organic compounds

9,10-Dibromophenanthrene

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The molecule of the title compound, $C_{14}H_8Br_2$, is almost planar [maximum deviation 0.0355 (7) Å] and possesses crystallographic twofold ($C2$) symmetry. In the crystal, the molecules form face-to-face slipped antiparallel π–π stacking interactions along the c axis with an interplanar distance 3.471 (7) Å, centroid–centroid distances of 3.617 (5)–3.803 (6) Å.

Related literature

For the first synthesis of the title compound, see: Schmidt & Ladner (1904). For the synthesis of 2,2′-bis(dibromomethyl)biphenyl, see: Bacon & Bankhead (1963). For a related structure, see: Yokota et al. (2012).
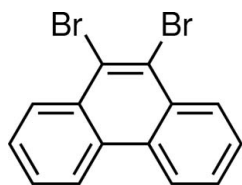
Experimental

Crystal data

$C_{14}H_8Br_2$	$M_r = 336.02$

Monoclinic, $C2/c$
$a = 18.2630$ (15) Å
$b = 9.0963$ (8) Å
$c = 7.3025$ (6) Å
$\beta = 114.499$ (2)°
$V = 1103.91$ (16) Å^3

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 7.31$ mm^{-1}
$T = 223$ K
$0.5 \times 0.1 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{min} = 0.160$, $T_{max} = 0.558$

5151 measured reflections
1257 independent reflections
1011 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.116$
$S = 1.25$
1257 reflections

73 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -1.49$ e Å^{-3}

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR2004* (Burla et al., 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

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supplementary materials

9,10-Dibromophenanthrene

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Comment

Phenanthrene is a polycylic aromatic hydrocarbon (PAH) as well as an important starting material toward fuctionalized π-conjugated molecules. The title compound, 9,10-dibromophenanthrene, was first prepared by Schmidt & Ladner (1904). However, the method involved relatively vigorous reaction conditions, and the title compound was not easily accessible. Therefore, the development of milder methods was pursued. Recently, we established a new method for the preparation of the title compound. Thus, treatment of 2,2′-bis(dibromomethyl)biphenyl (Bacon & Bankhead, 1963) with potassium *t*-butoxide yielded the title compound in a high yield. Securement of the title compound let to obtain single crystals suitable for X-ray analysis. We report herein the crystal structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The molecule possesses C_2 symmetry, and half of the formula unit is crystallographically independent. The molecule is almost planar with the maximum deviation of 0.0355 (7) Å for Br1. The bonds lengths and angles are in good agreement with the standard values. As shown in Fig. 2, the molecules form face-to-face slipped antiparrallel π-π stacking along the direction of the *c* axis. The interplanar distance is 3.471 (7) Å and controid–centroid distances of 3.617 (5)-3.803 (6) Å. Recently, we have reported the crystal structure of 3,6-dibromophenanthrene (Yokota *et al.*, 2012), whose feature was a herrinbone-like arrangement, indicating the difference in packing arrangement depending on the positions of bromo substituents.

Experimental

2,2′-Bis(dibromomethyl)biphenyl, as a starting material, was prepared according to the method described by Bacon & Bankhead (1963). To an ice-cooled solution of 2,2′-bis(dibromomethyl)biphenyl (300 mg, 0.60 mmol) in DMF (6 ml), pottasium *t*-butoxide (1.00 g, 9.05 mmol) was added. After stirring for 30 min, the reaction was quenched with 6*M* HCl. The resulting solid was extracted with toluene, washed with brine, and dried over Na_2SO_4. After evaporation, column chromatography on silica gel (hexane-CH_2Cl_2) produced the title compound (161 mg, 79%) as a pale yellow solid. Single crystals suitable for X-ray analysis were obtained by slow evaporation from a toluene solution.

