

Structure of *syn*-3,4-Dimethoxy-1,2-epoxy-1,2,3,4-tetrahydronaphthalene,\*C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>

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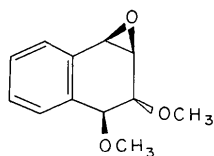
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**Abstract.**  $M_r = 206.0$ , orthorhombic,  $Pbca$ ,  $a = 20.440$  (2),  $b = 13.383$  (2),  $c = 7.648$  (1) Å,  $V = 2092.1$  (8) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.31$ ,  $D_m = 1.31$  (1) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70930$  Å,  $\mu = 1.01$  cm<sup>-1</sup>,  $F(000) = 760$ ,  $T = 295$  K. Final  $R = 0.037$  for 977 observed reflections. The title compound is a naphthalene derivative with the methoxy substituent groups bound axially to the ring. There are no intermolecular or intramolecular hydrogen bonds.

**Introduction.** Certain polycyclic aromatic hydrocarbons are known to be environmental pollutants and potent chemical carcinogens. The active forms of these carcinogens are believed to be metabolic derivatives of the parent hydrocarbons (Harvey, 1981, 1982). A series of naphthalene derivatives which model various metabolites of other carcinogenic hydrocarbons and which, in some cases, are themselves natural metabolites of naphthalene (Tsang, Griffin, Horning & Stillwell, 1982), have been chosen for structural and charge-density studies (Klein, Majeste, Tsang, Griffin & Stevens, 1983). The structural results confirm conformational assignments made on the basis of NMR spectral data. The title compound, shown below, provides information on the geometry of a *syn*-diol epoxide in the absence of an internal hydrogen bond (Glusker, Zacharias, Whalen, Friedman & Pohl, 1982).



**Experimental.** Colorless, needle-like crystal, approximate dimensions  $0.18 \times 0.18 \times 0.50$  mm.  $D_m$  by flotation in dioxane/CHCl<sub>3</sub>. Enraf–Nonius CAD-4 diffractometer with graphite-crystal-monochromatized Mo  $K\alpha$  radiation. Unit-cell dimensions and systematic absences  $0kl$ ,  $k = 2n + 1$ ,  $h0l$ ,  $l = 2n + 1$ , and  $hk0$ ,

\* (1R\*,2S\*,3R\*,4S\*)-3,4-Dimethoxy-1,2-epoxy-1,2,3,4-tetrahydronaphthalene.

$h = 2n + 1$ , uniquely determined space group  $Pbca$  with  $Z = 8$ . Lattice constants determined by least-squares fit of 25 reflections with  $28 \leq 2\theta \leq 44^\circ$  measured on diffractometer. Three-dimensional intensity data collected in  $\omega:2\theta$  scan mode; total of 2136 independent reflections, 977 observed with  $I \geq 3\sigma(I)$ ,  $2 \leq 2\theta \leq 50^\circ$ ,  $0 \leq h \leq 24$ ,  $0 \leq k \leq 15$ ,  $0 \leq l \leq 9$ . Data corrected for Lorentz–polarization. Three standard reflections measured every 2 h during data collection showed 13.5% intensity loss which was corrected in the data. Absorption as a function of  $\psi$  observed to be minimal and therefore not corrected. Structure solved by direct methods; data converted to normalized structure factors and a set of phases determined using MULTAN11/82 (Main *et al.*, 1982). Initial  $E$  map contained 15 non-H peaks corresponding to one asymmetric molecular unit. These 15 atoms refined isotropically on  $F$  using a full-matrix least-squares program to  $R = 0.138$ . All H atoms located on a difference Fourier map with exception of four methyl H atoms [H(11'), H(11''), H(12'), H(12'')] which were calculated on the basis of  $sp^3$  geometry and a C–H bond distance of 0.95 Å. All non-H atoms refined anisotropically. All H-atom coordinates were refined with isotropic thermal parameters allowed to vary. Final  $R = 0.037$ ,  $R_w = 0.044$  where  $w = 1/\sigma(F)^2$  and  $\sigma(F)^2 = [\sigma(F)^2_{cs} + (0.03)^2 (F^2)^2]^{1/2}$ ,  $S = 1.39$ . In final least-squares cycle  $(\Delta/\sigma)_{\max} = 0.03$ . Final difference Fourier map contained no peak larger than  $0.130 \text{ e } \text{Å}^{-3}$ . Scattering factors taken from *International Tables for X-ray Crystallography* (1974). CAD-4 SDP (Enraf–Nonius, 1980) programs used.

**Discussion.** Final fractional coordinates for the non-H atoms are given in Table 1.† The numbering system for the molecule may be found in Fig. 1. Bond lengths and angles may be found in Table 2.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38837 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The compound crystallizes with eight molecules in the unit cell. A stereoscopic diagram of the molecular packing in the unit cell is shown in Fig. 2. The shortest intermolecular contact is 2.53 (4) Å. As expected, there are no intermolecular or intramolecular hydrogen bonds.

