

## The Crystal and Molecular Structure of a *p*-Bromobenzoyl Derivative of $\epsilon$ -Caesalpin

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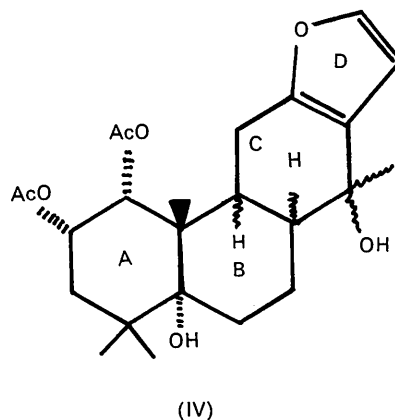
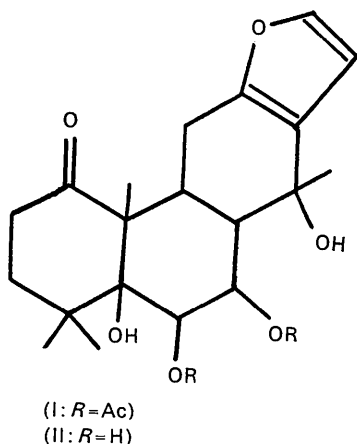
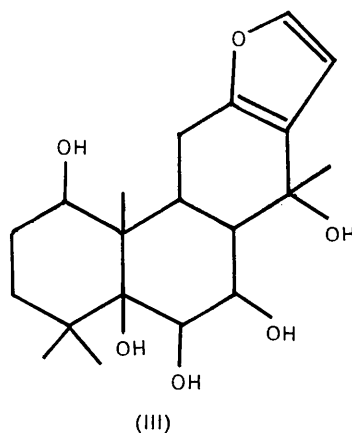
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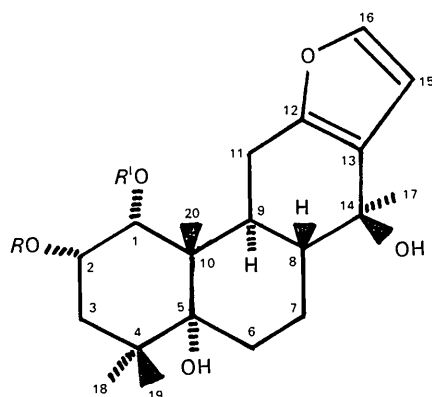
The crystal structure of a *p*-bromobenzoyl derivative,  $C_{27}H_{33}O_6Br$ , of the diterpene  $\epsilon$ -caesalpin has been determined by the heavy-atom method using three-dimensional X-ray data. The absolute configuration was established from the anomalous scattering of the bromine atom. The three six-membered rings *A*, *B* and *C* are fused to form a *trans-anti-trans* system. Rings *A* and *B* both occur in the chair form while the unsaturated ring *C* adopts a distorted half-chair conformation. An intramolecular hydrogen bond (2.649 Å) occurs between the two 1,3-diaxial hydroxyl groups. The crystals are monoclinic, space group  $P2_1$  with two molecules in a unit cell of dimensions  $a = 6.563$ ,  $b = 12.999$ ,  $c = 14.809$  Å;  $\beta = 94.50^\circ$ . The structure has been refined by least-squares methods to a final residual ( $R$ ) of 12.3% for 3115 reflexions.

### Introduction

From the seeds of *Caesalpinia bonducella* (Fleming), a plant abundantly available in East Pakistan, Qudrat-i-Khuda & Ali (1963) isolated  $\alpha$ -,  $\beta$ - and  $\gamma$ -caesalpins and determined their functional groups. Later the structures of  $\alpha$ -,  $\beta$ - and  $\delta$ -caesalpin were determined as (I), (II) and (III), respectively, and  $\gamma$ -caesalpin was reported to be a  $\delta$ -caesalpin ester of acetic and myristic acids (Canonica, Jommi, Manitto, Pagnoni & Pelizzoni, 1966). From the same source a new crystalline compound,  $\epsilon$ -caesalpin was isolated and assigned the structure (IV) or its enantiomer on the basis of chemical and spectroscopic evidence (Balmain, Bjämer, Connolly & Ferguson, 1967). This X-ray analysis was undertaken in order to determine the complete structure and the absolute configuration of  $\epsilon$ -caesalpin.



