

Crystal structure of *cis,cis,cis*-1,2-epoxy-3,5-dibromo-4-hydroxy tetralin

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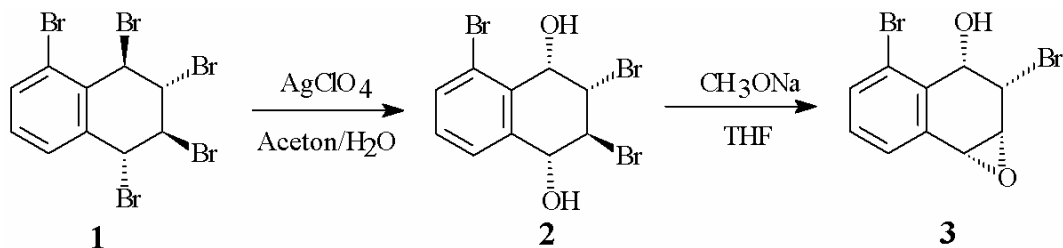
Key words *cis,cis,cis*-1,2-epoxy-3,5-dibromo-4-hydroxy tetralin, crystal structure.

The title compound, C₁₀H₈Br₂O₂, consists of a tetrahydronaphthalene skeleton composed of a six-membered ring A with arene oxide, monobromo and monohydroxy atoms in *cis,cis,cis* configuration held in a boat conformation and a six-membered planar ring B, where the ring B carries monobromo atom. The repulsive interactions between the Br and OH atoms affect the topology of the tetrahydronaphthalene moieties.

1 Introduction

Photobromination of 1-bromonaphthalene with elemental bromine is recently well-established [1]. Aromatic bromination generally requires the use of a catalyst and often gives a mixture of products [2]. However, the recent work on the photobromination of aryl compounds was carried out without catalyst and an optimum conditions to give mostly high yield of sole products or seperable two products [1] and bromoaryl compounds were converted to the methoxy and cyano derivatives [3]. These compounds regarded as a precursors for the many aryl compounds. Therefore, as an extension of this work, we have undertaken the preparation of poly substituted derivatives of naphthalene. We will also be interested in the synthesis of other derivatives.

For this purpose we carried out the hydroxy substitution of pentabromo derivative **1** a benzylic positions. In this study, the crystal structure of **3** was determined by X-ray analysis.



2 Experimental

1,4-dihydroxy-2,3,5-tribromotetralin (0.529 g, 1.32 mmol) was dissolved in dry THF (10 ml). To the solution was added sodium methoxide (0.157 g, 3 mmol). The reaction mixture was stirred magnetically for 92 h under nitrogen gas atmosphere at 0 °C (ice bath). The reaction progress was monitored by TLC. After completion of the reaction, the solvent was removed at reduced pressure and the residue was filtered on a short silica gel

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column (10 g) eluted with EA:Hex (1:9) to give title compound. The compound **3** was recrystallized from chloroform:hexane to give colourless crystals (0.34 g, 80%) (m.p. 409 K).

The X-ray diffraction data were collected on a Rigaku AFC7S diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) operating $\omega/2\theta$ scanning mode at room temperature. Accurate lattice parameters were determined from the angular settings of 25 well-centered reflections [$q > 10^\circ$]. During data collection three standard reflections were monitored at intervals of 120 min. The ranges of h, k, l are $0 \leq h \leq 9$, $0 \leq k \leq 17$, $-18 \leq l \leq 18$. Corrections for Lorentz and polarization factors were applied to the intensity values. Table 1 shows the crystal and experimental data. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 196031.

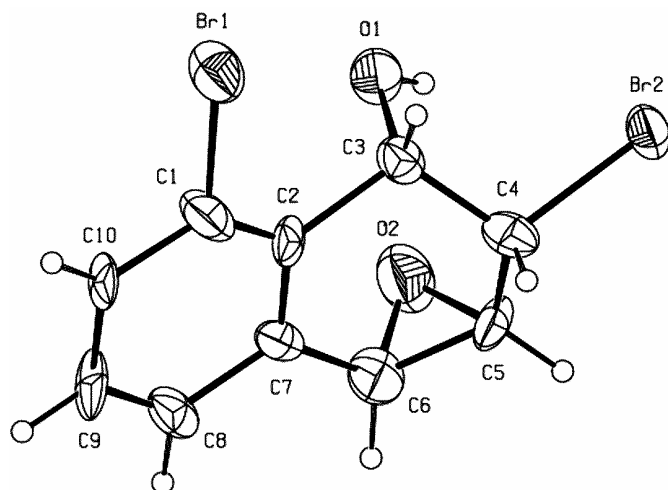


Fig. 1 An ORTEP drawing of the title molecule with the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability levels.

