

Crystal Structure Analysis of Epoxy Derivatives

T Sankar¹,
Potharaju Raju²,
Arasambattu K
Mohanakrishnan²,
S Naveen³,
NK Lokanath⁴ and
K Gunasekaran¹

Abstract

The halogen atoms (F, Br and Cl) substituted in epoxy compounds which were crystallized in slow evaporation method. Crystallographic data were collected by using BRUKER SMART APEX II CCD detector diffractometer. All the three compounds were solved by direct methods and refined by F² full matrix least squares method. Compounds I and III crystallize in monoclinic crystal system P21/c space group, but compound II crystallize in Triclinic P $\bar{1}$ space group, respectively. The final R-factor of the three compounds 0.0479, 0.0500 and 0.0787 respectively.

Keywords: Halogen atoms; Epoxides; Xenobiotic compounds

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Introduction

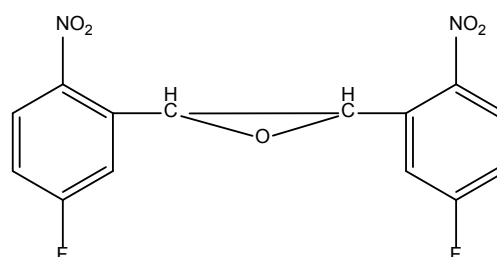
Compounds with epoxy group are found to be useful in paints, composite formations, and development of adhesives as well as in many microelectronic applications with biphenyl-type epoxy compounds [1-3]. Epoxides are three-membered oxygen compounds, generated when endogenous as well as xenobiotic compounds undergo oxidative metabolism via chemical and enzymatic oxidation processes. The epoxides are generally unstable in aqueous environments and highly reactive. These epoxide intermediates have been implicated as potential mutagenic and carcinogenic agents [4,5]. In view of the above said properties, structural analyses of such epoxy containing compounds are carried out by many investigators. The present study explains the structural details of three epoxy derivatives.

Experimental

Synthesis of Compound I

The reaction of 5-fluoro-2-nitrobenzaldehyde (0.5 g, 2.95 mmol) with triethyl phosphite (0.98 g, 5.91 mmol) in the presence of ZnBr₂ (0.07 g, 0.29 mmol) at room temperature for 20 min followed by different procedures using the above mentioned general procedure gave *trans*-epoxide as a colorless solid. Single crystals suitable for X-ray diffraction experiments were obtained by slow evaporation of the compound in chloroform/ethyl acetate. The schematic diagram of compound I is as

follows:



Schematic diagram for Compound I

- 1 Centre of Advanced Study in Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai, India
- 2 Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai, India
- 3 Institution of Excellence, University of Mysore, Manasagangotri, Mysore, India
- 4 Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, India

Corresponding author: K. Gunasekaran

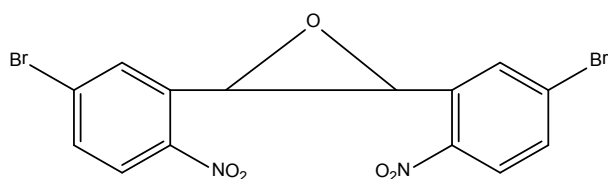
✉ gunaunom@gmail.com

Centre of Advanced Study in Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai-600 025, India.

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Synthesis of Compound II

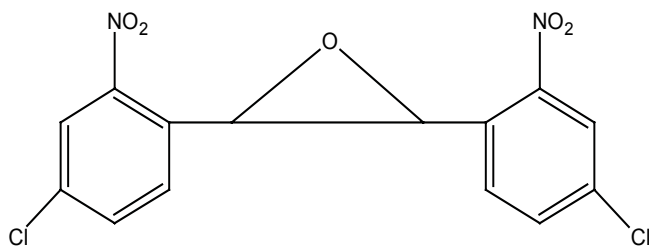
The reaction of 5-bromo-2-nitrobenzaldehyde (0.5 g, 2.17 mmol) with triethyl phosphite (0.72 g, 4.34 mmol) in the presence of $ZnBr_2$ (0.05 g, 0.21 mmol) at room temperature for 10 min followed by different procedures using the above mentioned general procedure furnished *trans*-epoxide as a colorless solid. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the compound in chloroform/ethyl acetate. The schematic diagram of compound II is as follows:



