

1,1-Di(9-fluorenyl)ethanol, a by-product from the acetylation of 9-fluorenyllithium

Cal Y. Meyers,^a Hisham G. Lutfi,^a Yuqing Hou^a and Paul D. Robinson^{b*}

^aDepartment of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, and ^bDepartment of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA
Correspondence e-mail: robinson@geo.siu.edu

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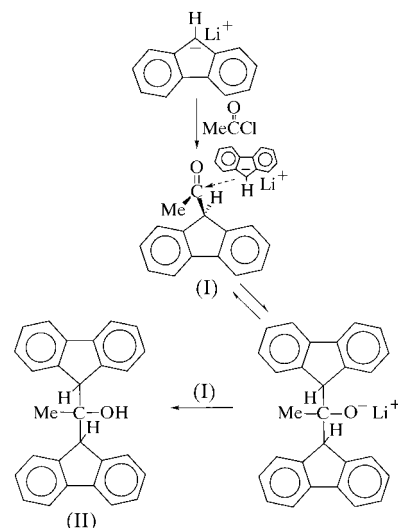
Treatment of 9-fluorenyllithium with acetyl chloride produces 9-acetylfluorene, (I), and several by-products. Among them is a compound unequivocally identified for the first time as the addition product of (I) with 9-fluorenyllithium, 1,1-di(9-fluorenyl)ethanol, C₂₈H₂₂O, (II). The two fluorene-ring planes of (II) are essentially perpendicular [89.90 (9)°]. A number of intermolecular non-bonding distances are well within or close to the sum of their respective van der Waals radii and may be responsible for the rarely observed large bowing of one of the fluorene rings. This bowing apparently arises from two molecules impinging on the convex face of the bowed ring, augmented by hydrogen bonding between the peripheral π electrons of the concave face and the hydroxyl H atom of another molecule adjacent to that face.

Comment

The reaction of 9-fluorenyllithium with acetyl chloride provided 9-acetylfluorene, (I), as the major product (Meyers *et al.*, 2000) along with by-products, among which was the 'diacetylfluorene', unequivocally identified as 9-(1-acetoxyethylidene)fluorene (Robinson *et al.*, 2000). A second by-product has now been isolated and characterized unequivocally as 1,1-di(9-fluorenyl)ethanol, (II). We believe that (II) results from an aldol addition of 9-fluorenyllithium to (I) (see Scheme). Although the acetylation of the 9-fluorenyl anion has been reported by several investigators, (II) was neither identified nor suggested as a by-product (*cf.* Naik *et al.*, 1988; Rouzaud *et al.*, 1965; Scherf & Brown, 1961; Greenhow *et al.*, 1953; Von & Wagner, 1944; Miller & Bachman, 1935), nor has it been noted in any previous literature.

The X-ray structure of (II) with the atomic numbering is shown in Fig. 1. The two fluorenyl-ring planes are nearly perpendicular to each other, subtending an angle of 89.90 (9)°. Some of the 18 short intramolecular contacts involving H atoms are as much as 0.36 Å less than the sum of their respective van der Waals radii [contact radii used for C, H, and

O are 1.70, 1.20, and 1.52 Å, respectively (Bondi, 1964)]. However, little angular distortion is exhibited other than that possibly suggested by the differences in angles subtended from the common *sp*³-hybridized C10 atom, which range from



105.7 (2) to 112.1 (2)°. A surprising feature exhibited by (II) is the significant bowing of one of its fluorene-ring planes, illustrated by the labeled central molecule of Fig. 2 and substantiated by the out-of-plane distances of the C atoms of the normally planar fluorene ring, *e.g.* C2' -0.192 (4), C7' -0.168 (4), C9' 0.200 Å (3), *etc.* A full list of the fluorene least-squares-plane parameters can be found in the CIF. No similar bowing is exhibited in the X-ray structures of the many other fluorene compounds we have reported.

Fig. 2 also shows the three surrounding molecules which impinge on both faces of the central bowed fluorene ring, and the resulting seven short intermolecular interactions. Of these, three are less than or equal to the sum of their respective van

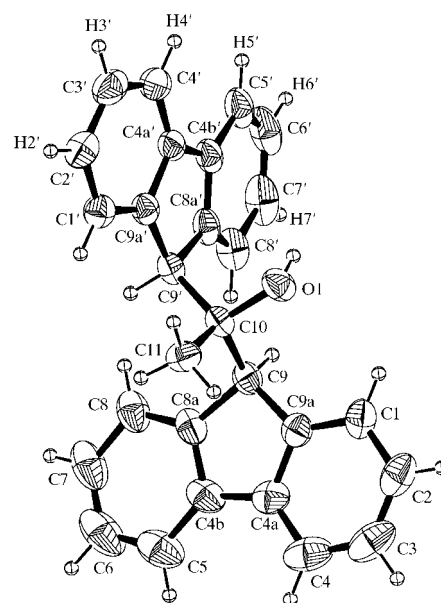


Figure 1
The molecular structure and atom-numbering scheme for (II) with displacement ellipsoids at the 30% probability level.

