organic compounds

2,7-Bis(bromomethyl)-9,9'-diethyl-fluorene

K. Chinnakali,[a]* R. Surendran,[a] M. Pushparani,[a] A. K. Mohanakrishnan[b] and Hoong-Kun Fun[c]*

[a]Department of Physics, Anna University, Chennai 600 025, India, [b]Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

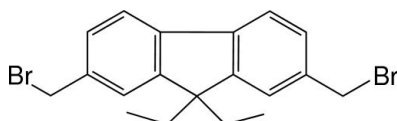Correspondence e-mail: kali@annauniv.edu, hkfun@usm.my

The asymmetric unit of the title compound, $C_{19}H_{20}Br_2$, contains one half-molecule, with the other half generated by a crystallographic twofold rotation axis passing through the Csp^3 ring atom and the mid-point of the Csp^2-Csp^2 single bond of the five-membered ring. The fluorene ring system is essentially planar. The non-H atoms of the two symmetry-related ethyl groups are coplanar. This plane and the plane of the fluorene ring system are perpendicular to one another, with a dihedral angle of 89.8 (1)°. The molecules are linked into zigzag layers parallel to the ab plane by C—H···Br hydrogen bonds. The adjacent layers are cross-linked by C—H···π interactions and Br···Br short contacts [3.3774 (3) Å] into a three-dimensional framework.

Related literature

For general background, see: Abdel-Rahman *et al.* (1994); Bazyl (1986); Johansson *et al.* (2001); Lee & Tsuysui (2000). For related structures, see: Hu *et al.* (2005, 2006); Leclerc *et al.* (1998); McFarlane *et al.* (2005, 2006).

Experimental

Crystal data

$C_{19}H_{20}Br_2$
M_r = 408.17
Orthorhombic, $Pbcn$
a = 10.9244 (2) Å
b = 8.8066 (2) Å
c = 17.4316 (4) Å

V = 1677.04 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.83 mm^{-1}
T = 100.0 (1) K
0.58 × 0.49 × 0.40 mm

Data collection

Bruker SMART APEX II CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.106, T_{max} = 0.246
(expected range = 0.063–0.145)

69232 measured reflections
5609 independent reflections
3854 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.140
S = 1.06
5609 reflections

96 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.23 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the C1–C6 benzene ring.

$D-$H$\cdots A$	$D-$H	H$\cdots A$	$D\cdots A$	$D-$H$\cdots A$
C4—H4···Br1[i]	0.95	2.88	3.8058 (16)	164
C7—H7B···Cg1[ii]	0.99	2.71	3.5589 (17)	144

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $-x, -y + 1, -z + 1$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2191).

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supplementary materials

2,7-Bis(bromomethyl)-9,9'-diethylfluorene

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Comment

Fluorene and its polymeric derivatives have been used as laser-generating (Bazyl, 1986) or photo-active fluorescent materials (Johansson *et al.*, 2001). Homopolymers and copolymers of fluorene derivatives have emerged as the most attractive blue-emitting materials due to their high effiency and excellent thermal stability (Lee & Tsuysui, 2000). Fluorene derivatives can also be used as potential anti-HIV and anticancer drugs (Abdel-Rahman *et al.*, 1994). In view of this wide range of activities associated with fluorene derivatives, the X-ray crystal structure determination of 2,7-bis(bromomethyl)-9,9-diethylfluorene was undertaken.

The asymmetric unit of the title compound contains one half-molecule (Fig.1). The other half is generated by a crystallographic twofold axis of symmetry; this axis passes through the atom C8 and the mid-point of the C6—C6A bond [symmetry code: (A) $-x$, y, $1/2 - z$] and is parallel to the *b* axis of the unit cell.

The C—C distances in the benzene ring lie in the range 1.388 (2)–1.403 (2) Å. The C6—C6A distance of 1.459 (3) Å is longer than the normal Csp^2—Csp^2 bond distance, but comparable to that observed in similar structures (McFarlane *et al.*, 2005, 2006; Leclerc *et al.*, 1998; Hu *et al.*, 2005, 2006). The angles subtended at C8 lie in the range 100.9 (2)–112.46 (8)°, deviating significantly from the ideal tetrahedral angle of *ca* 109.5°.

