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## Structure Reports

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## 3,6-Dibromophenanthrene

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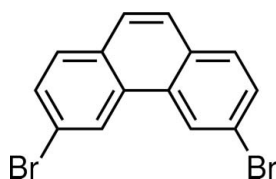
Received 28 September 2012; accepted 4 October 2012

Key indicators: single-crystal X-ray study;  $T = 223$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  
R factor = 0.018; wR factor = 0.037; data-to-parameter ratio = 15.5.

The phenanthrene ring in the title compound,  $\text{C}_{14}\text{H}_8\text{Br}_2$ , is approximately planar [maximum deviation =  $0.039$  (3) Å]. In contrast, the two bromo atoms are displaced slightly from the phenanthrene plane [maximum deviation =  $0.1637$  (3) Å]. In the crystal, the molecules adopt a herringbone-like arrangement and form face-to-face slipped  $\pi$ - $\pi$  stacking interactions along the  $b$  axis, with an interplanar distance of  $3.544$  (3) Å and slippage of  $1.81$  Å. The crystal studied was a racemic twin with a minor twin fraction of  $0.390$  (10).

## Related literature

For the synthesis of the title compound using the improved photocyclization of 4,4'-dibromo-*trans*-stilbene, see: Talele *et al.* (2009). For the original synthesis and applications of the title compound, see: Nakamura *et al.* (1996).



## Experimental

## Crystal data

 $\text{C}_{14}\text{H}_8\text{Br}_2$  $M_r = 336.02$ 

Monoclinic,  $P2_1$   
 $a = 6.8697$  (5) Å  
 $b = 3.9809$  (2) Å  
 $c = 20.5002$  (11) Å  
 $\beta = 93.813$  (2)°  
 $V = 559.39$  (6) Å<sup>3</sup>

$Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 7.21$  mm<sup>-1</sup>  
 $T = 223$  K  
 $0.62 \times 0.08 \times 0.03$  mm

## Data collection

Rigaku R-Axis RAPID  
diffractometer  
Absorption correction: numerical  
(NUMABS; Higashi, 1999)  
 $T_{\min} = 0.196$ ,  $T_{\max} = 0.793$

5372 measured reflections  
2267 independent reflections  
2084 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.037$   
 $S = 1.00$   
2267 reflections  
146 parameters  
1 restraint

H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
831 Friedel pairs  
Flack parameter:  $0.390$  (10)

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).

This work was supported by Grants-in-Aid for Scientific Research from the JSPS and MEXT.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QK2043).

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## supplementary materials

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## 3,6-Dibromophenanthrene

Ruri Yokota, Chitoshi Kitamura and Takeshi Kawase

### Comment

Phenanthrene is a polycyclic aromatic hydrocarbon (PAH) as well as a potential building block for higher-order  $\pi$ -extended PAHs. The title compound, 3,6-dibromophenanthrene, was first prepared by Nakamura *et al.* (1996). The bromo functional group on the aromatic ring is a suitable substrate for a variety of cross-coupling reaction. Recently, the improved synthesis was reported by Talele *et al.* (2009). However, the X-ray structure was not reported to date. We report herein the crystal structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1. The crystal was a racemic twin with a minor twin fraction of 0.390 (10). The molecule is approximately planar except for Br1 and Br2 [the maximum deviation is 0.1637 (3) Å for Br2]. The bonds lengths and angles are in good agreement with the standard values. As shown in Fig. 2, the crystal structure is characterized by a combination of a columnar stacking and a herrinbone-like arrangement. Along the *b* axis, there are two columns per unit cell in which the molecules form face-to-face slipped  $\pi$ -stacks with an interplanar distance of 3.543 Å. The interplanar tilt angle between the phenanthrene rings in two adjacent columns is 54.21°.

