

The Crystal and Molecular Structure of 8-Acetoxy-6-(2,4-dimethoxy-5-bromophenyl)-3-methyl-tricyclo[5,2,1,0^{3,8}]decan-2-one

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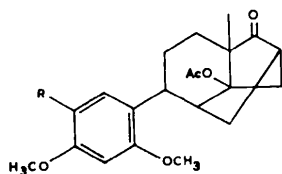
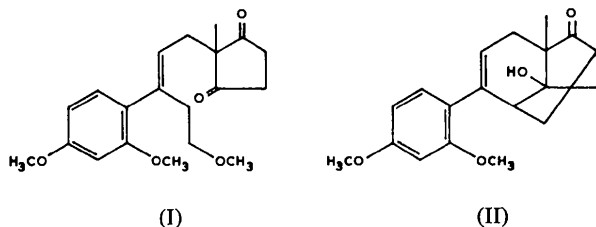
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The crystal and molecular structure has been determined by the heavy-atom method and refined by the least-squares procedure to $R=8.3\%$ for 2033 photographically observed reflexions. The compound crystallizes in the space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a=11.68 \pm 0.02$, $b=12.91 \pm 0.02$, $c=10.43 \pm 0.02$ Å, $\alpha=114.7 \pm 1$, $\beta=90.2 \pm 1$ and $\gamma=118.3 \pm 1^\circ$. The unit cell also contains one molecule of the solvent, benzene. The 'cage' part of the molecule exhibits a large number of elongated bonds and strained internal valency angles. The bridgehead angle in the bicyclic heptane ring system is 89° . The acetate group at C(16) and the methyl group at C(15) are *cis* to each other.

Introduction

As part of a series of investigations on some synthetic oxasteroids Kasturi, Ramachandra, Damodaran & Kalyani Vijayan (1972) prepared *B*-secodione (I) and studied the acid-catalysed cyclization under a variety of conditions. When compound (I) was refluxed with 20% ethanolic hydrochloric acid for one hour, a novel tricyclic ketoalcohol was formed and on the basis of spectral and analytical data, structure (II) was assigned to it. However, alternate structures could also be proposed on the basis of spectral data and on mechanistic grounds. Hence, with a view to determining the structure and stereochemistry of this compound unambiguously, the X-ray analysis of the bromo derivative (III*b*) of the dihydroacetate (III*a*) was undertaken.



(III) (a) R = H, (b) R = Br

Experimental

Transparent, needle-like crystals of (III*b*) were obtained by slow evaporation, with a mixture of benzene and petroleum ether used as solvent. The unit-cell dimensions and space group of the crystal were determined from oscillation and Weissenberg photographs. The unit cell chosen was not a reduced one. Density measurement by flotation in aqueous potassium iodide solution indicated the presence of one molecule of benzene along with two molecules of (III*b*) in the unit cell. Table I lists the relevant crystal data.

Table 1. *Crystal data*

Chemical formula	$C_{21}H_{25}O_5Br \cdot \frac{1}{2}C_6H_6$
M.W.	476.38
<i>a</i>	11.68 ± 0.02 Å
<i>b</i>	12.91 ± 0.02
<i>c</i>	10.43 ± 0.02
α	$114.7 \pm 1^\circ$
β	90.2 ± 1
γ	118.25 ± 1
Cell volume	1205 \AA^3
Density calculated, D_c	1.312 g cm^{-3}
Density experimental, D_x	1.345 g cm^{-3}
Number of molecules in the unit cell	2
Crystal system	Triclinic
Space group	$P\bar{1}$
μ for Cu $K\alpha$ radiation	30.16 cm^{-1}

Intensity data from reciprocal levels $hk0$ and hkl , $h=0$ to 7 were collected on multiple films using specimens cut along the crystallographic *c* and *a* directions respectively and ground to near cylindrical shapes. Nickel-filtered copper radiation was employed. The intensities were measured by visual comparison with a calibrated time-exposure strip prepared from the same specimen and were corrected for Lorentz and polarization factors and spots-hape effect. The data were also

corrected for absorption by the method of Palm (1964).

