

Crystal structure of 4,5-dibromophenanthrene

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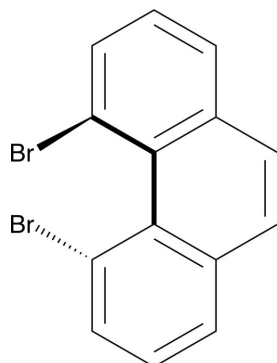
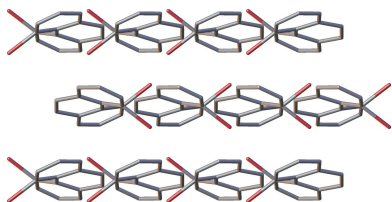
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The synthesis and crystal structure of the title compound, $C_{14}H_8Br_2$, is described. The molecule is positioned on a twofold rotation axis and the asymmetric unit consists of half a molecule with the other half being generated by symmetry. The presence of two large bromine atoms in the bay region significantly distorts the molecule from planarity and the mean planes of the two terminal rings of the phenanthrene system are twisted away from each other by $28.51(14)^\circ$. The torsion angle between the two C–Br bonds is $74.70(14)^\circ$ and the distance between the two Br atoms is $3.2777(13)$ Å. The molecules pack in layers in the crystal, with the centroids of the central rings of the phenanthrene units in adjacent layers separated by a distance of $4.0287(10)$ Å. These centroids are shifted by $2.266(6)$ Å relative to each other, indicating slippage in the stacking arrangement. Furthermore, the distance between the centroids of the terminal and central rings of the phenanthrene units in adjacent layers is slightly shorter at $3.7533(19)$ Å. While all of the molecules within each layer are oriented in the same direction, those in adjacent layers are oriented in the opposite direction, leading to anti-parallel stacks.

1. Chemical context

In the course of our research into non-planar polycyclic hydrocarbons, we became interested in the preparation of helical phenanthrene systems bearing bulky substituents in the 4- and 5-positions. Towards that end, we undertook the synthesis of 4,5-dibromophenanthrene (**2**) from the known dialdehyde **1** (Suzuki *et al.*, 2009) using a recently published procedure (Xia *et al.*, 2012), as shown in Fig. 1. Although there is one reference to the title compound **2** in the literature (Cosmo *et al.*, 1987*a*), neither the procedure for its synthesis nor its X-ray crystal structure has previously been reported.



2. Structural commentary

The asymmetric unit consists of half a molecule with the other half generated by symmetry as the molecule is positioned on a

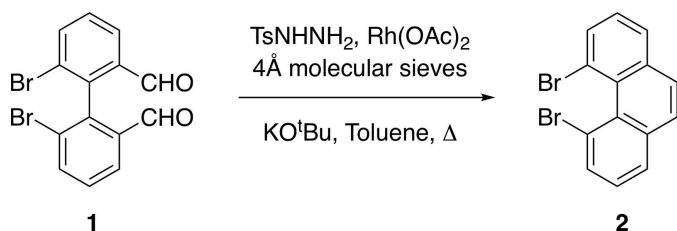


Figure 1
Synthesis of 4,5-dibromophenanthrene (**2**).

twofold rotation axis that bisects the central ring. The crystal structure shows a deformed phenanthrene framework (Fig. 2) in which the planes of the two terminal rings are twisted away from each other by $28.51(14)^\circ$ and the torsion angle between the two C–Br bonds (Br1–C4–C4'–Br1') is $74.70(14)^\circ$. The C4–C5–C5'–C4' torsion angle is $32.8(6)^\circ$, and the distance between the two bromine atoms is $3.277(13) \text{ \AA}$, a value consistent with a previous report (Cosmo *et al.*, 1987*a*). A comparison of the key structural features of the title compound **2** to those of other known 4,5-dihalophenanthrenes (Cosmo *et al.*, 1987*b*; Bock *et al.*, 1998) is presented in Table 1 with reference to the general structure shown in Fig. 3. The

