

The Crystal and Molecular Structure of α -Acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane

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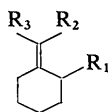
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The crystal and molecular structure of α -acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane, $C_{21}H_{22}O_2$, has been determined by a three-dimensional single-crystal X-ray diffraction study. The compound crystallizes in space group $P2_1/c$, with $a = 13.268$ (8), $b = 16.887$ (13), $c = 8.171$ (6) Å, and $\beta = 111.85$ (3)° ($Z = 4$). The intensities of 2878 unique reflections were measured on a Picker automatic diffractometer (Cu $K\alpha$ radiation), and the structure solved by the symbolic addition method. All hydrogen atoms were located. Full-matrix least-squares refinement of atom positions, hydrogen isotropic temperature factors and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 5.4\%$ for the 2222 reflections above background. The cyclohexylidene system adopts a chair conformation in which the 2-phenyl substituent assumes an axial position as predicted by the theory of $A^{1,3}$ strain. The torsion angles, which range from 49.0 to 59.6° (average value 53.5°) may indicate some distortion from normal cyclohexane geometry. Internal bond angles at the sp^3 hybridized carbon atoms average to 111.1°, and the C(2)–C(1)–C(6) angle measures 115.0°. The C(sp^3)–O bond lengths in the acetoxy group are 1.421 and 1.372 Å for bonds to methylene and carbonyl carbon atoms respectively. Bond distances and angles in the phenyl rings compare well with literature values.

Introduction

The theory of $A^{1,3}$ strain predicts (Johnson & Malhotra, 1965) that for substituted methylenecyclohexanes where R_1 and R_2 are sufficiently bulky,



- | | | | |
|------|----------------|-----------------|-----------------|
| (I) | $R_1 = C_6H_5$ | $R_2 = OCOCH_3$ | $R_3 = C_6H_5$ |
| (II) | $R_1 = C_5H_5$ | $R_2 = C_6H_5$ | $R_3 = OCOCH_3$ |

R_1 will occupy the axial instead of the equatorial position which is usually found in cyclohexanes. This theory has been questioned in certain cases (Zimmerman & Mariano, 1968; Bardwell & Yee, 1970). Accordingly we are undertaking direct proof of structure for substituted methylenecyclohexanes by X-ray diffraction. Our study of α -acetoxy- α ,2-*anti*-diphenylmethylenecyclohexane (I) (van Remoortere & Flynn, 1974) has unambiguously established that R_2 occupies an axial position on the saturated ring which takes the conformation of a chair with geometry similar to cyclohexane itself. The present paper describes the crystal and molecular structure of α -acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane (II).

Experimental

A sample of α -acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane, $C_{21}H_{22}O_2$ was obtained from F. Johnson as colorless platelets, m.p. 99–100°. Systematic absences on Weissenberg and precession photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), were consistent with space group $P2_1/c$ (C_{2h}^5) ($h0l$, $l = 2n + 1$; and $0k0$, $k = 2n + 1$).

A crystal of dimensions 0.93 × 0.30 × 0.09 mm sealed in a 0.3 mm diameter thin-walled glass capillary, was centered on a Picker automatic four-circle diffractometer and aligned with a coaxial with ϕ . Lattice constants were calculated from a least-squares refinement of setting angles of 13 reflections. The parameters of the monoclinic cell, $a = 13.268$ (8), $b = 16.887$ (13), $c = 8.171$ (6) Å and $\beta = 111.85$ (3)°, give a calculated density of 1.198 g cm⁻³ for $C_{21}H_{22}O_2$ and $Z = 4$. The errors given for the cell constants are those determined in the least-squares analysis multiplied by a factor of 10. This factor, chosen arbitrarily, allows for some systematic errors in measurement at a level consistent with our ability to reproduce results with different crystals and/or orientations.

Intensity data were collected in the θ - 2θ scan mode with Ni-filtered Cu $K\alpha$ radiation. The take-off angle was 3°, and a counter aperture 6.0 mm square was placed 30 cm from the crystal. Angles ranging between 2.2 and 3.1° of 2θ were scanned at a speed of 2° min⁻¹, and two stationary-crystal stationary-counter background counts of 15 s were taken at each end of the scan.