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(V:  $R=p\text{-Br}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ ,  $R^1=\text{H}$ )

(VI:  $R=R^1=\text{Ac}$ )

### Crystal data

1,2-Desacetyl- $\epsilon$ -caesalpin 2-*p*-bromobenzoate,  $\text{C}_{27}\text{H}_{19}\text{O}_6\text{Br}$ , F.W. = 533.2, m.p. 169–170°C. Monoclinic,  $a = 6.563 \pm 0.002$ ,  $b = 12.999 \pm 0.002$ ,  $c = 14.809 \pm 0.002$  Å;  $\beta = 94.50 \pm 0.03^\circ$ .  $V = 1259.5 \pm 0.5$  Å<sup>3</sup> from Cu  $K\alpha_1$  ( $\lambda = 1.54051$  Å) and Cu  $K\alpha_2$  ( $\lambda = 1.54433$  Å)  $D_m = 1.403$  g.cm<sup>-3</sup> (by flotation in aqueous potassium iodide),  $Z = 2$ ,  $D_x = 1.406$  g.cm<sup>-3</sup>.  $F(000) = 556$ . Space group  $P2_1$  (No. 4). Linear absorption coefficient  $\mu = 27.8$  cm<sup>-1</sup> for Cu  $K\alpha$  radiation.

### Experimental

The material crystallized from an acetone–ether solution as colourless, very soft plates with (001) as the predominant face. The cell dimensions were obtained by a least-squares method from  $0kl$  and  $h0l$  Weissenberg photographs calibrated with aluminum powder lines. The space group was determined from the absences ( $0k0$  absent when  $k$  is odd) and from knowing that the parent  $\epsilon$ -caesalpin is optically active ( $[\alpha]_D = +2^\circ$ ). Non-integrated equi-inclination Weissenberg data were collected with Ni-filtered Cu  $K\alpha$  radiation, using the multiple-film technique. Two crystals of the same size ( $0.35 \times 0.35 \times 0.10$  mm), mounted along the crystallographic  $a$  and  $b$  axes were used. From one crystal the layers  $0kl$  to  $6kl$  were obtained and from the other the layers  $h0l$  and  $h1l$ . The intensities were measured visually and 2399 reflexions were obtained from the  $a$ -mounting and 460 reflexions (91 of which had not been measured previously) from the  $b$ -mounting. Another 256 reflexions

which were too weak to be measured were included in the data with intensities  $\frac{1}{2}I_{\text{min}}$ . Of the total number (3115) of reflexions measured 2728 were independent and represented 95% of the reflexions accessible within the Cu sphere. The intensities were corrected for Lorentz and polarization factors but no absorption correction was applied.

### Structure determination

The structure was solved by the heavy-atom method; the ratio  $\frac{\sum f_H^2}{\sum f_L^2} = 0.88$  at  $\sin \theta = 0$ . The three-

dimensional data were sharpened to point atom with regard to bromine, and the Harker section at  $y = \frac{1}{2}$  was calculated. From the vector peak  $(2x, \frac{1}{2}, 2z)$  the bromine atom was found to be in the position  $x = 0.1863$  and  $z = 0.0482$ ; its  $y$  coordinate was arbitrarily chosen as  $\frac{1}{2}$ . A structure-factor calculation with the bromine atom in this position gave an  $R$  index of 47%. Since the space group is polar in the  $y$  direction the first electron-density distribution, based on observed structure factors and bromine phase angles, contained pseudo-mirror planes parallel to (010) at  $y = 0, \frac{1}{2}, 1$  etc. However, it was possible to locate the benzoate group and carbon atom C(2) [for numbering scheme see (V)]. In a subsequent structure-factor calculation based on these eleven atoms the  $R$  index was lowered to 41%. From the second electron-density distribution the remaining atoms were located and when all the atoms were included in the structure-factor calculations the  $R$  index was 27.7%. All the oxygen atoms had so far been treated as carbon atoms, but in the third electron-density distribution five of the peaks could be identified as oxygen atoms because of their greater heights. During the structure-factor calculations an overall isotropic temperature factor of  $U = 0.05$  Å<sup>2</sup> was applied, and the data were put on an approximate absolute scale by making  $k \sum |F_o| = \sum |F_c|$  for each layer.

### Structure refinement

Coordinates, temperature parameters and individual layer-scale factors were refined by least-squares methods using a block-diagonal approximation to the normal-equation matrix and minimizing the expression  $\sum_{hkl} w(|F_o| - |F_c|)^2$ . The weighting scheme used was one of the form recommended for photographic data (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961):

Table 1. *The course of the least-squares refinement*

Number of parameters refined	Cycle No.	Number of planes	Final ( $\sum w\Delta^2$ )	Final ( $R = \sum  \Delta  / \sum  F_o $ )	Final ( $R' = \sum w\Delta^2 / \sum wF_o^2$ )
142 ( $x, z, U_{\text{iso}}$ for Br; $x, y, z, U_{\text{iso}}$ for O, C; layer-scale factors)	1–10	2620	911	0.178	
314 [ $x, z, U_{ij}$ ( $i, j = 1, 2, 3$ ) for Br; $x, y, z, U_{ij}$ for O, C; layer-scale factors]	11	3115	1725	0.211	0.0760
314 (as above)	12–18	3115	485	0.123	0.0259

$w = 1/(p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)$ . The *p*-parameters were varied during the refinement in order to minimize the variation of  $w\Delta^2$  as a function of  $|F_o|$  and the final values were:  $p_1 = 1.20$ ,  $p_2 = 0.0159$ ,  $p_3 = 0.000632$ . A shift factor of 0.8 was used throughout the refinement except in the last three cycles of anisotropic refinement when a value of 0.5 was applied. The course of the refinement is outlined in Table 1. One oxygen atom [O(5)] was first considered as a carbon atom, but after the first isotropic least-squares cycle it was recognized as an oxygen atom because of a large drop (0.014 Å<sup>2</sup>) in its  $U_{iso}$  value.

