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2,7-Dibromo-9,9-dioctylfluorene–Chloroform (1/0.25)

Mario Leclerc, Maxime Ranger and Francine Bélanger-Gariépy

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7.
E-mail: leclerma@ere.umontreal.ca

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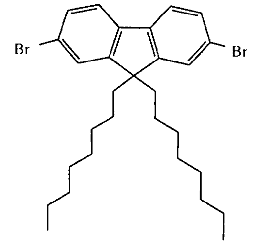
Abstract

In the solid state, the title compound, $C_{29}H_{40}Br_2.0.25CHCl_3$, crystallizes in the tetragonal system. The fluorene ring system is perfectly planar. The torsion angles in the octyl chains are all *trans*. These octyl chains are all orthogonal to the aromatic ring and are in the *ab* plane of the unit cell. The stacking of aromatic units is non-existent. In the cyclopentadiene ring, the angle at the benzilic carbon is 101.1 (3)° and is smaller than other angles in this part of the fluorene ring system.

Comment

There is growing interest in conducting polymers, especially those based on substituted conjugated polymers, since unsubstituted aromatic polymers decompose upon heating and are not soluble in most organic solvents, and are thus not easily processable. However, it has been shown that the presence of side chains lowers the melting point and makes, for instance, substituted polythiophenes soluble in most organic solvents, such as chloroform, tetrahydrofuran or toluene (Jen *et al.*, 1986; Sato *et al.*, 1986). Following this new method for preparing soluble conducting polymers, poly(paraphenylene)s (Kaeriyama *et al.*, 1997; Schlüter *et al.*, 1989) and polyfluorenes (Fukuda *et al.*, 1993; Pei & Yang, 1996) have been built with flexible side chains. In the case of polythiophenes and poly(paraphenylene)s, it seems that the presence of side chains does not greatly affect the conducting properties. On the other hand, most polyfluorenes show low conductivities (Fukuda *et al.*, 1989; Grell *et al.*, 1997; Ranger *et al.*, 1997; Miller *et al.*, 1997). The alkyl chains were suspected of hindering the stacking of the fluorene moieties and thus causing a major problem for electrical transport. To check this point, the structure of 2,7-dibromo-9,9-octylfluorene, (I), has been investigated. This molecule can serve as a model compound for poly-2,7-(9,9-dioctylfluorene).



(I)

A perspective representation of the title compound with the atomic numbering is shown in Fig. 1. The molecule, which possesses practically a rotation axis of order 2, consists of a planar fluorene ring system to which side chains are attached at the C9 atom. The dihedral angle C10—C11—C12—C13 is −0.1 (4)°. The angle between the plane composed of atoms C1–C4, C10 and C11, and the plane of the cyclopentadiene ring is 1.2 (2)°. The angle between the plane containing atoms C5–C8, C12 and C13, and the plane of the cyclopentadiene ring is 2.8 (2)°. These last results confirm that the fluorene moiety is practically planar. The C11—C12 distance is 1.474 (5) Å, while the C9—C10 and C9—C13 distances are 1.529 (6) and 1.503 (6) Å, respectively. These last distances show that the cyclopentadiene part of the fluorene ring system is

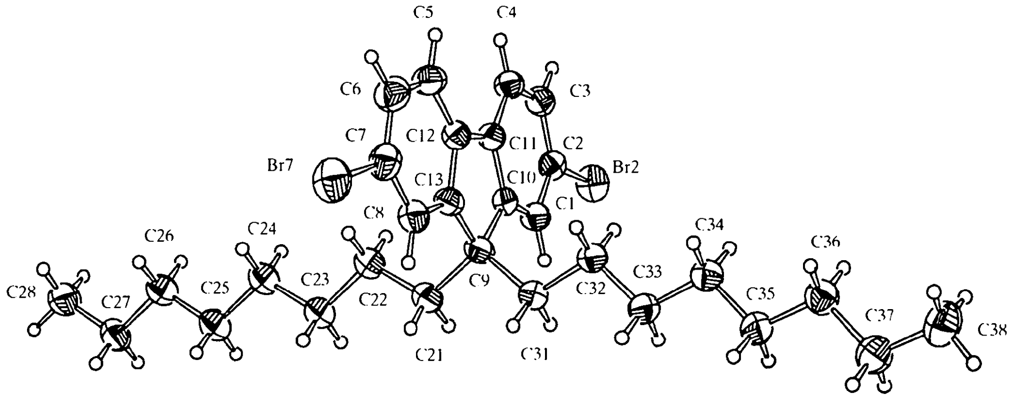


Fig. 1. *ORTEP*II view (Johnson, 1976) of $C_{29}H_{40}Br_2$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

not perfectly symmetric. On the other hand, the angle C10—C9—C13 is 101.1 (3)° and is smaller than other angles in this part of the ring. The octyl chains are orthogonal to the aromatic unit. All torsion angles in the octyl chains are *trans*. The stacking of aromatic units is non-existent because of the disposition of the octyl chains. The fluorene ring systems are disposed perpendicular to the one another with an interplanar angle of 90.00 (8)° and respect the rotation axis of order 4 of the unit cell.

