Acta Cryst. (1972). B**28**, 771

The Crystal and Molecular Structure of 2-phenyl-7-bromo-benz[*d*][1,3]oxazepine

By Birthe Jensen

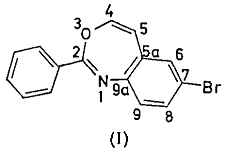
*Chemical Laboratory C, The Royal Danish School of Pharmacy, DK-*2100 *Copenhagen, Denmark*

(*Received* 2 *August* 1971)

2-Phenyl-7-bromo-benz[*d*][1,3]oxazepine crystallizes in space group $P2_12_12_1$ with $Z=4$ and unit-cell parameters $a=11{\cdot}09$ (2), $b=24{\cdot}83$ (3) and $c=4{\cdot}565$ (6) Å. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique to an R value of 0·086, using 706 three-dimensional diffractometer-collected single-crystal X-ray data. The oxazepine ring adopts a boat conformation, and the bond lengths are similar to those of a conjugated triene system.

Introduction

2-Phenyl-7-bromo-benz[*d*][1,3]oxazepine (I) was prepared by Dr O. Buchardt of the H. C. Ørsted Institute, University of Copenhagen, by photolysis of 2-phenyl-6-bromo-quinoline *N*-oxide, and its structure was established by a two-dimensional X-ray analysis (Buchardt, Jensen & Larsen, 1967).



(I)

It naturally follows that no conclusions as to the character of the bond system in the seven-membered ring could be drawn from the two-dimensional analysis and it was found worth while to extend the work to a three-dimensional structure determination.

Experimental

2-Phenyl-7-bromo-benz[*d*][1,3]oxazepine crystallizes (Buchardt, Jensen & Larsen, 1967) from pentane as orthorhombic needles, m.p. 81–82°. The unit-cell dimensions obtained from precession photographs (Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å) and refined by the least-squares method, using the program *CELSIUS* (Liminga, 1965) are: $a=11{\cdot}09$ (2), $b=24{\cdot}83$ (3) and $c=4{\cdot}565$ (6) Å. Since the only systematic absences were for $h00$ when h is odd, $0k0$ when k is odd and $00l$ when l is odd, the space group was determined as $P2_12_12_1$. The density calculated assuming $Z=4$ is 1·59 g.cm^{-3}. The density measured by flotation in an aqueous solution of potassium iodide was found to be 1·57(1) g.cm^{-3}. The linear absorption coefficient, μ(Mo $K\alpha$) is 34·5 cm^{-1}.

All X-ray data were measured from a needle with the dimensions 0·24 × 0·24 × 0·8 mm with quartz-monochromated Mo $K\alpha$ radiation using a NONIUS 3-circle automatic diffractometer. The crystal was mounted with the needle axis parallel to the φ-axis of the goniometer, and the ω-scanning mode was used with a scan speed of 0·6° per minute, each reflexion being scanned over a range of 1·2°. Of the 1350 independent reflexions within the range of $3{\cdot}5° \le \theta \le 25°$, 706 had intensities greater than 2·5 times their corresponding standard deviations and were considered as observed. The diffraction data were reduced to structure amplitudes by the use of a GIER-ALGOL-program *OUTDIFF*-5, written by A. M. Sørensen of this laboratory. No absorption corrections were applied.

Determination and refinement of the structure

The approximate x and y coordinates of all non-hydrogen atoms were known from the (001) projection (Buchardt, Jensen & Larsen, 1967). The z coordinate of the bromine atom was obtained from the three-dimensional Patterson synthesis. The positions of the other seventeen non-hydrogen atoms were deduced from a three-dimensional electron density map phased only on the contribution of the bromine atom.

