JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794 (revised 1970). Oak Ridge National Laboratory, Tennessee.

SMITH, D. C. (1964). *PLANES*. PhD Thesis, Univ. of Wisconsin, Madison, Wisconsin.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Crystal Structure Determination*, pp. 454–458. London: Collier–Macmillan.

TOROMANOFF, E. (1967). *Topics in Stereochemistry*, Vol. 2, pp. 161–163. New York: John Wiley.

VALENTE, E. J., SANTARSIERO, B. D. & SCHOMAKER, V. (1979). *J. Org. Chem.* **44**, 798–802.

ZALKIN, A. (1974). Unpublished.

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

BY JOSEPH S. CANTRELL AND ROBERT A. STALZER†

Department of Chemistry, Miami University, Oxford, Ohio 45056, USA

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^{-3} (by flotation in a mixture of pentachloroethane and tetrachloroethane); $V = 1231.8$ Å^3, μ(Mo $K\alpha$) = 3.52 mm^{-1}, $R = 0.056$ 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 $0.10 \times 0.10 \times 0.50$ 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 0*k*0 for *k* odd and *h*0*l* 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 2θ were measured using the θ–2θ 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).

	x	y	z	B (Å^2)
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)

---

refine anisotropically. The H atoms were given isotropic temperature factors and fixed initially. During the last three cycles of refinement the isotropic temperature factors of the H atoms were allowed to vary also. The final refinement results gave a conventional R value, $\sum ||F_o| - |F_c||/\sum |F_o|$, of 0·056 and a weighted R value, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0·052. The standard deviation in an observation of unit weight was 1·59.

There were no significantly large positive or negative electron-density peaks in a final difference Fourier synthesis; the largest positive region was 0·23 e Å^{-3} and the largest negative region was 0·27 e Å^{-3}, both of which occurred near C atoms in phenyl rings.

The atomic scattering factors of C, O and Br 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. 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).

Fractional atomic coordinates are given in Table 1.*

Discussion. Bond distances and angles and atom numbering are given in Fig. 1. The average C—C bond lengths in the benzo and phenyl ring are 1·384 (9) and 1·388 (9) Å respectively, with no bond more than one standard deviation from the mean. All three rings are essentially planar with the greatest deviation from the least-squares plane within each ring being 0·011, 0·024 and 0·008 Å for benzo, pyrone and phenyl rings respectively. The angle between the benzo and pyrone rings is 1·5° making them essentially coplanar. The angle between the phenyl ring and the plane of benzo and pyrone rings is 45·9°. This angle was larger than expected, considering the resonance stabilization that a planar structure would presumably have; however, the Br(1)—H(16) non-bonded intramolecular contact distance of 2·84 Å is considerably shorter than the van der Waals distance of 3·05 Å and results in a non-planar structure. The C(2)—O(1) and C(9)—O(1) bonds (1·370 and 1·395 Å respectively) are very similar to the values reported for similar flavonoid structures by Rossi, Cantrell, Farber, Dyott, Carrell & Glusker (1980). The C(2)—C(11) single bond (1·492 Å) has a value quite close to the expected 1·504 Å value (Pauling, 1960) for an sp^2—sp^2 single bond.

* Lists of structure factors, anisotropic thermal parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36420 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
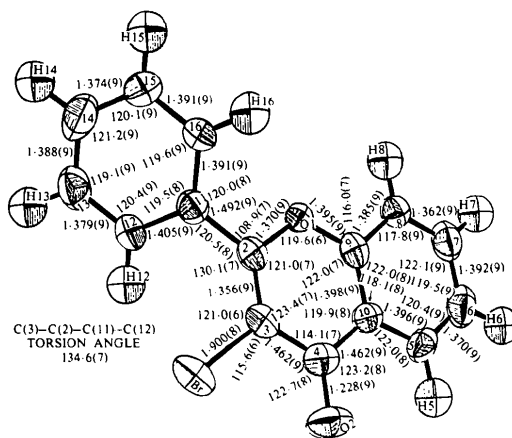

Fig. 1. *ORTEP* drawing of the molecule with thermal ellipsoids at 50% probability showing bond distances (Å) and angles (°). C atoms are numbered, O atoms are labeled O(1) and O(2) and H atoms are numbered corresponding to the C atom to which they are attached. H-atom distances and angles have been deposited.

In 4'-bromoflavanone (Cantrell, Stalzer & Becker, 1974) and licoricone monobromoacetate (Kaneda, Iitaka & Shibata, 1973) the corresponding C(2)—C(11) lengths are 1·516 and 1·51 Å respectively, compared to 1·532 Å for 3-bromoflavone.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

CANTRELL, J. S., STALZER, R. A. & BECKER, T. L. (1974). *Acta Cryst.* B30, 154–161.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794 (revised 1970). Oak Ridge National Laboratory, Tennessee.

KANEDA, M., IITAKA, Y. & SHIBATA, S. (1973). *Acta Cryst.* B29, 2827–2832.

PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 237. Ithaca: Cornell Univ. Press.

ROSSI, M., CANTRELL, J. S., FARBER, A. J., DYOTT, T., CARRELL, H. L. & GLUSKER, J. P. (1980). *Cancer Res.* 40, 2774–2784.

SMITH, D. C. (1964). *PLANES*. PhD Thesis. Univ. of Wisconsin, Madison, Wisconsin.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Crystal Structure Determination*, pp. 454–458. London: Collier–Macmillan.

ZALKIN, A. (1974). Unpublished.