The three fused rings are essentially coplanar, the dihedral angles formed by the five-membered ring with the two benzene rings being 0.46 (7)°. The non-hydrogen atoms of the two symmetry-related ethyl groups are coplanar, and this plane is perpendicular to the plane of the fused-ring system [dihedral angle 89.8 (1)°].

In the crystal structure the molecules are linked by C4—H4···Br1[i] [symmetry code: (i) $1/2 - x$, $1/2 + y$, z] hydrogen bonds into zigzag layers parallel to the *ab* plane. Such a layer, viewed approximately along the *c* axis, is shown in Fig.2. The adjacent layers are cross-linked by C—H···π hydrogen bonds (Table 1) involving the C1—C6 benzene ring (centroid *Cg*1) and Br1···Br1($1 - x$, $1 - y$, $1 - z$) short contacts [3.3774 (3) Å] into a three-dimensional framework (Fig.3).

Experimental

To prepare the title compound, a mixture of 9,9-diethylfluorene (1.11 g, 5 mmol), paraformaldehyde (0.33 g, 11.0 mmol) and 33% HBr solution in acetic acid (10 ml) was heated at 333–343 K for 20 h. The precipitate obtained after cooling the reaction mixture was collected by filtration and washed with water and dried *in vacuo*. The crude product was recrystallized from hexane.

supplementary materials

Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95–0.99 Å and $U_{iso}(H) = xU_{eq}$(carrier atom), where x = 1.5 for methyl C and 1.2 for all other C atoms. The highest residual electron density peak is located 0.70 Å from atom Br1 and the deepest hole is located 0.17 Å from atom Br1.
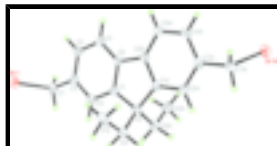
Figures

Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering. Atoms labelled with the suffix A are generated by the symmetry operation (−x, y, 1/2 − z).
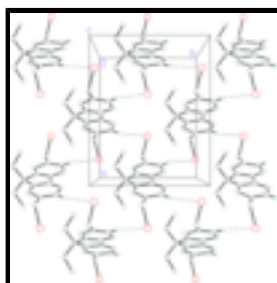

Fig. 2. A C—H···Br hydrogen-bonded (dashed lines) layer, viewed approximately along the c axis. H atoms not involved in hydrogen bonding have been omitted.
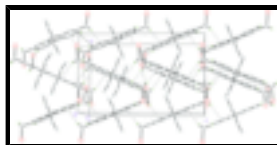

Fig. 3. The crystal packing of the title compound, viewed approximately along the b axis. Dashed lines indicate C—H···Br and Br···Br interactions while the dotted lines denote C—H···π interactions. H atoms not involved in hydrogen bonding have been omitted.

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Crystal data

$C_{19}H_{20}Br_2$	F_{000} = 816
M_r = 408.17	D_x = 1.617 Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 6378 reflections
a = 10.9244 (2) Å	θ = 2.3–35.8º
b = 8.8066 (2) Å	μ = 4.83 mm^{-1}
c = 17.4316 (4) Å	T = 100.0 (1) K
V = 1677.04 (6) Å^3	Block, yellow
Z = 4	0.58 × 0.49 × 0.40 mm

Data collection

Bruker SMART APEX II CCD area-detector diffractometer	5609 independent reflections
Radiation source: fine-focus sealed tube	3854 reflections with $I > 2\sigma(I)$

Monochromator: graphite	$R_{int} = 0.045$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{max} = 41.3°$
$T = 100.0(1)$ K	$\theta_{min} = 3.0°$
ω scans	$h = -20 \rightarrow 20$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -15 \rightarrow 16$
$T_{min} = 0.106$, $T_{max} = 0.246$	$l = -32 \rightarrow 32$
69232 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.140$	$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.7685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
5609 reflections	$\Delta\rho_{max} = 1.23$ e Å^{-3}
96 parameters	$\Delta\rho_{min} = -1.42$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2sigma(F^2)$ 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*	$U_{iso}*/U_{eq}$
Br1	0.348167 (16)	0.49225 (2)	0.517755 (10)	0.02468 (6)
C1	0.04152 (13)	0.38455 (16)	0.31212 (8)	0.0172 (2)
C2	0.09122 (14)	0.35223 (17)	0.38370 (8)	0.0189 (2)
H2	0.1030	0.2499	0.3993	0.023*
C3	0.12362 (15)	0.47126 (18)	0.43244 (9)	0.0196 (2)
C4	0.10699 (15)	0.62203 (18)	0.40870 (9)	0.0220 (3)
H4	0.1294	0.7025	0.4422	0.026*
C5	0.05831 (15)	0.65573 (17)	0.33714 (9)	0.0218 (3)
H5	0.0474	0.7581	0.3214	0.026*
C6	0.02571 (13)	0.53575 (17)	0.28861 (9)	0.0180 (2)

