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Crystal structure of 2,3-Bis(2-nitrophenyl)oxirane

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Abstract: Single crystals of 2,3-Bis(2-nitrophenyl)oxirane (**NOXI**) were grown by slow evaporation method and X-ray diffraction analysis reveals monoclinic $P2_1/c$ space group with unit cell dimensions of a = 7.936 (1) Å, b= 22.815 (3) Å, c= 7.0437 (9) Å and β= 94.484 (8)°. The oxirane group (O11/C10/C12) makes a dihedral angle of 74.08(1)° & 66.18(1)° with the two nitro substituted phenyl rings (C1—C6/N7/O8/O9) & (C13-C18/N19/O21/O20). The crystal structure is stabilized by C-H…O type intra & intermolecular interaction in addition to van der Waals forces.
Keywords : Oxirane, Bis nitrophenyl, crystal packing, hydrogen bonds.

Introduction

Compounds with epoxy group are found to be useful in paints, composite formations, development of adhesins as well as in many microelectronic applications with biphenyl-type epoxy compounds[1,2,3]. When endogenous as well as xenobiotic compounds undergoing oxidative metabolism via chemical and enzymatic oxidation processes, epoxides; three-membered oxygen compounds are generated. The epoxides are generally unstable in aqueous environments and reactive. These epoxide intermediates have been implicated as potential mutagenic and carcinogenic agents[4,5,6]. It becomes importance for the biological organism to regulate levels of these reactive species at any given time. In view of the above said important properties, structural analyses of such epoxy containing compounds are carried out by many investigators. The present study explains the structural details of one such derivative.

The ORTEP plot of the molecule is shown in Fig. 2. The oxirane group (O11/C10/C12) makes a dihedral angle of 74.15 (15)° with the nitro substituted phenyl ring 1 (C1—C6), it makes a dihedral angle of 66.21 (16)° with the nitro substituted phenyl ring 2 (C13—C18). The dihedral angle between the two phenyl rings is 76.94 (10)°. The packing of the crystal is stabilized by intermolecular C—H•••O hydrogen bonds (Fig. 3).

Experimental

The reaction of 2-nitrobenzaldehyde (0.5g, 3.30 mmol) with triethyl phosphite (1.09 g, 6.61 mmol) in the presence of ZnBr2 (0.075 g, 0.330 mmol) at room temperature. The reaction mixture was then stirred at the

same temperature for 30 minutes (slightly exothermic). After the consumption of the starting material (monitored by TLC), the reaction mass was poured over crushed ice (50 g) and extracted with ethyl acetate (2 x 15 mL). Then obtained trans-epoxide as a colorless solid· Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the compound in chloroform/ ethyl acetate.

Results and Discussion

Data Collection

X-ray diffraction intensity data were collected for **NOXI** on Bruker axs Kappa Apex II single crystal X-ray diffractometer equipped with graphite mono- chromate MoKα (λ=0.7103Å) radiation and CCD detector. Crystals were cut to suitable size and mounted on a glass fibre using cyano acrylate adhesive. The unit cell parameters were determined from 36 frames measured (0.5° phi-scan) from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.75 Å). The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using SAINT-NT (version7.06a) software. Empirical absorption correction (multi-scan) was performed using SADABS program. The Laue group assignment, systematic absences and intensity statistics were consistent with centro symmetry indicating space group $P2_1/c$ with lattice parameter a = 7.936 (1) Å, b = 22.815 (3) Å, c = 7.0437 (9) Å and β = 94.484 (8)°.

Structure Refinement

Crystal structure was solved by Direct Methods using *SHELXS-97*. All the non hydrogen atoms were located without any difficulty. The structure was then refined by full-matrix least-squares method using *SHELXL- 97*. The arrived model was refined using isotropic thermal parameters followed by anisotropic thermal parameters refinements. After completion of the refinement where R factor is converged with negligible shift/e.s.d and agrreable GooF and other parameters, hydrogen atoms were positioned geometrically C—H=0.93–0.98 Å and allowed to ride on their parent atoms, with U_{iso}(H) =1.5U_{eq}(C) for methyl H 1.2U_{eq}(C) for other H atoms.

Crystal Structure Analysis

Table 1 Crystal data for NOXI

Parameters	**Values**
Empirical formula	C_{14} H_{10} N_2 O_5
Formula weight	286.24
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 7.9360(10) Å
	b = 22.815(3) Å β = 94.484(8)°
	c = 7.0437(9) Å
Volume	1271.4(3) $Å^3$
Z, Calculated density	4, 1.495 Mg/m^3
Absorption coefficient	0.985 mm^{-1}
F(000)	592
Crystal size	0.30 x 0.27 x 0.25 mm
Theta range for data collection	5.59 to 64.61 °
Limiting indices	-9<=h<=8, -23<=k<=26, -8<=l<=8
Reflections collected / unique	8256 / 2097 [R(int) = 0.0624]
Completeness to theta = 64.61	98.10%
Max. and min. transmission	0.7908 and 0.7565
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	2097 / 0 / 191
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1244
R indices (all data)	R1 = 0.0604, wR2 = 0.1355
Extinction coefficient	0.0052(9)
Largest diff. peak and hole	0.227 and -0.183 e.$Å^{-3}$