During the structure determination and isotropic least-squares refinement the data collected from the *b* axis mounting were not included; they were added at the beginning of the anisotropic refinement. The common reflexions were not averaged but were treated as independent observations by the least-squares program. After the last cycle of refinement, the average parameter shift was 0.1 $\sigma$  and the largest shift was 0.67 $\sigma$ . The atomic scattering factors used throughout the analysis were taken from *International Tables for X-ray Crystallography* (1962).

The final coordinates and temperature parameters are given in Table 2 along with their average estimated standard deviations derived from the least-squares nor-

Table 2(a) (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(5)	0.7617	0.2756	0.3246
C(6)	0.7163	0.1752	0.3748
C(7)	0.8364	0.1741	0.4671
C(8)	0.7940	0.2693	0.5262
C(9)	0.8009	0.3733	0.4738
C(10)	0.6781	0.3689	0.3769
C(11)	0.7209	0.4629	0.5309
C(12)	0.7959	0.4485	0.6287
C(13)	0.8921	0.3683	0.6667
C(14)	0.9457	0.2721	0.6134
C(15)	0.9417	0.3950	0.7609
C(16)	0.8656	0.4871	0.7697
C(17)	1.1675	0.2698	0.5965
C(18)	0.8039	0.1923	0.1702
C(19)	0.4499	0.2387	0.2044
C(20)	0.4467	0.3642	0.3882
C(21)	0.5665	0.6414	0.1910
C(22)	0.6343	0.7281	0.1319
C(23)	0.7885	0.7178	0.0738
C(24)	0.8357	0.7980	0.0192
C(25)	0.7304	0.8894	0.0260
C(26)	0.5899	0.9044	0.0845
C(27)	0.5288	0.8208	0.1367
O(1)	0.9397	0.4853	0.3294
O(2)	0.6822	0.5586	0.1809
O(3)	0.9810	0.2827	0.3256
O(4)	0.9125	0.1823	0.6682
O(5)	0.7717	0.5252	0.6885
O(6)	0.4379	0.6475	0.2384
Br(1)	0.8105	1.0000	-0.0478

Table 2(a). Fractional coordinates

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(1)	0.7233	0.4713	0.3281
C(2)	0.6244	0.4659	0.2299
C(3)	0.7112	0.3760	0.1774
C(4)	0.6753	0.2716	0.2204

Mean standard deviations derived from the least-squares normal-equation matrix

C	0.0014 (0.009 Å)	0.0009 (0.011 Å)	0.0006 (0.008 Å)
O	0.0010 (0.006 Å)	0.0006 (0.008 Å)	0.0004 (0.006 Å)
Br	0.0002 (0.001 Å)	0	0.0001 (0.001 Å)

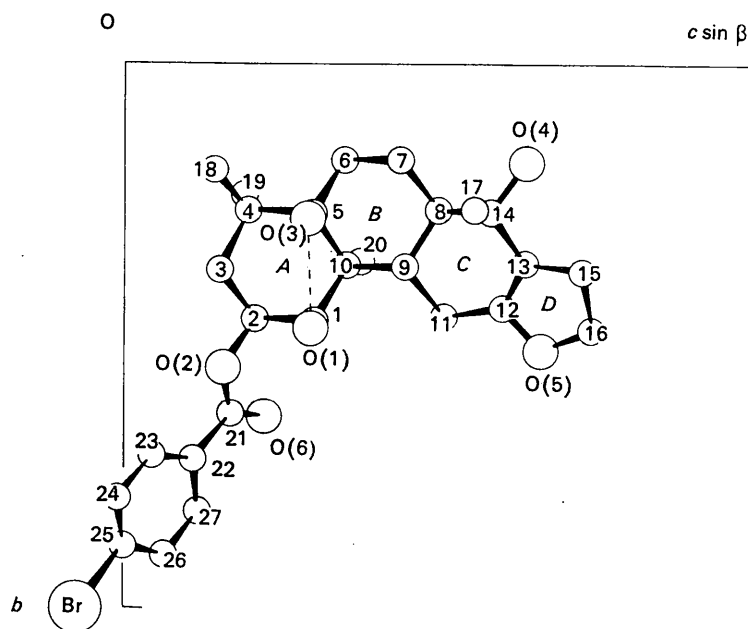


Fig. 1. View of the molecule along the *a* axis giving our numbering scheme. The intramolecular hydrogen bond is dashed.

