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2',7'-Dibromospiro[cyclopropane-1,9'-fluorene]

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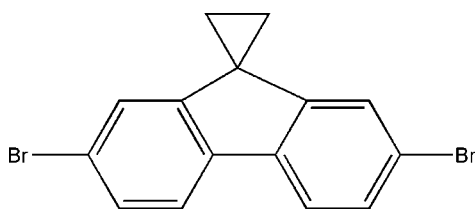
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.039; wR factor = 0.100; data-to-parameter ratio = 12.1.

In the title compound, $\text{C}_{15}\text{H}_{10}\text{Br}_2$, each molecule is situated on special position mm , so the asymmetric unit contains one-quarter of a molecule. The 2,7-dibromo-9H-fluorene fragment and three spirocyclopropane C atoms lie on different planes, which are perpendicular to each other. In the crystal, $\pi-\pi$ interactions between aromatic rings [intercentroid distance = $3.699(3)$ Å] pack the molecules into stacks extending in [001].

Related literature

For electroluminescence properties of fluorene derivatives, see: Cho *et al.* (2007); Jiang *et al.* (2005); Wei *et al.* (2008). For the crystal structures of related compounds, see: Jason *et al.* (1981); Wang *et al.* (2007).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{10}\text{Br}_2$	$V = 1277.3(3)$ Å ³
$M_r = 350.05$	$Z = 4$
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
$a = 16.9485(17)$ Å	$\mu = 6.32$ mm ⁻¹
$b = 11.0619(11)$ Å	$T = 293$ K
$c = 6.8127(10)$ Å	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	640 independent reflections
3276 measured reflections	471 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.155$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	53 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.30$ e Å ⁻³
640 reflections	$\Delta\rho_{\text{min}} = -0.68$ e Å ⁻³

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5463).

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supporting information

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2',7'-Dibromospiro[cyclopropane-1,9'-fluorene]**Yue-yuan Xue and Yong-qi Qin****S1. Comment**

Fluorene derivatives have a wide range of applications in electroluminescence materials (Jiang *et al.*, 2005; Wei *et al.*, 2008) because of their good thermal, light and chemical stability (Cho *et al.*, 2007). Herewith we present the title compound (I), which is a new derivative of fluorene.

In (I) (Fig. 1), all bond lengths and angles are normal and comparable with those observed in the related spiro(cyclopropane-1,9'-(9H)fluorene) (Jason *et al.*, 1981) and 2',7'-diiodospiro(cyclopropane-1,9'-fluorene) (Wang, *et al.*, 2007). In (I), the 2,7-dibromo-9H-fluorene fragment and three carbon atoms of spirocyclopropane lie on different planes *m*, which are perpendicular to each other, so asymmetric unit contains one fourth of the molecule.

In the crystal, π - π interactions between the aromatic rings [intercentroid distance of 3.699 (3) Å] pack molecules into stacks extended in [001].

S2. Experimental

The title compound was prepared by the reaction of 2,7-dibromo-9H-fluorene(0.01 mol), 1,2-dibromethane(0.01 mol) and KOH(0.03 mol) in 1,4-dioxane(20 ml) at 358 K for 3 h. Single crystals suitable for X-ray measurements were obtained by recrystallization from ethanol at room temperature.

S3. Refinement

H atoms were fixed geometrically and allowed to ride on their parent atoms, with C—H distances = 0.93–0.97 Å; and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