Experimental

The title compound was obtained by the dialkylation of fluorene in position 9 with 1-bromooctane using *n*-butyllithium as base. The bromination was carried out by the addition of liquid bromine to 9,9-dioctylfluorene using $FeCl_3$ as catalyst according to Ranger *et al.* (1997). Suitable single crystals were grown by slow evaporation of a chloroform solution.

Crystal data

$C_{29}H_{40}Br_2.0.25CHCl_3$
$M_r = 578.27$
Tetragonal
$I\bar{4}$
$a = 18.871\ (7)$ Å
$c = 16.249\ (11)$ Å
$V = 5787\ (4)$ Å^3
$Z = 8$
$D_x = 1.328$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 20–22°$
$\mu = 4.277$ mm^{-1}
$T = 210\ (2)$ K
Block
0.68 × 0.19 × 0.16 mm
Clear white

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.244$, $T_{max} = 0.556$
11 372 measured reflections
5484 independent reflections

4502 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 69.84°$
$h = -22 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = 0 \rightarrow 19$
5 standard reflections frequency: 60 min intensity decay: 11.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.106$
$S = 1.042$
5484 reflections
335 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.030$
$\Delta\rho_{max} = 0.387$ e Å^{-3}
$\Delta\rho_{min} = -0.668$ e Å^{-3}

Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00013 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.48 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br2	0.82918 (3)	0.13916 (3)	0.70521 (3)	0.07375 (15)
Br7	0.81680 (3)	0.14304 (3)	0.05698 (3)	0.08667 (18)
C1	0.8173 (2)	0.1767 (2)	0.5356 (3)	0.0575 (10)
C2	0.8374 (2)	0.1234 (2)	0.5900 (2)	0.0522 (9)
C3	0.8626 (2)	0.0584 (2)	0.5643 (3)	0.0584 (10)
C4	0.8686 (2)	0.0450 (2)	0.4800 (3)	0.0563 (10)
C5	0.8654 (2)	0.0465 (2)	0.2775 (3)	0.0652 (11)
C6	0.8552 (2)	0.0605 (2)	0.1951 (3)	0.0714 (12)
C7	0.8303 (2)	0.1259 (3)	0.1699 (3)	0.0659 (11)
C8	0.8129 (2)	0.1786 (2)	0.2263 (3)	0.0603 (10)
C9	0.80416 (19)	0.21093 (18)	0.3812 (3)	0.0524 (8)
C10	0.82387 (19)	0.16262 (18)	0.4532 (2)	0.0487 (9)
C11	0.84869 (18)	0.09834 (19)	0.4250 (3)	0.0512 (9)
C12	0.84799 (19)	0.09881 (19)	0.3342 (3)	0.0533 (9)
C13	0.8222 (2)	0.16439 (19)	0.3091 (3)	0.0514 (9)
C21	0.72369 (19)	0.2296 (2)	0.3824 (3)	0.0602 (9)
C22	0.6736 (2)	0.1668 (2)	0.3812 (3)	0.0613 (10)
C23	0.5965 (2)	0.1895 (2)	0.3768 (3)	0.0599 (10)
C24	0.5460 (2)	0.1264 (2)	0.3760 (3)	0.0621 (10)
C25	0.4682 (2)	0.1463 (2)	0.3729 (3)	0.0649 (11)
C26	0.4196 (2)	0.0826 (2)	0.3726 (3)	0.0640 (10)
C27	0.3415 (2)	0.1016 (2)	0.3730 (4)	0.0692 (12)
C28	0.2935 (2)	0.0369 (2)	0.3737 (4)	0.0765 (13)
C31	0.84511 (19)	0.28176 (19)	0.3812 (3)	0.0558 (9)
C32	0.92584 (19)	0.27615 (18)	0.3806 (3)	0.0563 (9)
C33	0.9609 (2)	0.34887 (19)	0.3782 (3)	0.0598 (9)
C34	1.0411 (2)	0.3481 (2)	0.3788 (3)	0.0605 (10)
C35	1.0734 (2)	0.4213 (2)	0.3734 (3)	0.0623 (10)
C36	1.1537 (2)	0.4233 (2)	0.3745 (3)	0.0651 (11)
C37	1.1839 (3)	0.4987 (2)	0.3735 (4)	0.0746 (13)
C38	1.2629 (3)	0.5015 (3)	0.3762 (4)	0.0926 (16)
C40†	−0.032 (3)	0.018 (2)	0.020 (2)	0.074 (12)
Cl41†	0.026 (4)	0.066 (3)	0.085 (3)	0.0973 (19)
Cl42†	0.0233 (13)	0.0011 (16)	−0.0681 (16)	0.0973 (19)
Cl43†	−0.031 (3)	−0.066 (3)	0.069 (3)	0.0973 (19)
C50†	0.003 (3)	−0.017 (2)	−0.018 (3)	0.074 (12)
Cl51†	0.031 (2)	0.0588 (18)	0.038 (2)	0.0973 (19)
Cl52†	0.069 (3)	−0.023 (4)	−0.098 (3)	0.0973 (19)
Cl53†	−0.068 (3)	0.018 (4)	−0.076 (4)	0.0973 (19)
C60†	0.002 (2)	−0.007 (2)	0.026 (2)	0.074 (12)
Cl61†	0.0554 (13)	−0.0669 (16)	−0.0294 (17)	0.0973 (19)
Cl62†	−0.035 (2)	−0.065 (2)	0.102 (3)	0.0973 (19)
Cl63†	−0.0697 (16)	0.0092 (19)	−0.042 (3)	0.0973 (19)
C70†	0.005 (2)	−0.027 (3)	0.037 (2)	0.074 (12)
Cl71†	0.018 (4)	0.062 (2)	0.072 (3)	0.0973 (19)
Cl72†	−0.0241 (19)	−0.0682 (17)	0.1313 (17)	0.0973 (19)
Cl73†	−0.0776 (13)	−0.0206 (16)	−0.0129 (5)	0.0973 (19)