Table 2(b). *Anisotropic temperature parameters* (Å<sup>2</sup>)

The parameters are defined by

$$\exp [-2\pi^2(U_{11}h^2a^*2 + U_{22}k^2b^*2 + U_{33}l^2c^*2 + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.040	0.036	0.067	0.017	0.019	-0.001
C(2)	0.050	0.040	0.077	0.014	0.039	0.001
C(3)	0.053	0.054	0.070	0.002	0.027	-0.004
C(4)	0.057	0.048	0.069	0.002	0.016	-0.020
C(5)	0.036	0.043	0.062	0.009	0.021	-0.004
C(6)	0.068	0.043	0.073	-0.005	-0.008	-0.017
C(7)	0.070	0.035	0.080	0.020	0.005	0.003
C(8)	0.049	0.042	0.067	0.013	0.010	0.001
C(9)	0.049	0.034	0.070	0.021	0.003	0.008
C(10)	0.036	0.036	0.059	0.016	0.011	-0.001
C(11)	0.092	0.039	0.070	0.005	-0.044	0.027
C(12)	0.067	0.044	0.070	0.010	0.006	0.013
C(13)	0.053	0.052	0.060	0.017	-0.000	-0.003
C(14)	0.045	0.041	0.065	0.030	0.027	0.006
C(15)	0.062	0.064	0.072	0.011	0.019	0.003
C(16)	0.078	0.053	0.081	0.001	0.023	-0.005
C(17)	0.034	0.075	0.066	0.019	0.008	0.010
C(18)	0.111	0.061	0.080	-0.016	0.028	0.023
C(19)	0.063	0.079	0.071	0.004	0.007	-0.076
C(20)	0.035	0.073	0.055	0.024	0.004	-0.008
C(21)	0.054	0.044	0.061	0.002	-0.007	0.007
C(22)	0.058	0.040	0.064	0.004	-0.001	0.008
C(23)	0.062	0.059	0.067	0.015	0.045	0.019
C(24)	0.088	0.049	0.057	0.005	0.005	0.003
C(25)	0.073	0.050	0.058	0.020	-0.018	-0.018
C(26)	0.062	0.057	0.092	0.004	0.011	0.023
C(27)	0.076	0.052	0.089	0.015	0.026	0.044
O(1)	0.042	0.040	0.088	0.026	0.008	-0.023
O(2)	0.053	0.045	0.070	0.026	0.012	0.006
O(3)	0.044	0.048	0.084	0.005	0.022	0.010
O(4)	0.058	0.052	0.073	0.042	0.027	0.032
O(5)	0.073	0.059	0.067	-0.007	0.004	0.000
O(6)	0.069	0.062	0.079	0.016	0.059	0.019
Br	0.100	0.063	0.088	0.036	0.012	-0.028

Mean standard deviations (Å<sup>2</sup>) derived from the least-squares normal-equation matrix.

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{23}$	$2U_{31}$	$2U_{12}$
C	0.005	0.005	0.004	0.009	0.007	0.010
O	0.003	0.003	0.003	0.007	0.005	0.007
Br	0.0008	0.0007	0.0006	0.0012	0.0011	0.0014

mal equations. However, use of the formula

$$\sigma(x) \sim \frac{R}{\bar{s}} \left( \frac{N}{4p} \right)^{1/2}$$

of Cruickshank (1960) to calculate mean coordinate standard deviations yielded values 50% greater than those obtained from the least-squares calculations. We feel that these larger values are more likely to be realistic especially as we used a block-diagonal approximation to the least-squares normal-equation matrix and neglected absorption and libration corrections. The mean e.s.d.'s in C-C, C-O and C-Br bond lengths are then 0.021, 0.017 and 0.015 Å respectively, and the mean e.s.d. in bond angle is 1.2°. Observed and calculated structure factors are given in Table 3. Some differences between  $|F_o|$ 's derived from the *a* axis and *b* axis mountings are most likely caused by differences in spot shapes for the two sets of data.

### Absolute configuration

The absolute configuration was determined by the anomalous dispersion method (Bijvoet, 1955) from an *hkl* precession photograph taken with Mo *K*α radiation and indexed in a right-handed cell (Peerdeman & Bijvoet, 1956). With Mo *K*α radiation the value of  $\Delta f''$  for bromine is 2.6 at  $\sin \theta = 0$ . The intensities of 17 Bijvoet pairs of reflexions, which appeared different, were measured visually and used in this determination. The ratios of the observed intensities and of the squares of calculated structure factors for these pairs can be seen in Table 4; their close correspondence indicates that the coordinates of Table 2 which were used in the structure-factor calculations *do* represent a molecule with the correct absolute configuration and not the mirror image. All the parameter tables and diagrams refer to a molecule with this correct absolute configuration.







