

Crystal and molecular structure of 2-(*S*-1-phenylethyl)-3-*p*-bromophenyloxaziridine

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Received: October 30, 1978

Abstract. The structure of the title compound, $C_{15}H_{14}NOBr$ was elucidated using X-ray diffraction technique. The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 7.73(1)$, $b = 29.83(2)$, $c = 5.92(1)$ Å, $Z = 4$. The structure was solved by the heavy-atom method followed by a block-diagonal and full-matrix least-squares refinement to an R of 0.043 for 983 counter reflexions. The S configuration of α -phenylethylamine asymmetric center allowed us to establish the absolute configuration of the examined compound as (+)-2*R*,3*R*-2(*S*-1-phenylethyl)-3-*p*-bromophenyloxaziridine.

Introduction

The reaction of imines with chiral peracids leads to formation of an optically active oxaziridines. Two types of asymmetric products were obtained. The first one possess asymmetric nitrogen and carbon atoms simultaneously (Boyd, 1968) and the second has its optical activity on account of chiral nitrogen only (Montanari et al., 1968, 1969).

The present investigations were undertaken to determine the absolute configuration of the chiral nitrogen and carbon atoms of the oxaziridine ring which had not been reported in the literature at the time the analysis started. Available data concerned only the relative configuration of oxaziridines (Jerslev, 1967; Cannon et al., 1972). The problem was solved by application of single crystal X-ray analysis to the model compound (Mostowicz, 1975; Bogucka-Ledóchowska et al., 1976; Bucciarelli et al., 1976). The last paper deals

with a substance containing only chiral nitrogen atom in the oxaziridine ring.

Experimental

The substance was kindly supplied by Professor C. Belżeczki of the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw. The crystals were grown from hexane to form colorless needles elongated along the *c*-axis. Preliminary crystallographic data were obtained from precession photographs with CuK_α radiation. The observed crystal density was measured by flotation in aqueous potassium iodide. Cell constants were calculated by least-squares fit of 14 high-angle reflexions. Crystal data are given in Table 1. The intensities were measured on a Syntex $P2_1$ diffractometer using a $\theta-2\theta$ scan method and graphite monochromatized CuK_α radiation. A crystal of $0.3 \times 0.3 \times 0.9$ mm mounted with the *c*-axis parallel to the goniostat φ -axis was used. The scan speed was one degree per minute and background counts of 20 s were measured at both ends of the scan. A standard reflexion was checked every 50 counts to ascertain stability and alignment of the crystal. Of the 1133 independent reflexions collected, 150 were rejected because their intensities were very weak. The data were corrected for Lorentz and polarization factors, but not for absorption.

Solution and refinement of the structure

The bromine atom was readily located on a three-dimensional Patterson function map. The bromine-phased Fourier synthesis made it possible to locate all non-hydrogen atoms. The structure was refined

Table 1. Crystal data

| | |
|---|--|
| $\text{C}_{15}\text{H}_{14}\text{NOBr}$ | M.W. 304 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| Cell dimensions | $a = 7.73(1) \text{ \AA}$, $b = 29.83(2)$, $c = 5.92(1)$ |
| Unit cell volume | 1365 \AA^3 |
| <i>Z</i> | 4 |
| D_{calc} | $1.47 \text{ g} \cdot \text{cm}^{-3}$ |
| D_{obs} (KI density gradient) | $1.40 \text{ g} \cdot \text{cm}^{-3}$ |

