

Tuncer Hökelek,^{a*} Ahmet Tutar^b
and Osman Çakmak^b^aHacettepe University, Department of Physics,
06532 Beytepe, Ankara, Turkey, and^bGaziosmanpasa University, Department of
Chemistry, Tokat, TurkeyCorrespondence e-mail:
merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$

R factor = 0.033

wR factor = 0.080

Data-to-parameter ratio = 16.5

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans,cis,trans*-1,2,3,4,9,10-Hexabromo-1,2,3,4-tetrahydroanthracene

The title compound, $\text{C}_{14}\text{H}_8\text{Br}_6$, consists of a tetrahydroanthracene skeleton composed of a six-membered ring *A* with four bromine atoms in *trans,cis,trans* configuration held in a boat conformation and two six-membered nearly coplanar rings *B* and *C*, where the ring *B* carries two Br atoms. The repulsive interactions between the Br atoms affect the topology of the tetrahydroanthracene moieties.

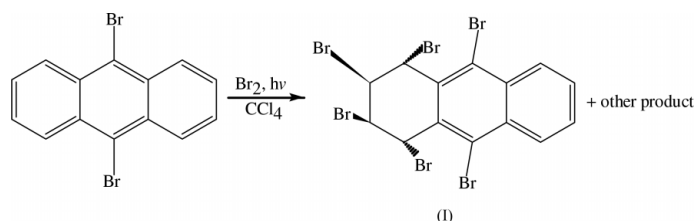
Received 27 November 2001

Accepted 30 November 2001

Online 8 December 2001

Comment

Bromination of aromatic compounds with elemental bromine is well known. Aromatic bromination generally requires the use of a catalyst and often gives a mixture of products (Hamanou *et al.*, 1984). Monohalogenation of benzenoid aromatics generally does not need any catalyst, unlike benzene, although further halogenation generally needs a catalyst. Therefore, synthesis of bromosubstituted anthracenes is restricted by the starting anthracene because reactivity is reduced towards bromine after some initial stages (Gieman, 1967).



Bromination of 9,10-dibromoanthracene is important in view of the synthesis of further brominated anthracene derivatives (Pac & Sakurai, 1969). For example, polyfunctionalization of anthracene may afford a synthesis of anthraquinone dyes, which provide the best example of the versatility of bromine in dye stuffs. Anthraquinone dyes comprise a large group, members of which can be indexed in different ways depending on their substituent group. Bromoanthraquinones are frequently used as intermediates. Brominated diaminodihydroxyanthraquinones are useful disperse dyes with good light fastness (Sumitomo Chem. Co. Ltd, 1984; Mitsubishi Chem. Ind. Co. Ltd, 1981).

9,10-Dibromoanthracene was photobrominated using a projector lamp in CCl_4 at room temperature. The reaction gives a mixture of products. The title compound, (I), was obtained as a major component. Because of the very close structural similarity, we were not able to make a clear-cut differentiation between the stereochemistries in any of these compounds containing four bromo substituents at sp^3 hybridized C atoms. Therefore, we carried out the structure deter-

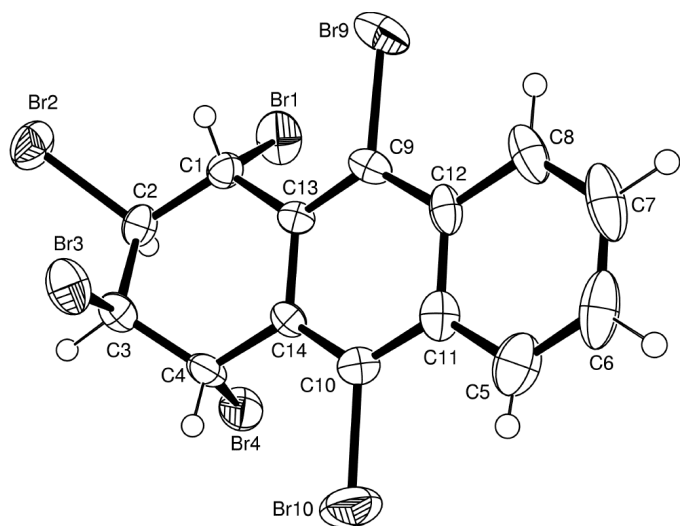


Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

mination of the isomer (I) shown in the Scheme.

The molecule (Fig. 1) contains the tetrahydroanthracene skeleton, composed of a six-membered ring *A* (C1–C4/C13/C14) with four Br atoms in a *trans,cis,trans* configuration, held in a boat conformation, and two six-membered nearly coplanar rings *B* (C9–C14) and *C* (C5–C8/C11/C12), where ring *B* carries two Br atoms. The Br3–C3–C2 [113.4 (4)°], Br1–C1–C13 [111.2 (4)°], Br2–C2–C3 [112.0 (4)°] and Br9–C9–C13 [119.7 (4)°] angles are larger than the other angles around the C3, C1, C2 and C9 atoms, respectively. This behaviour appears to be the result of the repulsive interactions between the related Br atoms. In contrast, the Br–C–C angles around C4 [Br4–C4–C3 109.1 (4)° and Br4–C4–C14 109.4 (4)°] and C10 [Br10–C10–C14 118.1 (4)° and Br10–C10–C11 118.2 (4)°] are the same.