der Waals radii, and four are very slightly longer (>0.0 but <0.10 Å). In our opinion, the three which involve direct impingement on the atoms toward the ends of the convex face of the origin molecule are mainly responsible for the observed bowing. These interactions, respectively, are 0.09 Å less than, equal to, and 0.02 Å greater than the sum of their van der Waals radii. In addition, there is a possible weak hydrogen bond from the hydroxyl group of molecule 3 (symmetry code: $x, -y, -\frac{1}{2} + z$) to the π cloud of the upper phenyl ring of the origin molecule (see Fig. 2). Using the centroid (Cg1) of this phenyl ring as the acceptor site, the hydrogen-bond geometry (O1—H1 \cdots Cg1) is $D-H$ 0.93 Å, $H\cdots Cg1$ 3.02 Å, $D\cdots Cg1$ 3.528 (2) Å and $D-H\cdots Cg1$ 123° . It should be noted that the $H\cdots Cg1$ distance is longer than that between this H atom and the closest C atoms of the upper phenyl ring of the origin molecule, *viz.* C1' 2.71 and C2' 2.96 Å. Thus, the suspected hydrogen bond may not be directed at the phenyl-ring centroid *per se*, but more toward its periphery, producing a minor attractive force which may contribute to the observed bowing. That this bowing of one of the fluorene rings is a solid-state phenomenon is supported by the molecular symmetry of (II) in solution, indicated by the NMR equivalency of the corresponding atoms of its two fluorene moieties.

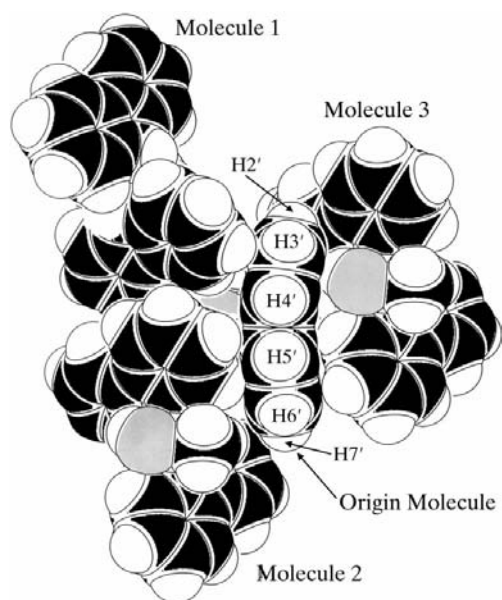


Figure 2
A space-filling representation of the origin molecule surrounded by the three equivalent molecules which impinge upon it. The hydroxyl O atoms are shaded grey. Note the bowing of the origin molecule. (Symmetry codes: molecule 1: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; molecule 2: $x, -y, \frac{1}{2} + z$; molecule 3: $x, -y, -\frac{1}{2} + z$.)

Experimental

Compound (II) was isolated by flash chromatography as one of the by-products in our preparation of (I) from the reaction of 9-fluorenyllithium with acetyl chloride in tetrahydrofuran under argon (Meyers *et al.*, 2000; Robinson *et al.*, 2000). Recrystallization from hexane provided colorless crystals, m.p. 454.0 – 455.5 K (corrected, no decomposition), used for the NMR and X-ray diffraction studies.

Crystal data

$C_{28}H_{22}O$
 $M_r = 374.46$
Monoclinic, $C2/c$
 $a = 34.792$ (5) Å
 $b = 10.0951$ (17) Å
 $c = 11.6821$ (17) Å
 $\beta = 102.962$ (12) $^\circ$
 $V = 3998.5$ (10) Å 3
 $Z = 8$

$D_x = 1.244$ Mg m $^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 7.6$ – 10.8°
 $\mu = 0.074$ mm $^{-1}$
 $T = 296$ K
Plate, colorless
 $0.36 \times 0.31 \times 0.05$ mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans (rate 1° min $^{-1}$)
3580 measured reflections
3521 independent reflections
1330 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$
 $\theta_{max} = 25.0^\circ$

$h = 0 \rightarrow 41$
 $k = 0 \rightarrow 12$
 $l = -13 \rightarrow 13$
3 standard reflections every 150 reflections
intensity decay: 0.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.138$
 $S = 0.968$
3521 reflections
265 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.11$ e Å $^{-3}$
 $\Delta\rho_{min} = -0.13$ e Å $^{-3}$
Extinction correction: SHELXL97
Extinction coefficient: 0.0014 (3)

The rotational orientations of the methyl and hydroxyl groups were refined by the circular Fourier methods available in SHELXL97 (Sheldrick, 1997). All H atoms were riding (C—H = 0.93 – 0.98 Å).

Data collection and cell refinement: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1996); data reduction: TEXSAN (Molecular Structure Corporation, 1997); structure solution: SHELXS97 (Sheldrick, 1990); structure refinement: TEXSAN and SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1965); software used to prepare material for publication: TEXSAN, SHELXL97 and PLATON (Spek, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1118). Services for accessing these data are described at the back of the journal.

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