Since the compound under study was a racemic mixture with two molecules in the unit-cell, the space group was initially assumed to be $P\bar{1}$. The position of the bromine atom was derived from the $0kl$ and the $hk0$ Patterson syntheses. Even though well defined peaks were observed in the subsequent bromine-phased Fourier maps, a molecular model could not be fitted satisfactorily owing to large overlap of atomic positions in projection. At this stage, three-dimensional data became available and the position of the bromine atom was confirmed from a 3D-Patterson map. Structure factor calculations with only bromine contribution gave an R value of 43.6%. The 3D-Fourier map computed with the bromine phases had a large number of spurious peaks. However, examination of the Patterson map and trial calculations led to the identification of the peaks corresponding to the lighter atoms in the molecule. In two cycles of block-diagonal structure-factor least-squares refinement using isotopic atomic thermal parameters and unit weight for all the reflexions, the R index was reduced to 20.1%. From an analysis of the function $\sum \Delta F^2$ vs F_{obs} , the weighting function was then changed to the form

$$w = \frac{1}{a + bF_o + cF_o^2}$$

where $a=1.0$, $b=0.02$ and $c=0.05$, and the R index dropped to 14.1% in six more least-squares cycles. Anisotropic thermal parameters were introduced at this stage for all the atoms and in three cycles of refinement the R value had been reduced to 8.6%. In the terminal least-squares cycle, the indicated shifts for all the parameters were less than the corresponding e.s.d.'s. A difference Fourier map was then computed and the positions of all but two hydrogen atoms (belonging to the methyl groups at C(11) and C(20) respectively) could be derived. (The numbering of atoms is as shown in Fig. 1 and does not follow chemical convention). However, the positions of these atoms could be fixed from geometric considerations. The hydrogen atom parameters were not refined. The inclusion of the hydrogen atoms, which were assumed to have the same isotropic temperature factors as those of the heavier atoms to which they were attached, in the structure factor calculations, reduced the discrepancy index to 8.3% for 2033 observed reflexions.

The scattering factors used in this analysis are those of Cromer & Waber (1965). The SFLS calculations were carried out using the computer program written by Shiono for the IBM 1130 computer and modified by B. S. Reddy for the IBM 360/44 computer.

