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trans,*trans*,*trans*-1,4-Dimethoxy-2,3,5,8-tetrabromotetralin

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.018 Å
R factor = 0.070
wR factor = 0.150
Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

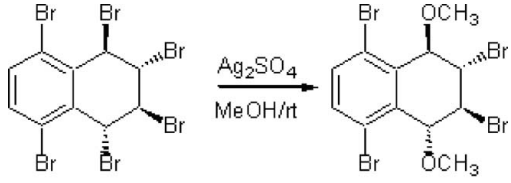
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The title compound, $C_{12}H_{12}Br_4O_2$, is a derivative of 1,2,3,4-tetrahydronaphthalene (tetralin), with 1,4-dimethoxy and 2,3-dibromo substituents on the saturated ring and 5,8-dibromo substituents on the aromatic ring. The molecule occupies a special position on a twofold axis and the saturated ring has a half-chair conformation.

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.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecules of (I) lies 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 Ag_2SO_4 (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

$C_{12}H_{12}Br_4O_2$
M_r = 507.82
Monoclinic, $C2/c$
a = 17.546 (5) Å
b = 12.522 (5) Å
c = 7.405 (5) Å
β = 113.207 (5)°
V = 1495.3 (12) Å^3
Z = 4
D_x = 2.256 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 10.76 mm^{-1}
T = 296 (2) K
Prism, colourless
0.28 × 0.23 × 0.16 mm

Data collection

Stoe IPDS II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.084, T_{max} = 0.203
6748 measured reflections
1611 independent reflections
797 reflections with $I > 2\sigma(I)$
R_{int} = 0.142
θ_{max} = 27.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.150
S = 1.01
1611 reflections
82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.9739P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}

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^{i}—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) $-x, y, -z+\frac{1}{2}$.

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 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.

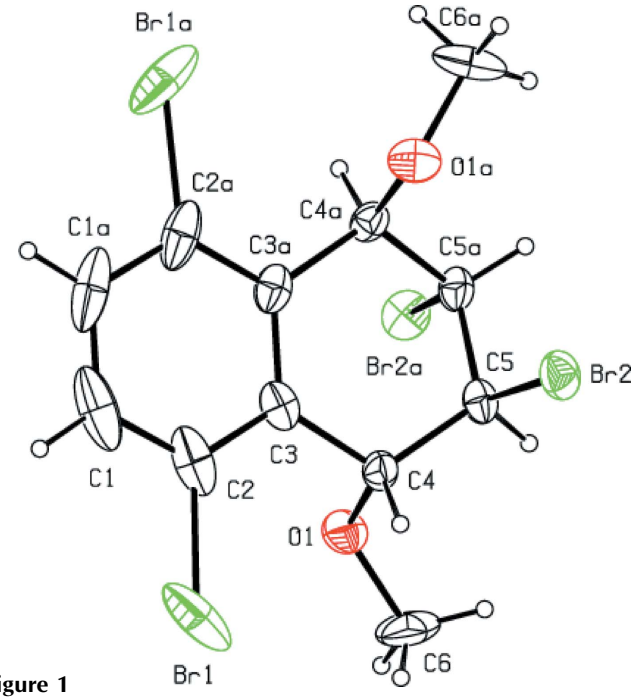


Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Atoms with the suffix a are at the symmetry position $(-x, y, \frac{1}{2}-z)$.

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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supporting information

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Crystal data

$C_{12}H_{12}Br_4O_2$
$M_r = 507.82$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 17.546$ (5) Å
$b = 12.522$ (5) Å
$c = 7.405$ (5) Å
$\beta = 113.207$ (5)°
$V = 1495.3$ (12) Å^3
$Z = 4$
$F(000) = 960$
$D_x = 2.256$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4073 reflections
$\theta = 2.1$–$24.3°$
$\mu = 10.76$ mm^{-1}
$T = 296$ K
Prism, colourless
0.28 × 0.23 × 0.16 mm

