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The Crystal and Molecular Structure of 3,3′-Methylene(bis-6-bromo-4-hydroxycoumarin): Unusual Molecular Interactions

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The crystal structure of 3,3′-methylene(bis-6-bromo-4-hydroxycoumarin), $C_{19}H_{10}O_6Br_2$, has been determined by single-crystal X-ray diffraction by the heavy atom method with 922 reflexions refined to an R value of 0·054. The molecular structure confirms that previously found for dicoumarol itself. The crystal investigated was tetragonal, space group $P4_12_12$ with $a=5{\cdot}496$, $c=54{\cdot}49$ Å, $Z=4$, $D_c=2{\cdot}012$ g.cm^{-3}. The unusual unit cell is attributed to packing of the molecules in layers, the 4_1 axis arising as a result of a good fit between the layers after a rotation of 90°.

Introduction

The structure of dicoumarol, [3,3′-methylene(bis-4-hydroxycoumarin)], has been in dispute until recently, and to resolve this problem X-ray studies of dicoumarol itself and of its dibromo derivative were started. Before this had progressed far, the structure of the parent compound was published (Bravic, Gaultier & Hauw, 1968). The dibromo derivative has a very unusual unit cell, (5·50, 5·50, 54·49 Å) in contrast to dicoumarol (8·47, 15·12, 11·71 Å, $\beta=99°$) and we have continued with its X-ray analysis in an attempt to understand the intermolecular interactions responsible for this packing.

Experimental

3,3′-Methylene(bis-6-bromo-4-hydroxycoumarin), (dibromodicoumarol), was prepared by the method of Huebner & Link, 1944. The compound was recrystallized, with very slow cooling, from cyclohexanone which had been carefully purified by distillation. It forms square plates with [001] developed, and is often twinned by reversal of c.

Crystal data

$C_{19}H_{10}O_6Br_2$. $M=494{\cdot}93$. Tetragonal, $a=5{\cdot}496$ (4), $c=54{\cdot}49$ (6) Å, $U=1645{\cdot}9$ Å^3, $Z=4$, $F_{000}=1936$. $D_c=2{\cdot}012$, $D_m=1{\cdot}979$ (10) g.cm^{-3} measured by flotation in benzene/methylene iodide. $\mu=73{\cdot}6$ for Cu $K\alpha$.

The Laue group $4/mmm$, systematic absences: $00l$ $l\neq4n$, $h00$ $h\neq2n$, indicate $P4_12_12$ or $P4_32_12$ and the former was chosen on the basis of the structure determination. The unit cell was determined at 18 °C with errors estimated from the agreement of observed and calculated axial 2θ values. The value of Z requires that the molecule lie on a crystallographic twofold axis.

Originally, photographic data were collected by the Weissenberg technique but these were superseded by more extensive data taken on a Siemens auto-diffractometer. Ni-filtered Cu $K\alpha$ radiation was used, and the diffractometer was operated in the $\omega/2\theta$ coupled mode. The '5-point' measurement procedure was used with a maximum step time of 0·6 sec. Data were collected to $\omega=70°$ and the 0,0,40 reflexion was used as an intensity reference. There was no evidence of crystal decay during the data collection. The crystal dimensions were $0{\cdot}6\times0{\cdot}6\times0{\cdot}5$ mm in the axial directions. The data were corrected for absorption, Lorentz and polarization factors. 1060 reflexions were collected of which 142 were classed as unobserved *i.e.* $I_{net}<2{\cdot}586\,\sigma(I_{net})$. A Patterson synthesis was interpreted to give a bromine atom position of 0·177, −0·012, 0·0101 (in $P4_12_12$).