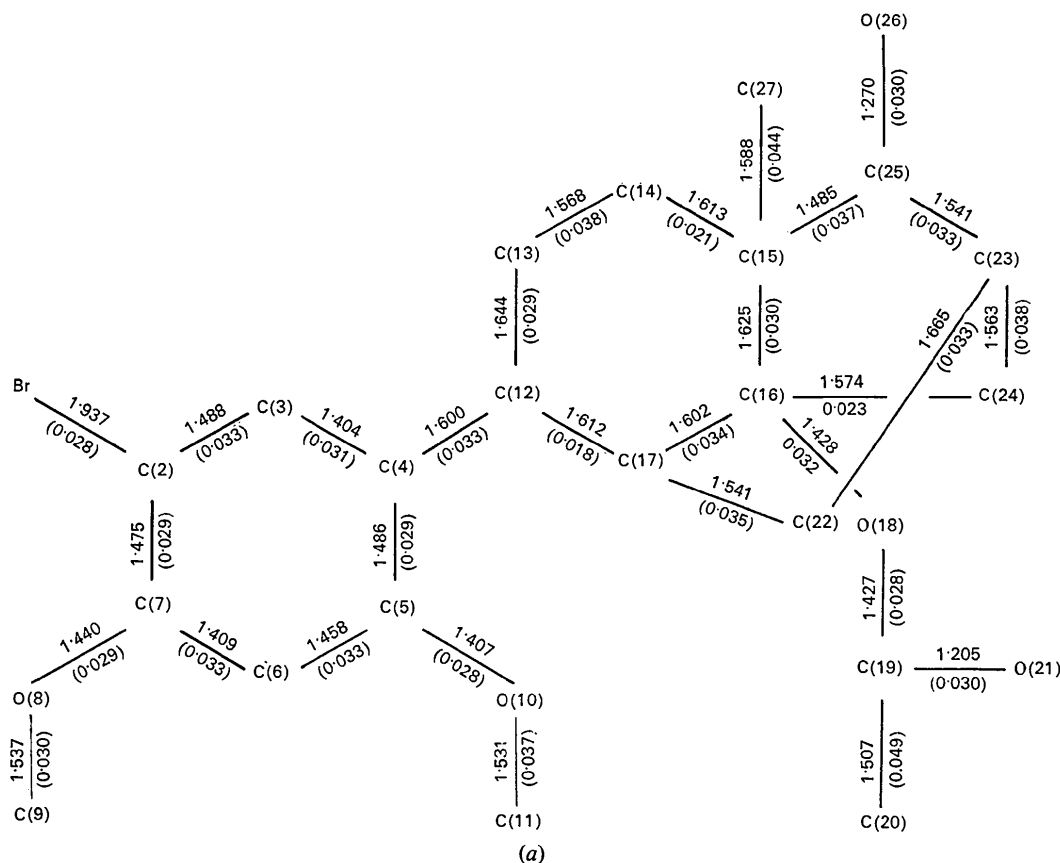
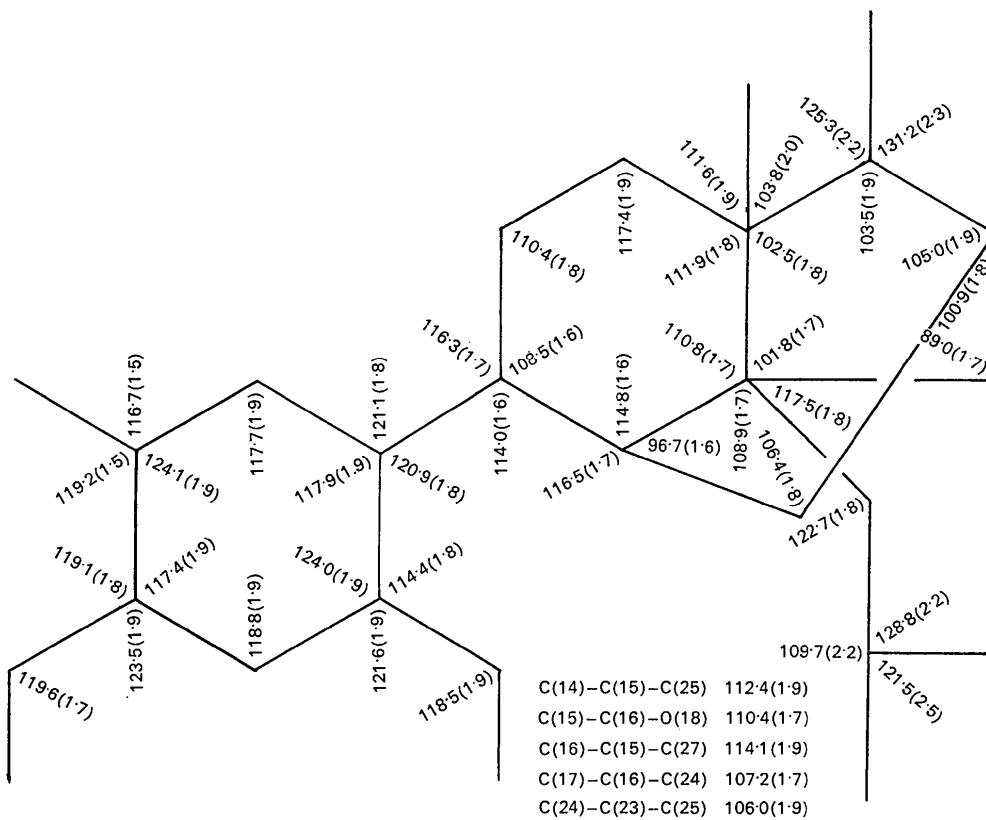


Fig. 1. (a) Interatomic distances in Å. (b) Valency angles in degrees. The values in parentheses represent the e.s.d.'s.



(b)

Fig. 1 (cont.)

