

Fig. 2. Modèle de superposition moléculaire: oestradiol-triphényl-éthylène.

Tableau 2. Angles de quelques plans moyens caractéristiques

Cycle		Entre	Angle (°)	Entre	Angle (°)
A	C(28) à C(78)	A et B	54	A et D	54
B	C(27) à C(77)	A et C	81	B et D	54
C	C(1) à C(6)	B et C	70	C et D	46
Plan					
D	C(4)–C(7)–C(8)–C(28)			C et E	4
E	C(1)–O(11)–C(21)			B et F	2
F	C(57)–O(87)–C(97)				

reportés sur le Tableau 2. Ces angles sont proches de ceux trouvés pour les autres dérivés du triphényl-éthylène: broparestrol (Fornies-Marquina, Courseille, Busetta & Hospital, 1972) et tamoxifène *cis* (Kilbourn & Owston, 1970). La position relative des cycles

*Acta Cryst.* (1979). **B35**, 2273–2276

### 4-[(4-Bromophenyl)methyl]-1,4-epoxy-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one

BY J. D. OLIVER,\* D. F. MULLICA, W. O. MILLIGAN, J. KARBAN, J. L. McATEE JR AND J. S. BELEW

*Department of Chemistry, Baylor University, Waco, Texas 76703, USA*

(Received 27 February 1979; accepted 30 May 1979)

**Abstract.**  $C_{22}H_{15}BrO_4$ ,  $M_r = 423.3$ , monoclinic,  $P2_1/a$ ,  $a = 12.224$  (4),  $b = 8.960$  (3),  $c = 17.074$  (4) Å,  $\beta = 96.83$  (2)°,  $V = 1856.8$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 2.21$  mm<sup>-1</sup>,  $D_x = 1.51$ ,  $D_m = 1.49$  (1) Mg m<sup>-3</sup>. Full-matrix least-squares refinement of 1048 unique reflections yielded  $R = 0.049$ . The five- and the six-atom rings of the bicyclic system exist in the half-chair and envelope conformations, respectively. The seven-atom ring of the bicyclic system consists of two planar segments which intersect to form an angle of 106°.

\* On sabbatical leave from the Department of Chemistry, West Texas State University, Canyon, Texas 79015, USA.

0567-7408/79/092273-04\$01.00

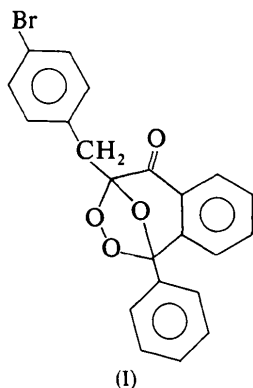
aromatiques peut être considérée en première approximation comme une constante géométrique des triphényl-éthylènes (Fig. 2). Le modèle proposé pour le squelette de la molécule oestrogène (Hospital, Busetta, Courseille & Précigoux, 1975) est en accord avec cette géométrie. Il doit donc y avoir une possibilité d'utiliser la molécule étudiée comme substrat d'une colonne d'affinité. Pour cela elle doit être attachée sur une résine par un 'bras' fixé sur l'atome d'azote N(10). Sur le modèle oestrogène cette position est voisine de la position C(7) de l'oestradiol qui est accessible sans entraîner une modification notable de l'affinité pour le récepteur (Bucourt *et al.*, 1978).

### Références

- BUCOURT, R., TORELLI, V., VIGNAU, M., RICHARD-FOY, H., GEYNET, C., SECCO-MILLET, C. & BAULIEU, E. E. (1978). *J. Biol. Chem.* **253**, 8221–8228.
- BUSETTA, B. (1978). *Acta Cryst.* **A34**, S44.
- FOURNIES-MARQUINA, J. M., COURSEILLE, C., BUSETTA, B. & HOSPITAL, M. (1972). *Cryst. Struct. Commun.* **1**, 261.
- GIACOVAZZO, C. (1977). *Acta Cryst.* **A33**, 933–944.
- HOSPITAL, M., BUSETTA, B., COURSEILLE, C. & PRÉCIGOUX, G. (1975). *J. Steroid Biochem.* **6**, 221–225.
- International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press.
- KILBOURN, B. T. & OWSTON, P. G. (1970). *J. Chem. Soc. B*, pp. 1–5.
- MIQUEL, J. F., SEKERA, A. & CHAUDRON, T. (1978). *C. R. Acad. Sci. Sér. C*, **286**, 151–154.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

**Introduction.** The synthesis and X-ray structure of an unusually stable secondary ozonide has recently appeared (Karbon, McAtee, Belew, Mullica, Milligan & Korp, 1978). In connection with our interest in the geometrical details of stable ozonides, the crystal structure determination of the ozonide (I) made from 2-[(4-bromophenyl)methyl]-3-phenylinden-1-one is reported.

