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sp-9-(*o*-Methylphenyl)fluorene

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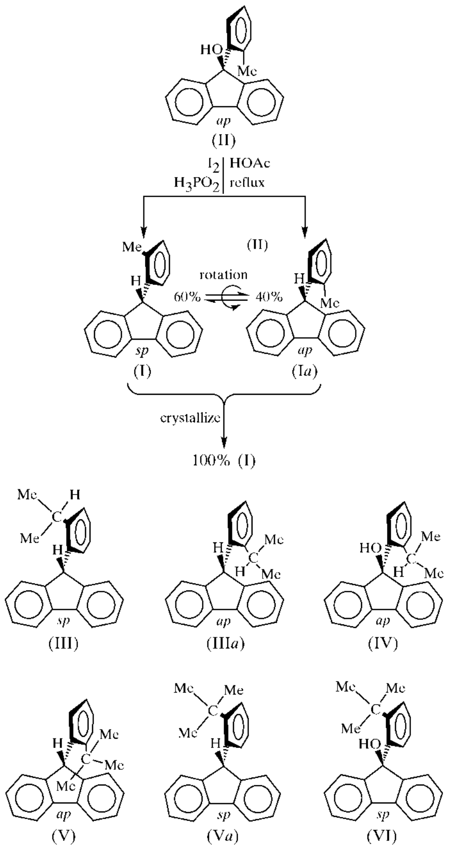
While the barriers of rotation of the *sp* and *ap* rotamers of 9-(*o*-methylphenyl)fluorene, $C_{20}H_{16}$, are sufficiently similar to permit them to equilibrate, both being observed (NMR) in solution, crystallization provides the *sp* rotamer, (I), exclusively. Although in the *sp* conformation the intramolecular distance between adjacent C atoms of the phenyl and fluorene rings is small [3.382 (4) Å, within 0.02 Å of the sum of the van der Waals radii], in the *ap* conformation the distance between the adjacent *o*-CH_3 group on the phenyl ring and C atom of the fluorene ring would be much closer, based on that exhibited in the crystalline *ap* progenitor 9-(*o*-methylphenyl)-9-fluorenol. The angle between the fluorene and 9-aryl planes of (I) is 75.82 (10)°.

Comment

Crystalline 9-(*o*-methylphenyl)fluorene, (I), prepared from *ap*-9-(*o*-methylphenyl)-9-fluorenol, (II) (Meyers, Robinson & McLean, 2003), is entirely composed of the *sp* rotamer (Fig. 1). The angle between the fluorene and 9-aryl planes is 75.82 (10)°.

Geometric intermolecular calculations suggest the possible presence of a weak C4—H4···*Cg*1^{i} interaction [where *Cg*1 is the centroid of the C1–C4/C4a/C9a ring; symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$], with an H···*A* distance of 2.82 Å, a *D*···*A* distance of 3.634 (3) Å and a *D*—H···*A* angle of 146°. This rather poor geometry suggests only a possible weak interaction at best. In addition, the fact that, after melting, (I) recrystallizes immediately at room temperature suggests the absence of any effective intermolecular hydrogen bonding, based on the tentative correlations raised by our related studies (Meyers, Robinson & McLean, 2003; Robinson *et al.*, 2003*a*,*b*; McLean *et al.*, 2003*a*,*b*, 2004; Meyers, McLean & Robinson, 2003).

Although in this *sp* conformation, the intramolecular distance between atoms C15 and C8 of (I) is small [3.382 (4) Å, within 0.02 Å of the sum of the van der Waals radii], in the *ap* conformation the distance between the CH_3 group (C16) and the fluorene ring (C8a) would be much closer, *e.g.* near the value of 3.140 (3) Å (within 0.26 Å of the sum of the van der Waals radii) in its crystalline *ap* progenitor (II). The *sp* conformation of the latter is so sterically hindered by the 9-OH group that it is not observed in solution (although the ^{1}H NMR resonance of *o*-CH_3 is broad; Meyers, Robinson & McLean, 2003). This restriction is alleviated in (I) by replacement of 9-OH by H. These factors plausibly account for the equilibration of *sp*-(I) (60%) and *ap*-(I) (40%) in solution, in which rotation is allowed but is slow enough to permit each to be observed. In turn, this interpretation appears much more valid than one suggesting that it is the intramolecular attractive interaction (van der Waals forces) between the *o*-methyl H atoms and the fluorene ring in (II) that promotes its *ap* rotamer exclusivity even in solution.