The structure determination shows that the two methoxy groups on C(3) and C(4) occupy axial positions. This is consistent with the fact that hydroxyl groups in *syn*-diol epoxides (Sims, Grover, Swaisland, Pal & Hewer, 1974) are known from <sup>1</sup>H NMR data also to occupy axial positions. Additionally, both the methyl groups and the hydroxyl groups in a methyl-substituted *syn*-hydroxyepoxide (Glusker *et al.*, 1982) show axial conformations. In contrast, the substituents are expected to be in equatorial positions in *anti*-isomers of similar compounds (Neidle, Subbiah, Cooper & Ribeiro, 1980).

Table 1. Positional and equivalent isotropic thermal parameters with their *e.s.d.*'s in parentheses

$$B_{eq} = \frac{8}{3}\pi^2 \text{tr } \mathbf{U}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
O(1)	0.1076 (1)	1.0920 (1)	0.2908 (3)	5.63 (5)
O(2)	0.02618 (8)	0.8645 (1)	0.1548 (2)	4.17 (4)
O(3)	0.09374 (8)	0.9451 (1)	0.5674 (2)	4.40 (4)
C(1)	0.1362 (1)	1.0328 (2)	0.1519 (4)	4.85 (7)
C(2)	0.0668 (1)	1.0245 (2)	0.1948 (4)	4.76 (6)
C(3)	0.0442 (1)	0.9330 (2)	0.2896 (3)	3.98 (6)
C(4)	0.0956 (1)	0.8874 (2)	0.4106 (3)	3.35 (5)
C(5)	0.1626 (1)	0.8827 (2)	0.3287 (3)	3.03 (5)
C(6)	0.2061 (1)	0.8071 (2)	0.3732 (3)	3.62 (5)
C(7)	0.2678 (1)	0.8023 (2)	0.2963 (4)	4.64 (6)
C(8)	0.2857 (1)	0.8718 (3)	0.1735 (4)	5.29 (7)
C(9)	0.2429 (1)	0.9461 (2)	0.1276 (3)	4.97 (7)
C(10)	0.1817 (1)	0.9533 (2)	0.2045 (3)	3.68 (5)
C(11)	-0.0255 (1)	0.8001 (3)	0.2011 (4)	6.11 (8)
C(12)	0.1188 (2)	0.8949 (3)	0.7155 (3)	5.18 (7)

Table 2. Bond distances (Å) and angles (°)

*E.s.d.*'s in the least significant digits are given in parentheses.

O(1)—C(1)	1.448 (4)	C(3)—C(4)	1.527 (3)
O(1)—C(2)	1.432 (3)	C(4)—C(5)	1.507 (3)
O(2)—C(3)	1.428 (3)	C(5)—C(6)	1.390 (3)
O(2)—C(11)	1.408 (4)	C(5)—C(10)	1.395 (3)
O(3)—C(4)	1.427 (3)	C(6)—C(7)	1.392 (3)
O(3)—C(12)	1.414 (3)	C(7)—C(8)	1.372 (4)
C(1)—C(2)	1.460 (4)	C(8)—C(9)	1.370 (4)
C(1)—C(10)	1.470 (4)	C(9)—C(10)	1.386 (4)
C(2)—C(3)	1.495 (4)		
C(1)—O(1)—C(2)	60.9 (2)	O(3)—C(4)—C(5)	113.4 (2)
C(3)—O(2)—C(11)	113.9 (2)	C(3)—C(4)—C(5)	113.0 (2)
C(4)—O(3)—C(12)	114.0 (2)	C(4)—C(5)—C(6)	120.7 (2)
O(1)—C(1)—C(2)	59.0 (2)	C(4)—C(5)—C(10)	120.6 (2)
C(2)—C(1)—C(10)	119.9 (3)	C(6)—C(5)—C(10)	118.7 (2)
O(1)—C(2)—C(1)	60.1 (2)	C(5)—C(6)—C(7)	120.7 (3)
O(1)—C(2)—C(3)	116.6 (2)	C(6)—C(7)—C(8)	120.0 (3)
C(1)—C(2)—C(3)	118.1 (2)	C(7)—C(8)—C(9)	119.8 (3)
O(2)—C(3)—C(2)	104.8 (2)	C(8)—C(9)—C(10)	121.2 (3)
O(2)—C(3)—C(4)	111.0 (2)	C(1)—C(10)—C(5)	120.0 (2)
C(2)—C(3)—C(4)	114.1 (2)	C(1)—C(10)—C(9)	120.4 (3)
O(3)—C(4)—C(3)	105.9 (2)	C(5)—C(10)—C(9)	119.6 (3)

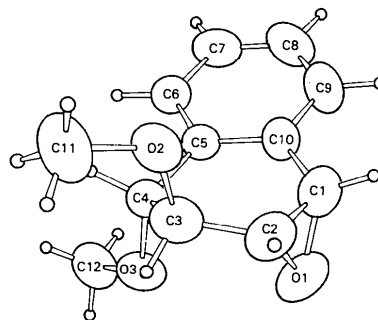


Fig. 1. Atomic-labeling scheme in one molecular unit of the title compound. H atoms have been plotted with arbitrary radii.

