organic papers

9,9-Bis(methoxycarbonylethyl)fluorene

Wei-Bing Hu,[a,b]* **Hong-Xia Liu,**[b] **Da-Ting Tian,**[b] **Cheng-Mei Liu**[a] **and Zu-Li Liu**[a]

[a]School of Science, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China, and [b]School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi, Hubei 445000, People's Republic of China

Correspondence e-mail: w.hu@tom.com

Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.005 Å
R factor = 0.060
wR factor = 0.187
Data-to-parameter ratio = 14.4

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

In the title compound, $C_{21}H_{22}O_4$, the three fused rings of the fluorene system are almost coplanar. There exists a weak intermolecular C—H···O interaction.

Comment

Since the discovery of an electroluminescent (EL) polymer in 1990, EL conjugated polymers and oligomers offer new opportunities for information technology because of potential application in light-emitting diodes (Yang *et al.*, 1996; Komaba *et al.*, 1997). Polyquinolines, polyquinoxalines and poly-fluorenes have recently been demonstrated as electron-transport layer light-emitting diodes because of their high thermal and oxidative stability, outstanding mechanical properties, and good film-forming ability (Kreyenschmidt *et al.*, 1998). However, polyquinolines, polyquinoxalines and polyfluorenes possess poor solution processability. Fluorene derivatives show interesting and unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at the 9-position (atom C13 in Fig. 1) can improve the solubility and processability of polymers without significantly increasing the steric interaction in the polymer backbone (Zhan *et al.*, 2002). As a result, homo-polymers 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; Johansson *et al.*, 2001). The synthesis of monomer (I) was carried out and the structure was determined by X-ray diffraction in order to confirm the molecular structure and to investigate its stereochemistry.

(I)
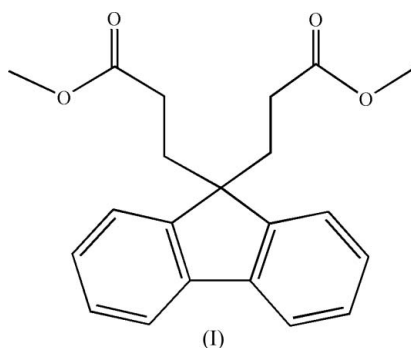
In (I), the three fused rings are essentially coplanar (Fig. 1), the dihedral angles formed by the five-membered ring with the two benzene rings being 0.6 (1)°. The two ester groups are nearly perpendicular to the fused-ring system. Selected bond lengths and angles are listed in Table 1. There is a weak intermolecular C—H···O interaction (Fig. 2 and Table 2).

3036 (Ar—H), 2948 (C—H), 1741 (C=O), 1449 (C=C), 1198, 1112 (C—O—C); ^{1}H NMR (CDCl$_3$): δ 7.71–7.31 (*m*, 8H), 3.46 (*s*, 6H), 2.43–2.39 (*m*, 4H), 1.58–1.53 (*m*, 4H). Elemental analysis calculated for C$_{21}$H$_{22}$O$_4$: C 74.54, H 6.55%; found: C 74.66, H 6.41%.

Crystal data

C$_{21}$H$_{22}$O$_4$	D_x = 1.204 Mg m^{-3}
M_r = 338.39	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2480
a = 12.0711 (18) Å	reflections
b = 10.0544 (15) Å	θ = 2.4–21.9°
c = 15.751 (2) Å	μ = 0.08 mm^{-1}
β = 102.390 (3)°	T = 292 (2) K
V = 1867.1 (5) Å^3	Block, colorless
Z = 4	0.30 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2243 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.025
Absorption correction: none	θ_{max} = 25.0°
9112 measured reflections	$h = -13 \rightarrow 14$
3274 independent reflections	$k = -11 \rightarrow 11$
	$l = -13 \rightarrow 18$

Refinement

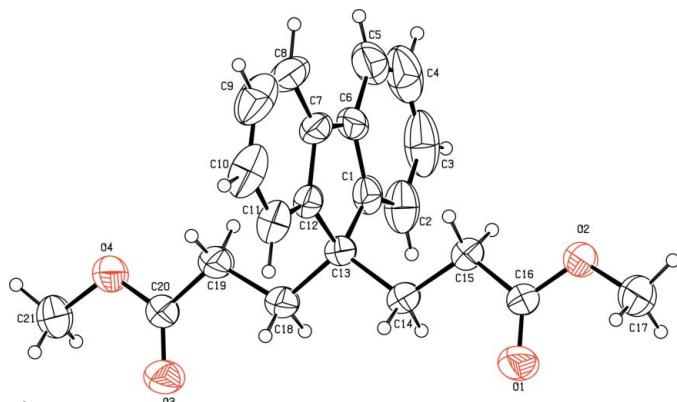|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0862P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.060	$+ 0.4752P]$
$wR(F^2)$ = 0.187	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
3274 reflections	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
228 parameters	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
H-atom parameters constrained	