2873 independent reflections were recorded out to the instrumental limit ($\sin \phi = 0.909$). The 140, 040 and 2,14,0 reflections, monitored every 50 measurements, showed good stability. An error

$$\sigma(I) = [(0.021)^2 + N_o + k^2 N_b]^{1/2}$$

was assigned to the net intensity $I = N_o - kN_b$ to establish weights $w = 4F^2/\sigma^2(F^2)$ for least-squares minimization of $\sum w(|F_o| - |F_c|)^2$. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and F^2 are the intensities corrected

for Lorentz and polarization effects. The 656 reflections having $I < 0$ or $I/\sigma(I) < 2$ were omitted from the refinement. $\mu(\text{Cu } K\alpha)$ is 6.01 cm^{-1} . Transmission factors were estimated to range from about 0.57 to 0.95, but no absorption corrections were made.

Solution and refinement of the structure

The phases of 286 of the largest structure factors were determined by the symbolic addition procedure using the program *MAGIC* of Dewar (1968). Eight cycles of

Table 1. Final structure parameters and standard errors

The anisotropic thermal parameters are in the form

$$\exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

Standard errors are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C(1)	0.8243 (2)	0.0320 (1)	0.7200 (3)	3.6 (1)	3.4 (1)	2.9 (1)	0.3 (1)	0.7 (1)	-0.2 (1)
C(2)	0.8561 (2)	0.0498 (1)	0.5629 (3)	4.1 (1)	3.1 (1)	3.7 (1)	-0.1 (1)	1.5 (1)	-0.5 (1)
C(3)	0.9756 (2)	0.0783 (2)	0.6307 (4)	4.0 (1)	5.1 (1)	5.0 (1)	-0.5 (1)	1.7 (1)	-0.5 (1)
C(4)	0.9937 (2)	0.1492 (2)	0.7522 (4)	4.8 (2)	5.7 (1)	6.0 (2)	-1.7 (2)	1.4 (1)	-1.4 (2)
C(5)	0.9655 (2)	0.1289 (2)	0.9115 (4)	5.2 (2)	5.5 (1)	4.9 (1)	-0.7 (2)	0.7 (1)	-1.4 (2)
C(6)	0.8489 (2)	0.0974 (1)	0.8560 (3)	5.0 (1)	4.3 (1)	3.4 (1)	0 (1)	1.3 (1)	-0.6 (1)
C(7)	0.7761 (2)	-0.0352 (1)	0.7306 (3)	3.8 (1)	3.5 (1)	2.8 (1)	0.6 (1)	0.9 (1)	0.4 (1)
C(8)	0.7415 (2)	-0.0999 (1)	0.5985 (3)	4.1 (1)	2.9 (1)	2.9 (1)	0.1 (1)	1.1 (1)	0.5 (1)
C(9)	0.6332 (2)	-0.1060 (1)	0.4851 (3)	4.2 (1)	3.7 (1)	3.7 (1)	-0.1 (1)	1.2 (1)	0.1 (1)
C(10)	0.6002 (2)	-0.1659 (1)	0.3614 (3)	4.9 (1)	4.4 (1)	4.2 (1)	-1.0 (1)	1.0 (1)	-0.3 (1)
C(11)	0.6752 (2)	-0.2204 (1)	0.3481 (3)	6.6 (2)	3.7 (1)	4.6 (1)	-0.3 (1)	1.9 (1)	-0.5 (1)
C(12)	0.7822 (2)	-0.2149 (1)	0.4596 (3)	6.2 (2)	3.9 (1)	5.1 (1)	1.2 (1)	2.1 (1)	0.1 (1)
