

## Structure of *cis*-3-Bromo-2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one (3-Bromoflavanone)

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**Abstract.** C<sub>15</sub>H<sub>11</sub>BrO<sub>2</sub>, monoclinic,  $P2_1/n$ ,  $a = 9.472$  (8),  $b = 15.035$  (10),  $c = 9.038$  (7) Å,  $\beta = 95.70$  (8)°,  $Z = 4$ ,  $D_c = 1.57$ ,  $D_o = 1.58$  (1) g cm<sup>-3</sup> (by flotation in a mixture of chloroform and tetrachloroethane),  $R = 0.073$  for 1637 reflections. The phenyl ring is rotated 42.2° with respect to the benzo ring, and the  $\gamma$ -pyrone ring is in the 1,2-diplanar conformation with the vicinal H atoms in the *cis* configuration.

**Introduction.** Light-yellow, elongated needle crystals of 3-bromoflavanone were grown by slow evaporation of an *n*-hexane solution. A single crystal of approximate dimensions 0.08 × 0.12 × 0.60 mm was mounted after being dipped in 2-butanone to remove the edges and points in order to reduce absorption effects. From indexed Weissenberg photographs the systematic absences  $0k0$  for  $k$  odd and  $h0l$  for  $h + l$  odd uniquely determined the space group to be  $P2_1/n$ .

Three-dimensional intensity data [Zr-filtered Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation] were collected on a Picker FACS-1 diffractometer equipped with a scintillation counter and pulse-height analyzer. In total 2131 reflections out to 50° in  $2\theta$  were measured in the  $\theta-2\theta$  scan mode. There were 1638 independent reflections with  $I > \sigma(I)$  which were included in subsequent calculations.

The heavy-atom method was employed to determine the structure followed by difference Fourier maps, and refined *via* full-matrix least-squares methods. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  where the weight,  $w$ , applied to each observation was taken to be  $1/\sigma^2(F)$ . The  $\sigma(F)$  were obtained from counting statistics (Stout & Jensen, 1968). Positions of all C, O, and Br atoms and their anisotropic Gaussian functions were refined. The H atoms (positions and isotropic Gaussian functions), located using difference Fourier maps, were not refined until the last three cycles of refinement. The final refinement results gave an  $R$  value,  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , of 0.073 and a weighted  $R$  value,  $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , of 0.085 for the 1637 observed reflections. The standard deviation in an observation of unit weight was 1.98.

There were no significantly large positive or negative electron-density peaks in a final difference Fourier synthesis; the largest positive region was 0.15 e Å<sup>-3</sup> and the largest negative region was 0.20 e Å<sup>-3</sup>. The atomic form factors for Br, O, and C were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Anomalous-scattering corrections taken from *International Tables for X-ray Crystallography* (1968) were introduced for Br for the final stage of refinement.

Table 1. Atomic fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters with e.s.d.'s in parentheses

$B$  values were obtained from the deposited anisotropic parameters by the relationship  $B = |B_{11}B_{22}B_{33}|^{1/3}$  where  $B_{11} = 4b_{11}/(a^*)^2$ ,  $B_{22} = 4b_{22}/(b^*)^2$ , and  $B_{33} = 4b_{33}/(c^*)^2$  (Stout & Jensen, 1968).