Crystals of the title compound, hereinafter referred to as OZOBR, were obtained by slow evaporation of an ethanol solution. A tablet-like crystal (0.35 × 0.33 × 0.091 mm) was mounted on a glass fiber and transferred to an Enraf–Nonius CAD-4 autodiffractometer. © 1979 International Union of Crystallography



tometer equipped with a Si(Li) solid-state detector. All X-ray measurements were made at 289 K using Mo  $K\alpha$  radiation ( $\lambda_{\text{mean}} = 0.71069 \text{ \AA}$ ). The Laue symmetry was  $2/m$  with systematic absences ( $0k0$  for  $k$  odd and  $h0l$  for  $h$  odd) consistent with space group  $P2_1/a$ . Lattice parameters were obtained by a least-squares refinement of 25 carefully centered reflections. Intensities were collected by the  $\theta$ - $2\theta$  scan method with a variable scan rate of  $1.12$  to  $6.7^\circ \text{ min}^{-1}$  determined by a fast ( $6.7^\circ \text{ min}^{-1}$ ) prescan. The intensities of two check reflections were monitored after every 2 h of data collection and revealed random variations from their mean intensities (average variation from mean intensity  $< 4\%$ ) that did not constitute any trend. Stability of the crystal and the diffractometer hardware and electronics was thus verified. Of the 3498 reflections measured ( $4.0^\circ < 2\theta < 50.0^\circ$ ), 1048 unique reflections with  $I_{\text{net}} > 2\sigma(I_{\text{net}})$  were obtained and used in the refinement of the structure.

The data were corrected for absorption as a function of crystal shape (J. M. Williams, Argonne National Laboratory program *MET176X*) and Lorentz and polarization effects. Standard deviations in structure factor amplitudes were calculated according to

$$\sigma(|F_o|) = 0.5 \times (\text{VLP})^{1/2} [(\text{Pk} + \text{Bg} + p^2 I_{\text{rel}}^2) / I_{\text{rel}}]^{1/2},$$

where VLP is the standard Lorentz-polarization term, Pk is the peak intensity, Bg is the sum of the background counts taken on both sides of the peak,  $p$  is the ignorance factor (0.02 in this work) and  $I_{\text{rel}}$  is  $\text{Pk} - \text{Bg}$ .

The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The phenyl ring and the six-atom ring of the *p*-bromotolyl moiety were treated as rigid bodies with idealized geometries ( $120^\circ$  bond angles, C-C distances  $1.397 \text{ \AA}$ , and C-H distances  $0.95 \text{ \AA}$ ) in the least-squares refinement. Full-matrix least-squares refinement of this model employing isotropic thermal parameters yielded  $R_1 = \sum \Delta F / \sum |F_o| = 0.088$  and  $R_2 = [\sum w(\Delta F)^2 / \sum w(F_o)^2]^{1/2} = 0.080$ , where  $w = \sigma^{-2}(|F_o|)$  and  $\Delta F = |F_o| - |F_c|$ .

Refinement was continued after inclusion of the remaining six H atoms of the structure at their idealized positions and conversion of the thermal parameters of the fifteen non-group, non-hydrogen atoms of the structure to anisotropic form. The isotropic thermal parameters of the H atoms were held constant at  $B = 5.5 \text{ \AA}^2$ . A variable isotropic extinction parameter (Zachariasen, 1968),  $1.5 (1) \times 10^{-6} e^{-2}$ , was also included. In the final least-squares cycle the largest shift for any parameter was 0.6 and the standard deviation of an observation of unit weight was 1.20. The final values for  $R_1$  and  $R_2$  are 0.049 and 0.044, respectively. A final difference electron density map revealed only a randomly fluctuating background below  $0.4 e \text{ \AA}^{-3}$ . Atomic scattering factors for all atoms and the anomalous-dispersion correction factors for the Br atom were taken from Ibers & Hamilton (1974). Final atomic parameters are listed in Tables 1 and 2.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34508 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ( $\times 10^4$ ) for the non-group atoms