From a Fourier synthesis, all the light atoms could be located and refinement proceeded smoothly to an R value of 0·064 with all atoms anisotropic, but with the hydrogen atoms not located. 10 reflexions (mostly of form $03l$), with inexplicably high deviations were given zero weight, and the statistical weights were used

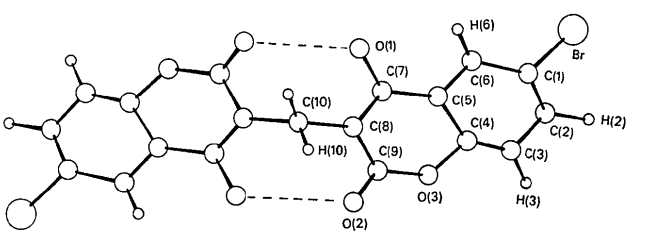

Fig. 1. The dibromodicoumarol molecule viewed down the twofold axis. Large circles represent bromine atoms, medium circles carbon and oxygen atoms, small circles hydrogen atoms (calculated positions). The hydrogen bond is dotted.

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for the rest. Form factors were taken from *International Tables for X-ray Crystallography* (1962). At this stage, anomalous dispersion for bromine was included (f' and f'' from *International Tables*). A cycle of refinement in space group $P4_32_12$ with all the z coordinates negative gave $R=0{\cdot}069$, and therefore $P4_12_12$ was taken as the correct space group for the crystal being examined. The hydrogen atoms were visible as weak peaks on a difference Fourier synthesis, but an attempt to refine their positions was not successful. They were therefore included at calculated positions (with the exception of the hydroxyl hydrogen atom) for a final cycle of least-squares calculations. This gave a final R value of 0·054.

The final atomic coordinates and temperature factors are shown in Tables 1 and 2 and the observed and calculated structure factors are given in Table 3. All calculations were performed using the X-RAY 63 and X-RAY systems running on an IBM 7094, an IBM 360 and the SRC ATLAS computers.

Table 1. *Atomic coordinates with standard deviations in brackets*

	x/a	y/b	z/c
Br	1·18304 (21)	−0·02989 (20)	0·10140 (1)
C(1)	1·0108 (16)	0·2250 (17)	0·0863 (2)
C(2)	0·8070 (19)	0·3078 (19)	0·0973 (1)
C(3)	0·6743 (18)	0·4961 (20)	0·0867 (1)
C(4)	0·7543 (17)	0·6013 (17)	0·0649 (1)
C(5)	0·9596 (16)	0·5135 (18)	0·0533 (1)
C(6)	1·0899 (16)	0·3180 (17)	0·0639 (1)
C(7)	1·0277 (17)	0·6274 (18)	0·0306 (1)
C(8)	0·9005 (16)	0·8291 (16)	0·0225 (1)
C(9)	0·6903 (17)	0·9086 (17)	0·0353 (1)
C(10)	0·9727 (17)	0·9727	0·0
O(1)	1·2161 (12)	0·5319 (12)	0·0184 (1)
O(2)	0·5628 (15)	1·0802 (15)	0·0290 (1)
O(3)	0·6195 (12)	0·7898 (15)	0·0560 (1)
H(2)	0·7541	0·2291	0·1148
H(3)	0·5042	0·5605	0·0954
H(6)	1·2475	0·2408	0·0547
H(10)	1·1692	0·9490	−0·0036

Results

The molecular structure and atomic numbering is shown in Fig. 1. The structure confirms that found for dicoumarol itself. The bond lengths and angles are given in Table 4 and information on molecular planes is given in Table 5. The dimensions correspond closely to standard values (Sutton, 1965) except for the bonds C(5)–C(7), C(7)–C(8) and C(8)–C(9), where C(7)–C(8), a double bond, is longer (at 1·38 Å) than the expected 1·34 Å, C(8)–C(9) is shorter (at 1·42 Å) than the expected 1·44 Å, and C(5)–C(7) is shorter (at 1·44 Å) than the expected 1·465 Å. These distances may indicate conjugation along this chain of atoms. It is very clear from the distances C(7)–O(1) of 1·34 Å, and C(9)–O(2) of 1·22 Å, that the possible tautomerism: C(7)–O(1)–H and C(9)=O(2): C(7)=O(1) and C(9)–O(2)–H does not occur, and the molecule is entirely in the first form. The hydrogen bond distance O(1)···O(2′) is 2·69 Å, a standard figure (Pimentel & McClellan, 1960).

