9,9-Di-*n*-octyl-9*H*-fluorene

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The title compound, $C_{29}H_{42}$, crystallizes from the melt as a triclinic crystal. The unit cell contains three crystallographically independent molecules. The three fluorene ring systems are oriented such that two non-equivalent ring systems related by a roto-translation are separated by a third ring system oriented orthogonally to them. The octyl chains of all three molecules are perpendicular to the fluorene ring system and force a 7.4 Å separation between the two coplanar molecules, thereby preventing molecular π-stacking.

Comment

The semiconducting polymer poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO) is currently being investigated scientifically and industrially 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). It is known that subtle changes in processing conditions produce dramatic structural and photophysical changes (Grell *et al.*, 1999). To add to the complexity, PFO chains are believed to order concomitantly in numerous phases, *i.e.* crystalline, liquid crystalline (Scherf & List, 2002) and non-crystalline (Chen *et al.*, 2005), in the solid state. In order to achieve a better understanding of PFO-based optoelectronic devices, and ultimately to control their electroluminescence maximum, researchers have been investigating correlations between polymer morphology and photophysical properties (Chen *et al.*, 2005). To illustrate the complex emission characteristics of PFO, researchers have examined the photophysics of PFO as single polymer chains (Grell *et al.*, 1999; Becker & Lupton, 2005) and found that small conformational changes can significantly alter the emission characteristics (Becker & Lupton, 2005). It has been proposed (Grell *et al.*, 1999) that PFO adopts a 'planar zigzag' conformation, in which the octyl chains on adjacent fluorene units are oriented antiparallel to each other, upon prolonged exposure to certain solvents. In light of the numerous conformations and phases that PFO polymer chains can adopt, a variety of packing models are necessary to understand fully its complex solid-state photophysics.

The 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 the chain packing, and hence the electro-optical properties, of PFO. The solid-state structures of both these monomers and of the present structure show that alkyl-substitutent steric requirements at the 9-position of the fluorene ring system effectively eliminate π-stacking. Unfortunately, while comparisons of these small-molecule structures provide some limited insight into the PFO structure, both have inherent limitations. The inclusion of a single solvent $CHCl_3$ molecule in the tetragonal unit cell and the Br atoms of 2,7-dibromo-9.9-dioctylfluorene chloroform solvate limit a direct PFO comparison, yet it has been used to model structural phases (Ariu *et al.*, 2001). While the crystal structure of 2,2′-bi(9,9-dihexylfluorene) (Suchod & Stéphan, 2000) possesses greater structural similarity with PFO and there is no inclusion of solvent, it crystallizes in a monoclinic space group inconsistent with the proposed packing of PFO (Grell *et al.*, 1999).

(I)
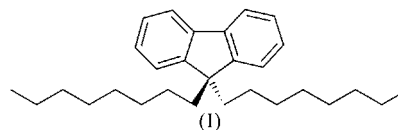
To understand further the structure–photophysical relationships of PFO, we have determined the solid-state crystal structure of the title compound, (I). The compound crystallizes from the melt, thus eliminating influences from solvent/ monomer interactions on the final structure. A molecular drawing of one of the three crystallographically independent molecules of the title compound is shown in Fig. 1. As is the case for the other aforementioned small molecule PFO models, all three non-equivalent molecules (*A*, *B* and *C*) in the present triclinic structure possess a planar central fluorene ring [none of the fluorene ring C atoms deviates from the calculated planes by more than 0.035 (2) Å]. In each molecule,
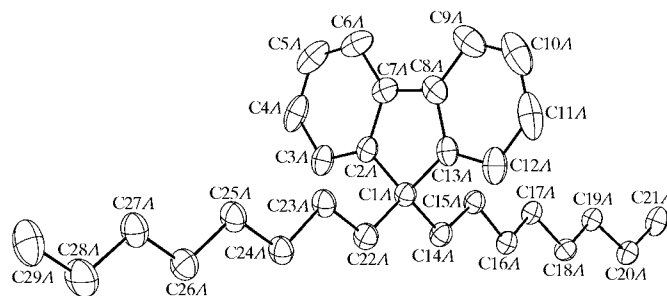