Table 5(a). Bond lengths

C(1)—C(2)	1.547 Å	C(13)—C(15)	1.450 Å
C(2)—C(3)	1.539	C(12)—C(13)	1.321
C(3)—C(4)	1.525	C(15)—C(16)	1.308
C(4)—C(5)	1.603	C(12)—O(5)	1.351
C(4)—C(18)	1.558	C(16)—O(5)	1.398
C(4)—C(19)	1.540		
C(5)—C(6)	1.542	C(21)—O(2)	1.333
C(5)—C(10)	1.562	C(21)—O(6)	1.142
C(6)—C(7)	1.524		
C(7)—C(8)	1.553	C(21)—C(22)	1.515
C(8)—C(9)	1.560		
C(8)—C(14)	1.568	C(22)—C(23)	1.385
C(9)—C(10)	1.591	C(23)—C(24)	1.370
C(9)—C(11)	1.555	C(24)—C(25)	1.382
C(10)—C(20)	1.542	C(25)—C(26)	1.329
C(14)—C(17)	1.497	C(26)—C(27)	1.409
		C(27)—C(22)	1.395
C(11)—C(12)	1.505		
C(13)—C(14)	1.534	C(25)—Br	1.905
C(1)—O(1)	1.430		
C(2)—O(2)	1.472		
C(5)—O(3)	1.441		
C(14)—O(4)	1.448		

Table 5(b). Bond angles

C(2)—C(1)—C(10)	108.5°	C(11)—C(12)—C(13)	128.1°
C(2)—C(1)—O(1)	111.2	C(11)—C(12)—O(5)	119.5
C(10)—C(1)—O(1)	109.1	C(12)—C(13)—C(14)	123.1
C(1)—C(2)—C(3)	111.4	C(14)—C(13)—C(15)	130.3
C(1)—C(2)—O(2)	108.8		
C(3)—C(2)—O(2)	104.6	C(12)—O(5)—C(16)	103.7
C(2)—C(3)—C(4)	112.9	C(12)—C(13)—C(15)	106.5
C(3)—C(4)—C(5)	108.6	C(13)—C(15)—C(16)	104.9
C(3)—C(4)—C(18)	106.4	C(15)—C(16)—O(5)	112.6
C(3)—C(4)—C(19)	111.1	C(13)—C(12)—O(5)	112.3
C(5)—C(4)—C(18)	108.5		
C(5)—C(4)—C(19)	114.8	C(2)—O(2)—C(21)	115.8
C(18)—C(4)—C(19)	107.0		
C(4)—C(5)—C(6)	111.7	C(22)—C(21)—O(2)	109.9
C(4)—C(5)—C(10)	113.1	C(22)—C(21)—O(6)	124.7
C(4)—C(5)—O(3)	106.8	O(2)—C(21)—O(6)	125.4
C(6)—C(5)—C(10)	109.2		
C(6)—C(5)—O(3)	106.3	C(21)—C(22)—C(23)	123.3
C(10)—C(5)—O(3)	109.6	C(21)—C(22)—C(27)	116.3
C(5)—C(6)—C(7)	109.6	C(23)—C(22)—C(27)	120.3
C(6)—C(7)—C(8)	113.3	C(22)—C(23)—C(24)	120.2
C(7)—C(8)—C(9)	113.4	C(23)—C(24)—C(25)	118.3
C(7)—C(8)—C(14)	110.6	C(24)—C(25)—C(26)	123.4
C(9)—C(8)—C(14)	110.4	C(24)—C(25)—Br	116.4
C(8)—C(9)—C(10)	112.6	C(26)—C(25)—Br	120.1
C(8)—C(9)—C(11)	110.8	C(25)—C(26)—C(27)	119.1
C(10)—C(9)—C(11)	110.4	C(22)—C(27)—C(16)	118.3
C(1)—C(10)—C(5)	110.3		

The mean e.s.d.s for C—C, C—O and C—Br bond lengths are 0.021, 0.017 and 0.015 Å respectively.