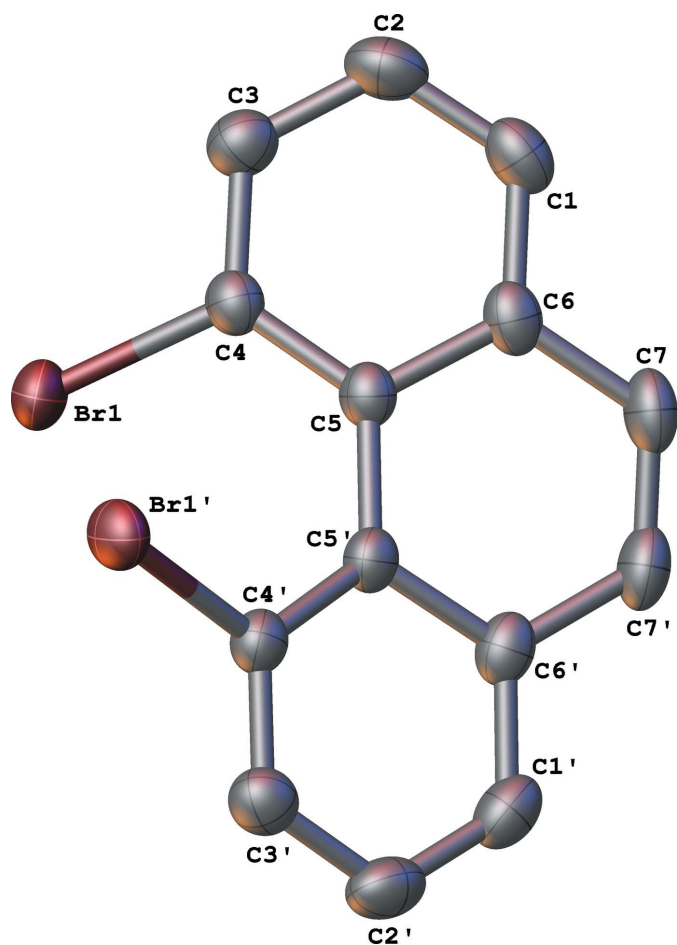


Figure 2
Crystal structure of **2** with displacement ellipsoids shown at the 50% probability level. H atoms omitted for clarity. [Symmetry code: (') $1 - x, + y, \frac{3}{2} - z$].

Table 1

A comparison of selected structural parameters (\AA , $^\circ$) in a series of known 4,5-dihalophenanthrene derivatives.

Refer to Fig. 3 for parameters used in this table.

Compound	angle between rings A and C	$X \cdots X$ distance	C4–C4'–C5'–C5 torsion angle	X –C4–C5– X torsion angle
3 ($X = \text{F}$) ^a	16.779	2.381	19.954	43.273
4 ($X = \text{Cl}$) ^a	32.282	3.097	37.738	69.980
2 ($X = \text{Br}$) ^b	28.51 (14) ^b	3.277 (13) ^c	32.8 (6)	74.70 (14)
5 ($X = \text{I}$) ^d	29.451	3.610	33.716	78.611

Notes: (a) Cosmo *et al.* (1987*b*); (b) this work; (c) Cosmo *et al.* 1987*a*); (d) Bock *et al.* (1998).

distance between the two halogen atoms, and the torsion angle between the two carbon–halogen bonds (X –C4–C5– X), increase as expected with the increasing size of the halogen atom. Interestingly, however, the distortion of the phenanthrene framework, as measured by either the angle between the mean planes of the terminal rings A and C, or the C4–C4'–C5'–C5 torsion angle (see Fig. 3), is the largest for the dichloro derivative **4** (Table 1), larger than for the dibromo and diiodo compounds. A combination of both size *and* electronegativity may account for compound **4** showing the largest twist of the phenanthrene system in the series of 4,5-dihalophenanthrene compounds.

