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2,7-Dibromo-9,9-di-*n*-octyl-9*H*-fluorene

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When grown from the melt, the title compound, $C_{29}H_{40}Br_2$, crystallizes in a tetragonal space group. The octyl chains lie in planes parallel to the (100) and (010) planes of the unit cell. These chains extend in a direction almost perpendicular to the fluorene ring system, forcing a 13.5 Å separation between potentially overlapping parallel fluorenes, thereby preventing molecular π–π stacking.

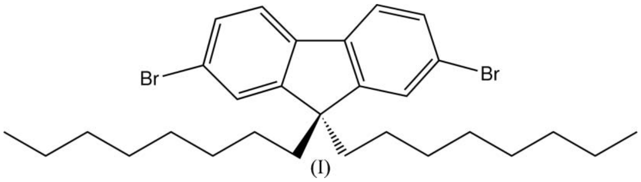
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.123
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The photoluminescent polymer poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO) is currently being investigated as a blue light-emitting material for polymer light-emitting diodes (PLEDS) (Scherf & List, 2002). The photophysical properties of PFO are complex and strongly dependent on the processing conditions of the material (Grell *et al.*, 1999), giving rise to crystalline, liquid crystalline (Scherf & List, 2002) and non-crystalline (Chen *et al.*, 2005) PFO phases in the solid state. In order to achieve a better understanding of PFO-based optoelectronic devices, and ultimately to control their electroluminescence maxima, researchers have investigated correlations between polymer morphology and photophysical properties (Chen *et al.*, 2005). Known crystal structures of 2,7-dibromo-9,9-dioctylfluorene chloroform solvate (Leclerc *et al.*, 1998) and 2,2′-bi(9,9-dihexylfluorene) (Suchod & Stéphan, 2000) have been used to explain chain packing and the electrooptical properties of PFO. Recently, a triclinic crystal of 9,9-dioctylfluorene (McFarlane *et al.*, 2005) grown from the melt revealed markedly different packing from the status quo tetragonal 2,7-dibromo-9,9-dioctylfluorene chloroform solvate (Leclerc *et al.*, 1998). Factors that may result in the different crystal packing motifs in these two reports may be the bromine substitution in the 2- and 7-positions of the fluorene ring, the chloroform molecule in the unit cell, and the different processing conditions used to prepare the crystals.



(I)

In order to understand further the structure–photophysical relationships of PFO, and potentially to isolate the influences of bromine substitution of the fluorene ring system and processing conditions on crystal packing, we have determined the solid-state crystal structure of the title compound, (I), obtained from melt-processing conditions, and present the results here.

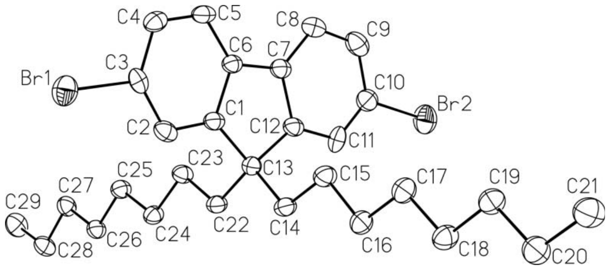


Figure 1
A plot of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

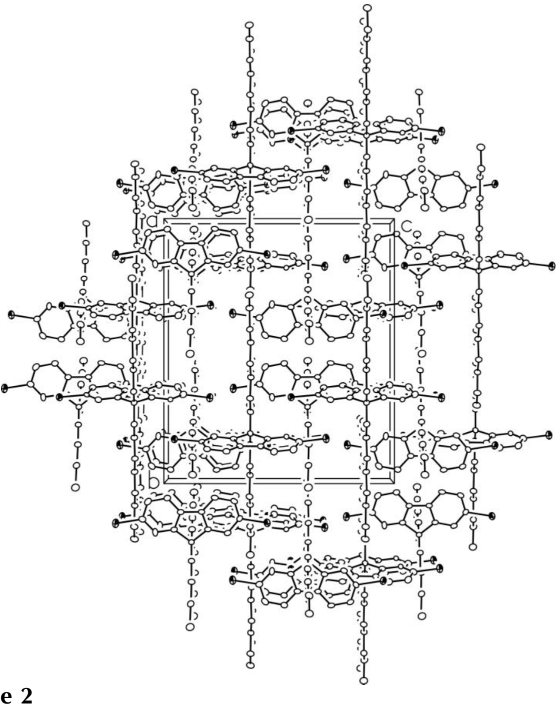


Figure 2
Illustration of the crystal packing of (I). The view direction is parallel to the crystal *a* axis.