C(13)	0.8158 (2)	-0.1552 (1)	0.5844 (3)	4.4 (1)	3.9 (1)	4.1 (1)	0.6 (1)	1.1 (1)	0.2 (1)
C(14)	0.7763 (2)	0.1056 (1)	0.4303 (3)	4.5 (1)	2.9 (1)	3.3 (1)	-0.2 (1)	1.4 (1)	-0.5 (1)
C(15)	0.6694 (2)	0.1141 (1)	0.4220 (3)	4.6 (1)	3.9 (1)	3.7 (1)	0.1 (1)	1.3 (1)	0.2 (1)
C(16)	0.5946 (2)	0.1589 (1)	0.2914 (3)	5.3 (2)	4.7 (1)	4.4 (1)	1.0 (1)	1.1 (1)	0.2 (1)
C(17)	0.6233 (3)	0.1970 (2)	0.1664 (3)	7.5 (2)	4.7 (1)	4.0 (1)	1.5 (2)	1.4 (1)	0.6 (1)
C(18)	0.7282 (3)	0.1894 (2)	0.1729 (3)	8.7 (2)	4.8 (1)	4.7 (2)	0.8 (2)	3.1 (1)	1.2 (1)
C(19)	0.8043 (2)	0.1447 (1)	0.3029 (3)	6.2 (2)	4.6 (1)	4.6 (1)	0.2 (1)	2.7 (1)	0.5 (1)
C(20)	0.6612 (2)	-0.0197 (1)	0.8957 (3)	4.5 (1)	4.9 (1)	4.0 (1)	-0.3 (1)	1.7 (1)	0.4 (1)
C(21)	0.6503 (3)	-0.0432 (2)	1.0645 (4)	7.9 (2)	8.3 (2)	4.3 (1)	-0.6 (2)	3.3 (1)	0.2 (2)
O(22)	0.7527 (1)	-0.0524 (1)	0.8829 (2)	4.9 (1)	4.4 (1)	3.2 (1)	0.6 (1)	1.6 (1)	0.7 (1)
O(23)	0.6009 (1)	0.0217 (1)	0.7845 (2)	5.3 (1)	8.7 (1)	5.2 (1)	2.3 (1)	2.2 (1)	1.4 (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(2)	0.853 (1)	0.000 (1)	0.498 (2)	3.5 (0.5)	H(11)	0.652 (2)	-0.261 (1)	0.253 (3)	6.4 (0.7)
H(31)	1.023 (2)	0.035 (1)	0.703 (3)	5.5 (0.6)	H(12)	0.835 (2)	-0.252 (2)	0.449 (3)	7.1 (0.8)
H(32)	0.995 (2)	0.088 (1)	0.528 (3)	5.0 (0.6)	H(13)	0.890 (2)	-0.151 (1)	0.666 (3)	5.6 (0.7)
H(41)	1.070 (2)	0.166 (1)	0.800 (3)	5.3 (0.6)	H(15)	0.650 (2)	0.086 (1)	0.508 (3)	4.4 (0.5)
H(42)	0.946 (2)	0.198 (1)	0.685 (3)	6.6 (0.7)	H(16)	0.520 (2)	0.164 (1)	0.288 (3)	6.8 (0.8)
H(51)	1.018 (2)	0.091 (1)	0.986 (3)	6.9 (0.8)	H(17)	0.565 (2)	0.229 (1)	0.072 (3)	6.7 (0.7)
H(52)	0.970 (2)	0.179 (1)	0.984 (3)	6.8 (0.7)	H(18)	0.748 (2)	0.215 (1)	0.085 (3)	6.6 (0.7)
H(61)	0.835 (2)	0.078 (1)	0.958 (3)	4.0 (0.5)	H(19)	0.880 (2)	0.138 (2)	0.306 (3)	7.9 (0.8)
H(62)	0.794 (2)	0.142 (1)	0.801 (3)	5.1 (0.6)	H(211)	0.716 (3)	-0.052 (2)	1.150 (5)	12.7 (1.6)
H(9)	0.579 (2)	-0.067 (1)	0.490 (3)	5.5 (0.6)	H(212)	0.640 (4)	-0.094 (2)	1.057 (6)	14.4 (1.9)
H(10)	0.525 (2)	-0.168 (1)	0.281 (3)	5.9 (0.7)	H(213)	0.608 (4)	-0.009 (3)	1.094 (6)	17.4 (2.0)

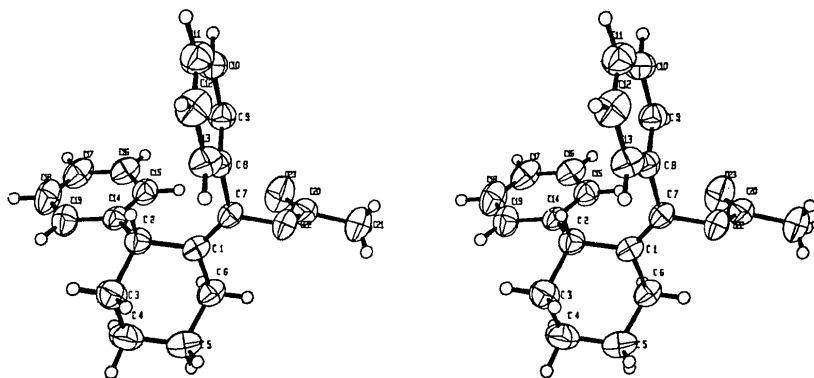


Fig. 1. Stereoscopic view of α -acetoxy- $\alpha,2$ -syn-diphenylmethylenecyclohexane showing the ellipsoids of thermal motion (at 50% probability) and the numbering system.