Data collection

Stoe IPDS II diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
ω scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
$T_{min} = 0.084$, $T_{max} = 0.203$
6748 measured reflections
1611 independent reflections
797 reflections with $I > 2\sigma(I)$
$R_{int} = 0.142$
$\theta_{max} = 27.1°$, $\theta_{min} = 2.1°$
$h = -22 \rightarrow 22$
$k = -16 \rightarrow 15$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.150$
$S = 1.01$
1611 reflections
82 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.9739P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.19717 (12)	1.04368 (15)	0.3341 (2)	0.1433 (8)
Br2	0.07083 (7)	1.36218 (9)	0.58829 (16)	0.0740 (4)
O1	0.1061 (4)	1.2535 (6)	0.1056 (9)	0.072 (3)
C1	0.0435 (10)	0.9536 (10)	0.268 (2)	0.127 (8)
C2	0.0824 (9)	1.0510 (10)	0.2830 (14)	0.095 (5)
C3	0.0427 (6)	1.1449 (7)	0.2669 (12)	0.061 (3)
C4	0.0898 (6)	1.2484 (7)	0.2789 (13)	0.054 (3)
C5	0.0468 (6)	1.3467 (7)	0.3054 (13)	0.057 (3)
C6	0.1765 (7)	1.3157 (13)	0.128 (2)	0.113 (6)
H1	0.07250	0.88990	0.28020	0.1530*
H4	0.14310	1.24310	0.39150	0.0650*
H5	0.06960	1.40860	0.26290	0.0680*
H6A	0.18360	1.31740	0.00600	0.1700*
H6B	0.22480	1.28470	0.22810	0.1700*
H6C	0.16900	1.38700	0.16540	0.1700*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1554 (15)	0.1830 (17)	0.0819 (9)	0.1213 (14)	0.0366 (9)	0.0053 (9)
Br2	0.0845 (8)	0.0729 (7)	0.0622 (6)	0.0003 (6)	0.0265 (5)	−0.0178 (6)
O1	0.073 (5)	0.093 (5)	0.057 (4)	−0.004 (4)	0.033 (4)	−0.018 (4)
C1	0.25 (2)	0.068 (8)	0.059 (7)	0.068 (10)	0.057 (15)	0.019 (7)
C2	0.159 (13)	0.069 (8)	0.045 (6)	0.047 (8)	0.026 (7)	0.009 (5)
C3	0.084 (6)	0.056 (5)	0.043 (5)	0.015 (5)	0.024 (5)	0.004 (5)
C4	0.047 (5)	0.047 (5)	0.057 (5)	0.003 (4)	0.009 (4)	−0.006 (4)
C5	0.072 (6)	0.041 (5)	0.060 (5)	0.004 (4)	0.028 (5)	0.000 (4)
C6	0.065 (7)	0.186 (14)	0.111 (10)	−0.042 (9)	0.059 (7)	−0.032 (10)

Geometric parameters (Å, º)

Br1—C2	1.899 (16)	C4—C5	1.497 (14)
Br2—C5	1.977 (9)	C5—C5^{i}	1.519 (15)
O1—C4	1.422 (12)	C1—H1	0.9312
O1—C6	1.414 (16)	C4—H4	0.9796
C1—C2	1.381 (19)	C5—H5	0.9793
C1—C1^{i}	1.44 (3)	C6—H6A	0.9596
C2—C3	1.348 (16)	C6—H6B	0.9609
C3—C4	1.521 (13)	C6—H6C	0.9591
C3—C3^{i}	1.419 (16)		