	$x$	$y$	$z$	$B_{eq}$ (Å <sup>2</sup> )
Br(1)	5322 (2)	2901 (2)	5681 (2)	5.59 (2)
O(1)	3315 (3)	4261 (3)	7256 (3)	3.06 (3)
O(2)	3489 (6)	1556 (3)	7874 (7)	4.33 (5)
C(2)	4439 (8)	3876 (5)	8196 (9)	2.70 (5)
C(3)	4749 (8)	2927 (5)	7704 (9)	2.83 (5)
C(4)	3410 (10)	2358 (5)	7648 (9)	3.45 (6)
C(5)	764 (10)	2399 (5)	7084 (10)	3.73 (6)
C(6)	-448 (9)	2843 (7)	6669 (10)	4.16 (6)
C(7)	-433 (9)	3749 (7)	6412 (11)	3.94 (6)
C(8)	844 (9)	4219 (5)	6612 (10)	3.58 (6)
C(9)	2086 (8)	3776 (5)	7047 (9)	2.66 (5)
C(10)	2088 (8)	2841 (5)	7293 (9)	3.08 (6)
C(11)	5730 (9)	4493 (5)	8231 (10)	2.80 (5)
C(12)	6786 (10)	4410 (5)	9375 (11)	4.13 (6)
C(13)	8022 (10)	4933 (7)	9474 (11)	4.78 (6)
C(14)	8133 (10)	5562 (6)	8361 (15)	4.30 (6)
C(15)	7103 (11)	5659 (5)	7248 (13)	4.07 (6)
C(16)	5881 (10)	5128 (5)	7163 (10)	3.99 (6)
H(2)	412 (2)	385 (3)	933 (3)	2.0 (6)
H(3)	556 (2)	264 (3)	848 (3)	3.5 (5)
H(5)	74 (3)	169 (2)	727 (3)	6.8 (7)
H(6)	-143 (3)	248 (3)	651 (3)	5.3 (7)
H(7)	-140 (3)	410 (2)	600 (3)	5.0 (7)
H(8)	87 (3)	493 (3)	639 (2)	6.2 (7)
H(12)	664 (3)	393 (2)	1025 (2)	4.5 (6)
H(13)	884 (2)	485 (2)	1041 (2)	2.4 (5)
H(14)	907 (2)	597 (3)	836 (3)	3.9 (6)
H(15)	721 (3)	616 (4)	643 (3)	8.5 (7)
H(16)	505 (2)	521 (2)	627 (2)	4.3 (5)

In addition to local programs for the IBM 370/165 computer, the programs used in this determination were *FORDAP* (A. Zalkin, 1974), *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *ORTEP* (Johnson, 1965), and *PLANES* (Smith, 1964).

The results are presented in Tables 1, 2, 3 and 4.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36395 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) involving H with their e.s.d.'s in parentheses

C(2)—H(2)	1.10 (3)	C(12)—H(12)	1.09 (4)
C(3)—H(3)	1.08 (3)	C(13)—H(13)	1.09 (4)
C(5)—H(5)	1.08 (3)	C(14)—H(14)	1.08 (4)
C(6)—H(6)	1.08 (3)	C(15)—H(15)	1.07 (4)
C(7)—H(7)	1.09 (3)	C(16)—H(16)	1.08 (4)
C(8)—H(8)	1.09 (3)		
H(2)—C(2)—O(1)	108 (2)	H(8)—C(8)—C(9)	120 (2)
H(2)—C(2)—C(11)	107 (2)	H(8)—C(8)—C(7)	121 (2)
H(2)—C(2)—C(3)	108 (2)	H(12)—C(12)—C(11)	118 (2)
H(3)—C(3)—C(4)	109 (2)	H(12)—C(12)—C(13)	119 (2)
H(3)—C(3)—C(2)	110 (2)	H(13)—C(13)—C(14)	120 (2)
H(5)—C(5)—C(6)	120 (2)	H(13)—C(13)—C(12)	120 (2)
Br(1)—C(3)—H(3)	111 (2)	H(14)—C(14)—C(15)	119 (2)
H(5)—C(5)—C(10)	118 (2)	H(14)—C(14)—C(13)	120 (2)
H(6)—C(6)—C(5)	119 (2)	H(15)—C(15)—C(14)	119 (2)
H(6)—C(6)—C(7)	120 (2)	H(15)—C(15)—C(16)	120 (2)
H(7)—C(7)—C(6)	121 (2)	H(16)—C(16)—C(11)	119 (2)
H(7)—C(7)—C(8)	119 (2)	H(16)—C(16)—C(15)	120 (2)

Table 3. Selected intermolecular distances (Å) (distances between atoms which are less than or close to the sum of the van der Waals radii for the individual atoms)

Br...C(5 <sup>ii</sup> )	3.36 (1)	H(12)...O(2 <sup>ii</sup> )	2.90 (3)
Br...H(5 <sup>ii</sup> )	3.20 (1)	H(12)...C(5 <sup>ii</sup> )	2.76 (3)
O(2)...H(7 <sup>ii</sup> )	2.99 (1)	H(12)...H(5 <sup>ii</sup> )	2.30 (3)
C(16)...H(5 <sup>iii</sup> )	2.86 (1)	H(15)...H(6 <sup>iii</sup> )	2.87 (3)
H(6)...Br	3.14 (3)	H(16)...H(5 <sup>iii</sup> )	2.70 (3)
H(8)...O(2 <sup>iii</sup> )	2.58 (3)		