Figure 1
A drawing of one of the three crystallographically independent molecules of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.
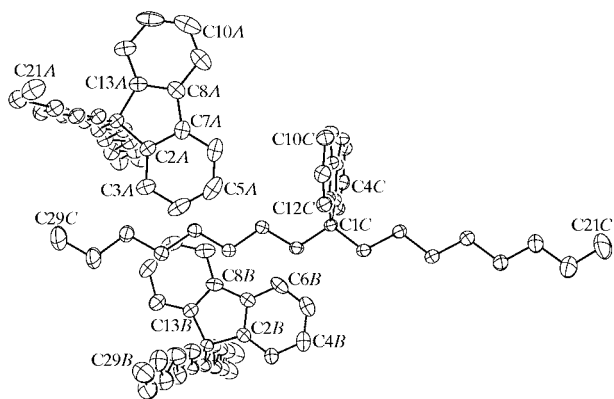
organic compounds

Figure 2
Illustration of the relative orientations of the three molecules of (I) as they occur in the unit cell.
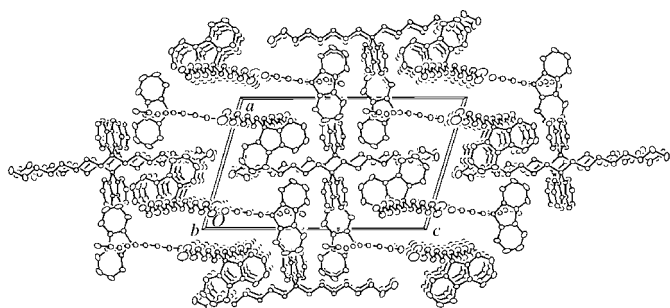

Figure 3
Illustration of the crystal packing of (I). The view direction is approximately along the crystallographic *b* axis.

the octyl chains extend in a direction orthogonal to the aromatic ring system; only molecule *C* shows any deviation from this planar zigzag conformation, with a 50% disorder of one of its terminal octyl C-atom positions. Fig. 2 illustrates the relative orientations of the adjacent independent molecules. The planes of the fluorene rings of molecules *A* and *B* are nearly parallel [the dihedral angle between their fluorene planes is 2.59 (5)°], while the fluorene plane of molecule *C* is almost orthogonal to those of molecules *A* and *B* [the *A–C* and *B–C* dihedral angles are 88.64 (4) and 89.22 (3)°, respectively]. Fig. 3 shows the crystal packing as viewed down the *b* axis.

Our crystallization process is similar to common processing conditions used in the fabrication of PFO-based PLEDs (Chen *et al.*, 2005) and, by extension, we expect that the molecular ordering presented here may provide a more accurate approximation of the PFO chain packing in functional PLEDs. Furthermore, the crystals display a blue luminescence (λ_{em} = 333 nm; λ_{ex} = 266 nm) consistent with the photo- and electroluminescence of PFO. We expect this triclinic crystal structure to provide valuable insight into the photophysics of PFO (Chen *et al.*, 2005).

Experimental

The title compound was prepared according to the previously published procedure of Ranger *et al.* (1997), followed by additional purification. To obtain suitable single crystals, the material was further purified by column chromatography (silica gel, hexane eluent). The hexane was removed under reduced pressure and the resulting white cloudy oil was cooled rapidly to 195 K and allowed to warm slowly to room temperature, yielding colourless prismatic crystals. The melting point of the resulting crystals was 300–301 K, as determined by differential scanning calorimetry.