3. Supramolecular features

A view of the crystal packing diagram, along the *b* axis, shows the centroids of the central B rings of the phenanthrene units

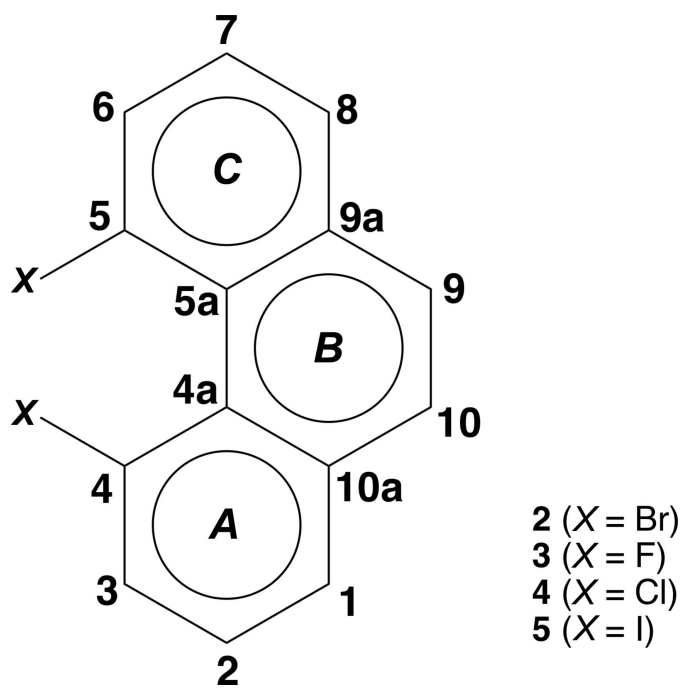


Figure 3
The 4,5-dihalo derivatives of phenanthrene shown with conventional chemical numbering. This figure is used as a reference for the data in Table 1.

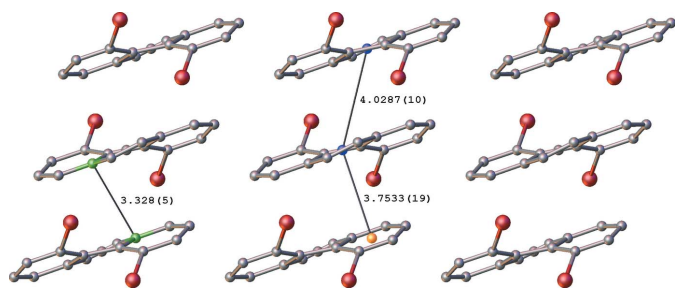


Figure 4

Crystal packing of **2** when viewed along the *b* axis. The separation between the centroids of the middle rings (blue spheres) is slightly longer than that between the centroids of the middle and terminal rings (blue and orange spheres) in adjacent layers. Close contacts are also observed between equivalent carbon atoms in the terminal rings (shown in green) that are offset from each other. All lengths are in Å.

in adjacent layers (marked in blue in Fig. 4, see Fig. 3 for ring numbering), separated by a distance of 4.0287 (10) Å. These (blue) centroids are shifted by 2.266 (6) Å relative to each other, indicating a slippage in the stacking arrangement. This ring slippage is also evidenced by the centroid of the *B* ring being at a shorter distance of 3.7533 (19) Å to the *A* ring centroid (shown in orange in Fig. 4) of the closest phenanthrene unit in an adjacent layer. In addition, short contacts of 3.328 (5) Å are found between C6 (or C6'; refer to Fig. 2. for atom numbering) and an equivalent carbon atom in an adjacent layer. These atoms, which are in terminal rings offset from each other, are shown in green in Fig. 4. A view along the *a* axis (Fig. 5) shows the opposing orientation of the molecules in going from one layer to the next, leading to anti-parallel stacks.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.38, update November 2016; Groom *et al.*, 2016) reveals entries for 4,5-difluorophenanthrene (refcode: FIXWOY; Cosmo *et al.*, 1987*a*), 4,5-dichlorophenanthrene (refcode: FIXWUE; Cosmo *et al.*, 1987*b*), and 4,5-diiodophenanthrene (refcode: PIPRUB;