least-squares refinement of the atomic positions and isotropic temperature factors of the 23 atoms found in the E map, using a small computer, blocks of 72 variables and a set of 1955 reflections, reduced $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ from 0.299 to 0.141, and $R_2 = \{\sum w[F_o - F_c]^2 / \sum wF_o^2\}^{1/2}$ from 0.353 to 0.159. A difference map clearly revealed all but methyl hydrogen atoms at reasonable bond distances. Refinement was continued on a larger computer with full-matrix least-squares calculations (Gvildys, 1967) (anisotropic thermal motion for the heavier atoms, isotropic for the hydrogens). After the first cycle, in which R_1 was reduced from 0.129 to 0.070 and R_2 from 0.137 to 0.072, the methyl hydrogens were readily identified in an electron density difference map. At this point ten strong low-order reflections, systematically less intense than their calculated values, were corrected for secondary extinction (Zachariasen, 1963). After introduction of the corrected structure factors, additional refinement on all parameters converged in three more cycles to the final discrepancy indices of $R_1 = 0.054$ and $R_2 = 0.050$ for the 2222 reflections above background. In the final cycle the average shift in position parameters was 0.04σ for the heavier atoms, and 0.067σ for the hydrogens. A final difference map revealed some residual electron density as high as $0.23 \text{ e } \text{\AA}^{-3}$, and nega-

tive peaks of magnitude up to $0.18 \text{ e } \text{\AA}^{-3}$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962); those for hydrogen were from Stewart, Davidson & Simpson (1965).

The final positional and temperature parameters, and their standard deviations as calculated in the least-squares refinement, are listed in Table 1. In Table 2 we summarize bond distances and angles, together with their standard errors. The errors listed in Table 2 were computed from the variance-covariance

Table 2. Bond distances and bond angles

Standard errors calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

(a) Bond distances (\AA)

Bonds in saturated ring		Carbon-oxygen bonds	
C(1)-C(2)	1.523 (3)	C(7)-O(22)	1.421 (2)
C(1)-C(6)	1.514 (3)	C(20)-O(22)	1.372 (3)
C(2)-C(3)	1.547 (3)	C(20)-O(23)	1.189 (3)
C(3)-C(4)	1.518 (4)		
C(4)-C(5)	1.522 (4)	Exocyclic carbon-carbon bonds	
C(5)-C(6)	1.537 (3)	C(1)-C(7)	1.321 (3)
		C(2)-C(14)	1.526 (3)
		C(7)-C(8)	1.484 (3)
		C(20)-C(21)	1.493 (4)

Table 2 (cont.)

(b) Bond angles ($^\circ$)

Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
C(1)	C(2)	C(6)	115.0 (2)	C(7)	C(1)	C(8)	127.7 (2)
	C(2)	C(7)	121.2 (2)		C(1)	O(22)	120.2 (2)
	C(6)	C(7)	123.7 (2)		C(8)	O(22)	112.1 (2)
C(2)	C(1)	C(3)	109.2 (2)	C(8)	C(7)	C(9)	120.2 (2)
	C(1)	C(14)	112.6 (2)		C(7)	C(13)	121.2 (2)
	C(1)	H(2)	108.1	C(9)	C(13)	118.8 (2)	
	C(3)	C(14)	114.2 (2)	C(9)	C(8)	C(10)	120.5 (2)
	C(3)	H(2)	107 (1)	C(10)	C(9)	C(11)	120.1 (2)
C(3)	C(14)	H(2)	106 (1)	C(11)	C(10)	C(12)	119.8 (2)
	C(2)	C(4)	111.7 (2)	C(12)	C(11)	C(13)	120.4 (2)
	C(2)	H(31)	109 (1)	C(13)	C(8)	C(12)	120.3 (2)
	C(4)	H(32)	108 (1)	C(14)	C(2)	C(15)	121.3 (2)
	C(4)	H(31)	106 (1)	C(2)	C(19)	121.0 (2)	
C(4)	C(4)	H(32)	113 (1)	C(15)	C(19)	117.5 (2)	
	H(31)	H(32)	109 (2)	C(15)	C(14)	C(16)	121.1 (2)
	C(3)	C(5)	110.6 (2)	C(16)	C(15)	C(17)	120.7 (3)
	C(3)	H(41)	112 (1)	C(17)	C(16)	C(18)	118.9 (3)
	C(3)	H(42)	111 (1)	C(18)	C(17)	C(18)	121.2 (3)
	C(5)	H(41)	106 (1)	C(19)	C(14)	C(18)	120.6 (3)
	C(5)	H(42)	109 (1)	C(20)	C(21)	O(22)	110.9 (2)
C(5)	H(41)	H(42)	108 (2)	C(21)	O(23)	126.4 (3)	
	C(4)	C(6)	111.5 (2)	O(22)	O(23)	122.8 (2)	
	C(4)	H(51)	109 (1)	C(21)	C(20)	H(211)	111 (2)
	C(4)	H(52)	109 (1)	C(20)	H(212)	105 (3)	
	C(6)	H(51)	112 (1)	C(20)	H(213)	111 (3)	
	C(6)	H(52)	107 (1)	H(211)	H(212)	89 (3)	
	H(51)	H(52)	108 (2)	H(211)	H(213)	115 (3)	
C(6)	C(1)	C(5)	112.7 (2)	H(212)	H(213)	124 (4)	
	C(1)	H(61)	109 (1)	O(22)	C(7)	C(20)	118.2 (2)
	C(1)	H(62)	107 (1)				
	C(5)	H(61)	111 (1)				
	C(5)	H(62)	110 (1)				
	H(61)	H(62)	108 (2)				

matrix obtained in the final least-squares cycle.* The numbering system is shown in Fig. 1, while the molecular packing can be seen in a three-dimensional view down the z axis in Fig. 2.

Discussion

As required by Johnson & Malhotra's theory of $A^{1,3}$ strain, α -acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane is found in the chair conformation with the R_1 substituent occupying an axial site. In general its structural features are very similar to the *anti* isomer. Although the average torsion angle of 53.5° for C-C bonds in the cyclohexane ring is only 1.8° smaller than in (I), the fairly large spread in individual values, which range from 49.0 to 59.6° (Table 4), indicates some

significant distortions from 'normal' chair geometry. The average torsion angles of 50° (Table 3) around the bonds in the sequence C(2)-C(1)-C(6)-C(5) result in more flattening than is observed for the *anti* isomer and for cyclohexanes, while more twisting is present around the C(3)-C(4) bond. Bond distances and angles in the saturated rings of both isomers are in excellent agreement. The average C(sp^3)-C(sp^3) bond lengths are 1.524 and 1.531 Å for (I) and (II) respectively. Similarly, the average for the endocyclic C(sp^2)-C(sp^3) single bonds of 1.519 Å differs by no more than 0.01 Å from the corresponding value in the *anti* isomer. The

Table 3. Torsion angles in the cyclohexylidene ring ($^\circ$)

Estimated standard deviations calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

C(6)-C(1)-C(2)-C(3)	51.0 (3)
C(1)-C(2)-C(3)-C(4)	-56.0 (3)
C(2)-C(3)-C(4)-C(5)	59.6 (3)
C(3)-C(4)-C(5)-C(6)	-55.6 (3)
C(4)-C(5)-C(6)-C(1)	50.0 (3)
C(5)-C(6)-C(1)-C(2)	-49.0 (3)

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30879 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Least-squares planes

The planes are defined by the equation $m_1x + m_2y + m_3z = d$. Δd_i refers to the deviation in Å of atom i from the least-squares plane.