The molecule consists of two approximately planar halves related by the twofold axis through C(10). Each half is itself composed of two closely planar

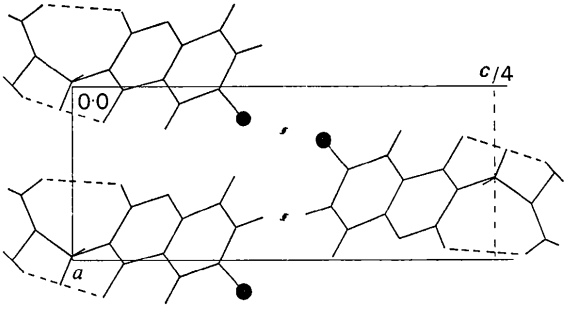

Fig. 2. One quarter of a unit cell viewed down **b**, showing halves of three molecules. The bromine atoms are indicated by solid circles and the hydrogen bonds by dashed lines.

Table 2. *Anisotropic temperature factors, with standard deviations in parentheses*

The values listed are 10^3u_{ij}, where the temperature factor has the form:

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

All hydrogen atoms have isotropic temperature factors, $U=0{\cdot}038$ Å^2.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	60·7 (7)	51·8 (7)	43·1 (5)	9·9 (5)	6·0 (5)	6·1 (4)
C(1)	45 (5)	39 (5)	35 (4)	1 (4)	−11 (3)	−4 (4)
C(2)	49 (5)	50 (5)	28 (3)	−2 (6)	2 (4)	2 (4)
C(3)	38 (5)	80 (7)	24 (3)	3 (5)	6 (4)	2 (4)
C(4)	42 (5)	45 (5)	25 (3)	1 (4)	−3 (3)	−2 (3)
C(5)	32 (4)	47 (5)	24 (3)	−5 (4)	−1 (3)	−2 (3)
C(6)	42 (5)	34 (4)	34 (4)	6 (4)	1 (4)	−5 (4)
C(7)	34 (4)	42 (5)	27 (3)	−2 (4)	1 (3)	−4 (4)
C(8)	37 (5)	34 (4)	25 (3)	−1 (4)	4 (3)	−6 (3)
C(9)	41 (5)	45 (5)	28 (3)	10 (4)	−1 (4)	−5 (4)
C(10)	42 (4)	42	26 (5)	−3 (6)	−3 (3)	3
O(1)	39 (3)	44 (4)	38 (3)	9 (3)	14 (3)	4 (3)
O(2)	53 (4)	61 (5)	37 (3)	14 (4)	12 (3)	−9 (3)
O(3)	37 (3)	68 (5)	30 (2)	13 (4)	11 (3)	1 (3)

Table 3. *Observed and calculated structure factors*

The columns are in the order l, $10F_o$, $10F_c$ and φ, the phase angle in millicycles.

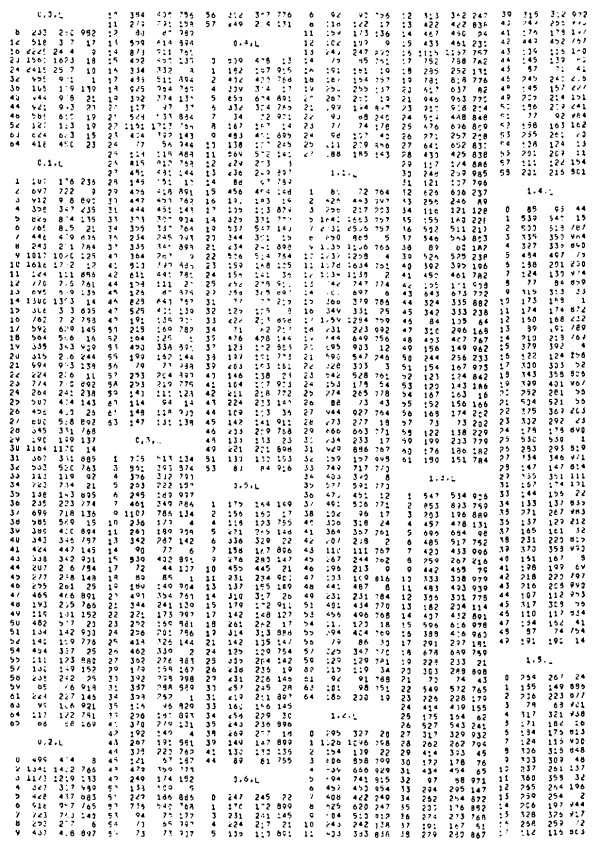

Table 4. *Bond lengths and angles, with standard deviations in brackets*

A primed atom is related to the corresponding unprimed one by the twofold axis passing through the molecule.