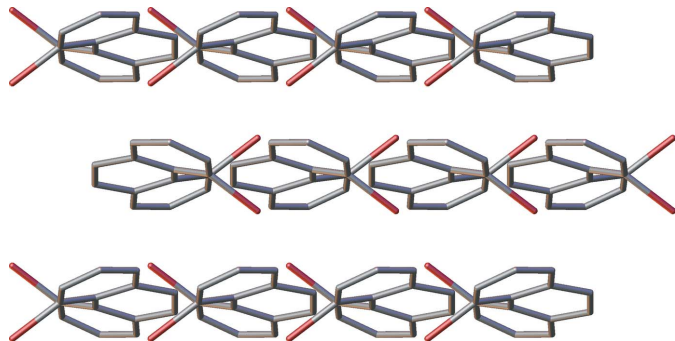


Figure 5

Crystal packing of **2** when viewed along the *a* axis, showing the opposite orientation of molecules in alternating layers.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₈ Br ₂
<i>M_r</i>	336.02
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.840 (3), 8.6112 (16), 8.1418 (15)
β (°)	103.735 (2)
<i>V</i> (Å ³)	1146.9 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	7.03
Crystal size (mm)	0.25 × 0.11 × 0.07
Data collection	
Diffractometer	Bruker D8 QUEST ECO
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.47, 0.64
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4708, 1203, 1070
<i>R_{int}</i>	0.033
(sin θ/λ) _{max} (Å ⁻¹)	0.634
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.083, 1.06
No. of reflections	1203
No. of parameters	73
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.01, −0.35

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2015), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Bock *et al.*, 1998). The title compound, 4,5-dibromophenanthrene (**2**), however, is not in the database.

5. Synthesis and crystallization

The dialdehyde **1** (108 mg, 0.3 mmol), *p*-toluenesulfonyl hydrazide (114 mg, 0.6 mmol), and toluene (2 mL) were successively added to a flame-dried flask under argon. The milky white mixture was heated at 333 K and stirred for 10 min. More toluene (14 mL) was added, and the solution was cooled to room temperature. Then, 4 Å molecular sieves (100 mg), KO^tBu (100 mg, 0.9 mmol), Rh₂(OAc)₄ (2 mg, 0.005 mmol), and toluene (14 mL) were added successively. The reaction system was degassed with argon and the resulting solution was stirred at 363 K for 1 h, producing a deep brown-red color after 20 min. The mixture was cooled to room temperature and the crude product was purified by silica gel column chromatography to give **2**, as colorless crystals (24 mg, 0.07 mmol, 23%). m.p. 443–444 K; ¹H NMR (500 MHz, CDCl₃) δ 7.40 (*m*, 1H), 7.50 (*m*, 1H), 7.70 (*m*, 1H), 7.80 (*m*, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 135, 132, 129, 128, 127, 126, 122. LRMS (EI) *m/z* 335.9 (*M*⁺), 255, 176. Crystals suitable for X-ray analysis were grown by the slow diffusion of pentane into a concentrated solution of **2** in dichloromethane.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Crystal structure of 4,5-dibromophenanthrene

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

4,5-Dibromophenanthrene

Crystal data

$C_{14}H_8Br_2$

$M_r = 336.02$

Monoclinic, $C2/c$

$a = 16.840$ (3) Å

$b = 8.6112$ (16) Å

$c = 8.1418$ (15) Å

$\beta = 103.735$ (2)°

$V = 1146.9$ (4) Å³

$Z = 4$

$F(000) = 648$

$D_x = 1.946$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3136 reflections

$\theta = 2.5$ – 26.8 °

$\mu = 7.03$ mm⁻¹

$T = 173$ K

Block, clear colourless

$0.25 \times 0.11 \times 0.07$ mm

Data collection

Bruker D8 QUEST ECO
diffractometer

Radiation source: sealed tube, Siemens
KFFMO2K-90C

Curved graphite monochromator

Detector resolution: 8.3660 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.47$, $T_{\max} = 0.64$

4708 measured reflections

1203 independent reflections

1070 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 26.8$ °, $\theta_{\min} = 2.5$ °

$h = -21 \rightarrow 21$

$k = -10 \rightarrow 10$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.083$

$S = 1.06$

1203 reflections

73 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.5337P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 1.01$ e Å⁻³