This explanation is strengthened by our earlier observations with the corresponding *o*-isopropyl compounds, which parallel those described above. Thus, like (I), 9-(*o*-isopropylphenyl)-fluorene (Meyers *et al.*, 1997) in solution also exhibited equilibrating *sp* [(III), 70%] and *ap* [(III*a*), 30%] rotamers, but crystallization provided the *sp* rotamer exclusively, while the corresponding 9-fluorenol, (IV) (Hou *et al.*, 1999), like 9-fluorenol (II), exists entirely as the *ap* rotamer both in solution and in the crystal. In contrast with these examples, the greater magnitude of steric hindrance between an *o*-*tert*-butyl group and the fluorene ring in *ap* conformation (V) reduces the rotational barrier of that rotamer substantially, forcing 9-(*o*-*tert*-butylphenyl)fluorene, (V*a*), and its corresponding

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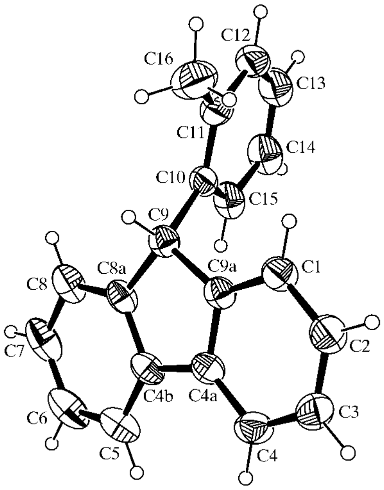

Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 30% probability level.

9-fluorenol, (VI), to exist exclusively in their *sp* rotamers in solution as well as in their crystalline forms (Robinson *et al.*, 1998). The very low rotational barrier of the highly hindered *ap*-9-(*o*-*tert*-butylphenyl)fluorene rotamer, (V), has been shown by the observation that, although it is exclusively formed *via* deprotonation–reprotonation inversion of *sp* rotamer (V*a*), it rapidly rotates back to 100% of the *sp* rotamer (Hou & Meyers, 2004).

Experimental

A solution of I_2 (0.018 g, 0.071 mmol), 50% aqueous H_3PO_2 (1.4 ml, 13.52 mmol) and glacial acetic acid (10 ml) was heated under argon until it became colorless, and 9-(*o*-methylphenyl)-9-fluorenol (Meyers, Robinson & McLean, 2003; 0.317 g, 0.663 mmol) was then added. The yellow mixture was refluxed under argon for 5 h and cooled. Water (50 ml) was added and the mixture was extracted with ether. The combined extracts were washed with saturated aqueous sodium bicarbonate, dried (anhydrous $MgSO_4$) and concentrated *in vacuo* to give a pale-yellow solid (0.283 g, 95% yield). Recrystallization (hexanes/methanol ~1:1) afforded pale-yellow crystals of (I) [m.p. 363–364 K; literature melting point 365–367.5 K (Bordwell *et al.*, 1982)]. The melt crystallized immediately upon cooling, the resulting crystals having the same melting point as those formed prior to melting. Spectroscopic analysis, ^1H NMR ($CDCl_3$, δ): 1.14 (*s*, *ap*, 1.2H), 2.79 (*s*, *sp*, 1.8H, CH_3, two rotamers), 5.03 (*s*, *ap*, 0.4H), 5.43 (*s*, *sp*, 0.6H, 9-H, two rotamers), 6.37–6.39 (*m*, 1H), 6.89–6.99 (*m*, 1H), 7.09–7.14 (*m*, 1H), 7.22–7.41 (*m*, 2H), 7.61–7.64 (*m*, 1H), 7.81–7.84 (*m*, 2H); ^{13}C NMR ($CDCl_3$, δ): 20.47, 49.92, 56.19, 98.98, 119.89, 124.69, 125.06, 125.72, 126.48, 126.58, 127.13, 127.27, 127.49, 130.32, 131.59, 132.63.

Crystal data

$C_{20}H_{16}$
$M_r = 256.33$
Monoclinic, $P2_1/c$
$a = 12.9887$ (17) Å
$b = 6.075$ (2) Å
$c = 18.7903$ (16) Å
$\beta = 104.701$ (8)°
$V = 1434.1$ (5) Å^3
$Z = 4$

$D_x = 1.187$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.8$–19.2°
$\mu = 0.07$ mm^{-1}
$T = 296$ K
Irregular fragment, colorless
0.49 × 0.46 × 0.35 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
2659 measured reflections
2539 independent reflections
1515 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 25.0°$

$h = 0 \rightarrow 15$
$k = 0 \rightarrow 7$
$l = -22 \rightarrow 21$
3 standard reflections every 100 reflections intensity decay: 4.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.166$
$S = 1.07$
2539 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.3078P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.016 (3)

The rotational orientation of the methyl group was refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). All H atoms were treated as riding, with C—H distances ranging from 0.93 to 0.98 Å and $U_{\rm iso}$(H) values equal to 1.5 (methyl H atoms) or 1.2 (all other H atoms) times $U_{\rm eq}$ of the parent atom.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); structure solution: *SIR*92 (Burla *et al.*, 1989); structure refinement: *TEXSAN* and *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1463). Services for accessing these data are described at the back of the journal.

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