

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

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Received 28 September 2000

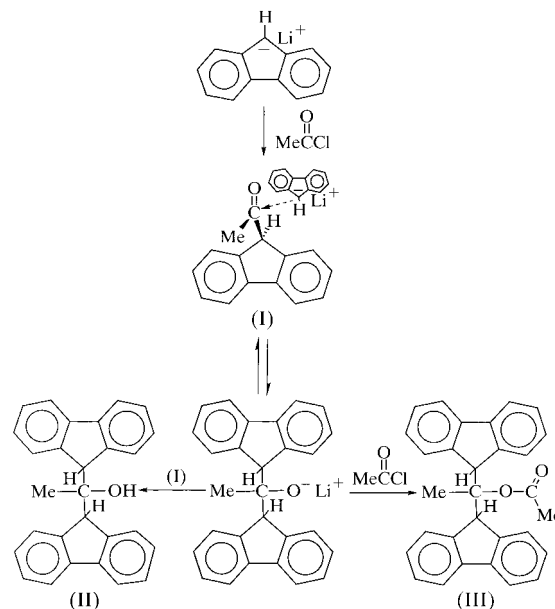
Accepted 25 January 2001

The preparation of *sp*-9-acetylfluorene from the reaction of 9-fluorenyllithium with acetyl chloride also provided 9-(1-acetoxyethylidene)fluorene ('diacetylfluorene') and 1,1-di(9-fluorenyl)ethanol, (II), as by-products recently characterized by X-ray analysis. A third by-product, 1,1-di(9-fluorenyl)ethyl acetate, (III), C₃₀H₂₄O₂, has now been unequivocally identified for the first time, and emanates from the acetylation of the oxyanion of (II). In the asymmetric unit, compound (III) exists as two almost identical structures which differ slightly, but significantly, in conformation. Neither possesses the significant fluorene-ring bowing or the perpendicularity of the two ring planes exhibited by (II). The angle between the least-squares planes of the two fluorene rings of (III) is 58.45 (9) and 60.95 (10)°, respectively, for the two conformations, and their corresponding bonding parameters also differ slightly in a number of instances.

Comment

Although the acetylation of 9-metallated fluorenes with acetyl chloride and related reagents has received much attention (*e.g.* Naik *et al.*, 1988; Rouzaud *et al.*, 1965; Scherf & Brown, 1961; Greenhow *et al.*, 1953; Von & Wagner, 1944; Miller & Bachman, 1935), the results have been controversial, mainly because of inadequate structure identification of the products. Moreover, difficulties in their separation and purification also led to discrepancies in the reported melting points. In light of this situation and the important stereochemistry associated with 9-substituted fluorenes, we undertook a re-examination of the reaction of 9-fluorenyllithium with acetyl chloride in tetrahydrofuran (THF). This study afforded the definitive characterization of the major product, *sp*-9-acetylfluorene, (I) (Meyers *et al.*, 2000), and two by-products, 9-(1-acetoxyethylidene)fluorene (Robinson *et al.*, 2001), and 1,1-di(9-fluorenyl)ethanol, (II) (Meyers *et al.*, 2001). A third by-

product, only slightly less polar than (II) and present in very small amounts, was detected by thin-layer chromatography (TLC) and separated *via* flash chromatography. There was insufficient material to obtain a definitive NMR spectrum, but the ¹H NMR spectrum of the separated material indicated that it contained (II) and another difluorenyl compound similar to (II). A single crystal was selected from the mass and submitted to X-ray analysis, which indicated this compound to be 1,1-di(9-fluorenyl)ethyl acetate, (III). Subsequently, larger amounts of (III) were synthesized directly by the acetylation of isolated (II) with acetic anhydride and dimethylaminopyridine, as well as with acetyl chloride and pyridine. ¹H and ¹³C NMR, as well as an additional X-ray analysis, unequivocally confirmed the suggested structure. As illustrated in the scheme below, a reasonable pathway leading to (III) in the acetylation involves nucleophilic attack of the 9-fluorenyllithium on initially formed (I) to provide the oxyanion of (II), which is subsequently either protonated to form (II) or acetylated with residual acetyl chloride to form (III). While, as already noted, (III) has not been previously identified as a product in the acetylation of the 9-fluorenyl anion, Von & Wagner (1944) reported that the major product in this reaction, (I), 'deteriorated rapidly on storage with conversion to dimeric acetylfluorene.' They suggested no structure for this dimer, and provided only elemental analysis and molecular weight, both of which are identical to those of (III). They noted that their dimer did not react with phenylhydrazine, which also would apply to (III). However, they reported a melting point of 520–521 K (corrected) for their dimer, while (III) melts sharply at 441.5–443.0 K (corrected). In light of the sharp difference in melting points and mode of formation of the two products, it is reasonable to assume that the Von & Wagner dimer and (III) are not the same.