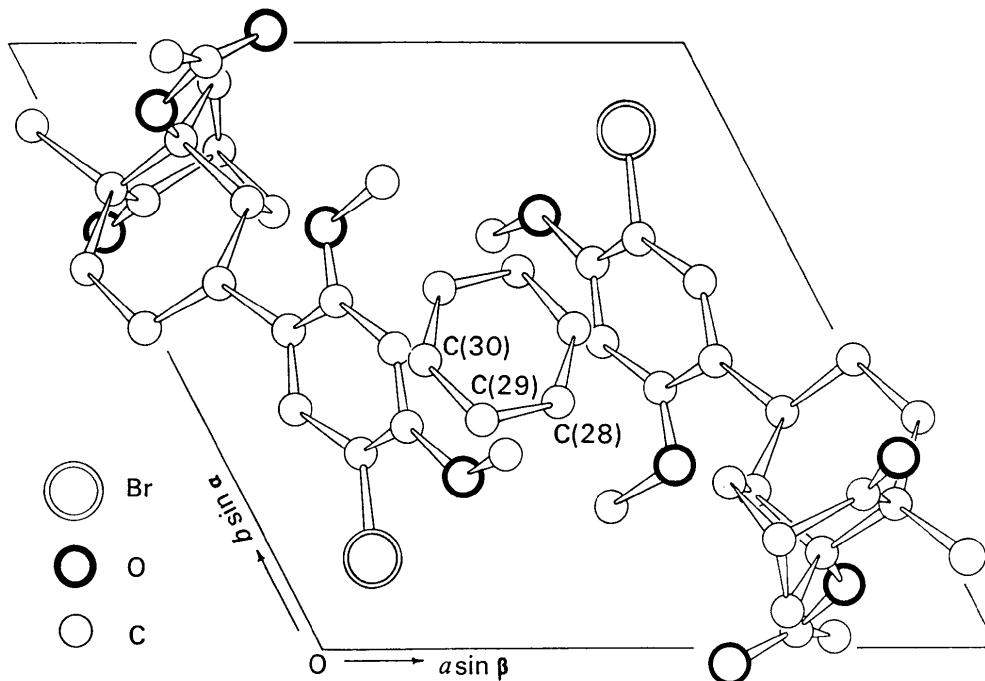


Fig. 2. A perspective view of the structure as seen perpendicular to the *ab* plane.

Results and discussion

The final positional coordinates of all the atoms are given in Table 2. In Table 3, the anisotropic thermal parameters along with the equivalent isotropic temperature factors (Hamilton, 1959) are listed. The observed and final calculated structure-factor table can be obtained from the authors on request. The bond lengths and bond angles involving the non-hydrogen atoms are marked in Fig. 1(a) and (b) respectively and those involving the solvent molecule in Table 4.

Table 2. Final positional coordinates in fractional units and their e.s.d.'s ($\times 10^4$)

Br	0.1473 (3)	0.1457 (2)	0.4803 (2)
C(2)	0.2071 (21)	0.3197 (16)	0.4972 (19)
C(3)	0.1506 (20)	0.3962 (17)	0.5933 (18)
C(4)	0.1939 (20)	0.5234 (16)	0.6088 (18)
C(5)	0.2932 (21)	0.5728 (16)	0.5284 (18)
C(6)	0.3459 (21)	0.4959 (18)	0.4320 (18)
C(7)	0.3009 (20)	0.3666 (17)	0.4123 (18)
O(8)	0.3452 (15)	0.2816 (12)	0.3186 (14)
C(9)	0.4234 (25)	0.3182 (21)	0.2109 (23)
O(10)	0.3301 (15)	0.7002 (13)	0.5482 (15)
C(11)	0.4514 (30)	0.7722 (28)	0.4962 (33)
C(12)	0.1312 (20)	0.6087 (16)	0.7015 (17)
C(13)	-0.0082 (21)	0.5272 (18)	0.7426 (20)
C(14)	-0.0631 (23)	0.6207 (19)	0.8223 (22)
C(15)	0.0395 (22)	0.7633 (19)	0.9618 (20)
C(16)	0.1830 (20)	0.8416 (17)	0.9287 (18)
C(17)	0.2357 (19)	0.7426 (16)	0.8482 (18)
O(18)	0.1707 (15)	0.8958 (13)	0.8385 (14)
C(19)	0.2810 (24)	0.9693 (18)	0.7920 (21)
C(20)	0.2296 (32)	0.9745 (29)	0.6630 (31)
O(21)	0.3994 (15)	0.0218 (15)	0.8407 (18)
C(22)	0.2649 (22)	0.7243 (19)	0.9790 (19)
C(23)	0.2330 (23)	0.8227 (20)	0.1182 (20)
C(24)	0.2779 (24)	0.9430 (19)	0.0870 (20)
C(25)	0.0786 (23)	0.7493 (20)	0.0865 (19)
O(26)	-0.0025 (19)	0.6860 (17)	0.1444 (17)
C(27)	-0.0278 (26)	0.8498 (23)	0.0254 (26)
C(28)	0.5438 (33)	0.4062 (28)	0.9259 (27)
C(29)	0.4128 (29)	0.3779 (25)	0.8719 (27)
C(30)	0.3738 (29)	0.4702 (31)	0.9428 (30)
H(031)	0.100	0.358	0.663
H(061)	0.417	0.525	0.367
H(091)	0.450	0.258	0.157
H(092)	0.388	0.375	0.179
H(093)	0.521	0.400	0.256
H(111)	0.460	0.717	0.396
H(112)	0.465	0.865	0.523
H(113)	0.550	0.800	0.567
H(121)	0.108	0.638	0.621
H(131)	0.004	0.500	0.819
H(132)	-0.067	0.442	0.642
H(141)	-0.150	0.592	0.863
H(142)	-0.067	0.625	0.719
H(171)	0.333	0.800	0.833
H(201)	0.213	0.883	0.567
H(202)	0.283	0.050	0.650
H(203)	0.140	0.985	0.696
H(221)	0.196	0.629	0.963
H(222)	0.369	0.752	0.979
H(231)	0.250	0.825	0.218
H(241)	0.250	0.009	0.142
H(242)	0.379	0.983	0.083
H(271)	-0.050	0.863	0.933
H(272)	-0.117	0.800	0.058
H(273)	0.042	0.938	0.100