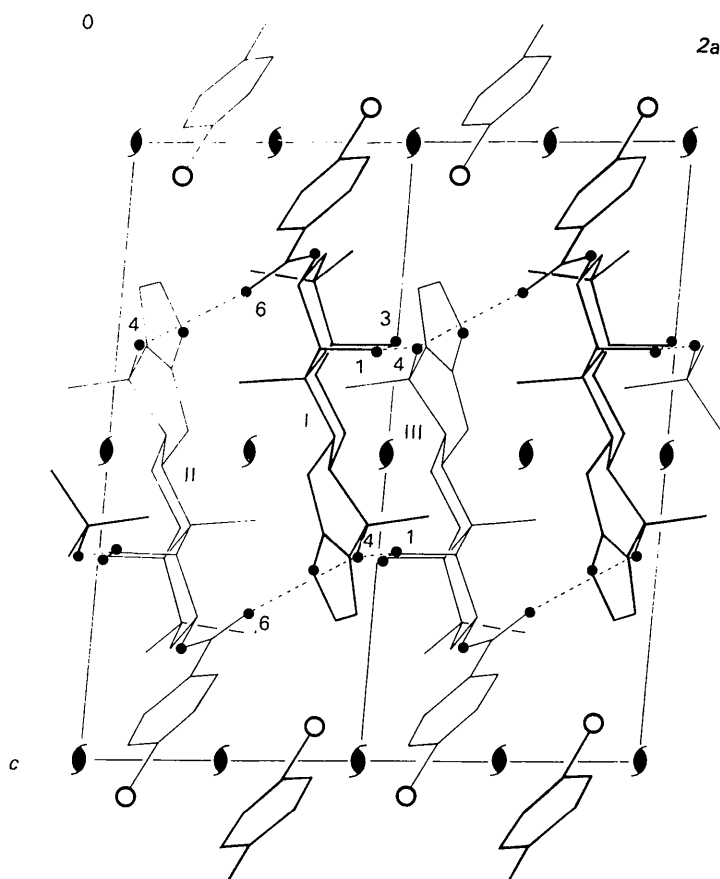


Fig. 2. Packing diagram viewed along the *b* axis. The hydrogen bonds are marked with dotted lines and the numbers refer to the oxygen atoms. The roman numerals refer to equivalent positions: I,  $x, y, z$ ; II,  $1-x, y \pm \frac{1}{2}, 1-z$ ; III,  $2-x, y \pm \frac{1}{2}, 1-z$ . (See also Table 7). Large open circles: bromine; small solid circles: oxygen.



Table 5(b) (cont.)

C(1)—C(10)—C(9)	106.7°	The mean e.s.d. in valency angle is 1.2°.
C(1)—C(10)—C(20)	108.1	
C(5)—C(10)—C(9)	107.6	
C(5)—C(10)—C(20)	114.2	
C(9)—C(10)—C(20)	109.7	
C(9)—C(11)—C(12)	109.3	
C(8)—C(14)—C(13)	106.7	
C(8)—C(14)—C(17)	115.2	
C(8)—C(14)—O(4)	109.2	
C(13)—C(14)—C(17)	111.6	
C(13)—C(14)—O(4)	108.5	
C(17)—C(14)—O(4)	105.5	

Table 5(c). Some intramolecular non-bonded distances

C(1)···C(5)	2.558	C(5)···C(8)	2.977
C(1)···O(3)	2.981	C(7)···O(3)	2.757
C(2)···O(6)	2.665	C(7)···O(4)	2.983
C(2)···C(5)	2.950	C(9)···O(1)	2.798
C(3)···O(1)	2.968	C(9)···O(3)	2.831
C(3)···O(3)	2.969	C(11)···C(20)	2.958
C(3)···C(10)	2.982	C(18)···O(3)	2.758
C(4)···C(10)	2.640	C(19)···C(20)	3.175
C(5)···O(1)	2.965	O(1)···O(2)	2.832

The only four atoms in ring *A* which are coplanar are C(2), C(3), C(5) and C(10) (all the least-squares planes are listed in Table 6). Atoms C(1) and C(4) are displaced above and below this plane by 0.725 and 0.668 Å respectively. In a regular cyclohexane chair these displacements would have been  $\pm 0.73$  Å. Since carbon atom C(4) is bent towards the ring-*A* plane by about 0.06 Å an increase in the adjacent angles from the tetrahedral value to about 111.5° is expected (Sim, 1965), assuming that all the bond lengths and other

angles are normal. The angles C(4)—C(3)—C(2) and C(4)—C(5)—C(10) are 112.9 and 113.1°, respectively. These slight distortions in ring *A* are mainly due to the interaction between the two diaxial methyl groups C(19) and C(20). In order to relieve the strain they are bent away from each other. This can be seen by comparing the C(4)···C(10) non-bonded distance (2.640 Å) with the much longer C(19)···C(20) distance (3.175 Å) [the van der Waals distance between two methyl groups is 4.0 Å (Pauling, 1960)]. The bending of the two diaxial methyl groups also causes significant increases from the normal value in the two angles C(19)—C(4)—C(5) (114.8°) and C(5)—C(10)—C(20) (114.2°). Similar distortions are normal in compounds with 1,3 diaxial methyl groups and the distance between them usually ranges from 3.0 to 3.3 Å [for example 2.95 Å in davalloiodoacetate (Oh & Maslen, 1966), 3.16 Å in a taxadiene-tetraol derivative (Bjåmer, Ferguson & Robertson, 1967), 3.12 and 3.31 Å in *p*-bromophenacyl labdanolate (Bjåmer, Ferguson & Melville, 1968), and 3.17 and 3.30 Å in methyl melaleucate iodoacetate (Hall & Maslen, 1965)]. The two 1,3-diaxial bonds of the hydroxyl groups O(1) and O(3) are approximately parallel to each other, the non-bonded distance C(1)···C(5) (2.558 Å) being only slightly shorter than the O(1)···O(3) distance (2.649 Å). The latter distance represents an intramolecular hydrogen bond which is discussed later.