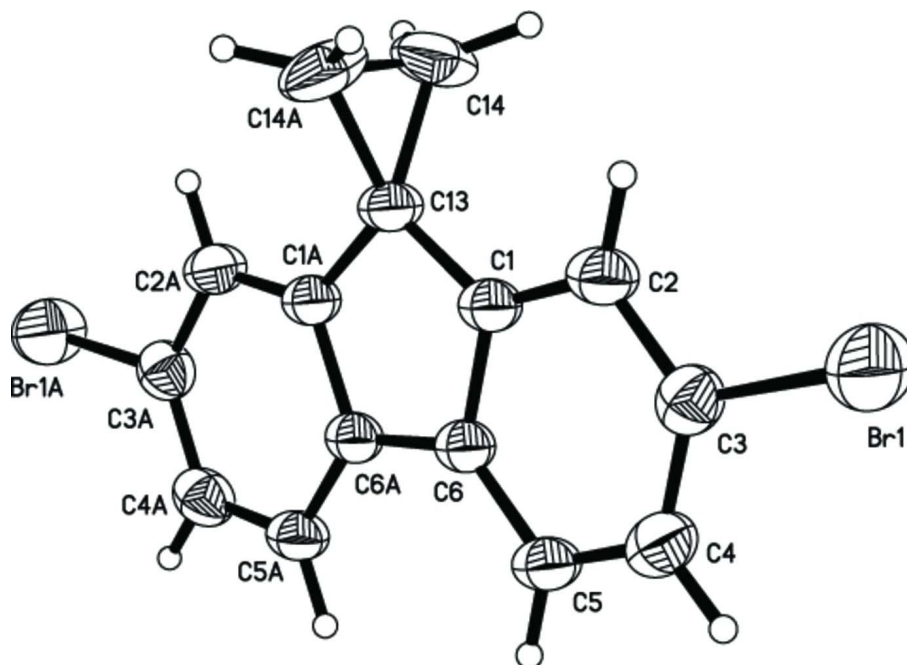


Figure 1

The molecular structure of (I) showing the atomic numbering and 40% probability displacement ellipsoids.

2',7'-Dibromospiro[cyclopropane-1,9'-fluorene]

Crystal data

$C_{15}H_{10}Br_2$

$M_r = 350.05$

Orthorhombic, $Cmcm$

$a = 16.9485$ (17) Å

$b = 11.0619$ (11) Å

$c = 6.8127$ (10) Å

$V = 1277.3$ (3) Å³

$Z = 4$

$F(000) = 680$

$D_x = 1.820$ Mg m⁻³

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

Cell parameters from 933 reflections

$\theta = 2.2$ – 25.0°

$\mu = 6.32$ mm⁻¹

$T = 293$ K

Block, colourless

$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

phi and ω scans

3276 measured reflections

640 independent reflections

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

$R_{int} = 0.155$

$\theta_{max} = 25.0^\circ$, $\theta_{min} = 2.2^\circ$

$h = -20 \rightarrow 17$

$k = -13 \rightarrow 12$

$l = -8 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.100$

$S = 0.98$

640 reflections

53 parameters

0 restraints

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$

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

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

$\Delta\rho_{max} = 0.30$ e Å⁻³

$\Delta\rho_{min} = -0.68$ e Å⁻³

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.

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	0.31110 (3)	0.12115 (5)	0.7500	0.0746 (4)
C1	0.0691 (3)	0.1592 (4)	0.7500	0.0396 (11)
C2	0.1489 (3)	0.1851 (4)	0.7500	0.0470 (12)
H2	0.1666	0.2647	0.7500	0.056*
C3	0.2011 (3)	0.0894 (5)	0.7500	0.0478 (12)
C4	0.1763 (3)	-0.0277 (4)	0.7500	0.0506 (12)
H4	0.2130	-0.0901	0.7500	0.061*
C5	0.0965 (3)	-0.0541 (4)	0.7500	0.0450 (12)
H5	0.0792	-0.1339	0.7500	0.054*
C6	0.0429 (2)	0.0393 (4)	0.7500	0.0380 (10)
C13	0.0000	0.2412 (5)	0.7500	0.0424 (16)
C14	0.0000	0.3609 (3)	0.6418 (11)	0.0725 (18)
H14	0.0485	0.3846	0.5754	0.087*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0506 (4)	0.0657 (5)	0.1074 (6)	0.0008 (3)	0.000	0.000
C1	0.054 (3)	0.0309 (19)	0.034 (2)	-0.001 (2)	0.000	0.000
C2	0.056 (3)	0.034 (2)	0.051 (3)	-0.004 (2)	0.000	0.000
C3	0.047 (3)	0.049 (3)	0.047 (3)	0.005 (2)	0.000	0.000
C4	0.059 (3)	0.046 (3)	0.047 (3)	0.012 (2)	0.000	0.000
C5	0.063 (3)	0.031 (2)	0.041 (3)	0.003 (2)	0.000	0.000
C6	0.052 (2)	0.032 (2)	0.031 (2)	0.0006 (19)	0.000	0.000
C13	0.051 (4)	0.028 (3)	0.048 (4)	0.000	0.000	0.000
C14	0.054 (3)	0.039 (3)	0.125 (5)	0.000	0.000	0.030 (3)