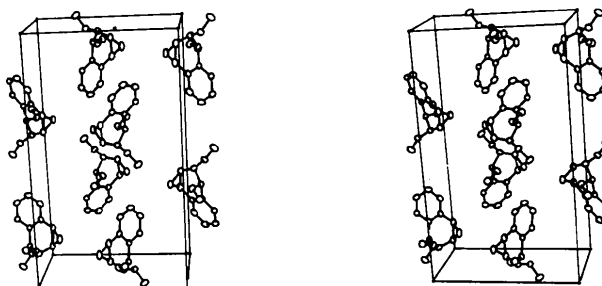


Fig. 2. Stereoview of the molecular packing diagram. *a* is the vertical direction, *b* is the horizontal direction and *c* is perpendicular to the plane of the page.

The intramolecular O(1)—O(3) distance, 2.901 (3) Å, is slightly longer than the comparable distance, 2.79 (1) Å, found in the methyl-substituted *syn*-hydroxyepoxide which shows an intramolecular hydrogen bond between the hydroxyl oxygen and the epoxide oxygen opposite in the ring (Glusker *et al.*, 1982). This is not surprising since a slight shortening of this O(1)—O(3) distance would be expected if an intramolecular hydrogen bond were present in the *syn*-dimethoxyepoxynaphthalene. The epoxide ring, however, is approximately symmetrical with C—O bond lengths of 1.448 (4) and 1.432 (3) Å showing no distortion due to steric effects (Glusker, Carrell, Zacharias & Harvey, 1974).

Deviations from the plane of the ring system [defined by a least-squares plane calculated for the aromatic portion of the molecule, C(5)C(6)C(7)C(8)C(9)C(10)] for all four of the saturated C atoms [C(1), C(2), C(3) and C(4)] occur in the same direction and on the opposite side of the plane from the epoxide oxygen. The saturated portion of the ring system is distorted such that C(3) deviates more from the aromatic ring than C(2) [−0.74 (1) and −0.38 (1) Å respectively].

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X-ray diffractometer was provided by the National Science Foundation (CHE-8208754). The authors are grateful to Drs W. S. Tsang and G. W. Griffin for providing crystals of the title compound.

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## 2-Amino-6,7-dihydroxytetralin Hydrobromide, C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>·HBr\*

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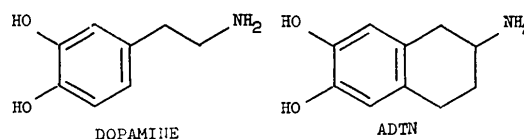
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**Abstract.**  $M_r = 260.1$ , monoclinic,  $P2_1/c$ ,  $a = 11.061(2)$ ,  $b = 20.939(3)$ ,  $c = 9.420(1)$  Å,  $\beta = 92.81(1)^\circ$ ,  $V = 2179.1$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.54(2)$ ,  $D_x = 1.586$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu = 4.987$  mm<sup>-1</sup>,  $F(000) = 1056$ ,  $T = 295$  K. Final  $R = 0.039$  for 2934 observed reflections. There are two independent molecules in the unit cell. Molecule *A* is essentially planar, except for two C atoms of the aliphatic ring which are displaced equally 0.33 Å above and below the plane of the molecule; the N atom also lies in the molecular plane defined by the aromatic ring. Molecule *B* exhibits partial disorder of the (+)- and (-)-enantiomers.

**Introduction.** In neurobiology one of the most intensively studied neurotransmitters is the catecholamine dopamine. The crystal and molecular structure of dopamine was first reported by Bergin & Carlström (1968). New dopamine receptor agonists are currently

being sought by the pharmaceutical industry due to their possible clinical applications in diseases such as Parkinsonism (Hornykiewicz, 1975). The tetrahydro-naphthalene derivative 2-amino-6,7-dihydroxytetralin† (ADTN) has been the object of much recent pharmacological interest since it is a very potent dopamine agonist (Horn, Grol, Dijkstra & Mulder, 1978; Horn, de Kaste, Dijkstra, Rollema, Feenstra, Westerink, Grol & Westerbrink, 1978; see also references therein). ADTN is also of interest from a structural point of view, as it is a semirigid analogue of dopamine and the conformation in the crystal could yield valuable information about the receptor-site preferred conformation of dopamine.



\* Contribution from the National Bureau of Standards.

† Tetralin®: 1,2,3,4-tetrahydronaphthalene.