### Experimental

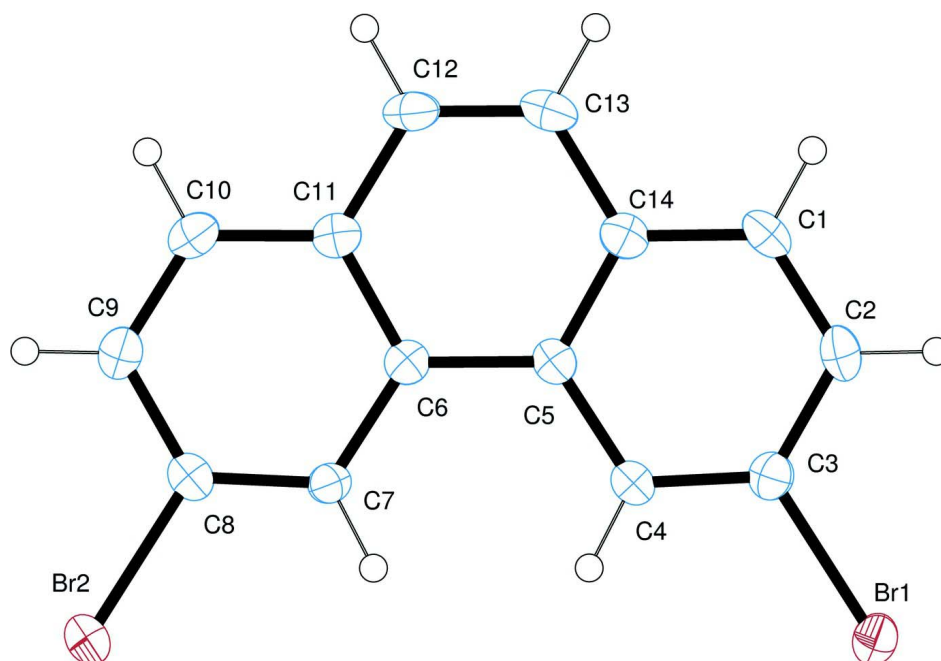
The title compound was prepared from 4,4'-dibromo-*trans*-stilbene according to the literature procedure of Talele *et al.* (2009). The title compound was dissolved in hot hexane. After cooling of the solution to room temperature, single crystals suitable for X-ray analysis were obtained.

### Refinement

All the aromatic H atoms were positioned geometrically and refined using a riding model with C—H = 0.94 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . In final refinement cycles, racemic twinning was taken into account with a TWIN and a BASF instruction of program *SHELXL97* (Sheldrick, 2008), giving a minor twin fraction of 0.390 (10).

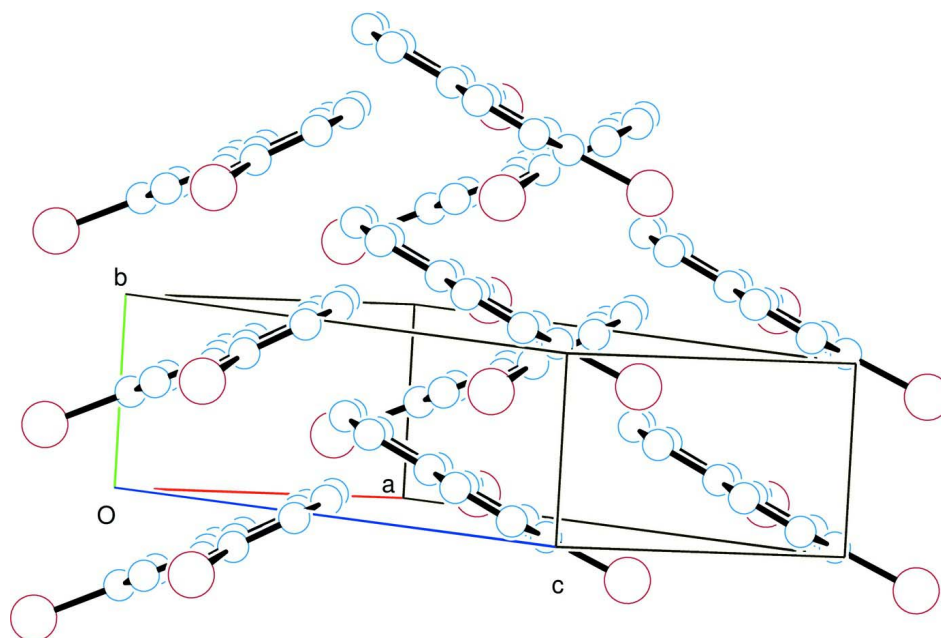
### Computing details

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 (I), showing the atomic numbering and 40% probability displacement ellipsoids.



**Figure 2**

The packing diagram of (I). Hydrogen atoms are omitted for clarity.

### 3,6-Dibromophenanthrene

*Crystal data*

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

Monoclinic,  $P2_1$   
 Hall symbol: P 2yb

$a = 6.8697$  (5) Å  
 $b = 3.9809$  (2) Å  
 $c = 20.5002$  (11) Å  
 $\beta = 93.813$  (2)°  
 $V = 559.39$  (6) Å<sup>3</sup>  
 $Z = 2$   
 $F(000) = 324$   
 $D_x = 1.995$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 4191 reflections  
 $\theta = 3.1$ – $27.5$ °  
 $\mu = 7.21$  mm<sup>-1</sup>  
 $T = 223$  K  
 Needle, colorless  
 $0.62 \times 0.08 \times 0.03$  mm