Plane	1	2	3	4	5	6
Atom						
1	C(1)	C(1)	C(1)	C(7)	C(8)	C(14)
2	C(2)	C(2)	C(7)	O(22)	C(9)	C(15)
3	C(6)	C(6)	C(8)	C(20)	C(10)	C(16)
4	C(7)	C(7)	O(22)	O(23)	C(11)	C(17)
5	C(8)			C(21)	C(12)	C(18)
6	O(22)				C(13)	C(19)
m_1	11.551	11.507	11.559	5.547	-5.667	0.725
m_2	-7.909	-7.775	-8.080	14.523	-9.158	14.123
m_3	1.230	1.546	0.896	2.390	5.912	4.457
d	10.144	10.338	9.915	5.523	0.252	3.975
$\Delta d, 1$	0.012	0.012	0.002	0.017	-0.001	-0.002
$\Delta d, 2$	0.044	-0.004	-0.004	0.000	-0.001	0.002
$\Delta d, 3$	-0.055	-0.004	0.001	-0.001	0.002	-0.001
$\Delta d, 4$	-0.051	-0.005	0.001	0.000	-0.002	0.000
$\Delta d, 5$	-0.002			0.000	0.000	-0.001
$\Delta d, 6$	0.052				0.002	0.002

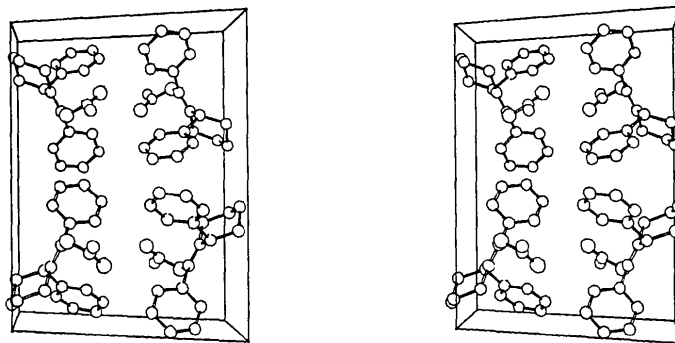


Fig. 2. Three-dimensional view of the molecular packing in α -acetoxy- α ,2-*syn*-diphenylmethylenecyclohexane as viewed down the z axis. The x axis is vertical and the y axis is horizontal. The origin of the box is at 0,0,0.

internal bond angles at the sp^3 -hybridized carbon atoms average to 111.1° , within experimental error of the 110.7° observed in (I), and the C(2)–C(1)–C(6) bond angle is $115.0(3)^\circ$ [$114.0(3)^\circ$ in (I)].

As in (I), the axial phenyl group is oriented symmetrically above the central ring in a manner that minimizes the non-bonded interactions between its *ortho* hydrogen atoms and the 4- and 6-axial hydrogens on the cyclohexylidene moiety. Although eased by the opening of the C(3)–C(2)–C(14) angle to $114.2(2)^\circ$, the resultant H(19)···H(32) contact is again short [$2.07(3) \text{ \AA}$] compared to the sum of the van der Waals radii 2.4 \AA (Pauling, 1960).

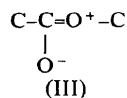
The double-bond system deviates significantly from planarity (Table 4, plane 1). These deviations originate from a distortion at C(1), which displaces C(7) and its substituents in the equatorial direction (Table 4, plane 2), and from twisting around the C(1)=C(7) bond. The latter effect creates a torsion angle of $5.6(3)^\circ$ [measured by the dihedral angle between the planes defined by {C(6), C(1), C(7)} and {C(1), C(7), O(22)}]. The additional opening of the C(1)–C(7)–C(8) angle to $127.7(2)^\circ$ combines with the above distortions to ease the C(8)···H(2) and O(22)···H(61) contacts to $2.57(2)$ and $2.43(2) \text{ \AA}$ respectively. No distortion occurs at C(7) which is coplanar with its substituents within experimental error (Table 4, plane 3).

The phenyl bonded to C(7) (phenyl *B*) is nearly perpendicular to the plane defined by {C(1), C(7), C(8)} (dihedral angle 88.5°). Consequently, its *ortho* hydrogens are separated by more than the van der Waals contact limits from other atoms in the structure, and its π system does not overlap with the π orbitals of the double bond. Although the C(7)–C(8) bond length of $1.484(3) \text{ \AA}$ exceeds the literature average for C–C single bonds between sp^2 -hybridized atoms by nearly 0.02 \AA , its value is only 4σ longer than the corresponding bond in the other geometrical isomer. The C(1)=C(7) bond distance measures $1.321(3) \text{ \AA}$, in good agreement with the $1.326(4) \text{ \AA}$ in (I) but slightly smaller than the accepted value for the ethylenic double bond of 1.335 \AA (Sutton, 1965).