The labelling of the hydrogen atoms is the same as that of the heavy atom to which they are linked; in the cases where there is more than one hydrogen atom attached to the heavy atom a new sequence is started and is included as the last digit of the labelling number.

The dimensions of the aromatic ring and the methoxyl groups at C(5) and C(7) do not differ significantly from the standard values. The C-Br length of 1.94 ± 0.02 Å is, however, longer than the normal value of 1.85 Å (Sutton, 1965). The tricyclic ring system consisting of the six-membered ring (ring *A*) through atoms C(12), C(13), C(14), C(15), C(16) and C(17), and the five-membered rings through atoms C(16), C(17), C(22), C(23) and C(24) (ring *B*) and atoms C(15), C(16), C(24), C(23) and C(25) (ring *C*) respectively, exhibits interesting structural characteristics. The most striking feature is perhaps the general lengthening of the bonds in the system. In particular, the C(12)-C(13), C(14)-C(15), C(15)-C(16) and the C(12)-C(17) bonds in ring *A* and the C(22)-C(23) bond in ring *B* differ significantly from the accepted value of 1.54 Å. However, the deviation of the average value of all the $C_{sp^3}-C_{sp^3}$ distances in the structure (1.60 ± 0.03 Å) from the standard distance is well within the limits of experimental error ($\Delta < 3\sigma$). It may be mentioned that the extension of C-C bonds is a feature commonly observed in cage molecules (Shimanouchi & Sasada, 1970; Gilardi, 1972; Kaneda & Iitaka, 1972), though the occurrence of as many as five long bonds in the same system appears to be rather rare. Hall & Maslen (1965) attribute the bond elongation to the fully substituted valence state of the carbon atoms. However, this could also be attributed to the strain arising from the fusion of several ring systems. The widely varying valency angles, especially in the bicyclic heptane ring system formed by rings *B* and *C* support this view. The internal angles in this system range from 89.0 to 108.9°, the average being 101.6°. The bridgehead angle of 89° at C(24) closely resembles the values observed in some substituted norbornanes (Destro, Filippini, Gramaccioli & Simonetta, 1969; Cesur & Grant, 1965; Flippen, 1972; Coetzer, Baxter & Gafner, 1971; Dwivedi & Srivastava, 1972). The dimensions of the acetate group and the solvent molecule are normal.

The equations of the mean planes through various groups of atoms and the corresponding atomic displacements are given in Table 5. The phenyl ring is highly planar, the largest displacement being 0.02 Å for C(7). The bromine atom is displaced by 0.05 Å from this plane. Ring *A* exists in a distorted chair form. Both the five-membered rings *B* and *C* assume envelope conformations. The six-membered ring through atoms C(15), C(16), C(17), C(22), C(23) and C(25) (Ring *D*) is in a distorted boat form. The torsional angles in these rings are presented in Table 6 and are comparable with the values reported earlier (Altona & Sundaralingam, 1970; Karle, 1972). The observed deviations from the ideal values could be attributed to the variation in the substitution and also to the fusion

Table 3. *Anisotropic thermal parameters* ($\times 10^4$)
of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl)]$ *and their e.s.d.'s* ($\times 10^4$)