Crystal data

$C_{29}H_{42}$	$Z = 6$
$M_r = 390.63$	$D_x = 1.014$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.9223$ (18) Å	Cell parameters from 7045
$b = 14.2423$ (18) Å	reflections
$c = 21.570$ (3) Å	$\theta = 2.2–25.9°$
$\alpha = 83.079$ (2)°	$\mu = 0.06$ mm^{-1}
$\beta = 72.024$ (2)°	$T = 193$ (2) K
$\gamma = 70.605$ (2)°	Prism, colourless
$V = 3836.6$ (9) Å^3	0.36 × 0.35 × 0.26 mm

Data collection

Bruker SMART 1000 CCD area-detector/PLATFORM diffractometer	13469 independent reflections
	8216 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction: integration (*SHELXTL*; Bruker, 2003)	$\theta_{max} = 25.0°$
	$h = -16 \rightarrow 16$
$T_{min} = 0.829$, $T_{max} = 0.986$	$k = -16 \rightarrow 16$
25454 measured reflections	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 0.6911P]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	
$wR(F^2) = 0.190$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
13469 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
796 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97* (Sheldrick, 1997)
	Extinction coefficient: 0.0092 (8)

Table 1
Selected geometric parameters (Å, °) for one of the crystallographically independent molecules of (I).

C1A—C2A	1.521 (3)	C6A—C7A	1.387 (3)
C1A—C13A	1.525 (3)	C7A—C8A	1.460 (3)
C1A—C14A	1.540 (3)	C8A—C9A	1.393 (4)
C1A—C22A	1.540 (3)	C8A—C13A	1.399 (3)
C2A—C3A	1.382 (3)	C9A—C10A	1.367 (5)
C2A—C7A	1.398 (3)	C10A—C11A	1.372 (5)
C3A—C4A	1.399 (4)	C11A—C12A	1.391 (4)
C4A—C5A	1.370 (4)	C12A—C13A	1.389 (3)
C5A—C6A	1.368 (4)		
C2A—C1A—C13A	100.79 (18)	C2A—C7A—C8A	108.8 (2)
C2A—C1A—C14A	111.39 (17)	C6A—C7A—C8A	130.6 (3)
C2A—C1A—C22A	112.01 (17)	C7A—C8A—C9A	132.1 (3)
C13A—C1A—C14A	111.77 (17)	C7A—C8A—C13A	108.2 (2)
C13A—C1A—C22A	112.05 (17)	C9A—C8A—C13A	119.8 (3)
C14A—C1A—C22A	108.72 (18)	C8A—C9A—C10A	119.6 (3)
C1A—C2A—C3A	129.0 (2)	C9A—C10A—C11A	120.9 (3)
C1A—C2A—C7A	110.99 (19)	C10A—C11A—C12A	120.8 (3)
C3A—C2A—C7A	120.0 (2)	C11A—C12A—C13A	118.8 (3)
C2A—C3A—C4A	118.7 (3)	C1A—C13A—C8A	111.23 (19)
C3A—C4A—C5A	120.2 (3)	C1A—C13A—C12A	128.6 (2)
C4A—C5A—C6A	121.9 (3)	C8A—C13A—C12A	120.1 (2)
C5A—C6A—C7A	118.5 (3)	C1A—C14A—C15A	116.12 (19)
C2A—C7A—C6A	120.6 (2)		

Disorder of one of the terminal C atoms of one octyl chain of one of the molecules was handled by splitting this atom into two equally occupied positions (C29*C* and C29*D*). The bond lengths and 1,3-distances involving these atoms were assigned fixed idealized values (C28*C*—C29*C* = C28*C*—C29*D* = 1.51 Å; C27*C*· · ·C29*C* = C27*C*· · ·C29*D* = 2.53 Å). Another *n*-octyl terminal atom (C21*C*) was also found to have a large U_{eq} value [0.203 (3) Å^2], but it could not be successfully split into two well behaved partial-occupancy positions; the bond distance [C20*C*—C21*C* = 1.497 (5) Å] and angle [C19*C*—C20*C*—C21*C* = 112.6 (3)°] involving this C atom are nonetheless acceptable. H atoms were generated in idealized positions, with C—H distances in the range 0.95–0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ1016). Services for accessing these data are described at the back of the journal.

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