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

Br1—C3	1.897 (5)	C5—C6	1.375 (6)
C1—C2	1.383 (6)	C5—H5	0.9299
C1—C6	1.398 (6)	C6—C6 ⁱ	1.454 (8)
C1—C13	1.481 (6)	C13—C1 ⁱ	1.481 (6)
C2—C3	1.380 (7)	C13—C14	1.516 (7)
C2—H2	0.9300	C13—C14 ⁱⁱ	1.516 (7)
C3—C4	1.361 (7)	C14—C14 ⁱⁱ	1.475 (14)
C4—C5	1.384 (6)	C14—H14	0.9741
C4—H4	0.9299		

C2—C1—C6	120.5 (4)	C4—C5—H5	120.5
C2—C1—C13	130.3 (4)	C5—C6—C1	120.2 (4)
C6—C1—C13	109.3 (4)	C5—C6—C6 ⁱ	131.3 (3)
C3—C2—C1	117.9 (4)	C1—C6—C6 ⁱ	108.5 (3)
C3—C2—H2	121.3	C1 ⁱ —C13—C1	104.5 (5)
C1—C2—H2	120.8	C1 ⁱ —C13—C14	122.36 (19)
C4—C3—C2	122.1 (5)	C1—C13—C14	122.36 (19)
C4—C3—Br1	118.7 (4)	C1 ⁱ —C13—C14 ⁱⁱ	122.36 (19)
C2—C3—Br1	119.2 (4)	C1—C13—C14 ⁱⁱ	122.36 (19)
C3—C4—C5	120.2 (4)	C14—C13—C14 ⁱⁱ	58.2 (6)
C3—C4—H4	120.0	C14 ⁱⁱ —C14—C13	60.9 (3)
C5—C4—H4	119.8	C14 ⁱⁱ —C14—H14	117.6
C6—C5—C4	119.1 (4)	C13—C14—H14	117.4
C6—C5—H5	120.4		
C6—C1—C2—C3	0.0	C2—C1—C6—C6 ⁱ	180.0
C13—C1—C2—C3	180.0	C13—C1—C6—C6 ⁱ	0.0
C1—C2—C3—C4	0.0	C2—C1—C13—C1 ⁱ	180.0
C1—C2—C3—Br1	180.0	C6—C1—C13—C1 ⁱ	0.0
C2—C3—C4—C5	0.0	C2—C1—C13—C14	35.1 (4)
Br1—C3—C4—C5	180.0	C6—C1—C13—C14	-144.9 (4)
C3—C4—C5—C6	0.0	C2—C1—C13—C14 ⁱⁱ	-35.1 (4)
C4—C5—C6—C1	0.0	C6—C1—C13—C14 ⁱⁱ	144.9 (4)
C4—C5—C6—C6 ⁱ	180.0	C1 ⁱ —C13—C14—C14 ⁱⁱ	110.6 (3)
C2—C1—C6—C5	0.0	C1—C13—C14—C14 ⁱⁱ	-110.6 (3)
C13—C1—C6—C5	180.0		

Symmetry codes: (i) $-x, y, z$; (ii) $x, y, -z+3/2$.