Table 2 Atomic coordinates(x10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for the non-hydrogen atoms of NOXI

Atom	x	y	Z	*U(eq)
C1	2464(2)	2887(1)	1420(2)	41(1)
C2	3680(3)	3327(1)	1742(2)	41(1)
C3	5341(3)	3141(1)	2107(3)	50(1)
C4	5756(3)	2551(1)	2212(3)	56(1)
C5	4516(3)	2130(1)	1902(3)	55(1)
C6	2870(3)	2295(1)	1477(3)	48(1)
N7	677(2)	3033(1)	1017(2)	53(1)
O8	117(2)	3461(1)	1773(3)	76(1)
O9	-184(2)	2713(1)	-58(3)	87(1)
C10	3309(3)	3967(1)	1643(2)	44(1)
O11	4764(2)	4333(1)	1518(2)	61(1)
C12	3911(3)	4358(1)	3216(3)	43(1)
C13	3060(2)	4932(1)	3571(2)	42(1)
C14	2276(2)	5075(1)	5212(2)	41(1)
C15	1598(3)	5625(1)	5496(3)	49(1)
C16	1656(3)	6045(1)	4104(3)	56(1)
C17	2390(3)	5915(1)	2448(3)	57(1)
C18	3094(3)	5368(1)	2193(3)	49(1)
N19	2099(2)	4644(1)	6730(2)	47(1)
O20	1499(2)	4803(1)	8172(2)	71(1)
O21	2514(2)	4136(1)	6463(2)	72(1)

*$U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i*a_j$***$a_i.a_j$**

Table 3 Anisotropic displacement parameters ($Å^2$x10^3) for thenon-hydrogen atoms of NOXI

Atom	U11	U22	U33	U23	U13	U12
C1	42(1)	40(1)	40(1)	-5(1)	3(1)	2(1)
C2	48(1)	40(1)	35(1)	-4(1)	1(1)	-1(1)
C3	46(1)	52(1)	51(1)	-9(1)	-1(1)	-4(1)
C4	48(1)	58(1)	61(1)	-6(1)	-1(1)	13(1)
C5	63(2)	42(1)	59(1)	-5(1)	5(1)	10(1)
C6	55(1)	38(1)	53(1)	-6(1)	8(1)	-1(1)
N7	47(1)	48(1)	64(1)	-6(1)	4(1)	0(1)
O8	61(1)	61(1)	108(1)	-20(1)	14(1)	16(1)
O9	54(1)	88(1)	117(2)	-35(1)	-17(1)	-3(1)
C10	52(1)	37(1)	43(1)	-1(1)	5(1)	-5(1)
O11	68(1)	47(1)	73(1)	-6(1)	32(1)	-11(1)
C12	41(1)	39(1)	49(1)	-4(1)	5(1)	-5(1)
C13	40(1)	34(1)	49(1)	-6(1)	-3(1)	-9(1)

C14	37(1)	35(1)	49(1)	-3(1)	-4(1)	-6(1)
C15	44(1)	41(1)	63(1)	-10(1)	1(1)	-1(1)
C16	49(1)	36(1)	83(1)	-3(1)	-6(1)	0(1)
C17	59(2)	42(1)	68(1)	10(1)	-7(1)	-11(1)
C18	54(1)	42(1)	52(1)	1(1)	1(1)	-10(1)
N19	43(1)	46(1)	52(1)	0(1)	0(1)	-4(1)
O20	92(1)	73(1)	49(1)	-1(1)	13(1)	4(1)
O21	86(1)	44(1)	90(1)	15(1)	26(1)	12(1)

The anisotropic displacement factor takes the form: $\exp\{-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]\}$

Table 4 Bond Length and Bond Angle of NOXI

Atoms	Length	Atoms	Angle
C1-C6	1.389(3)	C6-C1-C2	122.52(19)
C1-C2	1.398(3)	C6-C1-N7	116.52(17)
C1-N7	1.463(3)	C2-C1-N7	120.96(16)
C2-C3	1.390(3)	C3-C2-C1	116.35(17)
C2-C10	1.492(2)	C3-C2-C10	119.28(18)
C3-C4	1.385(3)	C1-C2-C10	124.33(18)
C4-C5	1.380(3)	C4-C3-C2	121.6(2)
C5-C6	1.370(3)	C5-C4-C3	120.3(2)
N7-O8	1.213(2)	C6-C5-C4	119.98(18)
N7-O9	1.221(2)	C5-C6-C1	119.22(19)
C10-O11	1.433(2)	O8-N7-O9	123.1(2)
C10-C12	1.471(3)	O8-N7-C1	118.79(17)
O11-C12	1.421(2)	O9-N7-C1	118.11(16)
C12-C13	1.503(3)	O11-C10-C12	58.56(11)
C13-C18	1.392(3)	O11-C10-C2	114.60(17)
C13-C14	1.394(3)	C12-C10-C2	120.41(16)
C14-C15	1.386(3)	C12-O11-C10	62.07(11)
C14-N19	1.467(2)	O11-C12-C10	59.37(11)
C15-C16	1.374(3)	O11-C12-C13	115.08(15)
C16-C17	1.376(3)	C10-C12-C13	121.93(17)
C17-C18	1.384(3)	C18-C13-C14	116.39(17)
N19-O20	1.211(2)	C18-C13-C12	118.32(17)
N19-O21	1.223(2)	C14-C13-C12	125.25(16)