*Data collection*

Rigaku R-AXIS RAPID  
 diffractometer  
 Radiation source: fine-focus sealed x-ray tube  
 Graphite monochromator  
 Detector resolution: 10 pixels mm<sup>-1</sup>  
 $\omega$  scans  
 Absorption correction: numerical  
 (NUMABS; Higashi, 1999)  
 $T_{\min} = 0.196$ ,  $T_{\max} = 0.793$

5372 measured reflections  
 2267 independent reflections  
 2084 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.1$ °  
 $h = -8 \rightarrow 8$   
 $k = -5 \rightarrow 4$   
 $l = -26 \rightarrow 26$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.037$   
 $S = 1.00$   
 2267 reflections  
 146 parameters  
 1 restraint  
 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0175P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 831 Friedel  
 pairs  
 Flack parameter: 0.390 (10)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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  $F^2 > \sigma(F^2)$  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<sup>2</sup>)*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.1808 (4)	0.2590 (6)	0.88179 (11)	0.0315 (7)
H1	-0.2947	0.3158	0.9023	0.038*
C2	-0.0292 (4)	0.1043 (7)	0.91762 (12)	0.0313 (6)
H2	-0.0389	0.0537	0.9621	0.038*
C3	0.1384 (4)	0.0249 (7)	0.88644 (11)	0.0270 (6)
C4	0.1569 (4)	0.0897 (6)	0.82192 (11)	0.0249 (6)
H4	0.2724	0.0318	0.8025	0.03*

C5	0.0013 (4)	0.2449 (6)	0.78399 (11)	0.0243 (6)
C6	0.0120 (3)	0.3192 (8)	0.71506 (10)	0.0236 (5)
C7	0.1731 (4)	0.2289 (6)	0.67943 (11)	0.0241 (6)
H7	0.2806	0.1184	0.7005	0.029*
C8	0.1728 (4)	0.3020 (7)	0.61427 (11)	0.0259 (5)
C9	0.0176 (4)	0.4707 (7)	0.58081 (12)	0.0301 (6)
H9	0.0215	0.522	0.5362	0.036*
C10	-0.1392 (4)	0.5590 (7)	0.61443 (12)	0.0309 (6)
H10	-0.2438	0.6729	0.5924	0.037*
C11	-0.1487 (4)	0.4842 (7)	0.68117 (11)	0.0260 (5)
C12	-0.3169 (4)	0.5686 (7)	0.71513 (13)	0.0325 (7)
H12	-0.4223	0.6774	0.6925	0.039*
C13	-0.3277 (4)	0.4956 (8)	0.77907 (13)	0.0330 (6)
H13	-0.4408	0.5519	0.8001	0.04*
C14	-0.1683 (4)	0.3330 (8)	0.81549 (11)	0.0270 (5)
Br1	0.35013 (4)	-0.17379 (7)	0.937295 (11)	0.03280 (8)
Br2	0.38478 (4)	0.16231 (7)	0.565973 (12)	0.03364 (8)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0312 (15)	0.0336 (18)	0.0310 (12)	0.0016 (11)	0.0128 (11)	-0.0049 (11)
C2	0.0392 (16)	0.0317 (16)	0.0237 (11)	-0.0038 (12)	0.0084 (11)	0.0023 (12)
C3	0.0291 (15)	0.0259 (12)	0.0256 (12)	-0.0017 (11)	0.0000 (11)	-0.0018 (11)
C4	0.0248 (14)	0.0252 (15)	0.0251 (11)	-0.0008 (10)	0.0054 (10)	-0.0017 (10)
C5	0.0248 (13)	0.0239 (15)	0.0245 (11)	-0.0031 (9)	0.0029 (10)	-0.0029 (10)
C6	0.0229 (12)	0.0214 (10)	0.0262 (11)	-0.0041 (13)	0.0002 (9)	-0.0010 (13)
C7	0.0222 (12)	0.0258 (15)	0.0241 (11)	0.0026 (9)	-0.0001 (9)	0.0001 (10)
C8	0.0265 (13)	0.0248 (12)	0.0268 (11)	-0.0043 (12)	0.0047 (10)	-0.0039 (12)
C9	0.0363 (16)	0.0281 (13)	0.0255 (12)	-0.0004 (13)	-0.0007 (11)	0.0012 (12)
C10	0.0296 (16)	0.0299 (14)	0.0324 (13)	0.0032 (11)	-0.0053 (11)	0.0001 (12)
C11	0.0247 (14)	0.0228 (12)	0.0301 (12)	-0.0018 (11)	-0.0009 (10)	-0.0032 (12)
C12	0.0223 (15)	0.0348 (16)	0.0396 (14)	0.0064 (11)	-0.0028 (12)	-0.0063 (13)
C13	0.0237 (15)	0.0344 (14)	0.0416 (14)	0.0030 (13)	0.0071 (11)	-0.0080 (14)
C14	0.0255 (13)	0.0244 (11)	0.0315 (11)	-0.0029 (14)	0.0040 (10)	-0.0012 (14)
Br1	0.03496 (16)	0.03660 (14)	0.02647 (12)	0.00097 (14)	-0.00083 (10)	0.00312 (13)
Br2	0.03388 (15)	0.04005 (15)	0.02791 (12)	0.00275 (14)	0.00893 (10)	0.00034 (13)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—C2	1.379 (4)	C7—C8	1.367 (3)
C1—C14	1.399 (3)	C7—H7	0.94
C1—H1	0.94	C8—C9	1.400 (3)
C2—C3	1.390 (4)	C8—Br2	1.898 (2)
C2—H2	0.94	C9—C10	1.363 (4)
C3—C4	1.362 (3)	C9—H9	0.94
C3—Br1	1.904 (2)	C10—C11	1.406 (3)
C4—C5	1.420 (3)	C10—H10	0.94
C4—H4	0.94	C11—C12	1.428 (4)
C5—C14	1.413 (3)	C12—C13	1.350 (4)