Br——C(1)	1·881 (9) Å	Br—C(1)—C(2)	118·2 (6)°
C(1)—C(2)	1·35 (1)	Br—C(1)—C(6)	120·1 (7)
C(2)—C(3)	1·39 (1)	C(1)—C(2)—C(3)	119·9 (8)
C(3)—C(4)	1·39 (1)	C(2)—C(3)—C(4)	119·9 (9)
C(4)—C(5)	1·38 (1)	C(3)—C(4)—C(5)	120·1 (8)
C(5)—C(6)	1·41 (1)	C(4)—C(5)—C(6)	119·6 (7)
C(6)—C(1)	1·39 (1)	C(5)—C(6)—C(1)	118·6 (8)
C(2)—H(2)	1·09	C(6)—C(1)—C(2)	121·8 (9)
C(3)—H(3)	1·11	C(3)—C(4)—O(3)	116·6 (8)
C(6)—H(6)	1·09	C(5)—C(4)—O(3)	123·3 (7)
C(4)—O(3)	1·36 (1)	C(4)—C(5)—C(7)	117·0 (8)
C(5)—C(7)	1·44 (1)	C(6)—C(5)—C(7)	123·4 (8)
C(7)—O(1)	1·34 (1)	C(4)—O(3)—C(9)	120·3 (7)
C(7)—C(8)	1·38 (1)	C(5)—C(7)—O(1)	117·3 (8)
C(8)—C(9)	1·42 (1)	C(5)—C(7)—C(8)	119·5 (8)
C(8)—C(10)	1·51 (1)	C(8)—C(7)—O(1)	123·2 (7)
C(9)—O(2)	1·22 (1)	C(7)—C(8)—C(9)	120·1 (7)
C(9)—O(3)	1·36 (1)	C(7)—C(8)—C(10)	123·0 (7)
O(1)—O(2′)	2·69 (1)	C(9)—C(8)—C(10)	116·8 (7)
C(10)–H(10)	1·11	C(8)—C(9)—O(2)	124·5 (8)
		C(8)—C(9)—O(3)	119·5 (8)
		O(3)—C(9)—O(2)	116·0 (8)
		C(8)—C(10)–C(8′)	112·5 (6)
		C(9)—O(2)—O(1′)	121·2 (6)

Table 5. *Least-squares planes*

The equations are given in terms of orthogonal coordinates (Å).

Plane 1

	Deviation	
Br	0·03 Å	Defining plane
C(1)	0·01	
C(2)	−0·01	
C(3)	−0·03	
C(4)	0·00	
C(5)	0·00	
C(6)	−0·02	
C(7)	0·00	
O(3)	0·03	
C(8)	0·12	
C(9)	0·11	
C(10)	0·24	
O(1)	−0·11	
O(2)	0·17	

Plane equation $0{\cdot}557X+0{\cdot}661Y+0{\cdot}503Z=6{\cdot}267$

Plane 2

	Deviation	
C(7)	−0·02 Å	Defining plane
C(8)	0·00	
C(9)	0·00	
C(10)	0·02	
O(2)	−0·02	
O(3)	0·02	
C(4)	0·09	
C(5)	0·09	
O(1)	−0·12	

Plane equation $0{\cdot}568X+0{\cdot}602Y+0{\cdot}561Z=6{\cdot}238$

Dihedral angles:

Plane 1 – Plane 2	4·8°
Plane 1 – Plane 1′ (other half of molecule)	118·9

portions hinged on the line O(1)–C(7)–O(3), with dihedral angle 4·8°. The dihedral angle between the benzene rings in the two halves of the molecule is 118·9°.