Estimated standard deviations are in parentheses.

	x	y	z
Br	6427 (1)	5928 (2)	145 (1)
O(1)	11524 (5)	10717 (8)	3386 (4)
O(2)	11220 (5)	9211 (9)	3606 (4)
O(3)	10017 (5)	10031 (9)	2584 (4)
O(4)	8841 (6)	8097 (9)	4032 (4)
C(1)	10504 (8)	11311 (11)	2995 (6)
C(4)	10143 (8)	8869 (13)	3159 (6)
C(5)	9300 (8)	9130 (16)	3765 (6)
C(6)	8510 (8)	11143 (14)	4535 (6)
C(7)	8407 (9)	12628 (16)	4727 (6)
C(8)	8982 (10)	13698 (12)	4371 (7)
C(9)	9673 (9)	13307 (13)	3816 (6)
C(10)	9756 (8)	11817 (14)	3620 (6)
C(11)	9186 (8)	10731 (15)	3969 (6)
C(12)	10156 (8)	7347 (11)	2795 (6)
H(6)	8103	10374	4804
H(7)	7902	12923	5126
H(8)	8896	14768	4531
H(9)	10113	14126	3574
H(12A)	10164	6534	3202
H(12B)	10867	7147	2574

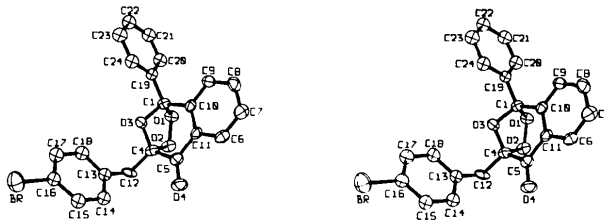


Fig. 1. Stereoview of OZOBR displaying ellipsoids of 30% probability.

Table 2. Parameters of the rigid phenyl groups

Estimated standard deviations are given in parentheses. For a description of these group parameters refer to Eisenberg & Ibers (1965). Angular coordinates are in radians. Positional parameters are  $\times 10^4$ .

	$X_0$	$Y_0$	$Z_0$	$\varphi$	$\varphi$	$\varphi$
Ph(1)	0.8383 (3)	0.6702 (4)	0.1562 (2)	-0.752 (5)	2.351 (4)	1.175 (5)
Ph(2)	1.1025 (3)	1.3516 (4)	0.1858 (2)	1.774 (4)	2.687 (4)	2.238 (4)

Derived group atoms	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )	
	Ph(1)				Ph(2)				
C(13)	9222 (4)	7039 (6)	2164 (3)	4.4 (2)	C(19)	10779 (5)	12461 (6)	2414 (3)	3.8 (2)
C(14)	8323 (5)	6176 (6)	2325 (2)	4.7 (2)	C(20)	11779 (4)	13234 (7)	2521 (2)	5.4 (3)
C(15)	7484 (3)	5839 (6)	1723 (3)	5.0 (2)	C(21)	12024 (3)	14287 (6)	1965 (3)	6.3 (3)
C(16)	7543 (4)	6364 (6)	958 (3)	4.7 (2)	C(22)	11269 (5)	14569 (6)	1301 (3)	5.6 (3)
C(17)	8442 (5)	7227 (6)	797 (2)	5.5 (3)	C(23)	10269 (4)	13797 (7)	1193 (2)	6.3 (3)
C(18)	9281 (4)	7564 (6)	1399 (3)	5.2 (3)	C(24)	10025 (3)	12743 (6)	1749 (3)	5.2 (3)
H(14)	8283 (7)	5819 (9)	2845 (3)	5.5	H(20)	12292 (6)	13042 (10)	2973 (3)	5.5
H(15)	6873 (5)	5253 (8)	1833 (5)	5.5	H(21)	12703 (4)	14812 (9)	2039 (5)	5.5
H(17)	8482 (7)	7584 (9)	277 (3)	5.5	H(22)	11435 (7)	15286 (8)	923 (4)	5.5
H(18)	9892 (5)	8151 (8)	1289 (5)	5.5	H(23)	9756 (6)	13988 (10)	742 (3)	5.5
					H(24)	9346 (4)	12218 (9)	1676 (5)	5.5