Refinement

All the aromatic H atoms were positioned geometrically and refined using a riding model with C—H = 0.94 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).
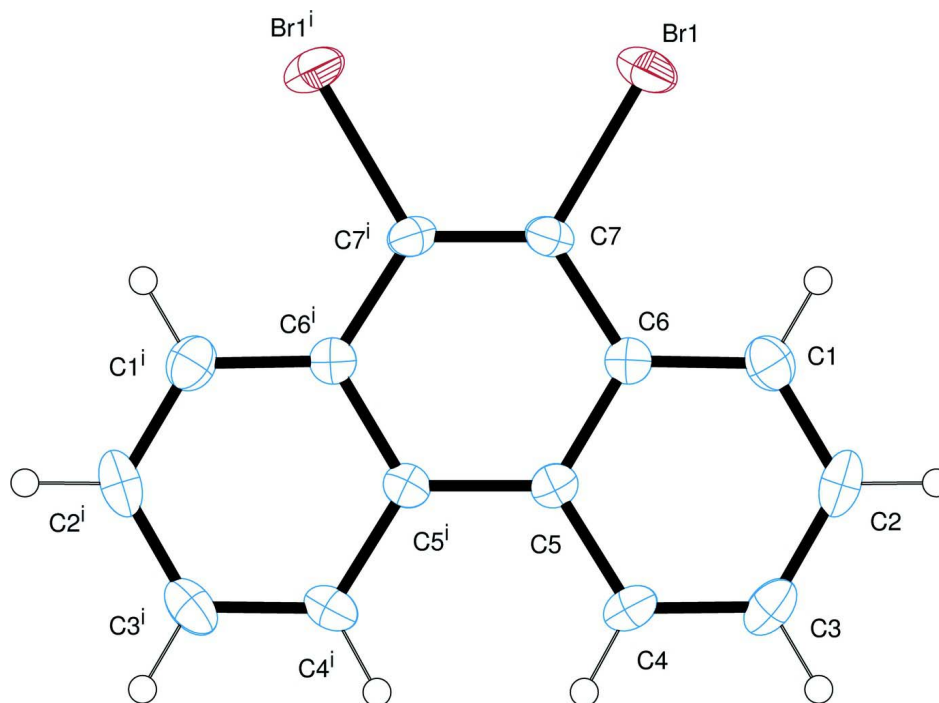
Figure 1

The molecular structure of the title compound, showing 40% probability displacement ellipsoids. Symmetry code: (i) $-x + 1, y, -z + 1/2$.
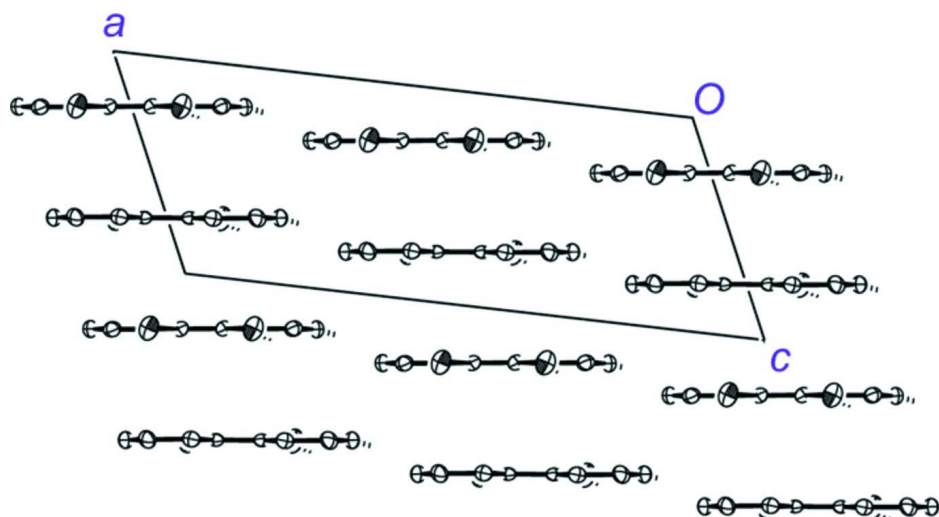
Figure 2

Packing diagram of the title compound viewed along the *b* axis. Hydrogen atoms are omitted for clarity.

9,10-Dibromophenanthrene

Crystal data

$C_{14}H_8Br_2$	Hall symbol: -C 2yc
$M_r = 336.02$	$a = 18.2630\ (15)$ Å
Monoclinic, *C*2/*c*	$b = 9.0963\ (8)$ Å

$c = 7.3025$ (6) Å

$\beta = 114.499$ (2)°

$V = 1103.91$ (16) Å^3

$Z = 4$

$F(000) = 648$

$D_x = 2.022$ Mg m^{-3}

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

Cell parameters from 3170 reflections

$\theta = 3.0$–27.5°

$\mu = 7.31$ mm^{-1}

$T = 223$ K

Needle, colourless

$0.5 \times 0.1 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID
  diffractometer

Radiation source: fine-focus sealed x-ray tube

Graphite monochromator

Detector resolution: 10 pixels mm^{-1}

ω scans

Absorption correction: numerical
  (*NUMABS*; Higashi, 1999)

$T_{min} = 0.160$, $T_{max} = 0.558$

5151 measured reflections

1257 independent reflections

1011 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$

$h = -23 \rightarrow 23$

$k = -11 \rightarrow 11$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.116$