C7	0.17355 (15)	0.4393 (2)	0.51043 (9)	0.0224 (3)
H7A	0.1629	0.3302	0.5223	0.027*
H7B	0.1269	0.4983	0.5489	0.027*
C8	0.0000	0.2745 (2)	0.2500	0.0177 (3)
C9	0.10677 (16)	0.17259 (18)	0.22344 (9)	0.0219 (3)
H9A	0.1343	0.1105	0.2675	0.026*
H9B	0.0759	0.1021	0.1837	0.026*
C10	0.21637 (17)	0.2570 (2)	0.19130 (10)	0.0278 (3)
H10A	0.2821	0.1845	0.1800	0.042*
H10B	0.2453	0.3312	0.2290	0.042*
H10C	0.1926	0.3096	0.1441	0.042*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02126 (9)	0.02858 (10)	0.02421 (9)	0.00002 (5)	−0.00302 (5)	−0.00119 (5)
C1	0.0166 (5)	0.0190 (5)	0.0158 (5)	0.0002 (4)	−0.0003 (4)	0.0001 (4)
C2	0.0199 (6)	0.0211 (6)	0.0159 (5)	0.0000 (4)	−0.0009 (4)	0.0002 (4)
C3	0.0177 (5)	0.0247 (6)	0.0165 (5)	−0.0014 (5)	−0.0005 (4)	−0.0021 (4)
C4	0.0223 (6)	0.0223 (6)	0.0214 (6)	−0.0019 (5)	−0.0023 (5)	−0.0039 (5)
C5	0.0231 (6)	0.0189 (5)	0.0234 (6)	−0.0014 (5)	−0.0028 (5)	−0.0015 (5)
C6	0.0175 (5)	0.0184 (5)	0.0180 (5)	0.0000 (4)	−0.0011 (4)	−0.0010 (4)
C7	0.0205 (6)	0.0288 (7)	0.0179 (6)	−0.0027 (5)	−0.0012 (5)	−0.0016 (5)
C8	0.0204 (8)	0.0184 (7)	0.0144 (7)	0.000	0.0005 (6)	0.000
C9	0.0266 (7)	0.0224 (6)	0.0167 (6)	0.0056 (5)	0.0014 (5)	0.0006 (4)
C10	0.0223 (6)	0.0363 (9)	0.0247 (7)	0.0069 (6)	0.0028 (6)	0.0037 (6)

Geometric parameters (Å, °)

Br1—C7	1.9679 (17)	C6—C6[i]	1.459 (3)
C1—C2	1.390 (2)	C7—H7A	0.99
C1—C6	1.404 (2)	C7—H7B	0.99
C1—C8	1.5226 (19)	C8—C1[i]	1.5226 (19)
C2—C3	1.395 (2)	C8—C9[i]	1.5426 (19)
C2—H2	0.95	C8—C9	1.5426 (19)
C3—C4	1.403 (2)	C9—C10	1.516 (3)
C3—C7	1.492 (2)	C9—H9A	0.99
C4—C5	1.388 (2)	C9—H9B	0.99
C4—H4	0.95	C10—H10A	0.98
C5—C6	1.400 (2)	C10—H10B	0.98
C5—H5	0.95	C10—H10C	0.98
C2—C1—C6	120.28 (13)	C3—C7—H7B	109.3
C2—C1—C8	128.63 (13)	Br1—C7—H7B	109.3
C6—C1—C8	111.08 (12)	H7A—C7—H7B	108.0
C1—C2—C3	119.47 (14)	C1—C8—C1[i]	100.90 (16)
C1—C2—H2	120.3	C1—C8—C9[i]	112.46 (8)
C3—C2—H2	120.3	C1[i]—C8—C9[i]	111.01 (8)