Symmetry code: none  $x, y, z$ ; (i)  $-x, -y, -z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

Table 4. Torsion angles for the pyrone ring (°)

	Angles of cyclohexane for 1,2-diplanar conformation	
C(9)—O(1)—C(2)—C(3)	52.4 (7)	60°
O(1)—C(2)—C(3)—C(4)	-56.0 (7)	-60
C(2)—C(3)—C(4)—C(10)	30.3 (8)	30
C(3)—C(4)—C(10)—C(9)	-0.9 (8)	0
C(4)—C(10)—C(9)—O(1)	-5.4 (7)	0
C(10)—C(9)—O(1)—C(2)	-21.6 (7)	-30

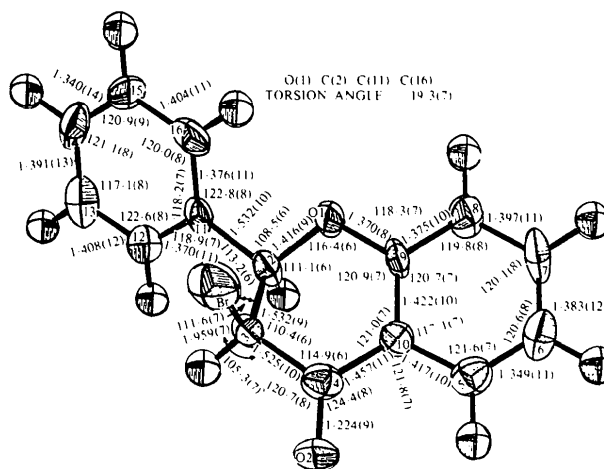


Fig. 1. ORTEP drawing of the molecule with the thermal ellipsoids at 50% probability, showing bond distances (Å) and angles (°). C atoms are numbered, O atoms are labeled O(1) and O(2). The H atoms take the number of the C atom to which they are bonded. See Table 2 for H-atom distances and angles.

**Discussion.** Bond distances and angles are shown in Fig. 1. The average C—C bond lengths in the benzo and phenyl rings are 1.391 (11) and 1.382 (12) Å respectively, with no bond more than two standard deviations from the mean. The benzo and phenyl rings are essentially planar while the  $\gamma$ -pyrone ring is in the 1,2-diplanar conformation. The phenyl ring is rotated 42.2° with respect to the benzo ring. C(3) is axially substituted with Br so that the H atoms at C(2) and C(3) are axial and equatorial respectively. These two vicinal H atoms have a torsion angle of 57.7°, giving them a *cis* configuration. The conformation of the pyrone ring follows that given by Toromanoff (1967) and by Valente, Santarsiero & Schomaker (1979). The absence of splitting of the proton peaks in the fine spectra by the two vicinal H atoms indicates that the C—H bonds are orthogonal in CCl<sub>4</sub> while they have a torsion angle of 57.5° in the crystal. The conformation of this crystal structure is similar to that reported for 4'-bromoflavanone (Cantrell, Stalzer & Becker, 1974).

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## Structure of 3-Bromo-2-phenyl-4H-1-benzopyran-4-one (3-Bromoflavone)\*

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(Received 16 July 1979; accepted 23 September 1981)

**Abstract.**  $C_{15}H_9BrO_2$ , monoclinic,  $P2_1/c$ ,  $a = 4.074$  (5),  $b = 22.735$  (31),  $c = 13.374$  (18) Å,  $\beta = 96.08$  (7)°,  $Z = 4$ ,  $D_c = 1.62$ ,  $D_o = 1.61$  (1) g cm<sup>-3</sup> (by flotation in a mixture of pentachloroethane and tetrachloroethane);  $V = 1231.8$  Å<sup>3</sup>,  $\mu(Mo K\alpha) = 3.52$  mm<sup>-1</sup>,  $R = 0.056$  for 1500 reflections. The phenyl ring at C(2) is rotated 45.9° with respect to the remainder of the molecule because of the steric interaction between the Br atom at C(3) and the adjacent H atom on the phenyl ring even though the molecule has a conjugated bond system and could have been coplanar.