Figure 1
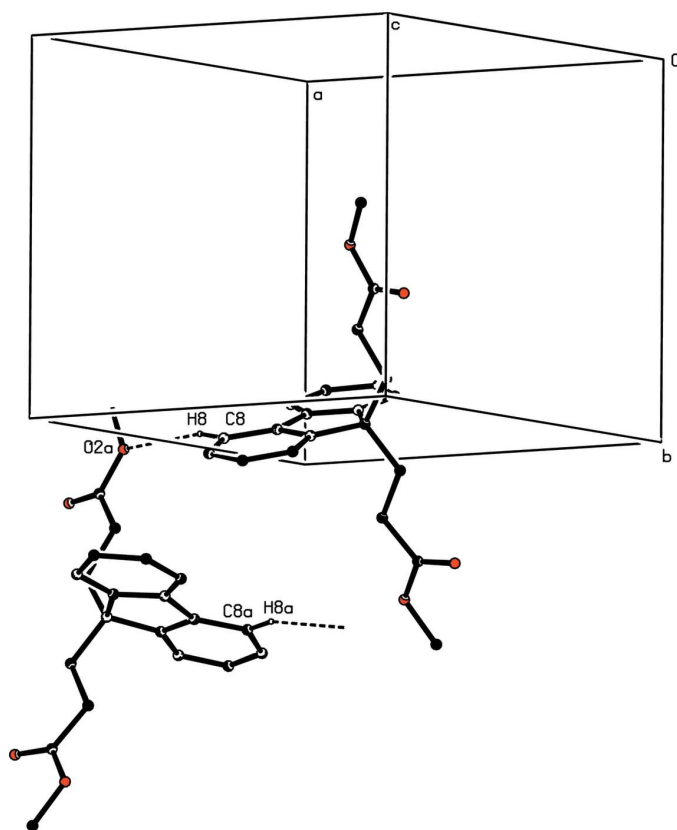The molecular structure of (I), showing 50% probability displacement ellipsoids.

Figure 2
Intermolecular C—H···O interactions (dashed lines) [symmetry code: (a) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

Table 1
Selected geometric parameters (Å, °).

C1—C6	1.395 (3)	C13—C18	1.539 (3)
C1—C13	1.515 (3)	C13—C14	1.544 (3)
C6—C7	1.463 (4)	C16—O1	1.187 (3)
C7—C12	1.378 (3)	C20—O3	1.195 (3)
C12—C13	1.508 (3)		
C6—C1—C13	110.4 (2)	C7—C12—C13	111.5 (2)
C1—C6—C7	108.4 (2)	C12—C13—C1	101.29 (18)
C12—C7—C6	108.3 (2)	C18—C13—C14	108.82 (17)
C6—C1—C2—C3	0.7 (4)	C7—C12—C13—C1	−0.7 (2)
C13—C1—C2—C3	179.9 (2)	C11—C12—C13—C18	60.1 (3)
C2—C1—C6—C5	0.6 (4)	C2—C1—C13—C14	62.5 (3)
C6—C7—C12—C11	−178.7 (2)	C1—C13—C14—C15	51.3 (3)
C8—C7—C12—C13	−178.8 (2)	C12—C13—C18—C19	55.9 (3)
C10—C11—C12—C13	179.7 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O2^i	0.93	2.57	3.462 (3)	161

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

All H atoms were initially located in difference Fourier maps. The methyl H atoms were then constrained to an ideal geometry, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å for phenyl H atoms, C—H = 0.97 Å for methylene H atoms and U_{iso}(H) = 1.2U_{eq}(C).

Experimental

A 50 ml three-necked round-bottomed flask was charged with fluorene (4 g) and methyl acrylate (5 ml) and heated to 308 K. Benzyltrimethylammonium methoxide (1 ml) was rapidly added dropwise with stirring, raising the temperature to 353 K. Excess methyl acrylate was evaporated by distillation to a kettle temperature of 343 K at a pressure of 10 mm Hg, then cooled to 263 K, and the residue was removed by filtration, air-dried and recrystallized from methanol to obtain the compound (I) in 83% yield. Suitable crystals for X-ray analysis were obtained by slow evaporation of a methanol solution at room temperature (m.p. 355–356 K). IR (KBr, v cm^{-1}):

organic papers

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

References

Bruker (2001). *SMART* (Version 5.628) and *SAINT-Plus* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.

Johansson, D. M., Ganlund, T., Theamder, M., Lnganas, O. & Andersson, M. R. (2001). *Synth. Met.* **121**, 1761–1762.

Komaba, S., Amano, A. & Osaka, T. J. (1997). *Electroanal. Chem.* **430**, 97–102.

Kreyenschmidt, M., Klaerner, G., Fuhrer, T., Ashenhurst, J., Karg, S., Chen, W. D., Lee, V. Y., Scott, J. C. & Miller, R. D. (1998). *Macromolecules*, **31**, 1099–1103.

Lee, S. H. & Tsuysui, T. (2000). *Thin Solid Films*, **363**, 76–80.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.

Yang, Y., Pei, Q. & Heeger, A. J. (1996). *Synth. Met.* **79**, 934–939.

Zhan, X. W., Liu, Y., Wu, X., Wang, S. & Zhu, D. B. (2002). *Macromolecules*, 35, 2529–2537.