$\Delta\rho_{\min} = -0.35$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.41183 (2)	0.94243 (3)	0.60761 (4)	0.03791 (16)
C1	0.35716 (18)	0.4938 (4)	0.8748 (4)	0.0403 (7)
H1	0.34	0.3985	0.914	0.048*
C2	0.31143 (18)	0.6255 (4)	0.8762 (4)	0.0440 (7)
H2	0.2652	0.6234	0.9242	0.053*
C3	0.33332 (16)	0.7628 (4)	0.8065 (4)	0.0384 (6)
H3	0.2992	0.8517	0.7974	0.046*
C5	0.45980 (15)	0.6426 (3)	0.7686 (3)	0.0295 (6)
C4	0.40447 (15)	0.7692 (3)	0.7508 (3)	0.0313 (5)
C6	0.42910 (17)	0.4984 (3)	0.8160 (3)	0.0332 (6)
C7	0.46876 (18)	0.3558 (3)	0.7880 (4)	0.0400 (7)
H7	0.4503	0.2602	0.8239	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0421 (2)	0.0281 (2)	0.0447 (2)	0.00648 (10)	0.01255 (15)	0.00529 (10)
C1	0.0409 (16)	0.0388 (16)	0.0393 (16)	-0.0115 (14)	0.0055 (12)	0.0039 (13)
C2	0.0334 (14)	0.055 (2)	0.0458 (17)	-0.0090 (14)	0.0138 (12)	-0.0033 (14)
C3	0.0327 (13)	0.0406 (16)	0.0411 (15)	0.0008 (12)	0.0073 (11)	-0.0026 (12)
C5	0.0313 (12)	0.0261 (13)	0.0296 (13)	-0.0020 (10)	0.0041 (10)	-0.0016 (9)
C4	0.0336 (13)	0.0275 (13)	0.0323 (12)	-0.0021 (10)	0.0069 (10)	-0.0008 (10)
C6	0.0361 (14)	0.0290 (14)	0.0309 (13)	-0.0031 (12)	0.0006 (11)	0.0027 (11)
C7	0.0508 (17)	0.0229 (13)	0.0420 (16)	-0.0040 (11)	0.0027 (13)	0.0012 (11)

Geometric parameters (\AA , $^\circ$)

Br1—C4	1.916 (3)	C3—H3	0.95
C1—C2	1.373 (5)	C5—C4	1.419 (4)
C1—C6	1.405 (4)	C5—C6	1.433 (4)
C1—H1	0.95	C5—C5 ⁱ	1.456 (5)
C2—C3	1.398 (5)	C6—C7	1.441 (4)
C2—H2	0.95	C7—C7 ⁱ	1.341 (6)
C3—C4	1.379 (4)	C7—H7	0.95
C2—C1—C6	120.7 (3)	C6—C5—C5 ⁱ	117.96 (17)
C2—C1—H1	119.6	C3—C4—C5	122.5 (3)
C6—C1—H1	119.6	C3—C4—Br1	114.7 (2)
C1—C2—C3	119.5 (3)	C5—C4—Br1	121.6 (2)

C1—C2—H2	120.2	C1—C6—C5	120.8 (3)
C3—C2—H2	120.2	C1—C6—C7	120.0 (3)
C4—C3—C2	120.0 (3)	C5—C6—C7	119.0 (3)
C4—C3—H3	120.0	C7 ⁱ —C7—C6	121.13 (18)
C2—C3—H3	120.0	C7 ⁱ —C7—H7	119.4
C4—C5—C6	115.0 (2)	C6—C7—H7	119.4
C4—C5—C5 ⁱ	126.84 (17)		
C6—C1—C2—C3	4.9 (4)	C2—C1—C6—C5	4.9 (4)
C1—C2—C3—C4	-5.9 (4)	C2—C1—C6—C7	-169.4 (3)
C2—C3—C4—C5	-3.1 (4)	C4—C5—C6—C1	-13.0 (4)
C2—C3—C4—Br1	164.5 (2)	C5 ⁱ —C5—C6—C1	171.6 (3)
C6—C5—C4—C3	12.2 (4)	C4—C5—C6—C7	161.3 (2)
C5 ⁱ —C5—C4—C3	-172.8 (3)	C5 ⁱ —C5—C6—C7	-14.1 (4)
C6—C5—C4—Br1	-154.6 (2)	C1—C6—C7—C7 ⁱ	171.4 (3)
C5 ⁱ —C5—C4—Br1	20.4 (4)	C5—C6—C7—C7 ⁱ	-2.9 (5)

Symmetry code: (i) $-x+1, y, -z+3/2$.

?