That C(7) is nearly coplanar with the acetoxy group is shown by plane 4 of Table 4. This plane forms a dihedral angle of 88.9° with the plane defined by {C(1), C(7), O(22)} [compare with an angle of 81° in (I)]. The carbonyl O is *cis* to C(7), but the twist angles around the C(7)–O(22) bond are in opposite directions in the two geometrical isomers. While the acetoxy group is rotated towards the equatorial side of the cyclohexylidene system in the present compound, the axial phenyl ring excludes a similar arrangement in (I), where the acetoxy group was found rotated away from the equatorial plane. The carbonyl group is eclipsed by a C–H bond of the methyl group; this feature was also present in (I).

The C(sp^2)–O single bonds of $1.421(2) \text{ \AA}$ for C(7)–O(22) and $1.372(3) \text{ \AA}$ for C(20)–O(22) do not differ by more than 5σ from their respective values in the

anti isomer, and, as in the latter the shortening of the C(7)–O(22) bond may involve resonance structure (III).



However, the carbonyl bond length of $1.189(3) \text{ \AA}$ does not show elongation, and is within experimental error of its value in (I). Correction for thermal motion, assuming O to ride on C brings this C–O bond distance to $1.221(3) \text{ \AA}$ in good agreement with most literature values (van Remoortere & Flynn, 1974; Sutton, 1965). Bond angles around C(20) (see Table 2) show severe deviations from ideal sp^2 values, but they agree within experimental error with corresponding angles in the *anti* isomer. The ester O may be closer to sp^2 hybridization than in (I), since it spans an angle of $118.2(2)^\circ$, significantly larger than the 116.1° observed for the latter molecule.

Both phenyl groups are planar within experimental error (Table 4, planes 5 and 6). The average C–C bond distance $\bar{d}=1.386$ obtained from 12 (*n*) individual measurements (d_i) has a standard deviation of 0.008 \AA ,

$$\sigma = \left[\sum_{i=1}^n (\bar{d} - d_i)^2 / (n - 1) \right]^{1/2}$$

approximately three times larger than the standard error obtained from the variance-covariance matrix. Except for the methyl H atoms, H positional and thermal parameters are better behaved and show a smaller spread than in the other isomer. Their isotropic temperature factors range from 3.5 to 7.9 \AA^2 [compare with 3.7 to 12.6 \AA^2 in (I)] and their bond distances vary from 0.96 to 1.06 \AA [compare with 0.84 to 1.13 in (I)]. The average values for C–H bond lengths are 0.97 and 0.98 \AA for bonds to sp^3 - and sp^2 -hybridized C atoms respectively.

The distribution of thermal motion is very similar in both geometrical isomers. Small and isotropic in the vicinity of the exocyclic double bond, thermal vibration increases in magnitude and anisotropy in the phenyl and acetoxy groups and in the cyclohexylidene system (Fig. 1). The thermal parameters are more anisotropic in phenyl *A* than in phenyl *B*, and their largest amplitude of vibration approximately coincides with the plane of the ring. The carbonyl O has the largest thermal parameters and its motion is fairly anisotropic.

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The Crystal Structure of $\text{Al}_2(\text{OH})_2\text{TeO}_3\text{SO}_4$

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$\text{Al}_2(\text{OH})_2\text{TeO}_3\text{SO}_4$ crystallizes in space group $P2_1/m$ with $a=7.013$ (2), $b=9.539$ (4), $c=4.880$ (2) Å, $\beta=92.65$ (3)°, $Z=2$. The structure was solved from Patterson and electron density calculations with 1289 independent reflexions, and a final R of 0.032 was obtained. The structure consists of tetrahedral SO_4^{2-} ions and pyramidal TeO_3 units connected by Al to form infinite sheets. The Al coordination is approximately octahedral with Al–O distances of 1.864–1.934 Å. The Te–O and the S–O lengths are 1.902–1.939 and 1.467–1.487 Å respectively.