The X-ray structure of (III) with the atom numbering for the two molecules in the asymmetric unit is illustrated in Fig. 1. The structure reveals two almost identical molecules which differ slightly, but significantly, in conformation and is a not-

too-common example of the concurrent cocrystallization of more than one molecular conformation. Differences between the two molecules in the asymmetric unit are manifested in their geometric parameters. Table 1 illustrates the largest differences in the geometric parameters between molecules 1 and 2. Note that equivalent torsion angles about one of the two bonds that join the two fluorene rings of each molecule (the C9X—C10 bond in molecule 1 and the C9Z—C10' bond in molecule 2) generally differ by 7–8°. These significant torsional differences are associated with all of the significant bond-angle variations listed in Table 1, which range from 5 to 8σ . By contrast, smaller differences are observed between equivalent torsion angles about the C9—C10 and C9Y—C10' bonds, which are the other bonds connecting the two fluorene rings in the respective molecules.

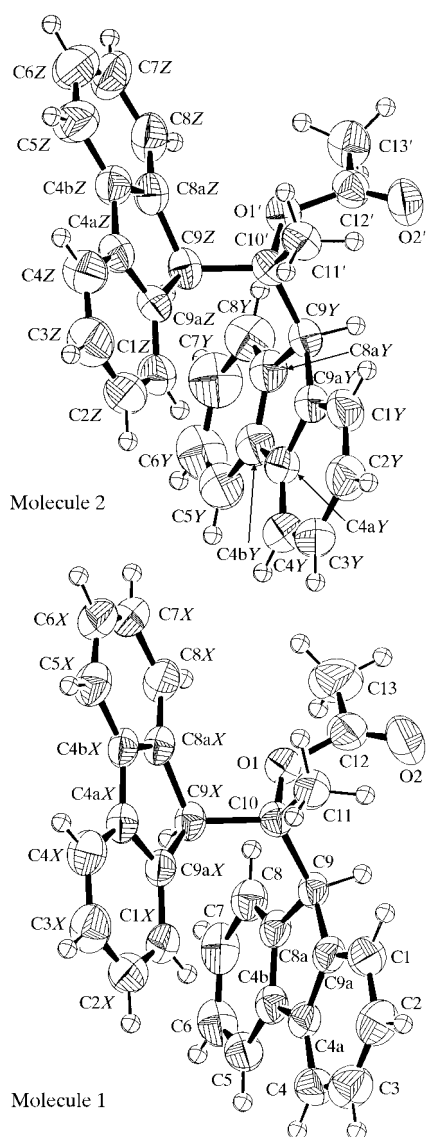


Figure 1
The molecular structure and atom-numbering scheme for (III) with displacement ellipsoids at the 50% probability level. Although both molecules reside in the asymmetric unit, they have been rotated relative to each other for clarity and to emphasize the fact that they are nearly identical.

Chemically, compound (II), a di-9-fluorenyl alcohol, differs only slightly from its acetate ester (III). However, significant conformational differences are apparent in their crystal structures. For example, while the two fluorene rings of (II) are normal to each other, those in (III) deviate from perpendicularity by 31.55 (9) (molecule 1) and 29.05 (10)° (molecule 2). In addition, the significant bowing of one of the fluorene rings of (II) has been suggested to emanate from its intermolecular interactions in the packing structure (Meyers *et al.*, 2001). Such bowing is much less obvious in (III). While all of the fluorene rings of (III) are reasonably flat, the two on the right side (Fig. 1) are significantly flatter (χ^2 values of 1517 and 753 for molecules 1 and 2, respectively) than those on the left (χ^2 values of 4811 and 7415 for molecules 1 and 2, respectively). Complete least-squares-plane data for all of the fluorene rings can be found in the CIF.

