4)—C(8)	0·09	C(6)	−0·03
C(8)—C(9)	0·15	C(7)	−0·03
C(9)—C(10)	0·10	C(8)	+0·02
C(4)—C(11)	0·17	C(9)	−0·03
C(1)—O(1)	*	C(10)	+0·04
C(1)—O(2)	*	C(11)	−0·02
C(2)—O(3)	0·06	C(12)	+0·02
C(5)—O(3)	0·02	O(1)	0
C(4)—O(1)	0·03	O(2)	+0·05
C(9)—O(4)	*	O(3)	0
C(11)-O(5)	*	O(4)	0
C(11)-O(6)	0·03	O(5)	+0·02
C(12)-O(6)	0·07	O(6)	0

* Means that no peak was found in the bond.

The residual density in the main plane of the lactone ring is shown in Fig. 5. The maxima in the C–C bonds and the negative regions both inside and outside the ring as well as their positions relative to one another are in general accordance with the predictions by Daw-
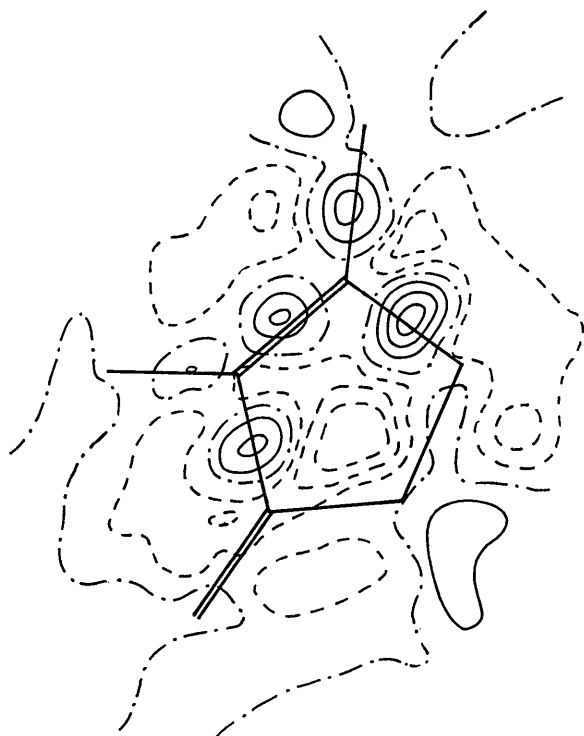

Fig. 5. Final difference map calculated in the main plane of the lactone ring. The zero contour is chain dotted, negative contours are dashed and positive contours are full lines. The distance between contours is 0·05 e.Å^{-3}.

son (1965) stating that a redistribution of electron density accompanies bonding giving an accumulation of charge, *i.e.* positive regions, in the bonds and antisymmetrically related negative regions. Similar features have been observed by a number of investigators and have been discussed in detail by *e.g.* O'Connell, Rae & Maslen (1966). The consistently lower peaks or flat regions in the C–O bonds agree qualitatively with what was found in 2,5-dimethyl-*p*-benzoquinone by Hirshfeld & Rabinovich (1967). The lone-pair electrons on oxygen will, provided they are neither pure *s* nor pure p_π orbitals, introduce a dipole moment directed away from the bond (*cf.* Coppens & Coulson, 1967). This lone-pair effect would be expected to reduce the conventionally calculated residual density in the C–O double bond compared with that in the C–C double bond. A similar relationship should exist between the C–O and C–C single bonds. Bratož, Daudel, Roux & Allavena (1960) have calculated the theoretical difference density in the O_2 molecule and indeed found the density to be non-positive in the molecular axis. Their method of calculation is directly relevant to the usual way of calculating difference maps in crystallography, where one subtracts from the measured total density the densities of postulated spherically symmetrical atoms. The broad maxima on the 'back' side of the double-bonded oxygen atoms in MHMP may at least in part be ascribed to lone-pair electrons.

The data in the present work are probably too inaccurate to warrant a more detailed study of the residual density. Nevertheless, it is interesting to notice the consistency with which the different residual density features occur in the molecule.

The following programs were used on a UNIVAC 1107:

FOUAL 3, a Fourier summation program.

LSFIV 4, a full-matrix least-squares program based on the Oak Ridge program *ORFLS* (TM–305), by Busing, Martin & Levy.

PAFIV 1, a function and error program based on the Oak Ridge program *ORFFE* (TM–306) by Busing, Martin & Levy.

BEPLA 1, a program for calculating best planes.

These programs were written or modified by O. Borgen & B. Mestvedt (Techn. Reports 46, 45, 47 and 40, Institute of Physical Chemistry, N.T. H.)

