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CONFORMATIONAL STUDIES OF SMALL RING DERIVATIVES BY X-RAY CRYSTALLOGRAPHY—I

THE CRYSTAL STRUCTURE OF *p*-NITROSTYRENE OXIDE

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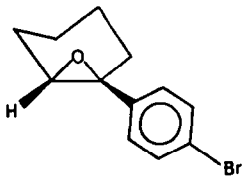
Abstract—The crystal structure of p-nitrostyrene oxide has been determined at room temperature from three-dimensional X-ray diffractometer data, and refined by full-matrix least-squares to a final $R = 0{\cdot}045$. The crystals are monoclinic, space group $P2_1/c$ with unit-cell dimensions $a = 7{\cdot}8244(2)$, $b = 7{\cdot}1277(2)$, $c = 14{\cdot}2059(4)$ Å, $\beta = 104{\cdot}193(3)°$. The value of the dihedral angle formed by the phenyl ring and the oxirane ring (80·2°) can be rationalised on the basis of pseudoconjugation between the two rings, and of non-bonding interactions of one of the ortho-hydrogens of the phenyl ring with the hydrogens of the oxirane ring. The oxirane ring contains a short C–C bond of length 1·448(4) Å.

In structures containing aryl groups directly linked to small ring alicyclic or heterocyclic derivatives (three- or four-membered rings), the relative conformation of these constituents can be influenced by both steric and electronic factors. The conformation may, in turn, influence the physical properties and chemical behaviour of these compounds. A study of their structures may, therefore, give a better insight into the electronic characteristics of these small rings, which at present are still the subject of some discussion.[1-5]

The spectroscopic techniques most frequently used in conformational problems (IR, NMR, ORD and CD) give, in the majority of cases,[6] only limited and very approximate information on the dihedral angle between two rings in a molecule. Furthermore, these techniques are unable to give detailed information on the exact molecular dimensions and other structural data such as bond angles, torsion angles, etc. Thus, an X-ray analysis of these compounds appeared to be the most promising approach to the determination of these parameters.

The solid state form of a molecule does not necessarily reflect its preferred conformation in solution or in the liquid state. However, there is increasing evidence that the conformation found in the solid state corresponds closely to one of the major conformers in solution or in the liquid state.[7-9]

Oxiranes are the most widely studied class of small-ring heterocyclics and those that are 1-aryl substituted are of particular interest because of their peculiar chemical behaviour.[10,11] The conjugative properties of the oxirane ring have been documented[12-14] and can be explained by the bent bond model developed for cyclopropane.[1] This theory shows that the geometry for maximum pseudoconjugative interaction between an oxirane ring and an adjacent π-system occurs when the plane of the three-membered ring is parallel to the axes of the π-orbitals of this system. An X-ray diffraction study of an 1-aryl substituted oxirane has been reported,[15] but in the compound examined, 1 - (p - bromophenyl) - 1,2 - epoxycyclohexane **1**, the oxirane and cyclohexane rings were fused. As a result there could be some doubt as to whether the conformational preference around the bond joining the aromatic and oxirane carbons may have been influenced by non-bonded interactions between the ring systems. The aim of the present work is to determine the geometry of a simple 1-aryl substituted oxirane, p-nitrostyrene oxide **2**, in order to define exactly its geometric parameters and the relative orientation of its two rings.



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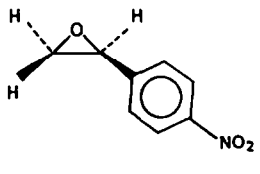

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EXPERIMENTAL

1-(p-*Nitrophenyl*)-2-*bromoethanol*

A stirred solution of $NaBH_4$ (0·90 g, 23·8 mmol) and p-nitrophenacyl bromide (Fluka AG) (5·00 g, 20·5 mmol) in anhydrous THF (40 ml) was treated dropwise with a solution of BF_3, Et_2O (4·00 ml, 31·6 mmol) in anhydrous THF (35 ml). The reaction mixture was stirred at room temperature for 12 h, treated with H_2O, and extracted with ether. Evaporation of the washed (10% aqueous Na_2CO_3 and H_2O) and dried ($MgSO_4$) ether extracts, gave the product (4·60 g), which was recrystallised from benzene-pet ether (b.p. 60–80°), m.p. (Kofler hot stage) 86–87° (lit.[16] 86–87°).