Br1···O1	3.192 (8)	C6···Br2^{vii}	3.730 (14)
Br1···C6	3.692 (16)	C6···Br1^{viii}	3.557 (16)
Br1···Br1^{ii}	3.861 (3)	C5···H6C	2.7710
Br1···C6^{iii}	3.557 (16)	C6···H5	2.7103
Br1···Br1^{iv}	3.861 (3)	H1···O1^{ii}	2.8738
Br2···C6^{v}	3.730 (14)	H4···Br1	2.7630
Br2···O1^{i}	3.168 (8)	H4···H6B	2.2710
Br1···H6C^{iii}	3.0588	H5···C6	2.7103
Br1···H4	2.7630	H5···H6C	2.1514
Br1···H6B	3.2031	H5···Br2^{ix}	3.1516
Br2···H6A^{v}	2.9956	H6A···Br2^{vii}	2.9956
Br2···H5^{vi}	3.1516	H6B···Br1	3.2031
O1···Br1	3.192 (8)	H6B···H4	2.2710
O1···Br2^{i}	3.168 (8)	H6C···C5	2.7710
O1···H1^{iv}	2.8738	H6C···H5	2.1514
C6···Br1	3.692 (16)	H6C···Br1^{viii}	3.0588

C4—O1—C6	113.3 (8)	C2—C1—H1	121.00
C1^{i}—C1—C2	117.9 (13)	C1^{i}—C1—H1	121.06
Br1—C2—C1	115.2 (11)	O1—C4—H4	107.89
Br1—C2—C3	122.0 (10)	C3—C4—H4	107.85
C1—C2—C3	122.8 (15)	C5—C4—H4	107.80
C2—C3—C4	119.2 (11)	Br2—C5—H5	108.63
C2—C3—C3^{i}	119.3 (10)	C4—C5—H5	108.54
C3^{i}—C3—C4	121.5 (8)	C5^{i}—C5—H5	108.54
O1—C4—C3	106.5 (7)	O1—C6—H6A	109.47
O1—C4—C5	111.9 (7)	O1—C6—H6B	109.40
C3—C4—C5	114.7 (9)	O1—C6—H6C	109.50
Br2—C5—C4	108.2 (6)	H6A—C6—H6B	109.45
Br2—C5—C5^{i}	107.8 (7)	H6A—C6—H6C	109.55
C4—C5—C5^{i}	115.0 (8)	H6B—C6—H6C	109.45

C6—O1—C4—C3	−154.3 (9)	C3^{i}—C3—C4—C5	15.3 (12)
C6—O1—C4—C5	79.6 (11)	C2—C3—C3^{i}—C4^{i}	177.8 (8)
C1^{i}—C1—C2—C3	0.5 (18)	C4—C3—C3^{i}—C2^{i}	177.8 (8)
C1^{i}—C1—C2—Br1	179.2 (10)	C4—C3—C3^{i}—C4^{i}	−4.2 (12)
C2—C1—C1^{i}—C2^{i}	−0.7 (19)	O1—C4—C5—C5^{i}	84.2 (10)
Br1—C2—C3—C3^{i}	−178.6 (6)	C3—C4—C5—Br2	83.3 (8)
Br1—C2—C3—C4	3.4 (12)	C3—C4—C5—C5^{i}	−37.3 (11)
C1—C2—C3—C4	−178.1 (10)	O1—C4—C5—Br2	−155.3 (7)
C1—C2—C3—C3^{i}	0.0 (15)	C4—C5—C5^{i}—C4^{i}	49.7 (11)
C2—C3—C3^{i}—C2^{i}	−0.3 (13)	Br2—C5—C5^{i}—C4^{i}	−71.1 (8)
C2—C3—C4—O1	69.0 (10)	C4—C5—C5^{i}—Br2^{i}	−71.1 (8)

C2—C3—C4—C5	−166.7 (8)	Br2—C5—C5^{i}—Br2^{i}	168.2 (4)
C3^{i}—C3—C4—O1	−109.0 (9)		

Symmetry codes: (i) −*x*, *y*, −*z*+1/2; (ii) *x*, −*y*+2, *z*+1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) *x*, −*y*+2, *z*−1/2; (v) *x*, *y*, *z*+1; (vi) *x*, −*y*+3, *z*+1/2; (vii) *x*, *y*, *z*−1; (viii) −*x*+1/2, *y*+1/2, −*z*+1/2; (ix) *x*, −*y*+3, *z*−1/2.