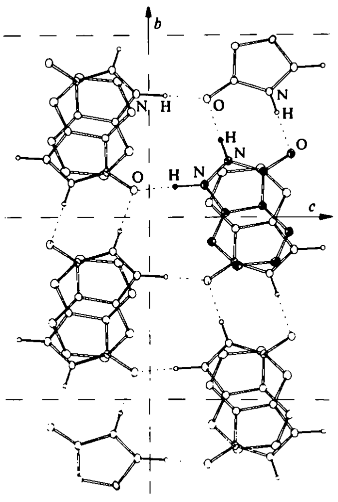

Fig. 2. *ORTEP* projection (Johnson, 1965) of the crystal structure along the *a* axis showing the hydrogen-bonding scheme. Non-bonding hydrogen atoms are omitted for clarity.

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Structure of 6-Bromo-1,2,3,4,4a,9a-hexahydro-4,9-dioxafluoren-2-one

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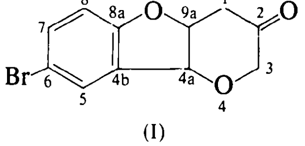
Abstract. $C_{11}H_9BrO_3$, $M_r = 269{\cdot}10$, monoclinic, $P2_1/a$, $a = 9{\cdot}145\ (1)$, $b = 10{\cdot}608\ (2)$, $c = 11{\cdot}104\ (2)$ Å, $\beta = 107{\cdot}08\ (1)^\circ$, $Z = 4$, $D_x = 1{\cdot}74$ Mg m^{-3}, μ(Cu $K\alpha$) $= 5{\cdot}89$ mm^{-1}, $V = 1029{\cdot}2$ Å^3. The structure was solved by direct methods and refined by the least-squares procedure to a final R value of 0·076 (unit weights) using 1745 independent reflections. The chemical structure was fully confirmed. The pyran ring is in a boat ($B_{O,3}$) conformation.

Introduction. The title compound was obtained (Grynkiewicz, Krajewski, Urbańczyk-Lipkowska, Gluziński & Zamojski, 1979) as a side-product by Lewis-acid-catalyzed substitution of 6-benzyloxy-2*H*-pyran-3(6*H*)-one by *p*-bromophenol. Its chemical structure was not clear initially and therefore X-ray structural investigations were performed in order to verify the conclusions drawn from the spectrochemical data.



(I)

A well shaped colorless single crystal of dimensions 0·4 × 0·25 × 0·25 mm was selected for X-ray measurements on a Syntex $P2_1$ single-crystal diffractometer (Institute of Organic Synthesis, Riga). The reflections were collected using the $\omega/2\theta$ scan technique up to $2\theta = 150°$. 1745 unique reflections with intensities $I > 2\sigma_I$ were chosen for the refinement procedure. The space group $P2_1/a$ was determined from the systematic absences of reflections ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The direct multisolution procedure (*SHELX* program; Sheldrick, 1976) revealed the positions of all the aromatic C atoms, the Br atom and the O atom bonded in the *para* position of the aromatic ring. A three-dimensional Fourier synthesis with these atoms gave the crude coordinates of all the non-hydrogen atoms in the molecule; the chemical structure of the compound is thus solved and shown to comprise three linearly condensed rings with the five-membered furan ring at the center.

A three-cycles refinement of the atomic coordinates by the full-matrix least-squares method with individual isotropic thermal parameters and unit weights (program *CRYLSQ* in the XRAY 70 system; Stewart, Kundell & Baldwin, 1970) gave $R = 0{\cdot}203$. Three subsequent cycles of refinement with anisotropic thermal parameters (unit weights) decreased the R factor to 0·102. The last refinement step with geometrically calculated H-atom positions resulted in $R = 0{\cdot}076$. The average shift/error value at the end of the refinement procedure was 0·012. The refined non-hydrogen atomic coordinates are presented in Table 1.*