$S = 1.25$

1257 reflections

73 parameters

0 restraints

Primary atom site location: structure-invariant
  direct methods

Hydrogen site location: inferred from
  neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 8.7358P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.67$ e Å^{-3}

$\Delta\rho_{min} = -1.49$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.3372 (3)	0.4275 (6)	0.2001 (7)	0.0341 (11)
H1	0.3099	0.3382	0.1903	0.041*
C2	0.2976 (3)	0.5571 (7)	0.1900 (8)	0.0395 (12)
H2	0.2438	0.5564	0.1738	0.047*
C3	0.3375 (3)	0.6900 (6)	0.2037 (8)	0.0388 (12)
H3	0.3103	0.7791	0.1962	0.047*
C4	0.4163 (3)	0.6916 (5)	0.2284 (7)	0.0320 (10)
H4	0.4425	0.7822	0.2387	0.038*
C5	0.4586 (3)	0.5595 (5)	0.2384 (6)	0.0248 (9)
C6	0.4168 (3)	0.4248 (5)	0.2245 (6)	0.0257 (9)

C7	0.4612 (3)	0.2907 (5)	0.2373 (7)	0.0268 (9)
Br1	0.40654 (4)	0.11098 (6)	0.22296 (10)	0.0491 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.034 (2)	0.039 (3)	0.031 (2)	−0.005 (2)	0.015 (2)	−0.001 (2)
C2	0.025 (2)	0.058 (3)	0.036 (3)	0.011 (2)	0.013 (2)	0.001 (2)
C3	0.033 (3)	0.042 (3)	0.037 (3)	0.014 (2)	0.010 (2)	0.001 (2)
C4	0.036 (2)	0.027 (2)	0.032 (2)	0.0076 (19)	0.012 (2)	−0.0008 (19)
C5	0.028 (2)	0.025 (2)	0.020 (2)	0.0015 (17)	0.0090 (18)	−0.0012 (16)
C6	0.027 (2)	0.028 (2)	0.020 (2)	0.0002 (17)	0.0083 (18)	0.0004 (17)
C7	0.033 (2)	0.021 (2)	0.029 (2)	−0.0036 (17)	0.015 (2)	−0.0008 (17)
Br1	0.0552 (4)	0.0270 (3)	0.0752 (5)	−0.0125 (2)	0.0373 (3)	−0.0035 (3)

Geometric parameters (Å, º)

C1—C2	1.369 (7)	C4—C5	1.415 (6)
C1—C6	1.389 (6)	C4—H4	0.94
C1—H1	0.94	C5—C6	1.424 (6)
C2—C3	1.393 (8)	C5—C5^i	1.449 (9)
C2—H2	0.94	C6—C7	1.447 (6)
C3—C4	1.375 (7)	C7—C7^i	1.349 (9)
C3—H3	0.94	C7—Br1	1.896 (4)
C2—C1—C6	121.5 (5)	C5—C4—H4	119.4
C2—C1—H1	119.2	C4—C5—C6	117.5 (4)
C6—C1—H1	119.2	C4—C5—C5^i	121.8 (3)
C1—C2—C3	119.7 (5)	C6—C5—C5^i	120.7 (3)
C1—C2—H2	120.2	C1—C6—C5	119.7 (4)
C3—C2—H2	120.2	C1—C6—C7	123.5 (4)
C4—C3—C2	120.4 (5)	C5—C6—C7	116.8 (4)
C4—C3—H3	119.8	C7^i—C7—C6	122.5 (2)
C2—C3—H3	119.8	C7^i—C7—Br1	120.42 (14)
C3—C4—C5	121.2 (5)	C6—C7—Br1	117.1 (3)
C3—C4—H4	119.4		
C6—C1—C2—C3	0.2 (8)	C5^i—C5—C6—C1	−179.3 (5)
C1—C2—C3—C4	−0.3 (8)	C4—C5—C6—C7	−179.3 (4)
C2—C3—C4—C5	0.6 (7)	C5^i—C5—C6—C7	0.8 (7)
C3—C4—C5—C6	−0.8 (7)	C1—C6—C7—C7^i	−179.4 (5)
C3—C4—C5—C5^i	179.2 (5)	C5—C6—C7—C7^i	0.5 (8)
C2—C1—C6—C5	−0.4 (7)	C1—C6—C7—Br1	−0.9 (6)
C2—C1—C6—C7	179.6 (5)	C5—C6—C7—Br1	179.1 (3)
C4—C5—C6—C1	0.6 (6)		

Symmetry code: (i) −x+1, y, −z+1/2.