Compound (I) crystallizes from the melt in the tetragonal space group $I\bar{4}$. A molecular drawing of (I) is shown in Fig. 1. The same compound processed from a chloroform solvent also packs into a tetragonal crystal system with the inclusion of chloroform solvent (Leclerc *et al.*, 1998). From this observation, we conclude that the bromine substitution markedly influences the crystal packing, while melt- or solution-processing is not a significant factor in this case. The unit-cell volume of the melt-processed compound is smaller than that of the solution-processed compound [5683.8 (4) Å^3 *versus* 5787 (4) Å^3], doubtless resulting from the exclusion of solvent from the unit cell. Fig. 2 shows the crystal packing as viewed down the *a* axis.

Experimental

The title compound was prepared according to the previously published procedure of Ranger *et al.* (1997). The compound was further purified according to the previously published procedure of Craig *et al.* (2003), followed by additional purification. To obtain suitable single crystals, the material was further purified by column chromatography (silica gel, hexane eluent). Hexane was removed under reduced pressure and the resulting white solid was warmed to 333 K and slowly cooled to 323 K, yielding colourless prismatic crystals.

Crystal data

$\mathrm{C_{29}H_{40}Br_2}$
$M_r = 548.43$
Tetragonal, $I\bar{4}$
$a = 18.7019$ (5) Å
$c = 16.2506$ (8) Å
$V = 5683.8$ (4) Å^3
$Z = 8$
$D_x = 1.282$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 5835 reflections
$\theta = 2.2$–26.2°
$\mu = 2.87$ mm^{-1}
$T = 193$ (2) K
Prism, colourless
0.49 × 0.43 × 0.36 mm

Data collection

Bruker SMART 1000 CCD area-detector/PLATFORM diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.280$, $T_{\max} = 0.356$
22528 measured reflections

5817 independent reflections
4767 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 26.4°$
$h = -23 \rightarrow 23$
$k = -23 \rightarrow 23$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.123$
$S = 1.06$
5817 reflections
281 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 1.0462P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 2792 Friedel pairs
Flack parameter: 0.544 (13)

Table 1
Selected geometric parameters (Å, °).

Br1—C3	1.936 (4)	C7—C8	1.393 (6)
Br2—C10	1.904 (5)	C7—C12	1.413 (5)
C1—C2	1.402 (5)	C8—C9	1.382 (7)
C1—C6	1.399 (5)	C9—C10	1.388 (7)
C1—C13	1.506 (5)	C10—C11	1.326 (6)
C2—C3	1.360 (6)	C11—C12	1.342 (5)
C3—C4	1.381 (5)	C12—C13	1.534 (5)
C4—C5	1.378 (6)	C13—C14	1.544 (4)
C5—C6	1.397 (5)	C13—C22	1.548 (4)
C6—C7	1.452 (4)		
C2—C1—C6	120.4 (3)	C7—C8—C9	119.3 (4)
C2—C1—C13	127.8 (3)	C8—C9—C10	118.8 (4)
C6—C1—C13	111.8 (3)	Br2—C10—C9	117.6 (4)
C1—C2—C3	116.3 (3)	Br2—C10—C11	120.9 (3)
Br1—C3—C2	118.4 (3)	C9—C10—C11	121.4 (4)
Br1—C3—C4	116.2 (3)	C10—C11—C12	122.1 (4)
C2—C3—C4	125.4 (4)	C7—C12—C11	118.9 (4)
C3—C4—C5	117.9 (4)	C7—C12—C13	109.4 (3)
C4—C5—C6	119.5 (3)	C11—C12—C13	131.6 (3)
C1—C6—C5	120.5 (4)	C1—C13—C12	101.4 (2)
C1—C6—C7	108.0 (3)	C1—C13—C14	111.7 (3)
C5—C6—C7	131.5 (4)	C12—C13—C14	110.8 (3)
C6—C7—C8	131.1 (4)	C1—C13—C22	113.0 (3)
C6—C7—C12	109.4 (4)	C12—C13—C22	112.5 (3)
C8—C7—C12	119.4 (4)	C14—C13—C22	107.4 (2)

H atoms were placed in idealized positions, with C—H = 0.95–0.99 Å, and treated as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The value of the Flack parameter (Flack, 1983) [0.544 (13)] is indicative of inversion twinning. The highest peak is located 0.57 Å from atom C3, and is not chemically significant.

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Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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