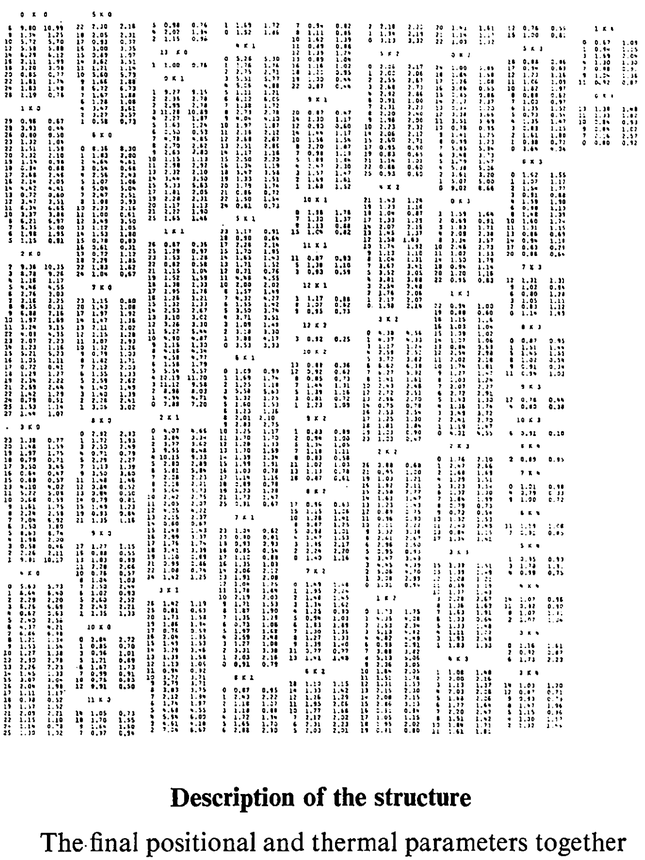
The refinement was performed by the full-matrix least-squares method and included the positional parameters and the individual isotropic temperature factors of all non-hydrogen atoms. When the refinement was nearly finished a difference Fourier synthesis was calculated, but the hydrogen atoms in the structure could not be located from this with any reasonable certainty, and they have not been included in any calculations. The chirality of the molecules in the crystal was determined from a number of Bijvoet pairs of reflexions (Table 1), and in the final two cycles of refinement account was taken for the anomalous dispersion of the bromine atom. The form-factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). Unit weight was given to each observed reflexion and no unobserved reflexions were included in the refinement. The final reliability index R is 0·086. The observed structure amplitudes and calculated structure factors are given in Table 2. Nearly all calculations have been performed on the IBM 7094 computer at the Northern Europe University Computing Center, Lyngby, Denmark, using the two integrated program systems *X-ray* 63 (Stewart, 1964) and *WATSUP* (Watson, 1969). The drawings were produced by *ORTEP* (Johnson, 1965).

Table 1. *Comparison of the observed and calculated structure amplitude ratios of the Bijvoet pairs of reflexions used for the establishment of the chirality*

h k l	$\frac{\lvert F_o(hkl)\rvert + \lvert F_o(\bar{h}\bar{k}l)\rvert}{\lvert F_o(h\bar{k}l)\rvert + \lvert F_o(\bar{h}kl)\rvert}$	$\frac{F_c(hkl)}{F_c(h\bar{k}l)}$
1 3 1	0·99	0·98
2 2 1	0·91	0·90
2 4 1	0·98	0·97
2 5 1	0·87	0·88
2 9 1	1·07	1·03
3 2 1	1·03	1·01
3 3 1	1·04	1·04
3 8 1	0·94	0·94
4 2 1	1·14	1·12
5 1 1	0·95	0·95
1 1 2	0·89	0·91
1 3 2	1·04	1·06
1 4 2	1·09	1·09
1 8 2	1·01	1 02
2 1 2	0·95	0·95
2 3 2	1·07	1·06
2 6 2	0·89	0·89
3 1 2	1·02	1·01
3 6 2	1·05	1·02

Table 2. *Observed structure amplitude and final calculated structure factors for* 2-*phenyl*-7-*bromo-benz*[*d*]-[1,3]*oxazepine*

The three columns give k, F_o and F_c.



Description of the structure

The final positional and thermal parameters together with their estimated standard deviations are given in Table 3, and the interatomic distances and angles are shown in Fig. 1 together with the atomic numbering system.

Table 3. *Final atomic positional* (×10⁴) *and isotropic thermal parameters*

The estimated standard deviations given in parentheses refer to the last decimal position.