C2—C3—C4	119.92 (14)	C1—C8—C9	111.01 (8)
C2—C3—C7	120.41 (15)	C1ⁱ—C8—C9	112.46 (8)
C4—C3—C7	119.66 (14)	C9ⁱ—C8—C9	108.88 (17)
C5—C4—C3	121.14 (14)	C10—C9—C8	115.02 (14)
C5—C4—H4	119.4	C10—C9—H9A	108.5
C3—C4—H4	119.4	C8—C9—H9A	108.5
C4—C5—C6	118.63 (14)	C10—C9—H9B	108.5
C4—C5—H5	120.7	C8—C9—H9B	108.5
C6—C5—H5	120.7	H9A—C9—H9B	107.5
C5—C6—C1	120.55 (14)	C9—C10—H10A	109.5
C5—C6—C6ⁱ	130.98 (9)	C9—C10—H10B	109.5
C1—C6—C6ⁱ	108.47 (8)	H10A—C10—H10B	109.5
C3—C7—Br1	111.64 (11)	C9—C10—H10C	109.5
C3—C7—H7A	109.3	H10A—C10—H10C	109.5
Br1—C7—H7A	109.3	H10B—C10—H10C	109.5
C6—C1—C2—C3	0.9 (2)	C8—C1—C6—C6ⁱ	−0.10 (19)
C8—C1—C2—C3	179.90 (12)	C2—C3—C7—Br1	110.20 (15)
C1—C2—C3—C4	−0.6 (2)	C4—C3—C7—Br1	−71.06 (18)
C1—C2—C3—C7	178.13 (14)	C2—C1—C8—C1ⁱ	−179.00 (18)
C2—C3—C4—C5	0.1 (2)	C6—C1—C8—C1ⁱ	0.04 (7)
C7—C3—C4—C5	−178.62 (15)	C2—C1—C8—C9ⁱ	62.65 (18)
C3—C4—C5—C6	0.0 (2)	C6—C1—C8—C9ⁱ	−118.31 (14)
C4—C5—C6—C1	0.3 (2)	C2—C1—C8—C9	−59.61 (18)
C4—C5—C6—C6ⁱ	−179.5 (2)	C6—C1—C8—C9	119.43 (14)
C2—C1—C6—C5	−0.8 (2)	C1—C8—C9—C10	−58.97 (16)
C8—C1—C6—C5	−179.91 (12)	C1ⁱ—C8—C9—C10	53.24 (17)
C2—C1—C6—C6ⁱ	179.03 (15)	C9ⁱ—C8—C9—C10	176.71 (16)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···Br1ⁱⁱ	0.95	2.88	3.8058 (16)	164
C7—H7B···Cg1ⁱⁱⁱ	0.99	2.71	3.5589 (17)	144