Table 3. Bond lengths (Å) not involving the hydrogen atoms

Br—C(16)	1.870 (6)	C(4)—C(12)	1.50 (2)
O(1)—C(1)	1.44 (1)	C(5)—C(11)	1.49 (2)
O(1)—O(2)	1.46 (1)	C(6)—C(7)	1.38 (2)
O(2)—C(4)	1.47 (1)	C(6)—C(11)	1.39 (2)
O(3)—C(1)	1.44 (1)	C(7)—C(8)	1.37 (2)
O(3)—C(4)	1.43 (1)	C(8)—C(9)	1.39 (2)
O(4)—C(5)	1.20 (1)	C(9)—C(10)	1.38 (2)
C(1)—C(10)	1.55 (1)	C(10)—C(11)	1.37 (2)
C(1)—C(19)	1.50 (1)	C(12)—C(13)	1.50 (1)
C(4)—C(5)	1.56 (2)		

**Discussion.** A stereoscopic drawing (Johnson, 1976) of OZOBR is shown in Fig. 1 which also illustrates the atom-labeling scheme used. Bond lengths and angles are listed in Tables 3 and 4, respectively. A comparison of the metrical details of OZOBR with those observed for another epoxy benzodioxepinone (Karban *et al.*, 1978) in which the Br atom is replaced by a NO<sub>2</sub> group, hereinafter referred to as OZONO, is appropriate. The maximum difference in corresponding bond lengths between the two structures is less than 1.5 times the sum of the standard deviations of their values, while the bond angles for the two structures agree to within twice the sums of their standard deviations. Thus no significant differences in these values are observed. The average bond angle within the five-atom ring in both structures is 104° and is representative of the values observed in other structures possessing a cyclopentyl ring.

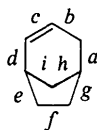
In addition to the unusual stability of this secondary oxonide, the principal structural interest involves the

Table 4. Bond angles (°) not involving the hydrogen atoms

Br—C(16)—C(15)	120.6 (4)	C(1)—C(10)—C(11)	117.5 (10)
Br—C(16)—C(17)	119.4 (4)	C(1)—C(19)—C(20)	121.1 (6)
O(1)—C(1)—O(3)	102.5 (7)	C(1)—C(19)—C(24)	118.9 (6)
O(1)—C(1)—C(10)	109.7 (8)	C(4)—C(5)—C(11)	112.8 (9)
O(1)—C(1)—C(19)	108.1 (7)	C(4)—C(12)—C(13)	114.9 (8)
O(1)—O(2)—C(4)	107.3 (7)	C(5)—C(11)—C(6)	119.8 (10)
O(2)—C(4)—O(3)	102.8 (8)	C(5)—C(11)—C(10)	121.1 (9)
O(2)—C(4)—C(5)	104.2 (8)	C(5)—C(4)—C(12)	116.8 (9)
O(2)—C(4)—C(12)	110.5 (8)	C(6)—C(7)—C(8)	120.1 (10)
O(3)—C(1)—C(10)	109.0 (8)	C(6)—C(11)—C(10)	119.1 (12)
O(3)—C(1)—C(19)	109.8 (7)	C(7)—C(8)—C(9)	120.8 (11)
O(3)—C(4)—C(12)	112.6 (9)	C(8)—C(9)—C(10)	118.5 (10)
O(3)—C(4)—C(5)	108.7 (9)	C(9)—C(10)—C(11)	121.6 (10)
O(4)—C(5)—C(4)	120.7 (11)	C(10)—C(1)—C(19)	116.8 (8)
O(4)—C(5)—C(11)	126.5 (10)	C(12)—C(13)—C(14)	120.6 (6)
C(1)—C(10)—C(9)	121.0 (9)	C(12)—C(13)—C(18)	119.4 (6)

conformation of the bicyclic residue. The 1,2,4-trioxacyclopentane ring in OZONO exists in a perfect envelope (C<sub>s</sub>) form. A comparison of endocyclic torsion angles for OZOBR, OZONO and 4-(2-aminoethyl)-1,8,8-trimethoxy-3-bicyclo[3.2.1]octene-2,6-dione, hereinafter referred to as BCO (Yonemitsu, Nakai, Kanaoka, Karle & Witkop, 1970), is given in Table 5. Due to a difference in chirality, the signs of all torsion angles for OZOBR need to be reversed in order to be comparable to those of OZONO and BCO. An alternative method for describing ring conformations in terms of ring-puckering coordinates has been discussed by Cremer & Pople (1975). The ring puckering coordinates of OZOBR are presented in Table 6.