	x/a	y/b	z/c	B
Br	5906 (2)	5855 (1)	4365 (6)	6·16 (7)
N(1)	4280 (14)	3641 (6)	0365 (40)	4·4 (3)
C(2)	3264 (17)	3429 (7)	0213 (52)	4·2 (4)
O(3)	2166 (14)	3666 (6)	0979 (44)	6·0 (4)
C(4)	2059 (19)	3902 (8)	3776 (55)	4·7 (5)
C(5)	2785 (17)	4265 (7)	4662 (50)	4·3 (4)
C(6)	4295 (17)	4967 (7)	4321 (55)	4·1 (4)
C(7)	5384 (19)	5176 (8)	3107 (54)	4·6 (5)
C(8)	6053 (20)	4877 (8)	1078 (57)	4·9 (5)
C(9)	5633 (18)	4377 (8)	314 (54)	4·9 (5)
C(5a)	3885 (18)	4478 (7)	3435 (47)	4·2 (5)
C(9a)	4549 (17)	4151 (8)	1370 (46)	4·4 (4)
C(1′)	3081 (18)	2909 (8)	−1151 (54)	4·6 (5)
C(2′)	4014 (21)	2675 (8)	−2895 (51)	5·2 (5)
C(3′)	3863 (20)	2168 (9)	−4113 (59)	5·8 (5)
C(4′)	2818 (24)	1869 (10)	−3819 (69)	6·4 (6)
C(5′)	1883 (24)	2102 (11)	−2102 (66)	7·0 (7)
C(6′)	1982 (21)	2634 (9)	−755 (69)	6·4 (6)

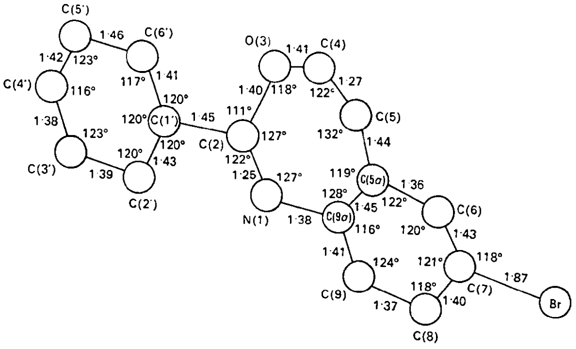


Fig. 1. Bond lengths and angles in 2-phenyl-7-bromo-benz-[*d*][1,3]oxazepine. The estimated standard deviations on bond lengths are about 0·03 Å and on angles 1·5–2°.

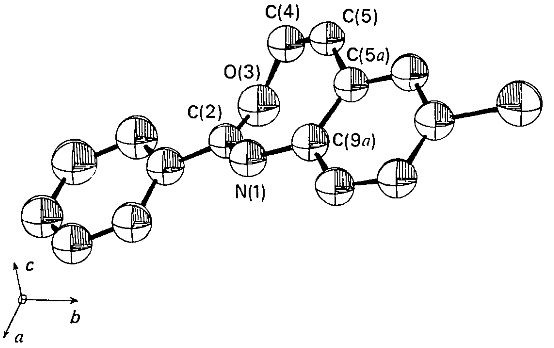


Fig. 2. A perspective view of 2-phenyl-7-bromo-benz[*d*][1,3] oxazepine. The atoms are represented by their individual thermal spheres. The boat-shaped oxazepine ring is seen bottom up. N(1), C(2), C(4), and C(5) are coplanar and the bow atom, O(3) and the stern atoms C(5*a*) and C(9*a*), are situated 'under' this plane.

The standard deviations in bond lengths and angles are very high. Nevertheless, the double-bond character of N(1)–C(2), 1·25 Å, and of C(4)–C(5), 1·27 Å, and the single-bond character of C(2)–O(3), 1·40 Å, O(3)–C(4), 1·41 Å, C(5)–C(5a), 1·44 Å, and C(9a)–N(1), 1·38 Å, is clearly indicated. No significant deviations from the conjugated triene-bond system are found.

A number of least-squares planes through parts of the molecule have been calculated. Their parameters are given in Table 4. The oxazepine ring adopts a boat conformation (Fig. 2). The stern angle [the angle between the least-squares planes *A* through the fused benzene ring and *B* through N(1), C(2), C(4), and C(5)] is 18° and the bow angle [the angle between plane *B*

Table 4. *Least squares planes and some angles between them*

The equations of the planes are in direct (unit-cell) space. Distances (Å) to atoms defining the plane are marked with an asterisk.

