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## *sp*-9-Acetylfluorene, the initial acetylation product of 9-fluorenyllithium

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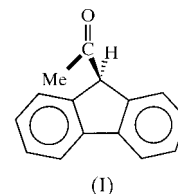
Data validation number: IUC0000220

The reaction of 9-fluorenyllithium with acetyl chloride (tetrahydrofuran, 213 K, under argon) provided four products which we have isolated and whose structures we have unequivocally identified for the first time. That of the initially formed component, 9-acetylfluorene (C<sub>15</sub>H<sub>12</sub>O), described here, shows it to be exclusively the *sp* rotamer in its crystalline form. The acetyl C—C=O plane is essentially perpendicular to the planar fluorene ring and there is no indication of rotational restriction. In contrast, related 9-pivaloylfluorene, which we reported previously, is rotationally restricted and exists exclusively as its *ap* rotamer, in which the pivaloyl C—C=O plane is also almost perpendicular to the fluorene ring.

### Comment

Acylation of 9-fluorenyl anion have been described in numerous reports, but the identities of the various products have not been characterized by X-ray diffraction and have been subjects of controversy (Naik *et al.*, 1988; Rouzard *et al.*, 1965; Scherf & Brown, 1961; Greenhow *et al.*, 1953; Von & Wagner, 1944; Miller & Bachman, 1935). The direct characterization of the initially formed component from acetylation is hampered by its great reactivity leading to other products under the reaction conditions, *e.g.* formation and X-ray crystal structure of the dipivaloylation product of 9-fluorenyllithium (Robinson *et al.*, 2000) and by its rapid degradation in the presence of air. We have isolated 9-acetylfluorene, (I), the initially formed crystalline acetylation product, and characterized it unequivocally for the first time by X-ray diffraction as the *sp* rotamer. Its solution NMR spectrum, which does not definitively convey a configuration, compared favourably with that previously reported (Ohwada & Shudo, 1988). The *sp* configuration of crystalline (I) is in contrast to that of crystalline 9-pivaloylfluorene whose *ap* configuration is fixed by the rotationally restricted pivaloyl group (Meyers *et al.*, 1991). The 87.78 (14)° dihedral angle between the fluorene-ring plane and the C9—C10—C11—O1 plane and the torsion angle H9—C9—C10—O1 of -1.2°

reflect the near perpendicularity of the C—C=O and fluorene-ring plane and the *sp* configuration of crystalline (I), respectively.



### Experimental

A molar equivalent of *n*-BuLi was added to a solution of fluorene in freshly distilled tetrahydrofuran maintained at 213 K under argon. After this mixture was stirred for 20 min, a molar equivalent of acetyl chloride in tetrahydrofuran was added. Stirring was maintained at 213 K for 20 min, then at room temperature for 90 min. An excess of dilute HCl was added, the mixture was extracted with ether and the combined extracts were dried (anhydrous MgSO<sub>4</sub>) and concentrated *in vacuo*. Thin-layer chromatography indicated the presence of several different compounds, which were separated and isolated by flash chromatography. Aside from recovered fluorene (*ca* 43%), the other major crystalline compound was identified by <sup>1</sup>H and <sup>13</sup>C NMR as 9-acetylfluorene (*ca* 32%), m.p. 347–348 K (corr.) from hexane and unequivocally characterized as the *sp* rotamer by X-ray diffraction.

#### Crystal data

|                                   |   |
|-----------------------------------|---|
| C <sub>15</sub> H <sub>12</sub> O | $D_x = 1.217 \text{ Mg m}^{-3}$           |
| $M_r = 208.25$                    | Mo $K\alpha$ radiation                    |
| Monoclinic, $P2_1/n$              | Cell parameters from 23 reflections       |
| $a = 11.253 (4) \text{ \AA}$      | $\theta = 2.3\text{--}8.1^\circ$          |
| $b = 5.740 (6) \text{ \AA}$       | $\mu = 0.075 \text{ mm}^{-1}$             |
| $c = 17.782 (6) \text{ \AA}$      | $T = 296 \text{ K}$                       |
| $\beta = 98.19 (3)^\circ$         | Prism, colourless                         |
| $V = 1136.9 (13) \text{ \AA}^3$   | $0.49 \times 0.43 \times 0.38 \text{ mm}$ |
| $Z = 4$                           |   |

#### Data collection

|                                       |                          |
|---------------------------------------|--------------------------|
| Rigaku AFC-5S diffractometer          | $h = 0 \rightarrow 13$   |
| $\omega$ scans                        | $k = 0 \rightarrow 6$    |
| 2109 measured reflections             | $l = -21 \rightarrow 20$ |
| 2001 independent reflections          | 3 standard reflections   |
| 981 reflections with $I > 2\sigma(I)$ | every 100 reflections    |
| $R_{\text{int}} = 0.043$              | intensity decay: -0.3%   |
| $\theta_{\text{max}} = 25.16^\circ$   |                          |

#### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.0629P]$    |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $wR(F^2) = 0.156$               | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| $S = 1.008$                     | $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$  |
| 2001 reflections                | $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$ |
| 146 parameters                  |  |
| H-atom parameters constrained   |  |

Compound (I) is quite air sensitive and several initial attempts at data collection failed. The data used in this study were obtained from a crystal which was coated with vacuum grease and sealed in a glass capillary. The rotational orientation of the methyl group was refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC*

*Diffraction Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*, *SHELXL97*, and *PLATON* (Spek, 2000).

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