The last column lists the equivalent isotropic temperature factors.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	<i>B</i>
Br	167 (4)	92 (2)	174 (3)	71 (2)	42 (2)	67 (2)	5.26
C(2)	123 (29)	51 (16)	129 (24)	41 (16)	-5 (19)	43 (17)	3.83
C(3)	109 (29)	78 (18)	108 (22)	54 (18)	11 (18)	43 (17)	3.60
C(4)	112 (28)	71 (17)	96 (21)	36 (17)	8 (18)	37 (16)	3.78
C(5)	136 (31)	64 (17)	107 (23)	53 (18)	11 (19)	34 (17)	3.93
C(6)	117 (30)	98 (20)	94 (22)	59 (19)	17 (18)	45 (18)	3.88
C(7)	99 (28)	87 (18)	96 (21)	50 (18)	17 (17)	37 (17)	3.62
O(8)	134 (21)	99 (14)	152 (18)	76 (14)	59 (15)	55 (14)	4.55
C(9)	177 (38)	130 (25)	156 (30)	102 (26)	90 (26)	79 (24)	5.23
O(10)	154 (22)	99 (14)	171 (20)	67 (14)	59 (16)	81 (15)	4.99
C(11)	192 (45)	186 (35)	316 (53)	125 (34)	143 (39)	171 (39)	7.27
C(12)	99 (27)	74 (17)	97 (21)	48 (17)	10 (17)	28 (16)	3.52
C(13)	117 (30)	81 (19)	128 (25)	41 (18)	16 (20)	45 (18)	4.32
C(14)	119 (32)	94 (21)	157 (29)	50 (20)	20 (22)	45 (21)	4.91
C(15)	127 (31)	102 (21)	123 (25)	72 (20)	43 (20)	51 (20)	4.20
C(16)	116 (29)	73 (18)	116 (24)	58 (18)	10 (19)	38 (17)	3.74
C(17)	102 (28)	73 (17)	118 (23)	57 (17)	7 (18)	48 (17)	3.37
O(18)	138 (21)	111 (15)	171 (20)	72 (14)	33 (15)	87 (15)	4.77
C(19)	165 (35)	80 (20)	145 (28)	64 (21)	26 (23)	50 (20)	4.90
C(20)	238 (50)	195 (38)	265 (49)	93 (36)	31 (37)	179 (39)	8.03
O(21)	105 (21)	133 (18)	237 (26)	34 (15)	13 (17)	100 (19)	6.17
C(22)	135 (32)	114 (22)	112 (24)	80 (21)	27 (20)	54 (19)	4.28
C(23)	138 (34)	120 (24)	126 (26)	87 (23)	22 (22)	55 (21)	4.54
C(24)	159 (35)	102 (22)	111 (24)	78 (22)	-5 (21)	30 (19)	4.83
C(25)	149 (33)	133 (24)	114 (24)	111 (23)	60 (21)	71 (20)	4.12
O(26)	217 (29)	202 (24)	199 (25)	136 (22)	95 (21)	143 (21)	6.56
C(27)	147 (37)	134 (27)	212 (38)	101 (26)	63 (28)	80 (27)	5.60
C(28)	278 (54)	196 (37)	174 (37)	162 (38)	64 (34)	101 (32)	7.33
C(29)	209 (45)	141 (30)	201 (39)	68 (29)	23 (30)	97 (29)	7.09
C(30)	191 (44)	247 (43)	261 (46)	132 (36)	80 (33)	205 (40)	7.13

Table 4. *Bond lengths* (Å) *and bond angles* (°) *in the solvent molecule*

C(28)–C(29)	1.44 (0.053)
C(29)–C(30)	1.40 (0.054)
C(30)–C(28)*	1.44 (0.030)
C(28)–C(29)–C(30)	120.6 (2.97)
C(29)–C(30)–C(28)*	123.3 (3.13)
C(29)–C(28)–C(30)*	116.1 (2.99)

* Centrosymmetrically related atom.

of the rings. Ring *A* is inclined at 142° to the phenyl ring. Rings *B* and *C* make angles of 87.8 and 84.9° respectively with ring *A*. The acetate group at C(16) and the methyl group at C(15) are *cis* to each other.

