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ap-9-(*meta-tert*-Butylphenyl)fluorene

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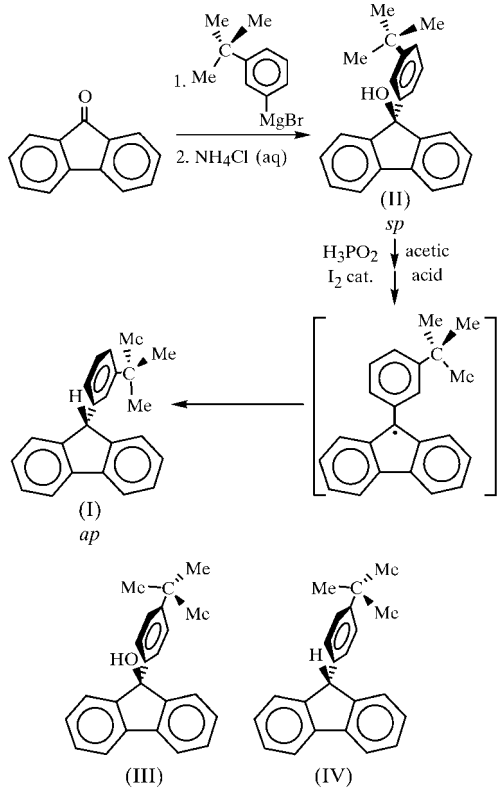
The title compound, $C_{23}H_{22}$, (I), crystallizes in an *ap* conformation[1] and its melt readily recrystallizes on cooling, in contrast to the corresponding 9-fluorenol compound, (II), which is *sp* and which melts without decomposition and fails to recrystallize over a long period. Both of these differences are ascribed to the intermolecular hydrogen bonding in (II), which is absent in (I) and which leads to distinctly different molecular packing in the two compounds.

Comment

We have been studying the characteristics and variability of *sp versus ap* conformations of 9-(*tert*-butylphenyl)- and 9-(isopropylphenyl)fluorenes and their corresponding 9-fluorenols both in solution and in the crystalline state (Hou, 1997; Meyers *et al.*, 1997, 1999; Robinson *et al.*, 1998; Hou *et al.*, 1999). The solution conformations were readily ascertained by ^{1}H NMR spectroscopy. In this context, we have now examined the title compound, *viz.* 9-(*meta-tert*-butylphenyl)fluorene, (I), prepared from 9-(*meta-tert*-butylphenyl)-9-fluorenol, (II). While (II), as we recently reported, is freely rotating in solution, it crystallizes as its *sp* conformer, exhibits O—H$\cdots\pi$(fluorene) intermolecular hydrogen bonds in its molecular packing and melts undecomposed, but the melt fails to recrystallize over a long period (Meyers *et al.*, 2003).

The structure of (I) with its atom-numbering scheme is shown in Fig. 1. No hydrogen bonding is evident, the shortest H9–fluorene distance being about 3.8 Å, which precludes the most reasonable C—H$\cdots\pi$(arene)-type bond. Solution NMR clearly shows free rotation of the 9-aryl group, and the angle between the fluorene and aryl planes of crystalline (I) [78.71 (6)°] would easily accommodate either the *sp* or the *ap* rotomeric conformation. However, Fig. 1 shows that crystalline (I) is *ap*, in contrast to its *sp*-9-fluorenol progenitor (II). This surprising difference in the rotational conformations in the crystalline state may be associated with a difference in the molecular packing. The intermolecular O—H$\cdots\pi$(fluorene) hydrogen bonding present in the molecular packing of (II) (Meyers *et al.*, 2003) requires the *tert*-butyl group and the C9—O bond to point in the same direction, hence the O1—C9—C10—C11 torsion angle of −11.6 (4)°, *i.e.* the *sp* conformation. In contrast, the preferred molecular packing of (I) requires the corresponding *tert*-butyl group and the C9—H bond to point in opposite directions, hence the H9—C9—C10—C11 torsion angle of 157°, *i.e.* the *ap* conformation.



When (I) is melted it recrystallizes readily, in contrast to the failure of melted (II) to recrystallize over a long period, a behavior which may be associated with the difficulty of

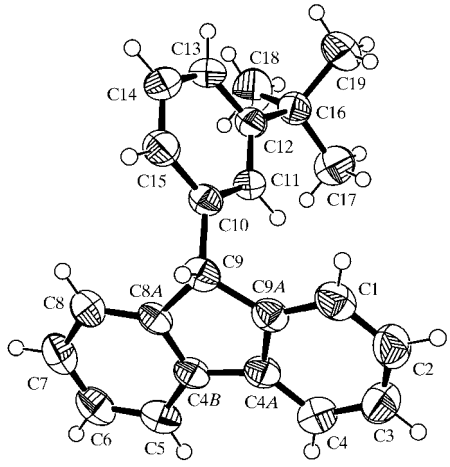


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level.