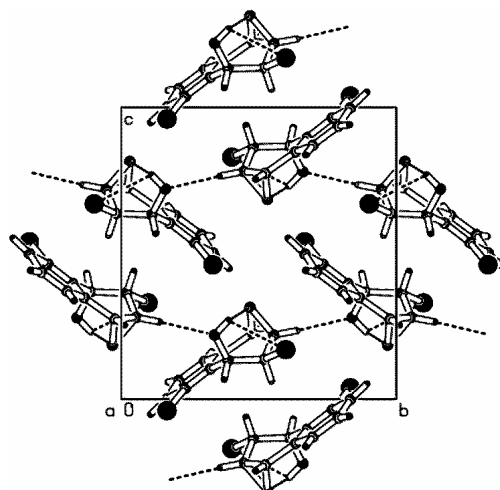


Fig. 2 Packing structure of **3**. The dotted lines indicate hydrogen contacts.

Table 1 Crystal and experimental data

| | |
|---|---|
| Crystal morphology | colorless, prism |
| Crystal dimensions (mm) | 0.20 x 0.30 x 0.35 |
| Chemical formula | C ₁₀ H ₈ Br ₂ O ₂ |
| Molecular weight (g/mol) | 319.98 |
| Crystal system | monoclinic |
| Space group | P 2 ₁ /n |
| Lattice parameters | <i>a</i> 7.575(4)Å |
| | <i>b</i> 11.262(5)Å |
| | <i>c</i> 11.931(6)Å |
| | <i>b</i> 91.47(5)° |
| Volume (Å ³) | 1017.5(8) |
| Number of formula units Z | 24 |
| Calculated density D _c (g.cm ⁻³) | 2.089 |
| Absorption coefficient (cm ⁻¹) | 7.935 |
| 2 θ_{\max} | 65.34° |
| Unique data measured | 1950 |
| Observed data | 1752 [$I \geq 2\sigma(I)$] |
| R(F^2) | 0.049 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0912P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Rw(F^2) | 0.1154 |

| | |
|---------------------------------------|--------|
| No. of parameters refined | 127 |
| GOF | 0.858 |
| Δr_{max} (e.Å ⁻³) | 0.441 |
| Δr_{min} (e.Å ⁻³) | -0.437 |

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters (Å²).

| Atom | x | y | z | Ueq |
|------|-------------|-------------|--------------|-----------|
| Br1 | 0.25595(16) | 0.16664(12) | -0.03933(13) | 0.0766(6) |
| Br2 | 0.43922(14) | 0.59819(10) | 0.16983(13) | 0.0715(5) |
| O1 | 0.3277(10) | 0.3396(7) | 0.2204(7) | 0.069(3) |
| O2 | 0.0713(12) | 0.4684(9) | 0.3149(8) | 0.094(4) |
| C1 | 0.0530(14) | 0.2328(13) | 0.0367(12) | 0.073(6) |
| C2 | 0.0655(13) | 0.3236(9) | 0.1032(9) | 0.043(3) |
| C3 | 0.2433(13) | 0.3888(10) | 0.1323(9) | 0.050(4) |
| C4 | 0.2170(12) | 0.5199(10) | 0.1363(10) | 0.057(4) |
| C5 | 0.0801(14) | 0.5545(9) | 0.2196(9) | 0.054(4) |
| C6 | -0.0670(16) | 0.4759(11) | 0.2253(11) | 0.070(5) |
| C7 | -0.0761(12) | 0.3664(10) | 0.1524(9) | 0.048(3) |
| C8 | -0.2386(13) | 0.3027(11) | 0.1294(9) | 0.057(4) |
| C9 | -0.2485(17) | 0.2106(9) | 0.0650(10) | 0.066(5) |
| C10 | -0.0986(14) | 0.1670(8) | 0.0017(10) | 0.060(4) |

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

Table 3 The H-atom coordinates and isotropic thermal parameters (Å²).

| Atom | x | y | z | Ueq |
|------|----------|---------|----------|--------|
| H1 | 0.34419 | 0.38993 | 0.26926 | 0.1027 |
| H3 | 0.31898 | 0.37464 | 0.06828 | 0.0599 |
| H4 | 0.17539 | 0.54605 | 0.06189 | 0.0687 |
| H5 | 0.06162 | 0.63908 | 0.23493 | 0.0649 |
| H6 | -0.17996 | 0.51111 | 0.24597 | 0.0841 |
| H8 | -0.34105 | 0.32931 | 0.16262 | 0.0683 |
| H9 | -0.35537 | 0.17031 | 0.05856 | 0.0786 |
| H10 | -0.10212 | 0.10700 | -0.05191 | 0.0715 |

Table 4 Bond lengths (Å) and bond angles (°).