Table 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$) $T = \exp -\pi^2 (U_{11}h^2 a^{*2} + 2 U_{12}hk a^* b^* + \dots)$. Estimated standard deviations in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Br(1) | 7537(2) | 3240(1) | 10613(2) | 856(6) | 581(4) | 598(4) | -96(7) | 51(6) | -73(4) |
| C(2) | 7178(12) | 2738(3) | 8654(16) | 356(19) | 464(22) | 494(17) | -38(21) | 88(16) | -1(17) |
| C(3) | 6372(13) | 2806(3) | 6623(18) | 450(24) | 374(20) | 564(22) | 37(17) | 39(17) | 115(21) |
| C(4) | 6091(12) | 2442(3) | 5243(19) | 467(19) | 464(21) | 425(19) | -3(17) | -12(18) | 73(20) |
| C(5) | 6695(12) | 2013(3) | 5826(17) | 395(21) | 410(20) | 383(20) | -44(18) | 12(18) | 71(19) |
| C(6) | 7503(17) | 1961(3) | 7910(16) | 492(20) | 424(18) | 575(21) | -33(18) | -70(19) | 121(20) |
| C(7) | 7779(14) | 2323(3) | 9308(16) | 503(19) | 527(22) | 407(19) | -23(19) | -23(18) | 75(17) |
| C(8) | 6376(12) | 1636(3) | 4245(19) | 418(16) | 406(17) | 588(18) | -1(15) | 103(19) | 21(17) |
| O(9) | 7849(10) | 1431(2) | 3295(13) | 598(16) | 563(16) | 748(18) | -87(18) | 171(20) | -22(17) |
| N(10) | 6714(10) | 1191(2) | 4967(14) | 433(17) | 415(15) | 566(18) | -40(17) | -27(19) | -8(16) |
| C(11) | 5648(14) | 850(3) | 3717(19) | 588(20) | 419(18) | 586(20) | -12(18) | -26(19) | -44(19) |
| C(12) | 6826(14) | 449(3) | 3258(23) | 628(20) | 550(21) | 1046(22) | 39(18) | 109(21) | -211(20) |
| C(13) | 4161(14) | 741(3) | 5300(23) | 487(19) | 316(19) | 648(21) | 27(17) | -74(21) | -1(17) |
| C(14) | 4388(15) | 503(4) | 7276(20) | 592(20) | 568(20) | 535(19) | -20(18) | -29(17) | 130(19) |
| C(15) | 3042(17) | 417(4) | 8719(23) | 907(22) | 591(21) | 525(20) | -123(21) | 90(19) | 59(19) |
| C(16) | 1404(20) | 577(4) | 8183(26) | 805(22) | 676(21) | 736(22) | -165(21) | 119(21) | -22(19) |
| C(17) | 1133(20) | 814(4) | 6229(30) | 415(21) | 631(22) | 1247(26) | -15(18) | -63(21) | -248(22) |
| C(18) | 2504(20) | 894(3) | 4796(19) | 620(21) | 469(21) | 731(22) | 49(19) | -142(20) | -62(20) |

Table 3. Fractional coordinates for hydrogen atoms ($\times 10^3$) (calculated geometrically)

| | <i>x</i> | <i>y</i> | <i>z</i> | | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|--------|----------|----------|----------|
| H(3) | 600 | 311 | 616 | H(15) | 323 | 24 | 1013 |
| H(4) | 544 | 248 | 380 | H(16) | 42 | 52 | 923 |
| H(6) | 789 | 166 | 840 | H(17) | -5 | 93 | 585 |
| H(7) | 840 | 228 | 1077 | H(18) | 230 | 107 | 337 |
| H(8) | 532 | 178 | 361 | H(121) | 609 | 23 | 231 |
| H(11) | 518 | 195 | 223 | H(122) | 787 | 55 | 239 |
| H(14) | 557 | 39 | 767 | H(123) | 719 | 30 | 470 |

by full-matrix least-squares using anisotropic temperature factors. The *R* value converged to 0.0802. The difference Fourier synthesis was calculated to reveal the positions of hydrogen atoms. The aromatic rings hydrogen atoms found had shown substantially distorted benzene ring geometry. 1.0 Å distance for C–H bond length was assumed and H-atom positions calculated geometrically. The non-hydrogen atoms were then refined anisotropically with three cycles of full-matrix least-squares. The hydrogen atoms were given fixed isotropic ($B_{\text{iso}} = 4$) temperature factor. The final *R* index was 0.043. The final parameters with its e.s.d's given in parentheses are shown in Table 2 and 3. The calculations were carried out with the Syntex Software System and NRC crystallographic computer programmes (Ahmed et al., 1966) adopted on an ICL-4/70.

Description and discussion of the structure

Figure 1 illustrates atoms numbering and *c*-axis projection of the molecule. Bond distances and valency angles are given in Tables 4 and 5.

In accordance with previously reported (Bełżecki and Mostowicz, 1975) physical and chemical evidences the conformation of 2-(*S*-1-phenylethyl)-3-*p*-bromophenyloxaziridine is *trans*.

Using the *S* configuration of α -phenylethylamine, the absolute configuration of both oxaziridine ring asymmetric centers was recognized as *R*.