p-*Nitrostyrene oxide* **2** was prepared by dehydrohalogenation of 1-(p-nitrophenyl)-2-bromoethanol, and crystals suitable for X-ray analysis, m.p. 85·5–86·5° (lit.[16] 85–86°), obtained by dissolving the product in ethyl ether, adding petroleum ether (b.p. 80–100°), and allowing the solution to evaporate slowly.

Crystal Data

Crystals of p-nitrostyrene oxide are regular yellow blocks, which are monoclinic, space group $P2_1/c$. Accurate lattice parameters were obtained by least-squares refinement of 22 high-angle reflections measured on a diffractometer using Cu-K_α radiation. The crystal data are: ($C_8H_7O_3N$), $M = 165$, $a = 7{\cdot}8244(2)$, $b = 7{\cdot}1277(2)$, $c = 14{\cdot}2059(4)$ Å, $\beta = 104{\cdot}193(3)°$, $U = 768{\cdot}07$ Å^3, $Z = 4$, $D_c = 1{\cdot}43$ g cm^{-3}, $\mu_{Cu} = 9{\cdot}5$ cm^{-1}.

Determination and refinement of the structure

A crystal of dimensions $0{\cdot}25 \times 0{\cdot}5 \times 0{\cdot}3$ mm^3 was cut from one of the blocks and mounted along its b direction. As previous cut crystals, after standing for a day or two, had shown signs of decomposition, this crystal was immediately coated with a film of picture varnish.

Intensities of 1459 reflections, up to $\theta = 70°$, (an unique quadrant of reciprocal space), were measured on a Siemens off-line automatic 4-circle diffractometer using Ni-filtered Cu-K_α radiation; of these 74 had $I < 2{\cdot}58\ \sigma\ (I)$ and were classed as unobserved.[17] As many of the lower angle reflections were exceptionally intense and exceeded the range of attenuators on the diffractometer, the data were collected in two concentric spheres, the inner sphere up to $\theta = 35°$ being collected with reduced X-ray tube current. A standard reflection, measured every 50 reflections, showed no change over the period of the data collection (2 days), indicating that no decomposition had occurred. The data were corrected for Lorentz and polarisation factors; an assessment of the overall scale and temperature factors was obtained by the method of Wilson[18] and a list of normalised structure factors (E's) produced. No absorption corrections were applied.

Phase determination was carried out by the symbolic-addition procedure[19] using a 98% probability acceptance criterion. Using 2 symbols, together with the 3 origin terms and 1 term determined from $\Sigma 1$, direct or symbolic indications were obtained for the phases of 120 reflections with $E \geq 1{\cdot}82$. During this process the sign of one of the symbols was unambiguously determined with high probability; the only indication for the other however, was an association with a reflection whose sign was indicated by $\Sigma 1$ to be positive. An E map computed using these terms gave plausible positions for all the non-hydrogen atoms in the structure. The structure, however, failed to refine and a second E map, with the sign of the second symbol reversed was computed. This map gave a much cleaner picture of the structure, this time in a different orientation in the cell. This solution quickly refined with isotropic temperature factors to $R = 0{\cdot}153$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. A difference electron-density map computed at this stage showed no major unassigned peaks.

The structure was then refined anisotropically reducing R to 0·084; standard deviations in bond lengths and angles averaged 0·005 Å and 0·35°, respectively. A second difference map was computed and clearly showed the positions of all the hydrogen atoms. The whole structure was refined by full-matrix least-squares, the hydrogen atoms isotropically and the rest anisotropically; R dropped to 0·048. Two reflections (004, 104) which had $|F_o| \ll |F_c|$, were suspected of being affected by extinction and therefore, removed. Subsequent refinement reduced R to a final value of 0·045.† The average shift/error for all atoms was 0·003 and the average standard deviations in bond lengths and angles were, for the non-hydrogen atoms 0·003 Å and 0·2°, and for the hydrogen atoms 0·02 Å and 1·5° respectively. Unit weights were used throughout the refinements. A final difference map showed no peak of height greater than 0·1 eÅ^{-3}. Scattering factors for C, O and N were taken from ref. 20 and those for H from ref. 21.