C5—C6	1.450 (3)	C12—H12	0.94
C6—C7	1.412 (3)	C13—C14	1.437 (4)
C6—C11	1.426 (3)	C13—H13	0.94
C2—C1—C14	121.2 (2)	C7—C8—C9	122.2 (2)
C2—C1—H1	119.4	C7—C8—Br2	119.72 (19)
C14—C1—H1	119.4	C9—C8—Br2	118.07 (17)
C1—C2—C3	118.4 (2)	C10—C9—C8	118.5 (2)
C1—C2—H2	120.8	C10—C9—H9	120.7
C3—C2—H2	120.8	C8—C9—H9	120.7
C4—C3—C2	122.5 (2)	C9—C10—C11	121.8 (2)
C4—C3—Br1	119.6 (2)	C9—C10—H10	119.1
C2—C3—Br1	117.94 (17)	C11—C10—H10	119.1
C3—C4—C5	119.9 (2)	C6—C11—C10	119.1 (2)
C3—C4—H4	120	C6—C11—C12	119.8 (2)
C5—C4—H4	120	C10—C11—C12	121.1 (2)
C14—C5—C4	118.1 (2)	C13—C12—C11	121.4 (2)
C14—C5—C6	119.4 (2)	C13—C12—H12	119.3
C4—C5—C6	122.5 (2)	C11—C12—H12	119.3
C7—C6—C11	118.3 (2)	C12—C13—C14	120.8 (3)
C7—C6—C5	123.0 (2)	C12—C13—H13	119.6
C11—C6—C5	118.7 (2)	C14—C13—H13	119.6
C8—C7—C6	120.0 (2)	C5—C14—C1	119.8 (2)
C8—C7—H7	120	C5—C14—C13	119.8 (2)
C6—C7—H7	120	C1—C14—C13	120.4 (2)
C14—C1—C2—C3	0.5 (4)	C7—C6—C11—C10	-1.7 (4)
C1—C2—C3—C4	-1.0 (4)	C5—C6—C11—C10	179.6 (2)
C1—C2—C3—Br1	177.77 (19)	C7—C6—C11—C12	177.8 (2)
C2—C3—C4—C5	0.2 (4)	C5—C6—C11—C12	-0.8 (4)
Br1—C3—C4—C5	-178.56 (17)	C9—C10—C11—C6	1.6 (4)
C3—C4—C5—C14	1.1 (3)	C9—C10—C11—C12	-177.9 (3)
C3—C4—C5—C6	-179.8 (2)	C6—C11—C12—C13	0.0 (4)
C14—C5—C6—C7	-177.7 (3)	C10—C11—C12—C13	179.5 (3)
C4—C5—C6—C7	3.2 (4)	C11—C12—C13—C14	0.7 (5)
C14—C5—C6—C11	0.9 (4)	C4—C5—C14—C1	-1.6 (4)
C4—C5—C6—C11	-178.2 (2)	C6—C5—C14—C1	179.3 (3)
C11—C6—C7—C8	0.5 (4)	C4—C5—C14—C13	179.0 (2)
C5—C6—C7—C8	179.0 (2)	C6—C5—C14—C13	-0.2 (4)
C6—C7—C8—C9	1.0 (4)	C2—C1—C14—C5	0.8 (4)
C6—C7—C8—Br2	-177.3 (2)	C2—C1—C14—C13	-179.7 (3)
C7—C8—C9—C10	-1.1 (4)	C12—C13—C14—C5	-0.6 (5)
Br2—C8—C9—C10	177.1 (2)	C12—C13—C14—C1	179.9 (3)
C8—C9—C10—C11	-0.2 (4)		