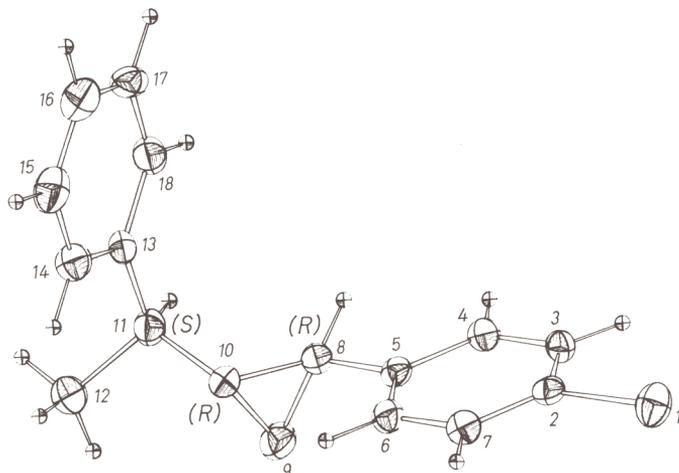


Fig. 1. The molecule and atom's numbering

Table 4. Bond distances (Å). Standard deviations in parentheses

| | | | |
|------------|-----------|-------------|-----------|
| Br(1)–C(2) | 1.915(9) | O(9)–N(10) | 1.504(11) |
| C(2)–C(3) | 1.370(15) | N(10)–C(11) | 1.504(13) |
| C(2)–C(7) | 1.379(13) | C(11)–C(12) | 1.528(15) |
| C(3)–C(4) | 1.375(14) | C(11)–C(13) | 1.519(17) |
| C(4)–C(5) | 1.406(13) | C(13)–C(14) | 1.379(18) |
| C(5)–C(6) | 1.392(15) | C(13)–C(18) | 1.393(19) |
| C(5)–C(8) | 1.483(14) | C(14)–C(15) | 1.372(18) |
| C(6)–C(7) | 1.376(13) | C(15)–C(16) | 1.391(20) |
| C(8)–O(9) | 1.411(13) | C(16)–C(17) | 1.372(23) |
| C(8)–N(10) | 1.420(12) | C(17)–C(18) | 1.379(21) |

Table 5. Bond angles (°). Standard deviations in parentheses

| | | | |
|-----------------|----------|-------------------|-----------|
| Br(1)–C(2)–C(3) | 118.9(7) | C(8)–N(10)–O(9) | 57.6(6) |
| Br(1)–C(2)–C(7) | 118.9(7) | C(8)–N(10)–C(11) | 112.6(8) |
| C(3)–C(2)–C(7) | 122.2(9) | O(9)–N(10)–C(11) | 108.5(7) |
| C(2)–C(3)–C(4) | 118.5(9) | N(10)–C(11)–C(12) | 106.9(9) |
| C(3)–C(4)–C(5) | 121.3(9) | N(10)–C(11)–C(13) | 104.8(8) |
| C(4)–C(5)–C(6) | 117.9(9) | C(12)–C(11)–C(13) | 113.2(9) |
| C(4)–C(5)–C(8) | 118.6(9) | C(11)–C(13)–C(14) | 122.5(10) |
| C(6)–C(5)–C(8) | 123.4(9) | C(11)–C(13)–C(18) | 119.6(10) |
| C(5)–C(6)–C(7) | 121.1(9) | C(14)–C(13)–C(18) | 117.9(11) |
| C(2)–C(7)–C(6) | 118.9(9) | C(13)–C(14)–C(15) | 121.9(11) |
| C(5)–C(8)–O(9) | 116.5(8) | C(14)–C(15)–C(16) | 118.9(12) |
| C(5)–C(8)–N(10) | 119.2(9) | C(15)–C(16)–C(17) | 120.6(13) |
| O(9)–C(8)–N(10) | 64.2(6) | C(16)–C(17)–C(18) | 119.4(13) |
| C(8)–O(9)–N(10) | 58.2(6) | C(13)–C(18)–C(17) | 121.2(12) |

Table 6. Selected dihedral angles (°)

| | | | |
|-----------------------|--------|-------------------------|--------|
| C(4)–C(5)–C(8)–O(9) | 116.7 | C(8)–O(9)–N(10)–C(11) | 105.5 |
| C(4)–C(5)–C(8)–N(10) | –169.5 | C(8)–N(10)–C(11)–C(12) | 140.0 |
| C(6)–C(5)–C(8)–O(9) | –66.1 | C(8)–N(10)–C(11)–C(13) | –99.6 |
| C(6)–C(5)–C(8)–N(10) | 7.7 | O(9)–N(10)–C(11)–C(12) | 78.2 |
| C(5)–C(8)–O(9)–N(10) | 111.4 | O(9)–N(10)–C(11)–C(13) | –161.4 |
| C(5)–C(8)–N(10)–O(9) | –107.4 | N(10)–C(11)–C(13)–C(14) | –70.0 |
| C(5)–C(8)–N(10)–C(11) | 154.4 | N(10)–C(11)–C(13)–C(18) | 108.1 |
| O(9)–C(8)–N(10)–C(11) | –98.2 | | |