The computations were carried out on the Imperial College CDC 6400 and the University of London CDC 6600 and 7600 computers. With the exception of the data processing, $\Sigma 2$ probability and molecular geometry programs, which were locally written, the programs used belonged to the X-ray 70 system.[22]

RESULTS AND DISCUSSION

The final fractional atomic coordinates and thermal parameters together with their standard deviations are listed in Tables 1 and 2. Figure 1 shows a perspective view of the molecule (ORTEP[23]) with thermal ellipsoids scaled to enclose 50 per cent probability, the hydrogens having been given arbitrary equal thermal values for illustrative purposes. The figure also shows the numbering scheme used; the hydrogen atoms carry the same numbers as the carbons to which they are bonded. Figures 2a, b show the bond lengths and angles with standard deviations in parentheses. Figure 3 shows a stereoscopic view (ORTEP) of the packing of the molecules.

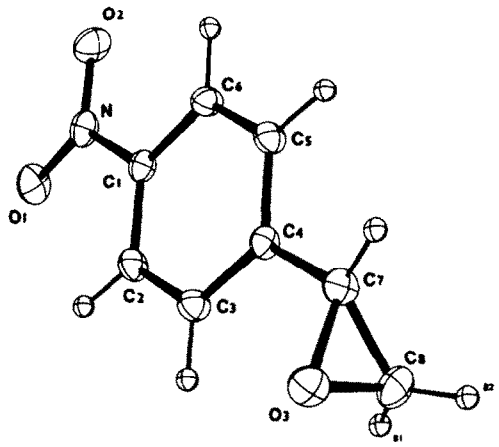

Fig. 1. Perspective view of the molecular structure of *p*-nitrostyrene oxide.

Fig. 2. (a) Bond lengths: standard deviations in parentheses. (b) Bond angles: standard deviations are, for angles not involving hydrogens, 0·2°, those involving a single hydrogen, 1·5°, and those involving two hydrogens, 2·0°.

Analysis of intermolecular contacts shows the structure to be fairly tightly packed with twelve contacts less than 3·5 Å, and two less than 3·2 Å. Despite this the packing seems consistent with van der Waals interactions, no

†Tables of observed and calculated structure factors may be obtained from the authors.

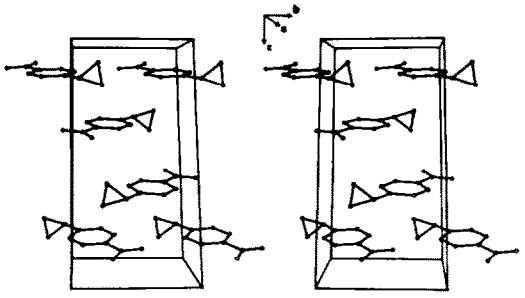

Fig. 3. Stereoscopic view of the packing of the molecules in the unit cell.

Table 1. Final fractional atomic coordinates $\times 10^4$ and isotropic thermal parameters. Standard deviations in parentheses

Atom	x	y	z	B(Å²)
O(1)	7514(2)	6672(3)	822(1)	*
O(2)	6068(2)	4238(3)	1100(1)	*
N	6247(2)	5938(3)	1034(1)	*
C(1)	4842(2)	7169(3)	1207(1)	*
C(2)	5039(3)	9084(3)	1158(2)	*
C(3)	3695(3)	10222(3)	1303(2)	*
C(4)	2187(2)	9443(3)	1493(1)	*
C(5)	2049(3)	7507(3)	1555(2)	*
C(6)	3376(3)	6355(3)	1409(2)	*
C(7)	711(3)	10646(3)	1626(2)	*
C(8)	58(3)	12199(4)	980(2)	*
O(3)	1150(2)	12541(2)	1930(1)	*
H(2)	6147(28)	9631(30)	1065(15)	5·0(5)
H(3)	3842(29)	11583(34)	1263(16)	5·9(6)
H(5)	940(29)	6909(32)	1637(16)	5·7(5)
H(6)	3277(31)	4953(38)	1488(18)	7·0(6)
H(7)	−94(32)	10016(35)	1974(17)	6·8(6)
H(81)	587(31)	12504(36)	443(18)	6·6(6)
H(82)	−1190(34)	12544(36)	901(18)	7·0(6)

*Anisotropic thermal parameters are given in Table 2.