A least-squares plane was calculated through the ring-*B* atoms C(10), C(5), C(7), and C(8). As can be seen from Table 6, these atoms are not quite coplanar. The 'best plane' through them makes a dihedral angle of 8.0° with the 'ring-*A* plane' instead of being parallel to it. The atoms C(9) and C(6) are displaced above and below this plane by 0.629 and 0.719 Å, respectively.

Table 6. Displacements from least-squares planes (Å)

Plane 1 ring <i>A</i>	Plane 2 ring <i>B</i>	Plane 3 ring <i>C</i>	Plane 4 ring <i>D</i>	Plane 5 <i>p</i> -bromobenzoate group
C(2) -0.009	C(10) -0.062	C(11) -0.000	C(12) 0.007	Br -0.017
C(3) 0.009	C(5) -0.065	C(12) 0.001	C(13) -0.008	C(21) 0.002
C(5) -0.009	C(7) -0.066	C(13) -0.001	C(15) 0.007	C(22) 0.019
C(10) 0.009	C(8) 0.063	C(14) 0.000	C(16) -0.004	C(23) 0.027
C(1)* 0.725	C(6)* -0.719	C(8)* -0.582	O(5) -0.002	C(24) -0.020
C(4)* -0.668	C(9)* 0.629	C(9)* 0.205	C(11)* 0.069	C(25) -0.029
			C(14)* 0.043	C(26) 0.041
				C(27) -0.007
				O(2) 0.054
				O(6) -0.025
				C(2) -0.046

Equations for the least-squares planes ( $X', Y, Z'$  are orthogonal coordinates in Å, i.e.  $X' = X \sin \beta$ ,  $Z' = Z + X \cos \beta$ ):

	r.m.s. distance
Plane 1: $0.923X' + 0.377Y + 0.079Z' = 6.307$	0.009 Å
Plane 2: $0.933X' + 0.355Y - 0.058Z' = 5.600$	0.064
Plane 3: $0.878X' + 0.409Y - 0.250Z' = 4.724$	0.001
Plane 4: $0.870X' + 0.395Y - 0.295Z' = 4.204$	0.006
Plane 5: $0.676X' + 0.295Y + 0.676Z' = 6.677$	0.030

\* Atoms not included in the calculation of the plane.

The distortion of ring *B* can probably be attributed to strain caused by the junction to the unsaturated ring *C*. The angle C(7)–C(8)–C(9) (113.4°) is significantly larger than tetrahedral.

Ring *C* is in a distorted half-chair conformation. Atoms C(11), C(12), C(13) and C(14) at the double bond are coplanar while C(9) and C(8) are displaced above below this plane by 0.205 and 0.582 Å, respectively. According to calculations by Corey & Sneen (1955) these displacements should be  $\pm 0.43$  Å and in pentachlorocyclohexene (Pasternak, 1951) the observed values were fairly similar, *viz.* 0.34 and 0.40 Å. On the basis of energy considerations Bucourt & Hainaut (1965) calculated that in a 4,5-disubstituted cyclohexene ring the angles at the trigonal carbon atoms should be 124.0° and at the other atoms in the ring 110.5°. The angle C(8)–C(14)–C(13) (106.7°) is significantly below 110.5° and the angle C(11)–C(12)–C(13) (128.1°) is considerably larger than 124.0° and these give a measure of the distortion in ring *C*. The hydroxyl group O(4) and the methyl group C(17) are respectively in the quasi-equatorial and quasi-axial positions. The methyl group is slightly bent towards the hydroxyl group giving rise to the significantly abnormal angles C(8)–C(14)–C(17) (115.2°) and C(17)–C(14)–O(4) (105.5°).

The furan ring *D* is flat (Table 6), but its plane is slightly tilted (2.7°) with respect to the ring-*C* plane. All the bond lengths and angles in the furan ring agree within experimental errors with the values found in furan itself (Bak, Christensen, Dixon, Hansen-Nygaard, Andersen & Schottländer, 1962) and with the values in 3,4-furandicarboxylic acid (Williams & Rundle, 1964). It is noteworthy that the three angles around carbon atom C(13) agree within 0.9° with the corresponding angles in 3,4-furandicarboxylic acid.