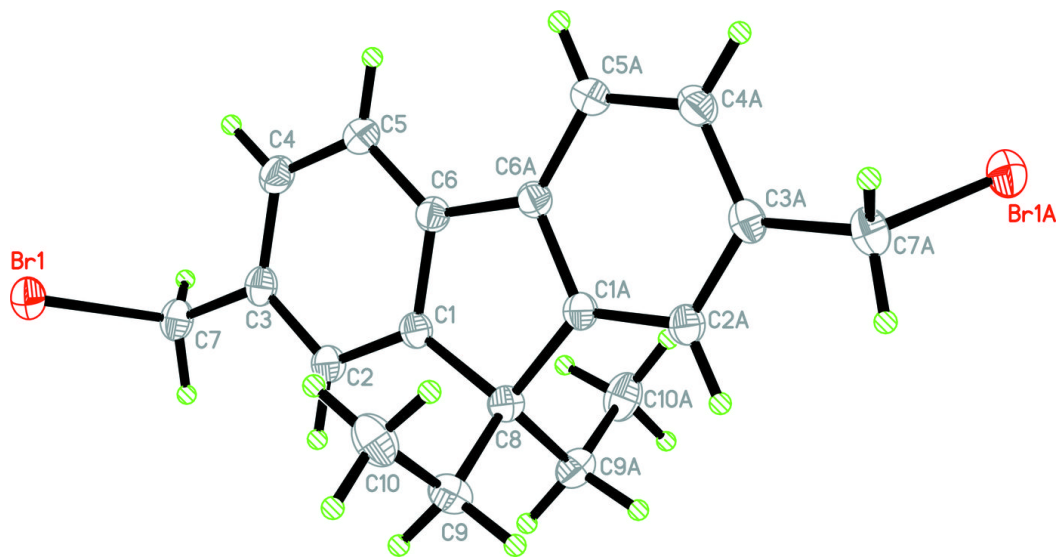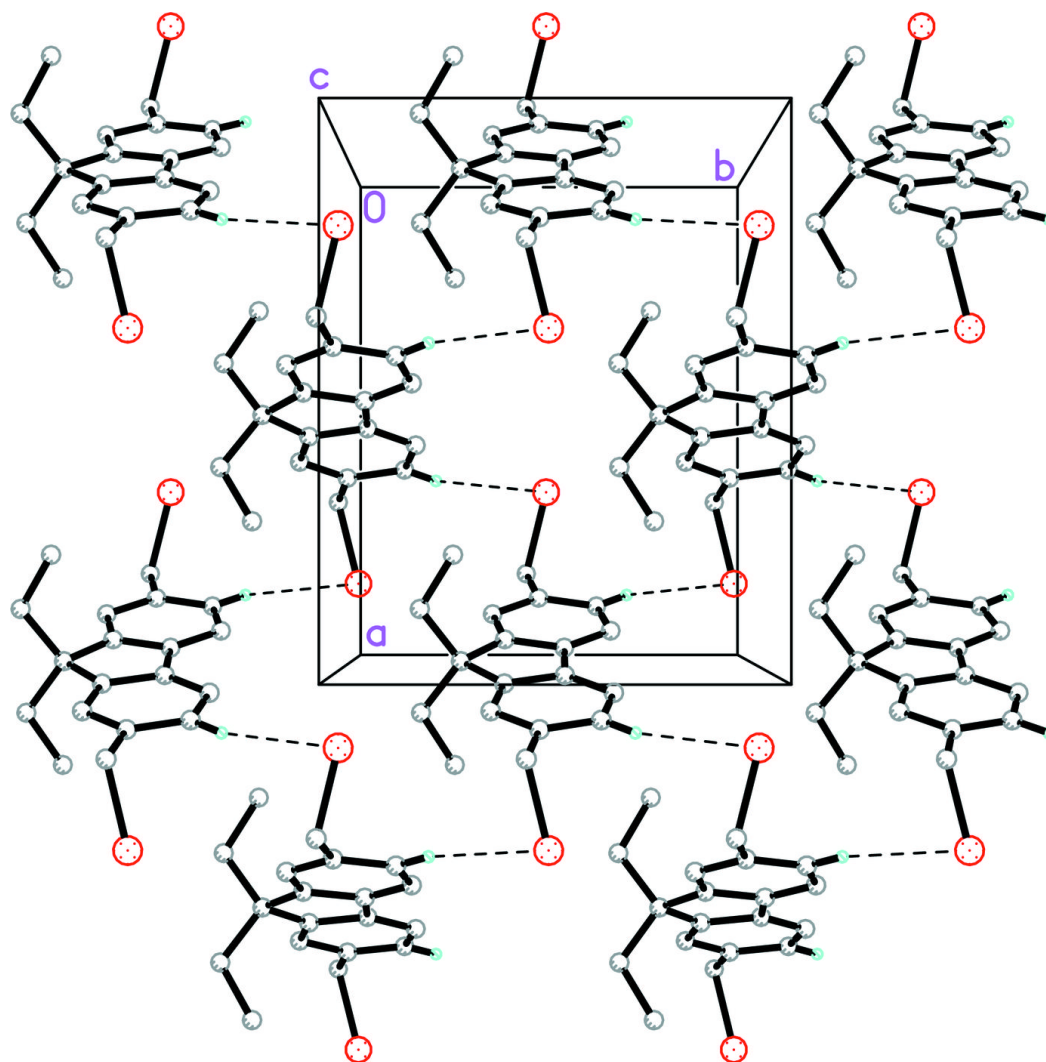Symmetry codes: (ii) $-x+1/2, y+1/2, z$; (iii) $-x, -y+1, -z+1$.

Fig. 1

Fig. 2

Fig. 3