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (*e.s.d.'s in parentheses*)

	x	y	z	$B_{\text{eq.}}$ (Å^2)*
Br	7045 (1)	609 (1)	7056 (1)	4·0
C(1)	7298 (10)	−282 (8)	2269 (7)	2·0
C(2)	8570 (11)	240 (9)	1730 (7)	2·4
C(3)	7953 (11)	756 (9)	436 (8)	2·8
C(4)	6702 (12)	1713 (10)	386 (8)	2·9
O(2)	6532 (11)	2667 (7)	−225 (8)	4·7
C(5)	5668 (12)	1382 (10)	1158 (9)	3·0
O(1)	5803 (7)	69 (6)	1510 (5)	2·5
C(6)	7748 (10)	305 (8)	3576 (7)	1·9
C(7)	7182 (10)	107 (9)	4585 (7)	2·3
C(8)	7796 (11)	826 (10)	5645 (8)	2·7
C(9)	8958 (11)	1708 (9)	5735 (8)	2·6
C(10)	9503 (11)	1905 (9)	4705 (8)	2·6
C(11)	8901 (10)	1196 (8)	3656 (8)	2·0
O(3)	9330 (7)	1287 (6)	2577 (5)	2·8

* Calculated from the refined anisotropic thermal parameters (deposited).

Discussion. Tables 2 and 3 give the calculated bond lengths and bond angles. Fig. 1 shows an *ORTEP* diagram (Johnson, 1965) of the molecule giving the crystallographic numbering scheme.

The $\mathrm{C_{ar}}$—O(3) bond length [1·37 (1) Å] in the dihydrofuran ring is significantly shortened as compared with the value for C(sp^3)—O(3) [1·49 (1) Å]. The bond angle at O(3) [107·4 (7)°] as well as the relatively large differences in the angle values inside the dihydrofuran ring seem to indicate the existence of some bond strain in the ring. The external bond angles at the aromatic carbon atoms C(6) and C(11) are strongly deformed: C(10)—C(11)—O(3) = 124·2 (9) and C(7)—C(6)—C(1) = 130·6 (8)° (Table 3). These angles are in agreement with the literature data for other structures containing the 2,3-dihydrobenzofuran

Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

Br—C(8)	1·90 (1)	C(6)—C(7)	1·38 (1)
C(1)—C(2)	1·56 (1)	C(6)—C(11)	1·40 (1)
C(1)—C(6)	1·52 (1)	C(7)—C(8)	1·38 (1)
C(2)—C(3)	1·49 (1)	C(8)—C(9)	1·40 (1)
C(3)—C(4)	1·51 (2)	C(9)—C(10)	1·39 (2)
C(4)—O(2)	1·20 (1)	C(10)—C(11)	1·36 (1)
C(4)—C(5)	1·49 (2)	C(11)—O(3)	1·37 (1)
C(5)—O(1)	1·44 (1)	O(3)—C(2)	1·49 (1)
O(1)—C(1)	1·43 (1)		

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(5)—O(1)—C(1)	113·7 (7)	C(1)—C(6)—C(11)	109·0 (8)
O(1)—C(1)—C(6)	113·6 (7)	C(11)—C(6)—C(7)	120·4 (7)
O(1)—C(1)—C(2)	112·0 (7)	C(6)—C(7)—C(8)	117·0 (8)
C(2)—C(1)—C(6)	101·4 (7)	C(7)—C(8)—Br	118·9 (8)
C(1)—C(2)—O(3)	106·6 (7)	Br—C(8)—C(9)	118·3 (7)
C(1)—C(2)—C(3)	112·8 (7)	C(7)—C(8)—C(9)	122·9 (9)
O(3)—C(2)—C(3)	108·1 (7)	C(8)—C(9)—C(10)	119·4 (8)
C(2)—C(3)—C(4)	110·5 (8)	C(9)—C(10)—C(11)	117·9 (9)
C(3)—C(4)—O(2)	124 (1)	C(10)—C(11)—O(3)	124·2 (9)
O(2)—C(4)—C(5)	122 (1)	C(10)—C(11)—C(6)	122·4 (9)
C(3)—C(4)—C(5)	114·8 (8)	O(3)—C(11)—C(6)	113·4 (7)
C(4)—C(5)—O(1)	111·3 (9)	C(11)—O(3)—C(2)	107·4 (7)
C(1)—C(6)—C(7)	130·6 (8)		