**Introduction.** Transparent, elongated needle crystals of 3-bromoflavone were grown by slow evaporation of a diethyl ether solution. A single crystal of approximate dimensions 0.10 × 0.10 × 0.50 mm was used for dipping in 2-butanone to remove the edges and points to reduce absorption effects. From indexed Weissenberg photographs the systematic absences  $0k0$  for  $k$  odd and  $h0l$  for  $l$  odd uniquely determined the space group to be  $P2_1/c$ .

Three-dimensional intensity data were collected on a Picker FACS-1 diffractometer equipped with scintillation counter and pulse-height analyzer; Zr-filtered Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation was used. In total 2118 reflections out to 50° in  $2\theta$  were measured using the  $\theta$ - $2\theta$  scan mode. There were 1500 independent reflections with  $I > \sigma(I)$  which were used in subsequent calculations.

The structure was determined using the heavy-atom method and difference Fourier maps, and refined using full-matrix least-squares methods. The quantity

minimized was  $\sum w(|F_o| - |F_c|)^2$  where the weight,  $w$ , applied to each observation was taken to be  $1/\sigma^2(F)$ . The  $\sigma(F)$  were obtained from counting statistics (Stout & Jensen, 1968). C, O and Br atoms were allowed to

Table 1. *Atomic fractional coordinates and isotropic temperature factors with e.s.d.'s in parentheses*

The isotropic temperature factors for non-H atoms were obtained from the deposited anisotropic parameters by the relationship  $B = |B_{11}B_{22}B_{33}|^{1/3}$  where  $B_{11} = 4b_{11}/(a^*)^2$ ,  $B_{22} = 4b_{22}/(b^*)^2$ , and  $B_{33} = 4b_{33}/(c^*)^2$  (Stout & Jensen, 1968).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Br(1)	0.908 (2)	0.4196 (1)	0.5247 (1)	4.83 (2)
O(1)	0.414 (1)	0.3213 (2)	0.2960 (4)	2.69 (3)
O(2)	0.660 (2)	0.3039 (3)	0.5994 (4)	4.79 (5)
C(2)	0.573 (2)	0.3658 (4)	0.3505 (6)	3.68 (5)
C(3)	0.664 (2)	0.3598 (4)	0.4505 (6)	3.78 (5)
C(4)	0.583 (2)	0.3082 (4)	0.5084 (6)	3.82 (5)
C(5)	0.291 (2)	0.2114 (4)	0.4919 (7)	4.07 (6)
C(6)	0.127 (3)	0.1691 (5)	0.4331 (9)	4.89 (6)
C(7)	0.058 (3)	0.1787 (4)	0.3303 (8)	4.81 (6)
C(8)	0.157 (2)	0.2283 (4)	0.2849 (7)	3.59 (5)
C(9)	0.322 (2)	0.2708 (4)	0.3452 (6)	3.58 (5)
C(10)	0.398 (2)	0.2629 (4)	0.4487 (6)	3.21 (5)
C(11)	0.617 (2)	0.4163 (4)	0.2821 (6)	3.34 (5)
C(12)	0.731 (2)	0.4070 (4)	0.1877 (6)	3.46 (5)
C(13)	0.761 (3)	0.4535 (5)	0.1231 (7)	4.49 (6)
C(14)	0.679 (3)	0.5095 (5)	0.1525 (9)	5.23 (6)
C(15)	0.571 (2)	0.5197 (5)	0.2450 (8)	4.35 (6)
C(16)	0.542 (2)	0.4731 (4)	0.3109 (7)	3.77 (6)
H(5)	0.341 (3)	0.204 (3)	0.572 (4)	5.6 (4)
H(6)	0.048 (2)	0.129 (2)	0.466 (2)	3.7 (2)
H(7)	-0.081 (2)	0.146 (3)	0.284 (3)	3.9 (4)
H(8)	0.108 (2)	0.234 (2)	0.204 (3)	4.6 (3)
H(12)	0.794 (4)	0.363 (3)	0.165 (3)	4.2 (3)
H(13)	0.849 (4)	0.446 (3)	0.050 (4)	7.4 (5)
H(14)	0.702 (3)	0.546 (4)	0.101 (3)	3.8 (4)
H(15)	0.507 (3)	0.564 (4)	0.266 (3)	5.8 (4)
H(16)	0.460 (4)	0.481 (3)	0.384 (3)	4.8 (4)

\* Based in part on the MS thesis of R. A. Stalzer, Miami University, 1974.

† Deceased.