SCALIN, a program for determining scale factor and temperature factor (Wilson plot), scaling to normalized structure factors and determination of probability distributions of E's.

SIGMA, a program for the listing of all possible Σ_2 relations.

These programs were written by J. A. Hjortås, at this Institute. In addition some routines written by B. Sivertsen were used.

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References

ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.

AMMON, H. L., SUNDARALINGAM, M. & STEWART, J. M. (1969). *Acta Cryst.* B**25**, 336.

ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffractometry.* Cambridge Univ. Press.

BAIRD, N. C., DEWAR, M. J. S. & SUSTMAN, R. (1969). *J. Chem. Phys.* **50**, 1275.

BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron,* **17**, 147.

BELLAMY, L. J. (1958). *The Infrared Spectra of Complex Molecules.* London: Methuen.

BERNER, E. & KOLSAKER, P. (1969). *Acta Chem. Scand.* **23**, 597.

BERNER, E. & LALAND, S. (1949). *Acta Chem. Scand.* **3**, 335.

BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.

BOLTON, W. (1964). *Nature, Lond.* **201**, 987.

BRATOŽ, S., DAUDEL, R., ROUX, M. & ALLAVENA, M. (1960). *Rev. Mod. Phys.* **32**, 412.

BROWN, G. M. & LEVY, H. A. (1964). *J. Phys.* **25**, 497.

CLAISEN, L. (1889). *Ber. dtsch. chem. Ges.* **22**, 3271.

COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.

COPPENS, P. & COULSON, C. A. (1967). *Acta Cryst.* **23**, 718.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

CURL, R. F. (1959). *J. Chem. Phys.* **30**, 1529.

DAWSON, B. (1965). *Austral. J. Chem.* **18**, 595.

DONOHUE, J. (1967). In A. RICH & N. DAVIDSON, *Structural Chemistry and Molecular Biology,* p. 459 (and references cited therein). London: Freeman.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390.

GAULTIER, J. & HAUW, C. (1966). *Acta Cryst.* **21**, 694.

GRANT, D. F., KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* B**25**, 374.

HEIKEL, A. (1935). *Acta chem. fenn.* B**8**, 33.

HEIKEL, A. (1938). *Acta chem. fenn.* B**11**, 5.

HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* **23**, 989.

HVOSLEF, J. (1968). *Acta Cryst.* B**24**, 23, 1431.

JEFFREY, G. A., ROSENSTEIN, R. D. & VLASSE, M. (1967). *Acta Cryst.* **22**, 725.

KALYANI, V. & VIJAYAN, M. (1969). *Acta Cryst.* B**25**, 252.

KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.

KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **20**, 555.

KITAIGORODSKIJ, A. I. (1961). *Organic Chemical Crystallo-graphy.* New York: Consultants Bureau.

KLUG, H. P. (1965). *Acta Cryst.* **19**, 983.

MATHIESON, A. McL. (1965). *Tetrahedron Letters,* No. 46, 4137.

MATHIESON, A. McL. & TAYLOR, J. C. (1961). *Tetrahedron Letters,* No. 17, 590.

O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

SUTTON, L. E. (1958). Special Publication No. 11. London: The Chemical Society.

SUTTON, L. E. (1965). Special Publication No. 18. London: The Chemical Society.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Crystal and Molecular Structure of Pyridoxamine-5'-phosphate Hydrochloride

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Crystals of pyridoxamine-5'-phosphate hydrochloride, $C_8H_{14}ClN_2O_5P$, have been studied by three-dimensional X-ray methods. They are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10.05 \pm 0.02$; $b = 7.83 \pm 0.01$; $c = 15.73 \pm 0.02$ Å; $\beta = 109.0 \pm 0.2°$. The structure was solved by a symbolic addition procedure, and refined by least-squares method to a final discrepancy index $R = 0.081$ including 1797 independent reflexions. The molecules lie in layers parallel to (101) and are held together through hydrogen bonds between phosphate groups.

Introduction

It is generally accepted that the biological activity of vitamin B_6 is due, in great part to the participation of a phosphorylated derivative, pyridoxal-5'-phosphate (Umbreit & Gunsalus, 1949; Heyl, Luz, Harris & Folkers, 1951) as the coenzyme in many enzymatic reactions of α-aminoacids, such as transamination, decarboxylation, racemization, *etc.* Despite the impor-tance of the system, it is only recently that the crystal structures of pyridoxine hydrochloride (Hanic, 1966) and, while this paper was in preparation, of pyridoxal