Fig. 2 gives a view of the structure as seen along the [001] direction. There is no significantly short intermolecular contact distance. Each molecule is in contact with 12 neighbours situated at $\pm a$, $\pm b$, $\pm c$, $\pm(a+b)$, $\pm(a+c)$ and $\pm(b-c)$. The packing coefficient of the structure is 0.692 and corresponds to a closest packed structure (Kitaigorodskii, 1961). The solvent molecule fits well into the hole formed between the two symmetry-related molecules in the unit cell.

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Table 5. *Equations of the mean planes through various groups of atoms, and the displacements, in Å, of the atoms from the respective planes*

Plane I	Through C(2), C(3), C(4), C(5), C(6) and C(7)	0.76296X + 0.00987Y + 0.64636Z = 3.77404				
Plane II	Through C(13), C(14), C(16) and C(17)	0.10465X - 0.17383Y + 0.97920Z = 3.7149				
Plane III	C(15), C(17), C(22) and C(25)	0.64836X + 0.75834Y + 0.06748Z = 7.2562				
Plane IV	C(16), C(17), C(22) and C(23)	0.93844X + 0.32358Y - 0.12189Z = 3.87638				
Plane V	C(15), C(16), C(23) and C(25)	0.11620X + 0.96481Y + 0.23589Z = 9.81515				
		I	II	III	IV	V
Br	0.054					
C(2)	0.021					
C(3)	-0.004					
C(4)	-0.011					
C(5)	0.010					
C(6)	0.006					
C(7)	-0.022					
C(12)			-0.731			
C(13)			-0.007			
C(14)			0.007			
C(15)			0.603	-0.011		0.016
C(16)			-0.007	0.837	-0.014	-0.011
C(17)			0.007	0.011	0.020	
C(22)				-0.011	-0.021	
C(23)				0.881	0.016	0.012
C(24)					0.906	0.914
C(25)				0.013		-0.017

Table 6. *Torsional angles*

Ring A		Ring B	
C(12)–C(13)–C(14)–C(15)	–53.5°	C(16)–C(17)–C(22)–C(23)	3.14°
C(13)–C(14)–C(15)–C(16)	47.7	C(17)–C(22)–C(23)–C(24)	–33.62
C(14)–C(15)–C(16)–C(17)	–46.0	C(22)–C(23)–C(24)–C(16)	53.34
C(15)–C(16)–C(17)–C(12)	55.8	C(23)–C(24)–C(16)–C(17)	–60.88
C(16)–C(17)–C(12)–C(13)	–58.2	C(24)–C(16)–C(17)–C(22)	40.57
C(17)–C(12)–C(13)–C(14)	54.8		
Ring C		Ring D	
C(23)–C(25)–C(15)–C(16)	2.68°	C(16)–C(17)–C(22)–C(23)	3.14°
C(25)–C(15)–C(16)–C(24)	–39.06	C(17)–C(22)–C(23)–C(25)	75.03
C(15)–C(16)–C(24)–C(23)	56.03	C(22)–C(23)–C(25)–C(15)	–71.10
C(16)–C(24)–C(23)–C(25)	–56.94	C(23)–C(25)–C(15)–C(16)	2.68
C(24)–C(23)–C(25)–C(18)	35.05	C(25)–C(15)–C(16)–C(17)	74.05
		C(15)–C(16)–C(17)–C(22)	–68.22

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The Crystal Structure of Lithium Maleate Dihydrate

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The structure of $Li_2C_4H_2O_4 \cdot 2H_2O$, with cell dimensions $a = 9.6306$, $b = 12.1307$, $c = 12.7051$ Å, $\beta = 107.96^\circ$, has been determined with counter-measured X-ray intensities (1535 planes). The maleate ion is non-planar and unsymmetrical, the principal bond distances (Å) being C(1)–C(2) 1.495 (3), C(2)–C(3) 1.330 (3), C(3)–C(4) 1.505 (3), C(1)–O(1) 1.277 (2), C(1)–O(2) 1.252 (2), C(4)–O(3) 1.273 (2), C(4)–O(4) 1.252 (2). Each lithium ion has an approximately tetrahedral coordination of oxygen atoms.

Experimental

(a) Preparation

The compound was prepared by the neutralization

of an aqueous solution of maleic acid with equivalent amounts of lithium hydroxide. Crystals obtained from the aqueous solution were monoclinic prisms, usually showing the forms {010}, {110}, {001} and occasionally elongated parallel to **a**. A melting point could not be determined as dehydration occurred at 160°C. The composition was confirmed by elemental chemical analysis (C, H, and Li).

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