A	$-5{\cdot}6542x+10{\cdot}430y-3{\cdot}4273z-1{\cdot}2854=0$
B	$-3{\cdot}2034x+15{\cdot}627y-3{\cdot}2935z-4{\cdot}2181=0$
C	$3{\cdot}4972x+21{\cdot}683y-1{\cdot}6958z-8{\cdot}5405=0$
D	$-6{\cdot}6426x+17{\cdot}512y-1{\cdot}7317z-4{\cdot}8115=0$
E	$-1{\cdot}1376x+8{\cdot}5079y-4{\cdot}2630z-2{\cdot}4552=0$
F	$-4{\cdot}1700x+10{\cdot}558y-3{\cdot}7584z-2{\cdot}2297=0$

Atom	*A*	*B*	*C*	*D*	*E*	*F*
Br	0·014					
C(6)	0·014*					
C(7)	−0·004*					
C(8)	−0·009*					
C(9)	0·013*					
C(9*a*)	−0·002*	−0·36			0·025	
C(5*a*)	−0·011*	−0·40		0·145		
C(5)	0·010	−0·019*		0·00*		
N(1)	0·033	0·020*			0·00*	
C(2)		−0·025*	0·00*		0·00*	0·050
O(3)		−0·49	0·00*	0·00*	0·00*	
C(4)		0·024*	0·00*	0·00*		
C(1′)					−0·160	0·010*
C(2′)						−0·009*
C(3′)						0·006*
C(4′)						−0·004*
C(5′)						0·005*
C(6′)						−0·009*

∠ Plane *A*	–	Plane *B*	18°
∠ Plane *A*	–	Plane *C*	61
∠ Plane *B*	–	Plane *C*	43
∠ Plane *E*	–	Plane *F*	17

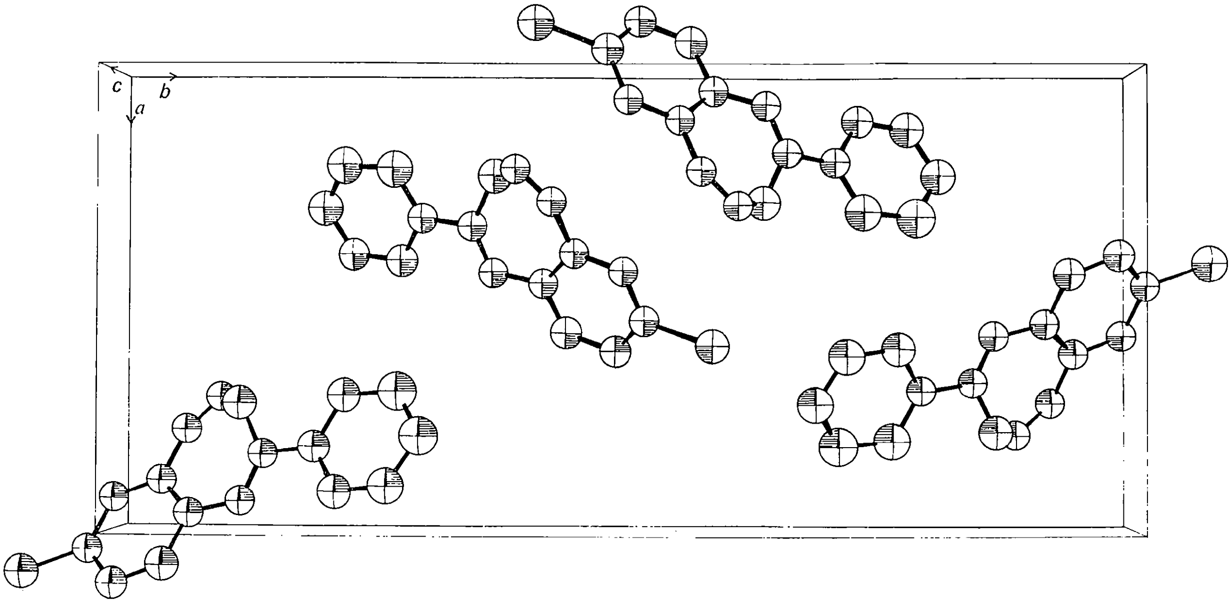


Fig. 3. The structure viewed in *perspective* along the *c* axis.

and plane *C* through C(2), O(3), and C(4)] is 43°. Some deviations from the ideal planarity in the areas of the double bonds are found. The ring atoms O(3), C(2), N(1), and C(9a) are coplanar (plane *E*), whereas C(1′) is out of the plane by 0·16 Å, and a twist of about 7° around the double bond C(4)–C(5) is observed. By this twist the $2p_z$ orbital of C(4) is brought nearer to the $2p_z$ orbital of C(2) under the boat (whereas the distances between the orbitals is increased over the boat). The distance C(2)–C(4) is 2·41 Å, and the overlap integral $S_{2.4}$ calculated according to Mulliken, Rieke, Orloff & Orloff (1949) is 0·08, a figure indicating some interaction between C(2) and C(4). The projection of the structure down [001] is shown in Fig. 3. A survey of the bond systems and conformations of some seven-membered rings will be given elsewhere (Jensen, 1972).