Experimental

Compound (III) 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 THF under argon (Meyers *et al.*, 2000, 2001; Robinson *et al.*, 2001). It was also prepared directly from (II) *via* treatment with acetic anhydride and dimethylamino-pyridine, or acetyl chloride and pyridine. Chromatographically (TLC and column) it was slightly less polar than (II); m.p. 441.5–443.0 K (corrected). $^1\text{H NMR}$: δ 1.67 (s, 3H), 2.25 (s, 3H), 4.87 (s, 2H), 7.01 (m, 4H), 7.16 (ddd, 2H, $J = 7.5, 1.2$ Hz), 7.26 (dd, 2H, $J = 7.5$ Hz), 7.35 (dd, 2H, $J = 7.5$ Hz), 7.59 (d, 2H, $J = 7.5$ Hz), 7.64 (d, 2H, $J = 7.5$ Hz), 7.68 (d, 2H, $J = 7.5$ Hz); $^{13}\text{C NMR}$: δ 20.92, 22.82, 54.52, 89.53, 119.53, 119.57, 126.24, 126.40, 126.80, 126.85, 127.29, 127.43, 141.93, 142.02, 142.66, 143.52, 169.89. Von & Wagner (1944) reported an m.p. of 520–521 K for ‘dimeric 9-acetylfluorene’, and the same M_r and elemental analysis as (III).

Crystal data

$\text{C}_{30}\text{H}_{24}\text{O}_2$
 $M_r = 416.49$
Triclinic, $P\bar{1}$
 $a = 13.211$ (3) Å
 $b = 19.044$ (3) Å
 $c = 9.5505$ (12) Å
 $\alpha = 98.852$ (11)°
 $\beta = 108.115$ (14)°
 $\gamma = 74.565$ (14)°
 $V = 2194.7$ (6) Å³

$Z = 4$
 $D_x = 1.260$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.0$ – 11.3°
 $\mu = 0.077$ mm⁻¹
 $T = 296$ K
Irregular fragment, colorless
0.43 × 0.41 × 0.27 mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
8103 measured reflections
7737 independent reflections
2792 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 25.0^\circ$

$h = 0 \rightarrow 15$
 $k = -21 \rightarrow 22$
 $l = -11 \rightarrow 10$
3 standard reflections
every 100 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.140$
 $S = 0.972$
7737 reflections
581 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0460P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C2X—C3X	1.386 (5)	C8X—C8aX	1.378 (4)
C2Z—C3Z	1.372 (5)	C8Z—C8aZ	1.391 (5)
C8a—C9—C10	116.8 (3)	O1—C10—C11	111.3 (2)
C8aY—C9Y—C10'	114.7 (3)	O1'—C10'—C11'	110.3 (2)
C8aX—C9X—C10	111.7 (3)	O1—C10—C9X	100.3 (2)
C8aZ—C9Z—C10'	113.7 (3)	O1'—C10'—C9Z	101.9 (2)
C9aX—C9X—C10	116.2 (3)	C9—C10—C9X	116.8 (2)
C9aZ—C9Z—C10'	114.2 (3)	C9Y—C10'—C9Z	115.2 (3)
C9aX—C9X—C10—O1	−175.8 (2)	C8aX—C9X—C10—O1	−59.9 (3)
C9aZ—C9Z—C10'—O1'	−164.6 (3)	C8aZ—C9Z—C10'—O1'	−49.6 (3)
C9aX—C9X—C10—C11	−58.4 (3)	C8aX—C9X—C10—C11	57.5 (3)
C9aZ—C9Z—C10'—C11'	−47.5 (4)	C8aZ—C9Z—C10'—C11'	67.4 (3)
C9aX—C9X—C10—C9	72.6 (3)	C8aX—C9X—C10—C9	−171.5 (3)
C9aZ—C9Z—C10'—C9Y	83.3 (3)	C8aZ—C9Z—C10'—C9Y	−161.8 (3)

The rotational orientations of the methyl 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: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); program(s) used to refine structure: *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON* (Spek, 2000).

Partial support of this research from Southern Illinois University through Distinguished Professorship funding (CYM) and from the University Research Foundation (La Jolla) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1121). Services for accessing these data are described at the back of the journal.

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