Table 5. Torsion angles (°), with standard deviations of 1°, in OZOBR, OZONO, and BCO



Bonds involved	OZOBR	OZONO	BCO
a-b-c	2	6	-6
a-h-i	74	-67	-68
b-c-d	1	-1	4
c-d-e	-79	73	72
c-d-i	33	-39	-38
d-i-h	-70	75	69
d-e-f	79	-91	-92
e-f-g	15	-1	5
f-g-a	-100	89	81
f-g-h	13	-25	-32
g-a-b	69	-81	-71
g-h-i	-36	42	48
h-a-b	-40	29	40
h-i-e	46	-42	-43
i-e-f	-36	26	24

Table 6. Ring-puckering coordinates

Ring	q <sub>2</sub> (Å)	q <sub>3</sub> (Å)	φ <sub>2</sub> (°)	φ <sub>3</sub> (°)	θ (°)
Cyclopentyl	0.412		199.1		
Cyclohexyl	0.484	0.358	355.1		53.5
Cycloheptyl	1.063	0.374	339.3	61.1	

An envelope conformation of the six-atom ring is indicated. An ideal envelope conformation for an isometric six-atom ring has puckering coordinates  $\phi_2 = 0^\circ$  and  $\tan \theta = 2^{1/2}$ . The geometry of the seven-atom ring may be described in terms of two planar residues. One residue contains the atoms C(1), C(10), C(11), C(5) and C(4), while the other consists of C(1), O(1), O(2) and C(4). These residues intersect to form an

angle of 106.0°. The ring-puckering coordinates for the five-atom ring are intermediate between the values expected for the envelope form and those expected for the half-boat form. The magnitudes of the positional shifts for atoms O(1) and O(2) required for the ring to assume the envelope form are less than 0.15 Å; thus the conformational difference between OZOBR and OZONO may be due to the different packing environments within their crystals.

No intermolecular contact distances are shorter than the sum of the respective van der Waals radii of the atoms (Pauling, 1960).

The financial support of this work by The Robert A. Welch Foundation (Grant Numbers AA-668 and AA-110) is gratefully acknowledged.

### References

- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354-1358.
- EISENBERG, R. & IBERS, J. A. (1965). *Inorg. Chem.* **4**, 773-778.
- IBERS, J. A. & HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 72-151. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KARBAN, J., MCATEE, J. L. JR, BELEW, J. S., MULLICA, D. F., MILLIGAN, W. O. & KORP, J. (1978). *Chem. Commun.* **17**, 729-730.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- YONEMITSU, O., NAKAI, H., KANAOKA, Y., KARLE, I. L. & WITKOP, B. (1970). *J. Am. Chem. Soc.* **92**, 5691-5700.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212-218.

*Acta Cryst.* (1979). **B35**, 2276-2278

## 2-Phenylquinazoline 1,3-Dioxide

BY KEVIN L. BROWN AND GRAEME J. GAINSFORD

*Chemistry Division, DSIR, Private Bag, Petone, New Zealand*

(Received 30 April 1979; accepted 4 June 1979)

**Abstract.** C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 238.2, orthorhombic, *Pca*2<sub>1</sub>, *a* = 12.868 (1), *b* = 5.3709 (5), *c* = 15.784 (1) Å (Cu *K*α, λ = 1.5418 Å), *Z* = 4, *D<sub>m</sub>* = 1.44, *D<sub>c</sub>* = 1.45 Mg m<sup>-3</sup>; *R* = 0.030 for 683 diffractometer data. The N—O bonds and the phenyl ring disturb the electronic structure of the parent quinazoline.

0567-7408/79/092276-03\$01.00

**Introduction.** Quinazoline *N*-monooxides undergo interesting photochemical rearrangements (Rees, Somanathan, Storr & Woolhouse, 1975; Field & Sternbach, 1968). The title compound (I) was prepared to investigate the photochemistry of a quinazoline *N,N'*-dioxide. The analysis was undertaken to characterize

© 1979 International Union of Crystallography