The *p*-bromobenzoate group, attached to ring *A* in the equatorial position, is approximately planar. Mathieson (1965) made a survey of several structures containing ester groups in the equatorial position of six-membered rings in the chair conformation. In all these structures the ester group was oriented so that it was coplanar with the axial hydrogen atom of the ring carbon atom [here C(2)]. The preference for this was ascribed to an interaction between this hydrogen atom and the double-bonded oxygen atom [here O(6)] of the ester group. In this structure the ester group is

rotated around the O(2)–C(2) bond by 43.3° from the position predicted by Mathieson. This orientation is most likely due to the intermolecular hydrogen bond between O(6) and O(4) which is energetically favoured.

#### Hydrogen bonds

The molecular arrangement parallel to (010) can be seen from Fig. 2 where the hydrogen bonds are marked with dotted lines. The dotted lines from the atoms O(1) and O(4) in equivalent position (I) connect, respectively, O(4) and O(1) in equivalent position (III) but belonging to two different molecules, the first one at  $y + \frac{1}{2}$ , the other at  $y - \frac{1}{2}$ . Similarly O(4) and O(6) in equivalent position (I) are, respectively, connected with O(6) and O(4) in equivalent position (II) belonging to the molecules at  $y - \frac{1}{2}$  and  $y + \frac{1}{2}$  respectively. All the hydroxyl groups are involved in hydrogen bonding; one in an intramolecular [O(3)–H...O(1)] and two in intermolecular [O(1)–H...O(4) and O(4)–H...O(6)] bonds. Each molecule is therefore connected with four neighbouring ones and the crystal structure can be described as consisting of helices formed by molecules linked by hydrogen bonds. Although the hydrogen positions were not determined, the donor-acceptor scheme can be unequivocally deduced from the fact that O(6) can only accept a proton. The oxygen atoms O(1) and O(4) act both as donors and as acceptors while O(3) acts only as a donor. The hydrogen bond lengths and angles with their *e.s.d.*'s are listed in Table 7. The intramolecular bond is the shortest one. The C–O...O angles lie within the usual range for hydrogen bonds indicated by Fuller (1959). All intermolecular distances < 4.0 Å were calculated; except for the above-mentioned hydrogen bonds none of them are shorter than van der Waals distances.

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Table 7. Hydrogen bond lengths (Å) and angles (°)

Bond	Distance	Angle	Type
O(3)–H...O(1)	2.649	C(5)–O(3)...O(1) 87.7	O–H...OH
O(4)–H...O(6) <sub>II</sub>	2.812	C(14)–O(4)...O(6) 124.8	O–H...O=C
O(1)–H...O(4) <sub>III</sub>	2.738	C(1)–O(1)...O(4) 118.0	O–H...O–H

The subscripts refer to the following equivalent positions:

I	$x, y, z;$
II	$1-x, y - \frac{1}{2}, 1-z;$
III	$2-x, y + \frac{1}{2}, 1-z$ (see also Fig. 2).

The mean *e.s.d.* in O–H...O distance is 0.015 Å and for bond angle 0.8°.

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## Crystal and Molecular Structure of 3,4'-Biisoxazole

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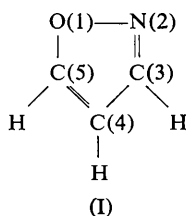
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The crystal structure of 3,4'-biisoxazole has been determined from three-dimensional X-ray data. The atomic coordinates and anisotropic temperature factors have been refined by the block-diagonal least-squares method to give a final *R* index of 0.10 for 816 observed reflexions. The space group is  $P2_1/c$ , with  $Z=4$  and unit-cell dimensions  $a=3.797$ ,  $b=11.175$ ,  $c=14.790$  Å and  $\beta=94.8^\circ$ . Bond distances and angles are within the expected values and suggest that there is no conjugation between the rings. The rings are not coplanar, the angle between their planes being  $2.8^\circ$ . Some values of the intermolecular distances are very close to the van der Waals limits.

### Introduction

When two isoxazole rings (I) are bonded together six iso-



mers are expected. Four out of the six have so far been synthesized: 3,3' (Quilico, Gaudiano & Ricca, 1957); 5,5' (Quilico, Gaudiano & Merlini, 1958); 3,5' (Ricca &

Gaudiano, 1959) and 3,4' (Maggioni, Gaudiano & Bravo, 1966). The infrared and ultraviolet spectra of these isomers suggested a different conjugation effect between the rings, according to the carbon atoms involved in the inter-ring bond. This effect has been shown to be negligible in 3,3', limited in 3,4', bigger in 3,5' and very strong in 5,5' (Speroni, 1962; Maggioni, Gaudiano & Bravo, 1966). On the other hand structural studies of the two symmetrical isomers, performed by X-ray analysis (Cannas & Marongiu, 1967, 1968), suggested that the conjugation effect might be greater in 3,3' than in 5,5' at least in the solid state. Structural investigations have now been extended to the asymmetrical members of the series and in this paper the results of a three-dimensional analysis of 3,4'-biisoxazole (II) are reported.