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The surprising *sp* rotameric structure of 9-methyl-9-pivaloylfluorene[1]

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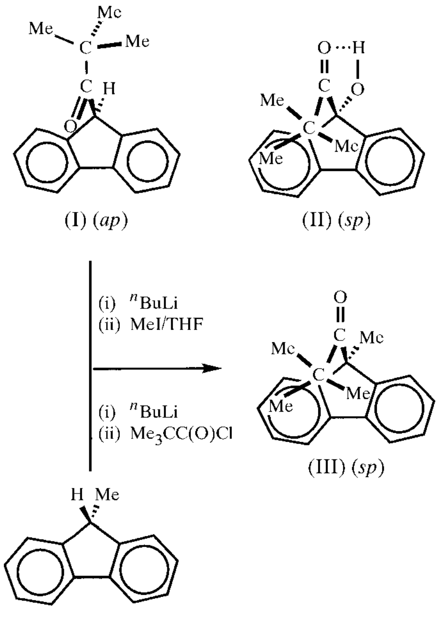
Methylation of 9-lithiated *ap*-9-pivaloylfluorene, (I), as well as pivaloylation of 9-lithiated 9-methylfluorene provided rotationally stable *sp*-9-methyl-9-pivaloylfluorene, (III), $C_{19}H_{20}O$, which lies about a crystallographic mirror plane. Fluorene (I) exists exclusively in the *ap* configuration in solution (NMR) as well as in the crystalline state, reflecting the unfavorable interaction between the *tert*-butyl and fluorene-ring π electrons in the *sp* configuration. The existence of (III) exclusively in the *sp* configuration indicates that, in *this* case, the interaction between the *tert*-butyl group and the fluorene-ring π electrons provides relatively more thermodynamic stability than the steric interaction between the *tert*-butyl and 9-methyl groups (*ap* configuration).

Comment

We previously reported that the *ap* rotamer of 9-pivaloylfluorene, (I), is the exclusive configuration in solution (NMR) as well as in the crystalline state (Meyers *et al.*, 1991). Shortly afterwards, we reported the surprising observation that the related 9-hydroxy-9-pivaloylfluorene, (II), exists solely in the *sp* configuration, both in solution and as crystals (Meyers *et al.*, 1992). The exclusive *ap* configuration of (I) reflects its thermodynamic stability relative to the *sp* configuration, in which there is unfavorable interaction between the *tert*-butyl group and fluorene-ring π electrons. While this same unfavorable interaction would be realized in the *sp* configuration of (II), it was suggested that, in this case, intramolecular hydrogen bonding (*viz*. C=O···HO) in this configuration lowered the energy sufficiently to make the *sp* rotamer thermodynamically preferred. Replacement of the 9-OH group by CH_3 would not afford such hydrogen bonding. However, it was not known *a priori* whether the steric interaction between the *tert*-butyl and the fluorene-ring π electrons (*sp* rotamer) or between the *tert*-butyl and 9-CH_3 groups (*ap* rotamer) would impart the lesser thermodynamic stability.

9-Methyl-9-pivaloylfluorene was prepared by two quite different routes (see Scheme and *Experimental*), namely methylation of (I) and pivaloylation of 9-methylfluorene. The crystalline products were identical, melting sharply without decomposition. ^1H NMR at room temperature exhibited a singlet for the pivaloyl protons at δ 0.67, indicating their strong shielding by the fluorene ring, characteristic of the *sp* rotamer of 9-methyl-9-pivaloylfluorene, (III), in solution (Meyers *et al.*, 1992), and an absence of the signal near δ 1.25 which is exhibited by the deshielded pivaloyl protons of related *ap* counterparts (Robinson *et al.*, 1994; Meyers *et al.*, 1991).



This study firmly establishes the *sp* configuration of crystalline (III) (Fig. 1). The geometric parameters of (III) (Table 1) are very similar to the parameters of the corresponding bonds of (II) (Meyers *et al.*, 1992), for the most part differing by no more than about 1° or 0.01 Å. Those that differ to a larger extent are in the direction which could be asso-

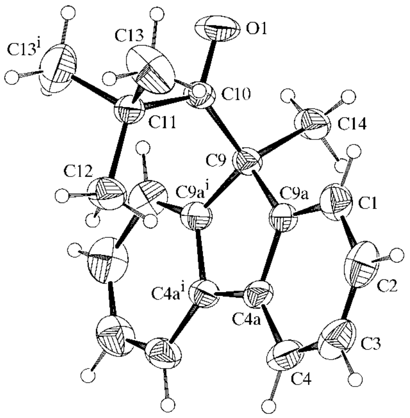


Figure 1
The molecular structure and atom-numbering scheme for (III) with displacement ellipsoids at the 30% probablilty level. Atoms C9, C14, C10, O1, C11 and C12 lie on a plane of symmetry. [Symmetry code: (i) $2 - x, y, z$.]

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[1] The designations *sp* (synperiplanar) and *ap* (antiperiplanar) for these configurations are in accord with Rule E-6.6 of IUPAC Tentative Rules (IUPAC, 1970).

ciated with intramolecular hydrogen bonding in (II), exemplified by the following comparisons of corresponding angles and torsion angles of (II) and (III), respectively: O1—C10—C9 115.4 (4)/118.5 (3)°; C10—C9—C9a—C4a 125.6 (4)/122.8 (2)°; C10—C9—C9a—C1 −53.5 (5)/−58.9 (4)°; and C14—C9—C9a—C1 67.8 (5)/63.2 (4)°.