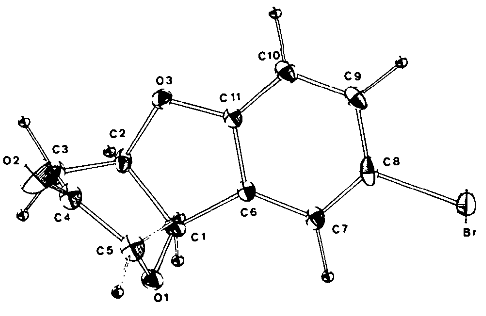


Fig. 1. *ORTEP* diagram of the molecule. The thermal-motion ellipsoids are set at the 40% probability level.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34589 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Least-squares planes*

Plane	Atoms defining the plane	σ_s (Å)
1	C(1), C(6), C(7), C(8), C(9), C(10), C(11), O(3)	0·01064
2	C(1), C(2), O(3)	–
3	C(1), C(5), O(1)	–
4	C(1), C(2), C(4), C(5)	0·09742
5	C(2), C(3), C(4)	–

Distances of atoms from the planes (Å) (e.s.d.'s in parentheses)

Plane 1		Plane 2		Plane 4	
Br	0·036 (1)	C(3)	1·203 (9)	C(3)	−0·562 (9)
C(2)	−0·220 (8)	C(4)	2·467 (9)	O(1)	−0·583 (6)
C(3)	0·728 (9)	C(5)	2·386 (9)	O(2)	0·138 (8)
C(4)	2·160 (9)	C(6)	−0·371 (8)	O(3)	1·544 (6)
C(5)	2·368 (9)	C(7)	−0·681 (8)	C(6)	1·335 (8)
O(1)	1·248 (5)	C(8)	−0·931 (9)	C(7)	1·837 (8)
O(2)	3·073 (8)	Br	−1·341 (1)	Br	3·948 (1)

system (Foresti Serantoni, Merlini, Mongiorgi & Riva di Sanseverino, 1974; Fontaine, Dideberg & Dupont, 1975; Rodgers, Goaman & Blow, 1976).

The C(sp^3)—O(1) bond lengths in the pyran ring are approximately symmetric: 1·43 and 1·44 (1) Å. The bond angle at O(1) is 113·7 (7)°.

All the atoms of the benzofuran system except C(2) approximately form a plane (Table 4, plane 1). C(2) deviates from this plane by *ca* −0·2 Å. Plane 1 forms a dihedral angle of 166° with the plane of C(1), C(2) and O(3) (Table 4, plane 2), thus indicating the envelope shape of the dihydrofuran ring.

The tetrahydropyran ring reveals the boat conformation of $B_{O,3}$ type [for the nomenclature see Schwartz (1973)], deformed by the presence of C(4) with sp^2 hybridization. Three least-squares planes may be distinguished in the ring (Table 4, planes 3, 4 and 5). They form the following dihedral angles: planes 3–4 132° and planes 4–5 139°. The central plane 4 is somewhat distorted (the mean deviation of atoms is 0·04 Å), and forms a dihedral angle of 93° with plane 2, causing the nearly rectangular shape of the molecule.

The authors are much indebted to Professor Dr A. Zamojski and Dr G. Grynkiewicz for valuable discussions.

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Structure of Spiro[3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1′-cyclopropane]

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Abstract. $C_{25}H_{20}O_2$, $M_r = 352{\cdot}4$, orthorhombic, *Pbca*, $a = 10{\cdot}690$ (1), $b = 10{\cdot}792$ (1), $c = 31{\cdot}131$ (4) Å, $U = 3591$ Å^3, $D_m = 1{\cdot}303$ (2), $D_x = 1{\cdot}303$ Mg m^{-3}, $Z = 8$, μ(Cu $K\alpha$) = 0·558 mm^{-1}. The structure was solved by direct methods and refined to $R = 0{\cdot}068$ for 2612 counter-collected reflections. In the crystalline state the molecule adopts an asymmetrical conformation. The two naphthyl planes are twisted through an angle of 71·5°; this value differs significantly from that of the torsion angle at the single bond of the binaphthyl system inside the nine-membered ring (64·2°), showing a strain in the binaphthyl system.

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