Table 2. Final anisotropic thermal parameters* $\times 10^4$ with standard deviations in parentheses

Atom	β11	β22	β33	β12	β13	β23
O(1)	175(3)	394(5)	106(1)	31(3)	67(2)	−10(2)
O(2)	271(4)	248(4)	102(1)	94(3)	56(2)	9(2)
N	164(3)	295(5)	58(1)	52(3)	25(2)	−4(2)
C(1)	140(3)	223(5)	52(1)	31(3)	25(2)	0(2)
C(2)	144(4)	241(5)	69(1)	−12(4)	40(2)	1(2)
C(3)	177(4)	195(5)	75(1)	−6(4)	45(2)	−2(2)
C(4)	150(3)	212(5)	51(1)	13(3)	31(2)	1(2)
C(5)	161(4)	217(5)	71(1)	−8(3)	47(2)	8(2)
C(6)	186(4)	193(5)	71(1)	9(4)	42(2)	9(2)
C(7)	188(4)	229(5)	74(1)	21(4)	57(2)	−9(2)
C(8)	217(5)	308(7)	85(2)	87(5)	45(3)	11(3)
O(3)	260(4)	236(4)	87(1)	31(3)	61(2)	−27(2)

*The form of the anisotropic thermal function is:

$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)].$$

contact being shorter than the sum of the van der Waals radii of the constituent atoms. Table 3 lists these contacts together with their symmetry relations. The closest H–H contact is 2·48(4) Å between H(3) and H(6) of neighbouring molecules related by a cell translation in y.

The bond lengths and angles of the nitro and phenyl groups are within the normal spread of values found for

Table 3. Short intermolecular contacts < 3·5 Å

Atoms	Distance (Å)	Symmetry relation
O(1)–C(5)	3·494(3)	1 + x, y, z
O(2)–C(8)	3·485(3)	1 + x, y − 1, z
C(3)–O(2)	3·463(3)	x, 1 + y, z
O(3)–C(6)	3·407(3)	x, 1 + y, z
O(2)–O(1)	3·461(2)	1 − x, 1 − y, z
O(2)–O(2)	3·342(2)	1 − x, 1 − y, z
O(2)–N	3·129(2)	1 − x, 1 − y, z
N–N	3·378(2)	1 − x, 1 − y, z
O(2)–C(1)	3·332(3)	1 − x, 1 − y, z
O(3)–O(1)	3·168(2)	1 − x, ½ + y, ½ − z
C(4)–O(2)	3·361(3)	1 − x, ½ + y, ½ − z
O(3)–N	3·306(2)	1 − x, ½ + y, ½ − z

nitro substituted phenyls. The bond linking the oxirane and phenyl rings is of the same length as that found in 1-(p-bromophenyl)-1,2-epoxycyclohexane.[15] The two C–O bonds of the oxirane ring are, to within one standard deviation, of the same length, (average 1·432 Å), and compare well with the value of 1·435 Å determined from microwave spectra for ethylene oxide.[24,25] The C–C bond in the ring (1·448(4) Å) is, however, somewhat shorter than the value in ethylene oxide (1·472 Å) and appreciably shorter than that found in tetracyanoethylene oxide (1·496 Å).[26] These differences are significant.

CNDO/2 MO calculations kindly performed for us have shown however, that the distance we found (1·448 Å) corresponds to the minimum energy configuration: any increase or decrease of this length causes an increase in the total energy of the system.