Table 7. Least-squares planes and atomic deviations (Å). All equations are expressed in orthogonal Ångstrom space. Atoms not included in planes calculation are denoted by (+)

| | |
|-----------|---|
| Plane (1) | $-0.560 X - 0.352 Y - 0.750 Z = -6.364$ |
| | C(8) 0.0 |
| | O(9) 0.0 (oxaziridine ring) |
| | N(10) 0.0 |
| Plane (2) | $0.879 X + 0.181 Y - 0.440 Z = 4.113$ |
| | Br(1) –0.0008 |
| | C(2) –0.0056 |
| | C(3) 0.0120 |
| | C(4) –0.0156 |
| | C(5) 0.0112 |
| | C(6) –0.0113 |
| | C(7) 0.0077 |
| | C(8) 0.0023 |
| | O(9) ⁺ 1.1403 |
| | N(10) ⁺ –0.1970 |
| | sigma (delta squared) = 0.0007 |
| Plane (3) | $-0.187 X - 0.850 Y - 0.492 Z = -4.040$ |
| | C(11) –0.0177 |
| | C(13) 0.0139 |
| | C(14) 0.0067 |
| | C(15) 0.0012 |
| | C(16) –0.0125 |
| | C(17) –0.0039 |
| | C(18) 0.0123 |
| | C(12) ⁺ 0.9615 |
| | sigma (delta squared) = 0.0009 |

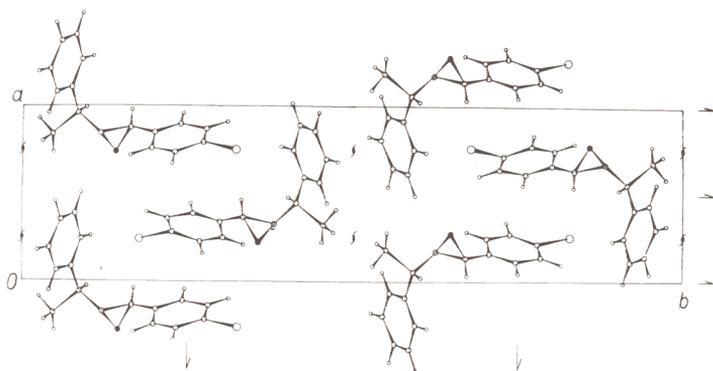


Fig. 2. The packing of the molecules in the crystal viewed along the *c*-axis

There are no significant differences in bond lengths between this and the previously reported structures (Cannon et al., 1972; Jerslev, 1967). The C—C bond 1.468 Å connecting the benzene and oxaziridine rings is a little shorter than that expected for sp^2-sp^3 hybridization. The distance agrees fairly well with the one 1.469 Å observed in (*RS*)-*trans*-2-methyl-3-(2,6-dimethyl-4-chlorophenyl)-oxaziridine (Jerslev, 1967). The corresponding bond length found in *cis*-2-isopropyl-3-(4-nitrophenyl)oxaziridine is 1.487 Å (Cannon et al., 1972). Though it is still possible that the difference may be a result of legitimate e.s.d's, it is worthwhile to notice that a different substituent in the benzene ring and *cis* conformation of the molecule may account for this observation.

The benzene and oxaziridine planes intersect at an angle of 103°. The mean planes of the benzene and α -phenylethylamine form an angle of 96°. Torsional angles are given in Table 6. The least-squares planes are presented in Table 7. The packing of the molecules in the unit cell is shown in Figure 2.

In the crystal structure of the compound there are no intermolecular contacts significantly shorter than 3.5 Å. One may therefore assume that the van der Waals forces are the main intermolecular interactions occurring in this structure. Thus, the packing of the molecules in the crystal cannot be considered very compact.

Acknowledgement. The authors wish to thank Dr. T. Głowiak from the Institute of Inorganic Chemistry, Wrocław University, Poland for measuring the diffraction data and for preliminary crystallographic computing. We also acknowledge the financial support of the Institute of Organic Chemistry of the Polish Acad. of Sci., Warsaw.

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