

trans,trans,trans-1,4-Dimethoxy-2,3,5,8-tetra-bromotetralinİsmail Çelik,^a Mehmet Akkurt,^{b*} Ramazan Erenler,^c Osman Çakmak^c and Cem Cüneyt Ersanlı^d^aDepartment of Physics, Faculty of Arts and Sciences, University of Cumhuriyet, 06532 Sivas, Turkey, ^bDepartment of Physics, Faculty of Arts and Sciences, University of Erciyes, 38039 Kayseri, Turkey, ^cDepartment of Chemistry, Faculty of Arts and Sciences, Gaziosmanpaşa University, 60240 Tokat, Turkey, and ^dDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

Correspondence e-mail: akkurt@erciyes.edu.tr

Key indicators

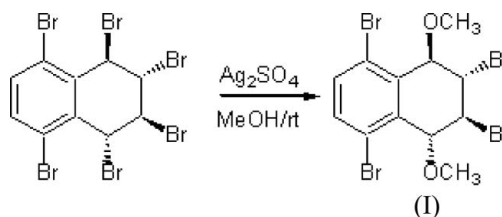
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.018$ Å
 R factor = 0.070
 wR factor = 0.150
Data-to-parameter ratio = 19.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{12}\text{H}_{12}\text{Br}_4\text{O}_2$, is a derivative of 1,2,3,4-tetrahydronaphthalene (tetralin), with 1,4-dimethoxy and 2,3-dibromo substituents on the saturated ring and 5,8-dibromo substituents on the aromatic ring. The molecule occupies a special position on a twofold axis and the saturated ring has a half-chair conformation.

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Comment

Naphthalene derivatives often play an important role as structural units or key intermediates in the synthesis of naturally occurring compounds, and they also show promising biological activities (Huang & Wang, 2001). Therefore, they attract considerable attention from synthetic and natural product chemists. The bromination of hydrocarbons is an important process, since it leads to useful intermediates for the synthesis of a large variety of bromoorganic compounds (Hileman, 1993; Chambers & James, 1979; Ruasse, 1993). Methoxynaphthalenes have great synthetic importance, as they can be used in ring-enlargement reactions with halocarbenes to give benzotropone derivatives (Sato *et al.*, 1976) and as precursors for other substituted naphthalene derivatives such as naphthoquinones (Song *et al.*, 2000). Taking into account the weakness of the C–Br bond and the reactivity of the Br atoms attached to the benzene ring, we proposed to perform the substitution of these Br atoms with methoxy groups *via* a silver-mediated reaction. In this study, the crystal structure of the product of this reaction, the title compound, (I), was determined using single-crystal X-ray diffraction.



The molecular structure of (I) is shown in Fig. 1. The molecules of (I) lie on a twofold axis, which passes through the mid-points of the C1–C1a, C3–C3a and C5–C5a bonds. The saturated ring has a half-chair conformation, with atoms C5 and C5a on opposite sides of the plane through the other four atoms (C3, C3a, C4 and C4a).

In compound (I), the mean Br–C distance is 1.938 (16) Å, and the Br–C–C bond angles are within the range 107.8 (7)–122.0 (10)°. In a similar structure, *trans,trans,trans*-2,3,5,8-tetrabromo-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene (Akkurt *et al.*, 2004), very similar values for the corresponding

parameters [1.938 (5) Å and 107.0 (3)–121.6 (4)°, respectively] were observed.

Experimental

To a solution of 1,2,3,4,5,8-hexabromo-1,2,3,4-tetrahydronaphthalene (2.21 g, 3.65 mmol), obtained according to the method of Akkurt *et al.* (2004), in dry methanol (40 ml) was added Ag₂SO₄ (2.39 g, 7.66 mmol) under a nitrogen atmosphere. The resulting reaction mixture was stirred at room temperature for 3 d. The consumption of the starting material, indicating the progress of the reaction, was monitored by thin-layer chromatography. After the reaction was complete, the residual solid was removed by filtration and the solvent was evaporated. The crude product was submitted to column chromatography (silica gel, 100 g). Elution with hexane–EtOAc (9:1 v/v, 2.0 l) gave colourless crystals of (I) (m.p. 412 K; yield 0.85 g, 46%).