Schematic diagram for Compound II

Synthesis of Compound III

The reaction of 4-chloro-2-nitrobenzaldehyde (0.5 g, 2.69 mmol) with triethyl phosphite (0.89 g, 5.39 mmol) in the presence of $ZnBr_2$ (0.06 g, 0.27 mmol) at room temperature for 10 min followed by different procedures using the above mentioned general procedure furnished *trans*-epoxide 2b as a colorless solid. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the compound in chloroform/ethyl acetate. Schematic diagram of compound III is as follows:



Schematic diagram for Compound III

Data collection

X-ray diffraction intensity data were collected for all three compounds on Bruker Kappa Apex II single crystal X-ray diffractometer equipped with graphite mono-chromate $CuK\alpha$ ($\lambda=1.54178 \text{ \AA}$) 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 \AA). The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using SAINT-NT (version 7.06a) software. Empirical absorption correction (multi-scan) was performed using SADABS program.

Result and Discussion

Structure solving and 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*. They 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 agreeable GooF and other parameters, hydrogen atoms were positioned geometrically $C-H=0.93-0.98 \text{ \AA}$ 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. The relevant details of crystal data table is given in **Table 1**.

For Compound I

The molecular structure (ORTEP diagram) of compound I is shown in **Figure 1**. The bond lengths and bond angles are listed in **Table 2**. The epoxy ring (O12/C11/C13) plane is oriented axially with two fluoro phenyl rings (C1—C6) and (C14—C19) makes dihedral angles of $66.75(19)^\circ$ and $64.79(18)^\circ$, respectively. The dihedral angle between the two fluoro phenyl rings is $55.89(11)^\circ$. The nitro group (N20/O21/O22) is lie in a plane with one of the fluoro phenyl ring (C14-C19/F23) which evidenced by the torsion angle values are $[C14/C15/N20/O21=] 3.2(3)^\circ$ and $[C16/C15/N20/O22=] 2.3(3)^\circ$ and another nitro group (N7/O8/O9) is not lie in a plane with the fluoro phenyl ring (C1-C6/F10). C-H...O types of intermolecular interaction makes $R^2_2(22)$ dimer ring motifs. C-H...O and C-H...F types hydrogen bond stabilize the crystal packing (**Figure 2**). Relevant hydrogen bond details are given in **Table 3**.

For Compound II

The molecular structure (ORTEP diagram) of compound II is shown in **Figure 3**. The bond lengths and bond angles are listed in **Table 4**. The epoxy ring (O3/C5/C6) plane is oriented axially with two bromo phenyl rings (C1—C4/C11/C12/Br₂) and (C7—C14/Br₁) makes dihedral angles of $66.5(3)^\circ$ and $70.3(3)^\circ$, respectively. The dihedral angle between the two bromo phenyl rings is $71.01(2)^\circ$. The nitro group (N1/O1/O2) is oriented with one of the bromo phenyl ring (C1-C4/C11/C12/Br₂) the values of $32.0(2)^\circ$ and another nitro group (N2/O4/O5) is oriented with the bromo phenyl ring (C7-C14/Br₁) the values of $32.1(2)^\circ$. C-H...O types of intermolecular interaction makes $R^2_2(22)$ dimer ring motifs. C-H...O types intra and inter molecular hydrogen bond stabilize the crystal packing (**Figure 4**). Relevant hydrogen bond details are given in **Table 5** [6-12].

For Compound III

The molecular structure (ORTEP diagram) of compound III is shown in **Figure 5**. The bond lengths and bond angles are listed in **Table 6**. The epoxy ring (O12/C11/C13) plane is oriented axially with two chloro phenyl rings (C1—C6/Cl7) and (C14—C19/Cl20) makes dihedral angles of $68.6(4)$ and $68.0(4)^\circ$, respectively. The dihedral angle between the two chloro phenyl rings is $63.6(3)^\circ$. The nitro group (N8/O9/O10) is oriented with one of the chloro

phenyl ring (C1-C6/Cl7) with the angle of $10.6(4)^\circ$ and another nitro group (N21/O22/O23) is oriented with the chloro phenyl ring (C14-C19/Cl20) with the angle of $10.2(3)^\circ$. C-H...O types of intermolecular interaction makes $R_2^2(20)$ and $R_2^2(10)$ dimer ring motifs. C-H...O types intra and inter molecular hydrogen bond stabilize the crystal packing (**Figure 6**). Relevant hydrogen bond details are given in **Table 7**.

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