[1] The designations *sp* (synperiplanar) and *ap* (antiperiplanar) for these fluorene rotamers are in accordance with Rule E-6.6, IUPAC Tentative Rules, Section E, Fundamental Stereochemistry [*J. Org. Chem.* (1970), **35**, 2861].

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reforming the intermolecular hydrogen bonds required for the molecular packing of crystals of (II). This explanation, rather than one involving conformational differences, is supported by our recent observation that the melt of 9-(*para-tert*-butylphenyl)-9-fluorenol, (III), which is devoid of this type of conformational isomerism but which exhibits intermolecular hydrogen bonding, likewise fails to recrystallize when cooled (McLean *et al.*, 2003). In contrast, the corresponding fluorene (IV), which has no OH group and cannot undergo hydrogen bonding, produces a melt that readily recrystallizes on cooling.

Experimental

Compound (I) was prepared from (II) in a manner similar to that used for the conversion of other 9-fluorenols to fluorenes (Hou, 1997; Robinson *et al.*, 1998; Meyers *et al.*, 1999). A stirred solution of iodine (14.2 mg, 0.0559 mmol), 50% aqueous H_3PO_2 (1.4 ml, 13.52 mmol) and glacial acetic acid (10 ml) was heated under argon until the mixture became colorless, whereupon 9-(*meta-tert*-butylphenyl)-9-fluorenol (0.251 g, 0.799 mmol; Meyers *et al.*, 2003), (II), was added. The mixture was refluxed for 3 h, cooled to room temperature, diluted with water (50 ml) and extracted with ether. The extract was washed with saturated aqueous sodium bicarbonate, dried (anhydrous $MgSO_4$) and concentrated *in vacuo*, yielding a white solid [0.226 g, yield 95%, colorless crystals (from hexanes), m.p. 328.5–330.0 K]. The melt recrystallized on cooling and remelted at the same temperature. ^{1}H NMR ($CDCl_3$): δ 1.31 (*s*, 9H), 5.05 (*s*, 1H), 6.71–6.74 (*m*, 1H), 7.12–7.40 (*m*, 9H), 7.787 (*s*, 1H), 7.813 (*s*, 1H); ^{13}C NMR ($CDCl_3$): δ 31.38, 34.66, 54.70, 119.81, 123.71, 124.87, 125.32, 125.82, 127.20, 128.32, 140.98, 141.06, 147.86, 151.46. Compound (IV) was prepared from (III) by the method described above and recrystallized from hexanes [m.p. 433.5–435.5 K; literature m.p. 436–438 K (Tolbert *et al.*, 1992)]. The crystals that reformed from the cooled melt exhibited an identical melting point. ^{1}H NMR ($CDCl_3$): δ 1.29 (*s*, 9H), 5.04 (*s*, 1H), 7.01–7.03 (*m*, 2H), 7.22–7.40 (*m*, 8H), 7.78–7.81 (*m*, 2H); ^{13}C NMR ($CDCl_3$): δ 31.59, 34.41, 54.18, 120.04, 125.61, 125.79, 127.44, 128.07, 138.55, 141.21, 148.22, 149.74, 154.93.

Crystal data

$C_{23}H_{22}$
M_r = 298.41
Monoclinic, $P2_1/n$
a = 10.069 (3) Å
b = 14.981 (3) Å
c = 11.714 (3) Å
β = 100.17 (2)°
V = 1739.2 (8) Å^3
Z = 4
D_x = 1.140 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 17.3–20.7°
μ = 0.06 mm^{-1}
T = 296 K
Irregular fragment, colorless
0.54 × 0.43 × 0.33 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
3263 measured reflections
3080 independent reflections
2043 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.1°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 17$
$l = -13 \rightarrow 13$
3 standard reflections
every 100 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.109
S = 1.04
3080 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.2217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0174 (17)

The rotational orientations of the methyl H atoms of the *tert*-butyl group were 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_{iso}(H) values equal to 1.5 (methyl H atoms) or 1.2 (all other H atoms) times U_{eq} of the parent atom.

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: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1435). Services for accessing these data are described at the back of the journal.

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