Crystal data

C ₁₂ H ₁₂ Br ₄ O ₂	Z = 4
M _r = 507.82	D _x = 2.256 Mg m ⁻³
Monoclinic, C2/c	Mo Kα radiation
a = 17.546 (5) Å	μ = 10.76 mm ⁻¹
b = 12.522 (5) Å	T = 296 (2) K
c = 7.405 (5) Å	Prism, colourless
β = 113.207 (5)°	0.28 × 0.23 × 0.16 mm
V = 1495.3 (12) Å ³	

Data collection

Stoe IPDS II diffractometer	6748 measured reflections
ω scans	1611 independent reflections
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)	797 reflections with I > 2σ(I)
T _{min} = 0.084, T _{max} = 0.203	R _{int} = 0.142
	θ _{max} = 27.1°

Refinement

Refinement on F ²	w = 1/[σ ² (F _o ²) + (0.0498P) ²
R[F ² > 2σ(F ²)] = 0.070	+ 0.9739P]
wR(F ²) = 0.150	where P = (F _o ² + 2F _c ²)/3
S = 1.01	(Δ/σ) _{max} = 0.001
1611 reflections	Δρ _{max} = 0.70 e Å ⁻³
82 parameters	Δρ _{min} = -0.77 e Å ⁻³
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Br1–C2	1.899 (16)	O1–C4	1.422 (12)
Br2–C5	1.977 (9)	O1–C6	1.414 (16)
C4–O1–C6	113.3 (8)	O1–C4–C5	111.9 (7)
Br1–C2–C1	115.2 (11)	Br2–C5–C4	108.2 (6)
Br1–C2–C3	122.0 (10)	Br2–C5–C5 ⁱ	107.8 (7)
O1–C4–C3	106.5 (7)		
C6–O1–C4–C3	-154.3 (9)	Br1–C2–C3–C4	3.4 (12)
C6–O1–C4–C5	79.6 (11)	C3–C4–C5–Br2	83.3 (8)
C1–C1–C2–Br1	179.2 (10)	Br2–C5–C5 ⁱ –C4 ⁱ	-71.1 (8)
Br1–C2–C3–C3 ⁱ	-178.6 (6)		

Symmetry code: (i) -x, y, -z + ½.

Crystals of the title compound were of limited quality. Even though it was possible to select a specimen suitable for the X-ray diffraction experiment, the data obtained were rather poor and the value of R_{int} remained high (0.142). H atoms were placed in ideal positions and allowed to ride on their parent atoms, with aromatic

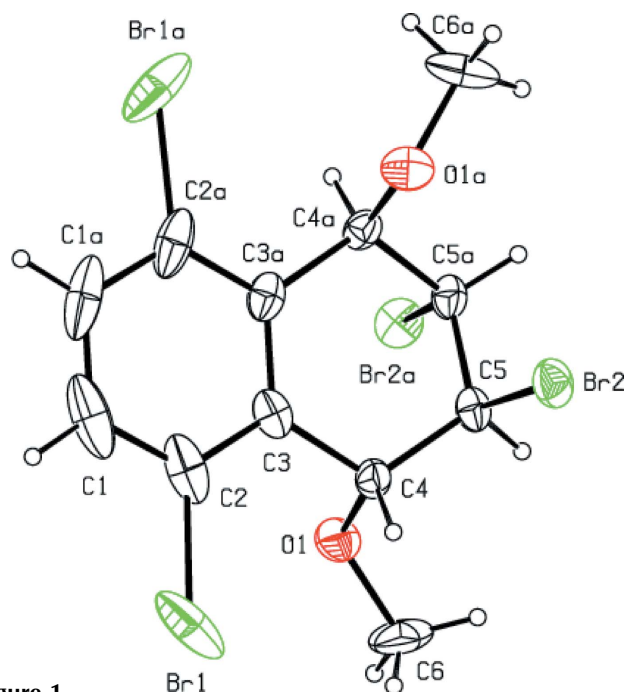


Figure 1

The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Atoms with the suffix a are at the symmetry position (-x, y, ½ - z).

C–H = 0.93 Å, methyl C–H = 0.96 Å and methine C–H = 0.98 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms and 1.2U_{eq}(C) for all other H atoms.

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA; data reduction: X-RED32 (Stoe & Cie, 2002); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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