An examination of the deviations from the least-squares planes through the individual rings shows that ring *A* is not planar, with a maximum deviation for atom C3 [–0.346 (6) Å], while rings *B* and *C* are planar. These rings are also twisted with respect to each other; the dihedral angles between the least-squares planes are *A/B* = 14.9 (2)°, *A/C* = 16.3 (2)° and *B/C* = 1.8 (2)°. In ring *A*, the puckering parameters, *i.e.* the angles between the mean plane C1/C2/C4/C14 with C1/C13/C14 and C2/C3/C4 are 6.2 (5)° and 46.3 (4)°, respectively. Ring *A* has a boat conformation.

Experimental

A mixture of dibromoanthracene (1.00 g, 2.98 mmol) and bromine (1.20 g, 7.44 mmol) in chloroform (15 ml) was externally irradiated with a 150 W projector lamp for 2 h at 303 K. The reaction was monitored by TLC and the solvent together with excess bromine was removed under reduced pressure. The residue was chromatographed

using silica gel. Compound (I) was recrystallized from chloroform; yield 1.56 g (m.p. 353 K).

Crystal data

$C_{14}H_8Br_6$
 $M_r = 655.60$
 Triclinic, $P\bar{1}$
 $a = 7.929 (1) \text{ \AA}$
 $b = 8.402 (1) \text{ \AA}$
 $c = 13.285 (1) \text{ \AA}$
 $\alpha = 79.759 (5)^\circ$
 $\beta = 82.136 (6)^\circ$
 $\gamma = 72.503 (5)^\circ$
 $V = 827.31 (14) \text{ \AA}^3$

$Z = 2$
 $D_x = 2.632 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9\text{--}18^\circ$
 $\mu = 14.55 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Rod, colourless
 $0.3 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.190$, $T_{\max} = 0.234$
 3596 measured reflections
 3347 independent reflections
 2228 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 26.3^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 9$
 $l = -16 \rightarrow 16$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.080$
 $S = 1.02$
 3347 reflections
 203 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 1.4128P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C4–Br4	1.993 (6)	C2–Br2	1.955 (5)
C1–Br1	1.991 (5)	Br9–C9	1.887 (5)
C3–Br3	1.967 (6)	Br10–C10	1.899 (5)
C14–C4–Br4	109.4 (4)	C3–C2–Br2	112.0 (4)
C3–C4–Br4	109.1 (4)	C1–C2–Br2	110.9 (4)
C13–C1–Br1	111.2 (4)	C13–C9–Br9	119.7 (4)
C2–C1–Br1	104.8 (4)	C12–C9–Br9	117.0 (4)
C4–C3–Br3	106.0 (4)	C14–C10–Br10	118.1 (4)
C2–C3–Br3	113.4 (4)	C11–C10–Br10	118.2 (4)
Br4–C4–C3–Br3	171.5 (2)	C13–C14–C10–Br10	–177.5 (4)
Br3–C3–C2–Br2	–58.4 (5)	Br9–C9–C12–C11	–179.2 (4)
Br1–C1–C2–Br2	–91.4 (4)	Br10–C10–C11–C12	178.2 (4)
Br9–C9–C13–C14	179.8 (4)		

Most of the H atoms were located from difference maps and refined isotropically; the C–H lengths are 0.80 (7)–1.02 (5) Å. The positions of the remaining H atoms (H6 and H8) were calculated geometrically at distances of 0.93 Å (CH) from the corresponding C atoms, and a riding model was used during the refinement process.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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).

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gieman, H. (1967). Editor. *Organic Syntheses*, p. 207. New York: Wiley.
- Hamanoue, K., Tai, S., Hidaka, T., Nakayama, T., Kimoto, M. & Teranishi, H. (1984). *J. Phys. Chem.* **88**, 4380–4384.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Mitsubishi Chem. Ind. Co. Ltd (1981). Japanese Pat. JP 56/163151 A2 (Dec. 1981), to Mitsubishi Chem. Ind. Co. Ltd.; *Chem. Abs.* (1982). **96**, 124524a.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pac, C. & Sakurai, H. (1969). *Tetrahedron Lett.* pp. 3829–3832.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sumitomo Chem. Co. Ltd (1984). Japanese Pat. JP 84/150185 (Aug 1984), to Sumitomo Chem. Co. Ltd.; *Chem. Abs.* (1985). **102**, 9690y.