Molecular packing

Intermolecular distances less than 3·5 Å are given in Table 6. The unit cell contains four complete molecules with the halves of each related by the diagonal two-fold axis. The molecules form layers and these are stacked up, one upon the other (Fig. 2). The strongest intermolecular contacts probably occur between one

Table 6. *Intermolecular distances* (Å) *less than* 3·5 Å (*translated atom second*)

To the molecule at $(1+x, y, z)$			
C(1)–H(3)	3·32	H(6)—C(3)	3·24
C(6)–H(3)	3·15	H(6)—C(4)	3·46
O(1)–C(9)	3·45	H(6)—H(3)	3·16
O(1)–O(3)	3·33	H(10)–O(2)	2·89
To the molecule at $(x, 1+y, z)$			
C(8)—H(6)	3·44	O(2)—C(5)	3·49
C(10)–O(1)	3·54	H(10)–O(1)	3·43
To the molecule at $(1+x, y-1, z)$			
Br—H(3)	2·88	H(6)—C(9)	3·22
C(6)–O(2)	3·48	H(6)—O(2)	2·40
O(1)–O(2)	3·18	H(6)—O(3)	3·21
To the molecule at $(1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z)$			
C(2)–H(2)	3·12	H(2)—H(2)	2·97
C(3)–H(2)	2·97	H(3)—Br	3·12
H(2)–Br	3·31	H(3)—H(3)	2·71

molecule and its neighbours in the same *x*-*y* layer. The forces in the *z* direction may be fairly weak, with the packing taking the form it does because the bottom of one layer fits well to the top of another after a rotation of 90°, *i.e.* with a 4_1 symmetry operation. In fact, because of the molecular twofold axis, the ends of two molecules, near $z=0{\cdot}125$, are related by a 2_1 axis (Fig. 3). The nearest neighbours are Br, H(2) and H(3) in the two molecules related by the screw axis $\frac{3}{4}, y, \frac{1}{8}$.

The space groups $P4_12_12$ and $P4_32_12$ are uncommon although not unknown, but the present example has an extreme axial ratio (9·91). One group of compounds is of particular interest (Öyum & Foss, 1956) typified by tellurium di(toluene-*p*-thiosulphonate), $[Te(S_2O_2C_6H_4CH_3)_2]$, the only other structure determined in this space group (Foss & Öyum, 1955). This has $a=7{\cdot}73$, $c=29{\cdot}88$ Å, with $c/a=3{\cdot}87$. There are again 4 molecules per unit cell, and the tellurium atom lies on the twofold axis. The phenyl rings are rather

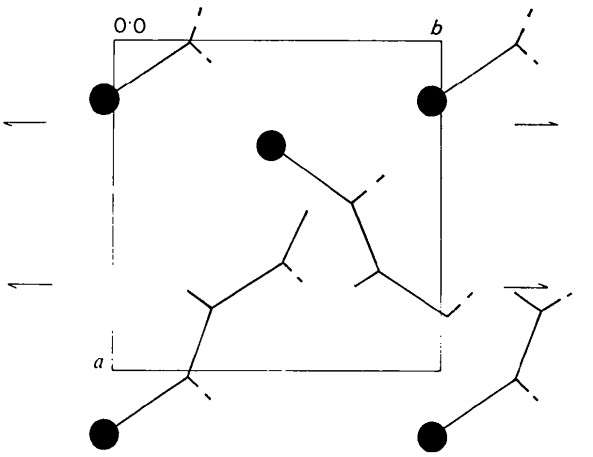

Fig. 3. The unit cell viewed down **c**, showing *only* the portions of molecules close to $z=0{\cdot}125$, in the order: Br (solid circles), C(1), C(2) and H(2), C(3), H(3).

further apart than in dibromodicoumarol, and so there is some penetration by the methyl groups from one layer to the next. However, the overall packing is similar, and may again result from fairly strong forces within the layers, with the layer stacking depending mainly on geometry. One other compound is known with a similar unit cell, silver gibberellate (personal communication by D. Rogers of preliminary observations) which is tetragonal with $a\simeq 7$, $c\sim 80$ Å. The space group was not identified but the evidence of the compounds discussed here suggests that $P4_12_12$ is likely.

We wish to thank Dr D. W. Hutchinson for drawing our attention to the problem and for preparing dibromodicoumarol, and Professor D. Rogers for the facilities for collecting the data for this compound.

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