† Site occupancy = 0.0625.

Table 2. *Selected geometric parameters (Å, °)*

C1—C10	1.370 (6)	C8—C13	1.383 (6)
C1—C2	1.392 (6)	C9—C13	1.503 (6)
C2—C3	1.380 (5)	C9—C10	1.529 (6)
C3—C4	1.398 (6)	C9—C31	1.544 (5)
C4—C11	1.399 (5)	C9—C21	1.559 (5)
C5—C6	1.378 (7)	C10—C11	1.379 (5)
C5—C12	1.389 (6)	C11—C12	1.474 (5)
C6—C7	1.382 (7)	C12—C13	1.391 (5)
C7—C8	1.392 (6)		
C13—C9—C10	101.1 (3)	C4—C11—C12	130.3 (4)
C21—C9—C31	107.0 (3)	C5—C12—C11	131.1 (4)
C9—C10—C1	127.6 (3)	C11—C12—C13	107.6 (3)
C10—C11—C12	109.0 (3)	C12—C13—C9	111.8 (3)

H atoms were placed in ideal positions and refined as riding atoms with different C—H distances for different types of C—H bond. The isotropic displacement factors, U_{iso}, were adjusted to values 50 (methyl) and 20% (others) higher than those of the bonded C atom. Highly disordered solvent molecules located in the vicinity of a $\bar{4}$ center were found distributed over symmetry-related positions. The proportion and identity of the solvent, $CHCl_3$, were confirmed using the *SQUEEZE* routine of the *PLATON* program (Spek, 1995) (V_s = 492.5 Å^3 and 114.5 electrons per cell). Final refinements were carried out using a disordered description of the solvent and no *SQUEEZE* correction was applied to the data for the solvent contribution. Solvent was refined using a constraint (*DFIX*) and restraints (*SAME*/*SADI*) in order to improve the solvent model. All C atoms have the same isotropic displacement parameters and all Cl atoms have the same isotropic displacement parameters. A small hole remained in this structure accounting for zero electrons and 36.2 Å^3 of the volume of the cell. The absolute structure was determined by way of the *SHELXL*96 (Sheldrick, 1996) instructions *TWIN*, with a matrix ($\bar{1}00$, $0\bar{1}0$, $00\bar{1}$), and one *BASF* parameter to give a value of the Flack (1983) parameter of 0.48 (2). The crystal is thus an equicomponent inversion twin.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96. Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1412). Services for accessing these data are described at the back of the journal.

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Methyl 7α,12α-Dihydroxy-3α-methacryloyloxy-5β-cholan-24-oate

Huiyou Liu, Francine Bélanger-Gariépy, Mehdi Akram, Mariana Moskova and Xiao-Xia Zhu

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: zhuj@ere.umontreal.ca

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Abstract

The structure determination of the title compound, $C_{29}H_{46}O_6$, establishes the selective esterification of the hydroxyl group on position 3 of the steroid skeleton of the cholic acid methyl ester. The asymmetric unit contains one molecule and the crystal structure is stabilized by intermolecular hydrogen bonds. The two side chains on the steroid skeleton are quite flexible and each has two orientations; a disorder model was introduced and two sets of atoms were refined for the side chains.

Comment

The biological importance, the amphiphilic properties and the acid–base properties of bile acids make them interesting starting materials in the preparation of new polymers with potential biomedical and pharmaceutical applications.

The title compound, (I), was synthesized from one of the most commonly occurring bile acids, cholic acid, and was one of the monomers synthesized for the preparation of the new polymers. It can be readily polymerized by a free-radical polymerization in solution (Ahlheim & Hallensleben, 1992; Zhu *et al.*, 1996) and co-polymerized with methacrylic monomers such as methacrylic acid and 2-hydroxyethyl methacrylate (Zhu *et al.*, 1996).