Table 5 Intermolecular Hydrogen bond interactions for NOXI [Å and º]

Compound	D-H…A	D-H	H…A	D…A	D…H…A
NOXI	C10-H10…O20[i]	0.98	2.56	3.336(2)	137
	C15-H15...O8[ii]	0.93	2.45	3.212(3)	140
	C18-H18...O11[iii]	0.93	2.47	3.299(3)	148

Symmetry codes:

i. -x,-y,2-z
ii. 1-x,-y,1-z
iii. x,y,-1+z

The crystal data and structure refinement details are given in Table 1. The chemical diagram of **NOXI** is shown in Fig.1. The molecular structure (ORTEP diagram) of **NOXI** is shown in Fig. 2. The portion of molecular packing is shown in Fig. 3. The atomic coordinates are given in Table 2. The anisotropic displacement parameters are listed in Table 3. Selected bond lengths and bond angles are listed in Table 4. The various hydrogen bond geometrical parameters are presented in Table 5.

The ORTEP plot of the molecule is shown in Fig. 2. The oxirane (O11/C10/C12) plane is oriented with two nitro phenyl rings (C1—C6) & (C13—C18) by assuming dihedral angles of 74.08(1)° & 66.18(1)°, respectively. The dihedral angle between the two phenyl rings is 76.88(1)°.

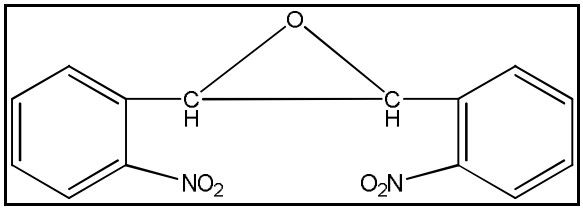

Fig. 1 Schematic Diagram of the NOXI

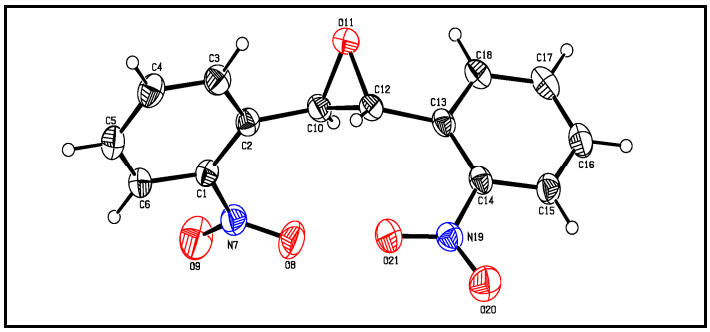

Fig. 2 Perspective view of the NOXI with the atom numbering scheme Displacement ellipsoids are drawn at 30% probability level.

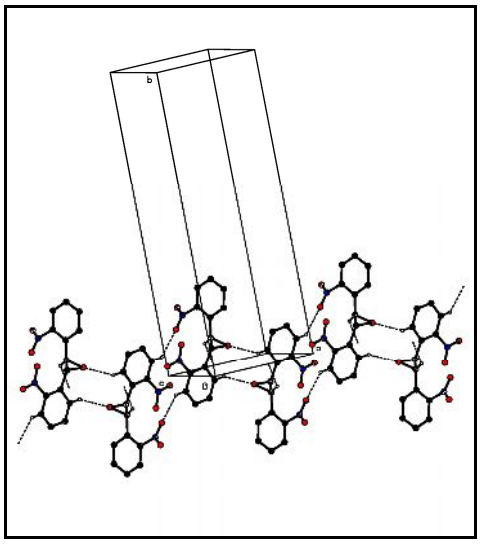

Fig. 3. Portion of packing of the molecules viewed down the *c-axis* for NOXI

Packing Features

C-H…O types of intermolecular interaction makes $R^2_2(5)$ & $R^2_2(10)$ ring motifs. This kind of hydrogen bond network along a and c axis stabilize the crystal packing (Fig 3)**.**

Computational detail

Data collection: APEXII; cell refinement: SAINT; data reduction: SAINT; program(s) used to solve structure: SHELXS97; program(s) used to refine structure: SHELXL97; molecular graphics: PLATON; software used to prepare material for publication: SHELXL97 and PARST.

CCDC 1408772 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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