| | | | |
|------------|-----------|----------|-----------|
| Br1-C1 | 1.953(12) | C2-C3 | 1.565(14) |
| Br2-C4 | 1.933(10) | C3-C4 | 1.491(16) |
| O1-C3 | 1.336(13) | C4-C5 | 1.506(15) |
| O2-C5 | 1.497(14) | C5-C6 | 1.426(16) |
| O2-C6 | 1.480(16) | C6-C7 | 1.510(17) |
| C1-C2 | 1.296(18) | C7-C8 | 1.445(14) |
| C1-C10 | 1.420(16) | C8-C9 | 1.292(16) |
| C2-C3 | 1.565(14) | C9-C10 | 1.465(16) |
| C5-O2-C6 | 57.2(7) | O2-C5-C4 | 112.2(9) |
| Br1-C1-C2 | 122.6(8) | O2-C5-C6 | 60.8(8) |
| Br1-C1-C10 | 107.7(9) | C4-C5-C6 | 115.0(9) |
| C2-C1-C10 | 129.6(11) | O2-C6-C5 | 62.0(8) |
| C1-C2-C7 | 120.7(10) | O2-C6-C7 | 113.0(10) |
| C3-C2-C7 | 115.6(9) | C5-C6-C7 | 120.2(10) |
| C1-C2-C3 | 123.7(9) | C2-C7-C8 | 115.5(10) |
| O1-C3-C4 | 116.6(9) | C6-C7-C8 | 122.8(9) |

| | | | |
|-----------|----------|-----------|-----------|
| C2-C3-C4 | 110.9(8) | C2-C7-C6 | 121.8(9) |
| O1-C3-C2 | 111.8(9) | C7-C8-C9 | 123.2(10) |
| Br2-C4-C5 | 110.9(8) | C8-C9-C10 | 122.8(11) |
| C3-C4-C5 | 111.9(9) | C1-C10-C9 | 107.8(10) |
| Br2-C4-C3 | 110.0(7) | | |

3 Structure analysis

The crystal structure was solved using direct methods [4] and refined by the full-matrix least square techniques [5]. The final atomic coordinates and equivalent isotropic thermal parameters and the H-atom parameters are listed in Table 2 and Table 3, respectively. Bond lengths and bond angles are given in Table 4. The H atom of the hydroxyl group was not appeared in difference Fourier maps and placed geometrically as a idealized hydroxyl group in staggered geometry and refined as a riding atom. Other H atoms were placed geometrically and were treated as riding on their parent atoms. An ORTEP [6] drawing showing the atom-labelling scheme is presented in Fig. 1, and a view of the crystal packing along the *a*-axis in Fig. 2.

4 Discussion

The structure of the title compound shown in Fig 1, contains the expected arene oxide tetralin skeleton. The X-ray structure analysis of the title compound has revealed that epoxy formation has occurred in (3) as expected. It is because of the trans-configuration of the 1-hydroxy-2-bromo atoms. However, the second epoxy did not occur due to the *cis* configuration of the 3-bromo-4-hydroxy atoms.

The Br-C-C bond angles are 107.7(9)° and 122.6(8)°, with an average value of 112.8(8)°, compared with 112.6(7)° in 5,7,7,8,10-pentabromo-7,8-dihydro-benzocyclooctene [7], 112.4(3)° in 2,2-exo-3,5,5-exo-6-hexabromo-bicycloheptane [8], 112.7(6)° in *exo,endo,exo,exo*-2,3,5,6-tetrabromonorbornane [9], 1.960(14)Å and 111.2(4)° in *exo,endo,endo*-9,9,10,11,12-pentabromo-tricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene [10]. For a six-membered ring with arene oxide, monobromo and monohydroxy atoms in *cis,cis,cis* configuration, the total puckering amplitude Q_T is 0.49(1) Å [11].

As shown in the packing of the title compound (Fig. 2), there exist one intermolecular short hydrogen contact [C5--H5...O1ⁱ: H5...O1ⁱ = 0.981 Å, C5--O1ⁱ = 3.359(13) Å, C5--H5--O1ⁱ = 151.85°; (*i*) = 0.5-x, 0.5+y, 0.5-z], and three intramolecular ones [O1--H1...Br2 : H1...Br2 = 0.820 Å, O1--Br2 = 3.096(8) Å, O1--H1--Br2 = 108.75°; O1--H1...O2 : H1...O2 = 0.820 Å, O1--O2 = 2.694(12)Å, O1--H1--O2 = 107.99°; C3--H3...Br1 : H3...Br1 = 0.980 Å, C3--Br1 = 3.236(11) Å, C3--H3...Br1 = 114.26°]. The crystal structure is stabilized by these short H-contacts and weak van der Waals interactions.

The quantum-chemical calculation using the semi-empiric AM1 method showed that the charges at the Br1, Br2, O1 and O2 atoms are 0.060, -0.016, -0.304 and -0.171e⁻, respectively. The molecule dipole moment calculated is 2.642 Debyes (1D = 3.33564x10⁻³⁰ C.m) for C₁₀H₈Br₂O₂. The final heat of formation and the HOMO and LUMO energy levels are found as -36.86 kcal, -9.87 and -0.34 eV, respectively.

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