With the exclusion of C(8) and O(3) the molecule is essentially planar with a maximum deviation from planarity for the remaining atoms of 0·047 Å and a standard deviation from this plane of 0·027 Å. C(8) lies 0·93 Å below this plane and O(3), 0·46 Å above. Considering the phenyl ring alone, the standard deviation from planarity is 0·006 Å with a maximum deviation of 0·008 Å; C(8) lies 0·94 Å below and O(3), 0·46 Å above. The angle between this plane and the plane of the oxirane is 80·2°. The nitro group is rotated slightly out of the plane of the aromatic by an angle of 2·7°. Table 4 lists some selected torsion angles. The torsion angles C(3)C(4)C(7)O(3), C(5)C(4)C(7)H(7) and C(3)C(4)C(7)C(8), giving the rotation of the bonds C(7)–O(3), C(7)–H(7) and C(7)–C(8) out of the plane of the aromatic ring are illustrated by the Newman projection[27] (Fig. 4). Torsion angle calculations show that the hydrogen H(81) and H(82), and H(7) and C(4) are symmetric, within about one standard deviation, with the plane of the oxirane ring. Figure 5 shows the corresponding Newman projections. Figure 6, which depicts the 'splay' angle of the planes of these substituents to the C–C bond of the oxirane ring, shows that the 3-membered ring causes these groups to be splayed

Table 4. Selected torsion angles

Atoms	Torsion angle
C(3)C(4)C(7)O(3)	24·0°
C(3)C(4)C(7)C(8)	−45·0
C(5)C(4)C(7)H(7)	−20
O(3)C(8)C(7)H(7)	102
O(3)C(7)C(8)H(81)	103
O(3)C(7)C(8)H(82)	−104
O(3)C(8)C(7)C(4)	−104·1

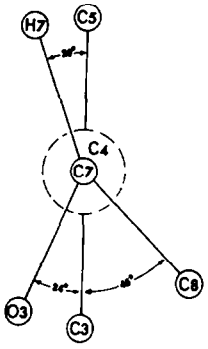

Fig. 4. Newman projection down the bond linking the phenyl and oxirane rings.

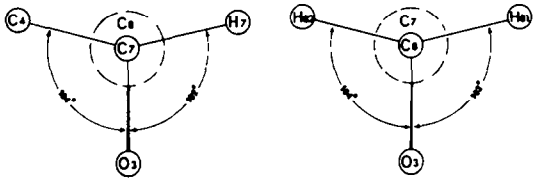

Fig. 5. Newman projections of the substituents to the oxirane ring.

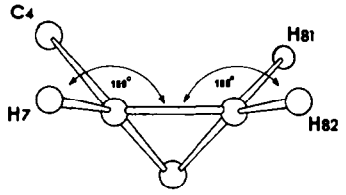

Fig. 6. "Splay" of the groups attached to the oxirane ring.

out at an angle more than 30° greater than the normal tetrahedral value of 125°. A splay angle of 158° has also been reported for ethylene oxide.[24,25]

The dihedral angle (80·2°) found between the phenyl and oxirane rings in **2** agrees well with the analagous angle (83°) found in **1**.[15] This agreement seems to lend credence to the conclusion that the rotameric position of the phenyl group is not due to the packing of the molecules in the crystal, and that the value found in **1** was not influenced by nonbonded interactions between the rings. The relative arrangement of the two rings, as previously pointed out,[15] should be essentially determined by the pseudoconjugation between them. However, the values found in both cases do not coincide exactly with the orientation expected for maximum conjugation, where the axes of the π-orbitals are symmetrically arranged with respect to the bent bonds. These differences may be caused by the relief of the interaction of the ortho-hydrogen of the phenyl group linked to C(5) with the hydrogen linked to C(7), (2·45(3) Å), and of the other ortho-hydrogen H(3) with the cis-hydrogen atom linked to C(8) (2·61(3) Å). On the other hand, when the phenyl ring is slightly rotated from the position of maximum overlap between the two sp^5-hybridized orbitals of the oxirane ring and those of the adjacent π-electron system, the pseudoconjugation does not change markedly.[1] Recent molecular orbital studies on styrene oxide[6c] show a preferred conformation in agreement with our study.

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