Introduction

A new Te^{IV} compound, $\text{Al}_2(\text{OH})_2\text{TeO}_3\text{SO}_4$, has been prepared as part of an investigation of tellurate(IV, VI) chemistry under hydrothermal conditions (Moret, 1972) and single crystals were kindly provided by Dr Moret. In most of the previously known M-tellurate(IV) structures, the metal atoms (Zn, Cu, Fe) are involved in three-dimensional covalent M–O– Te^{IV} nets (Lindqvist, 1973; Zeeman, 1971). Only in $\text{BaTeO}_3 \cdot \text{H}_2\text{O}$ (Rottersten-Nielsen, Grønbæk-Hazell & Rasmussen, 1971) can the building units be regarded as Ba^{2+} and TeO_3^{2-} ions.

The aim of the present investigation was to examine the effect of the Al atoms on the Te^{IV} coordination.

Data collection

Crystals of $\text{Al}_2(\text{OH})_2\text{TeO}_3\text{SO}_4$ were first investigated with Weissenberg techniques, the reflexion pattern indicating the space groups $P2_1$ or $P2_1/m$. Accurate cell dimensions were determined from a Guinier powder photograph (Table 1) with KCl as an internal standard ($d_{\text{KCl}}=6.2919_4$ Å at 20°C; Hambling, 1953), (*POWDER*; Lindqvist & Wengelin, 1967). Crystallographic data are given in Table 2. The density was determined by flotation in aqueous thallium(I) formate and malonate ('Clericis Lösung').

The crystal was mounted along c (for dimensions see Fig. 1) and intensities were collected on a two-

Table 1. Powder data for $\text{Al}_2(\text{OH})_2\text{TeO}_3\text{SO}_4$; Cu $K\alpha_1$ radiation (1.54050 Å)

h	k	l	$\sin^2 \theta$ (obs)	$\sin^2 \theta$ (calc)	d (calc) (Å)	I
1	0	0	0.01213	0.01209	7.006	<i>vw</i>
1	1	0	0.01864	0.01861	5.647	<i>w</i>
0	2	0	0.02625	0.02608	4.769	<i>m</i>
0	1	$\bar{1}$	0.03155	0.03149	4.340	<i>w</i>
1	0	$\bar{1}$	0.03566	0.03545	4.091	<i>w</i>
1	0	1	0.03859	0.03866	3.917	<i>m</i>
1	1	$\bar{1}$	0.04226	0.04197	3.760	<i>w</i>
1	1	1	0.04513	0.04518	3.624	<i>w</i>
2	1	0	0.05489	0.05487	3.288	<i>w</i>
1	2	$\bar{1}$	0.06160	0.06154	3.105	<i>m</i>
1	2	1	0.06483	0.06475	3.027	<i>w</i>
2	0	$\bar{1}$	0.07020	0.07011	2.909	<i>m</i>
1	3	0	0.07087	0.07077	2.895	<i>w</i>
2	2	0	0.074061	0.07443	2.823	<i>w</i>
2	0	1	0.07646	0.07653	2.784	<i>s</i>
2	1	$\bar{1}$	0.07646	0.07663	2.782	<i>s</i>
0	3	$\bar{1}$	0.08370	0.08366	2.663	<i>m</i>
1	3	$\bar{1}$	0.09424	0.09414	2.510	<i>m</i>
0	0	$\bar{2}$	0.10006	0.09988	2.437	<i>m</i>
2	2	1	0.10271	0.10261	2.405	<i>s</i>
0	4	0	0.10435	0.10433	2.385	<i>m</i>
0	1	$\bar{2}$	0.10631	0.10640	2.361	<i>m</i>
1	0	$\bar{2}$	0.10887	0.10876	2.269	<i>w</i>
1	1	$\bar{2}$	0.11511	0.11528	2.269	<i>s</i>
0	4	$\bar{1}$	0.12933	0.12930	2.142	<i>w</i>
3	1	$\bar{1}$	0.13514	0.13546	2.093	<i>us</i>
3	0	1	0.13862	0.13858	2.069	<i>w</i>
1	4	1	0.14302	0.14299	2.037	<i>w</i>
2	0	2	0.15478	0.15466	1.959	<i>w</i>
0	3	$\bar{2}$	0.15865	0.15857	1.934	<i>w</i>
1	3	2	0.17384	0.17387	1.847	<i>w</i>
3	3	1	0.19734	0.19726	1.734	<i>w</i>
4	1	0	0.20014	0.19992	1.723	<i>w</i>