It is concluded that the *sp* configuration of (III) is not associated with intramolecular hydrogen bonding or crystal-packing forces, this being the exclusive rotamer also in solution, and is therefore the sterically induced thermodynamically favored rotamer. The fact that *both* (II) and (III) exist solely as their *sp* rotamers while the 9-H parent compound (I) exists exclusively as its *ap* rotamer might not have been predicted from our recent observations of the related but more sterically restricted 9-H, 9-OH and 9-CH_3 9-(*o-tert*-butylphenyl)fluorenes (Hou & Meyers, 1999; Meyers *et al.*, 1999; Robinson *et al.*, 1998), in which intramolecular hydrogen bonding is not a possibility. In the latter series, both the 9-H and 9-OH fluorenes exist exclusively in the same singular configuration (crystalline form and solution), while the 9-CH_3 fluorene exists in the *opposite* configuration, showing that an H atom and an OH group have similar steric influence, while a CH_3 group imparts a substantially greater effect. With this in mind, the fact that (II) and (III), but not (I), are both *sp* configured further supports the probability that this configuration for (II) is promoted by intramolecular hydrogen bonding, but for (III), is induced by steric factors.

Experimental

Preparation of *sp*-9-methyl-9-pivaloylfluorene, (III). Method 1: pivaloylation of 9-methylfluorene. Based on the method reported by McCollum (1977), after earlier reports by Ullman & Wustemburger (1905) and Wanscheidt & Moldavski (1931), treatment of 9-fluorenone with CH_3MgI followed by aqueous NH_4Cl provided 9-methyl-9-fluorenol, which was reduced to 9-methylfluorene with H_3PO_2/I_2 in HOAc. In the manner reported for the preparation of 9-pivaloylfluorene from fluorene (Meyers *et al.*, 1991), 9-lithiated 9-methylfluorene treated with pivaloyl chloride at 213 K readily produced (III). Flash chromatography provided colorless crystals [71% yield, m.p. 431–431.5 K (uncorrected); same m.p. after heating to 458 K and allowing to recrystallize from the melt], shown by X-ray analysis to be exclusively the *sp* rotamer, which was likewise the case for solutions of (III) as determined by ^1H NMR at room temperature. IR (concentrated $CDCl_3$): δ 1680 cm^{-1} (sharp, strong; C═O); ^1H NMR (Varian VXR 300; $CDCl_3$): δ 1.54 (*s*, 3H, 9-CH_3), 0.67 [*s*, 9H, $C(CH_3)_3$]; ^{13}C NMR (Varian VXR 300, 75 MHz for ^{13}C; $CDCl_3$): δ 46.42 [$\mathit{C}(CH_3)_3$], 28.26 [$C(\mathit{C}H_3)_3$], 25.73 (9-CH_3). Method 2: methylation of 9-pivaloylfluorene. To a stirred solution of *ap*-9-pivaloylfluorene (Meyers *et al.*, 1991) in THF under argon and maintained at 213 K, ^{n}BuLi (Aldrich, in hexanes) was injected. The deep-red stirred solution was then maintained at 273 K and methyl iodide was injected. The solution became slightly yellow within 20 min. This mixture was stirred at room temperature for an additional 30 min. Thin-layer chromatography indicated the presence mainly of (III). The reaction was quenched with aqueous NH_4Cl, the mixture extracted with ether, and the extract dried and rotary evaporated. Column chromatography (silica gel, 230–400 mesh; hexanes/ether 10:1) provided colorless crystals identified by ^1H NMR as (III) [93% yield, m.p. 430.5–431.5 K (corrected)].

Crystal data

$C_{19}H_{20}O$
$M_r = 264.35$
Orthorhombic, $Cmc2_1$
$a = 13.908$ (2) Å
$b = 15.3513$ (18) Å
$c = 7.1860$ (6) Å
$V = 1534.3$ (3) Å^3
$Z = 4$
$D_x = 1.144$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.0$–$10.5°$
$\mu = 0.069$ mm^{-1}
$T = 296$ K
Fragment, colorless
0.51 × 0.49 × 0.43 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 6° min^{-1})
1137 measured reflections
997 independent reflections
691 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.53°$

$h = 0 \rightarrow 18$
$k = 0 \rightarrow 19$
$l = -1 \rightarrow 9$
3 standard reflections
every 150 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.138$
$S = 1.024$
997 reflections
102 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.0776P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (4)

Table 1
Selected geometric parameters (Å, °).

O1—C10	1.195 (5)		
C10—C9—C14	108.9 (3)	C9a—C9—C10	112.85 (19)
C9—C10—C11	123.9 (3)	O1—C10—C9	118.5 (3)
C9a—C9—C14	110.34 (19)	O1—C10—C11	117.6 (3)
C10—C9—C9a—C1	−58.9 (4)	C10—C9—C9a—C4a	122.8 (2)
C14—C9—C9a—C1	63.2 (4)	C14—C9—C9a—C4a	−115.2 (2)

The 140 Friedel pairs measured were merged in the final cycles of refinement because the f'' terms in the scattering-factor expression are insignificant for this structure. All H atoms are riding.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON* (Spek, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1104). Services for accessing these data are described at the back of the journal.

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