No intermolecular contacts significantly shorter than the sum of the respective van der Waals radii of the atoms are found in the structure.

Solutions of 2-phenyl-7-bromo-benz[*d*][1,3]oxazepine show no optical activity (Buchardt, 1967) and an interconversion between the two enantiomorphic conformers of the benzoxazepine ring is assumed to take place as is known for benzcycloheptatrienes (Tochtermann, Schnabel & Mannschreck, 1968) and related heterocyclic compounds (Mannschreck, Rissmann, Vögtle & Wild, 1967). In the crystal all the molecules have the same chirality, and crystals of each chirality are assumed to co-exist in any batch.

References

BUCHARDT, O. (1967). Private communication.

BUCHARDT, O., JENSEN, B. & KJØLLER LARSEN, I. (1967). *Acta Chem. Scand.* **21**, 1841.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JENSEN, B. (1972). *Acta Cryst.* B**28**, 774.

JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal Ellipsoid Plot Program For Crystal Structure Illustrations.* Oak Ridge National Laboratory, Oak Ridge, Tennessee.

LIMINGA, R. (1965). *Acta Chem. Scand.* **19**, 1631.

MANNSCHRECK, A., RISSMANN, G., VÖGTLE, F. & WILD, D. (1967). *Chem. Ber.* **100**, 335.

MULLIKEN, R. S., RIEKE, C. A., ORLOFF, D. & ORLOFF, H. (1949). *J. Chem. Phys.* **17**, 1248.

STEWART, J. M. (1964). Technical Report Tr 64-6, NSG-398. Computer Science Center of the Univ. of Maryland, College Park.

TOCHTERMANN, W., SCHNABEL, G. & MANNSCHRECK, A. (1968). *Liebigs Ann.* **711**, 88.

WATSON, K. J. (1969). *WATSUP, A Set of Unified Computer Programmes for the Determination of Crystal Structures.* Chemical laboratory IV, H. C. Ørsted Institute, The University of Copenhagen, Denmark.

Acta Cryst. (1972). B**28**, 774

The Crystal and Molecular Structure of 2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine

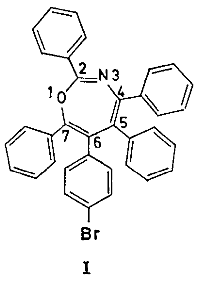
BY BIRTHE JENSEN

Chemical Laboratory C, The Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark

(*Received* 2 *August* 1971)

2,4,5,7-Tetraphenyl-6-(4-bromophenyl)[1,3]oxazepine crystallizes in space group $P\bar{1}$ with $Z=2$ and unit-cell parameters $a=11\cdot403$ (4), $b=6\cdot394$ (5), $c=19\cdot376$ (7) Å, $\alpha=86\cdot52(5)$, $\beta=100\cdot36(1)$, and $\gamma=98\cdot97$ (9)°. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique to a final *R*-value of 0·068, using 3077 three-dimensional diffractometer-collected single-crystal X-ray data. A conjugated triene bond system is found in the oxazepine ring, which adopts a boat conformation as usually found in seven-membered carbocyclic and heterocyclic rings with three double bonds. No considerable norcaradiene character of the oxazepine ring is found.

Ultraviolet irradiation of a variety of heteroaromatic *N*-oxides results in ring expansion (Spence, Taylor & Buchardt, 1970). The photoproducts of some quinoline *N*-oxides, isoquinoline *N*-oxides, and quinoxaline *N*-oxides were identified by infrared, ultra-violet, and n.m.r. spectroscopy and by two-dimensional X-ray determinations as benz[*d*][1,3]oxazepines (Buchardt, Jensen & Kjøller Larsen, 1967), benz[*f*][1,3]oxazepines (Simonsen, Lohse & Buchardt, 1970), and benz[*d*][1,3,6]oxazepines (Buchardt & Jensen, 1968) respectively. This paper describes the crystal structure of the main photoproduct of 2,3,5,6-tetraphenyl-4-(4-bromophenyl)-pyridine *N*-oxide, *i.e.* 2,4,5,7-tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine (I).



I