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ap-9-(*o*-Methylphenyl)-9-fluorenol, a structure exhibiting several aryl-H···π(arene) intermolecular interactions

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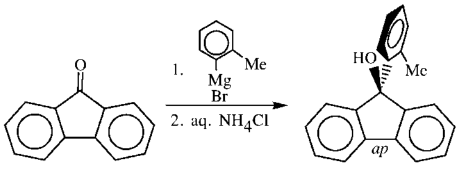
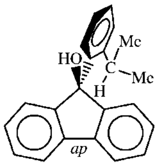
The title compound, $C_{20}H_{16}O$, (I), which crystallized exclusively as its *ap* rotamer, exhibits several intermolecular aryl-H···π(arene) interactions, resulting in planar molecular arrays in which each molecule interacts with six adjacent molecules. Surprisingly, there were no O—H···O—H or O—H···π(arene) interactions within hydrogen-bonding distances. Crystalline (I) melted sharply without molecular decomposition (NMR), but the cooled melt recrystallized only after several hours.

Comment

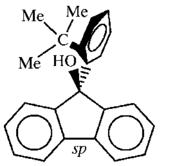
ap-9-(*o*-Methylphenyl)-9-fluorenol, (I), prepared from the reaction of fluorenone with *o*-tolylmagnesium bromide, crystallized as its *ap* rotamer, as illustrated with the atom-numbering in Fig. 1, which was also its exclusive conformation in solution, determined by NMR resonance. Several intermolecular aryl-H···π(arene) interactions were observed (Table 1), resulting in planar molecular arrays in which each molecule interacts with six adjacent molecules, shown in Fig. 2.



(I)



(II)



(III)

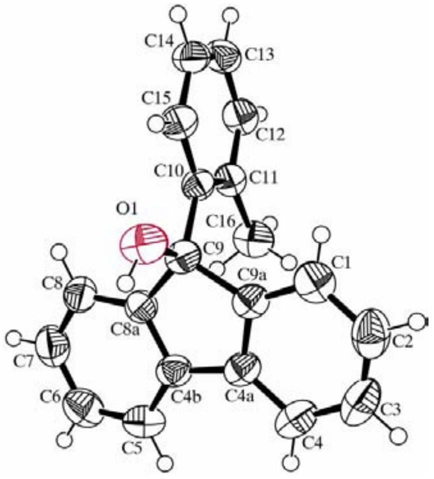


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probablilty level.

Surprisingly, there were no O—H···O—H or O—H···π(arene) interactions within hydrogen-bonding distances, the only remote possibility being the latter, in which a near interaction with an H1···C2^{ii} distance of 3.02 Å, an O1···C2^{ii} distance of 3.783 (3) Å, and an O1—H1···C2^{ii} angle of 157° was observed [symmetry code: (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. While (I) exhibited a sharp melting point, the melt recrystallized only after standing at room temperature overnight, and the melting point of the reformed crystals was identical to that of the original crystals, showing that no decomposition had occurred during melting. The fact that the cooled melt recrystallized within several hours but not immediately may be associated with the extensive intermolecular aryl-H···π(arene) interactions in the absence of stronger interactions involving O—H···O—H hydrogen bonds. Like (I), related 9-(*o*-isopropylphenyl)-9-fluorenol, (II), crystallized as its *ap* rotamer, which also was shown by NMR to be its only rotamer in solution (Hou *et al.*, 1999). However, while crystalline (II), like (I), exhibited no O—H···O—H hydrogen bonding, it did provide parameters suggesting O—H···π(fluorene) intermolecular hydrogen bonding. Also like (I), the cooled melt of (II) recrystallized only after about 24 h, and the NMR spectra of the melts of (I) and (II) were identical to that of their crystals, again showing that molecular decomposition did not occur on melting. In the case of (II), it is suggested that this phenomenon is associated with the weak O—H···π(fluorene) intermolecular hydrogen bonding in the absence of stronger O—H···O—H hydrogen-bonding interactions. In contrast, related 9-(*o*-*tert*-butylphenyl)-9-fluorenol, (III), crystallized exclusively as its *sp* rotamer, which was also true of its solution, the very large barrier restricting rotation of the 9-(*o*-*tert*-butylphenyl) group being responsible for the absence of its *ap* rotamer even in solution (Robinson *et al.*, 1998). In further contrast, the molecular packing of (III) exhibited O—H···O—H as well as O—H···π(fluorene) intermolecular hydrogen bonding, and its melt failed to recrystallize on cooling even after long standing, in line with the suggested explanation of the behavior of (I) and (II).

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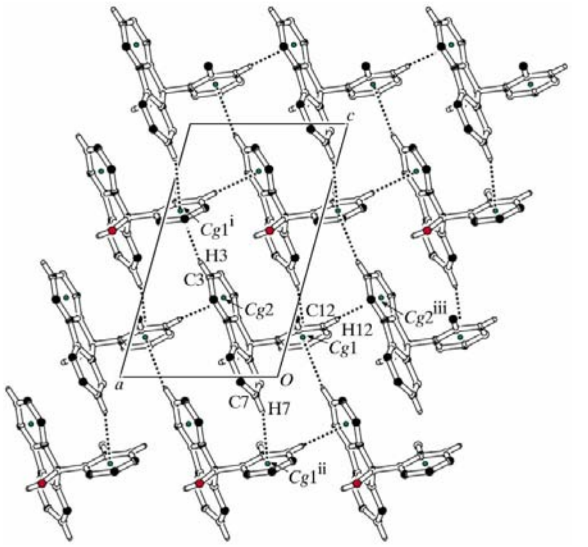

Figure 2

The molecular packing and aryl–H···π(arene) interactions in (I). Note that there are three crystallographically distinct interactions which form tightly knit planar arrays of molecules normal to [010]. Only one of the two parallel planes that pass through the unit cell is shown. *Cg*1 and *Cg*2 represent the centroids of rings C10–C15 and C1–C4/C4a/C9a, respectively. [Symmetry codes: (i) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$.]

As seen from the torsion angles O1—C9—C10—C11 of −177.60 (14)°, O1—C9—C10—C15 of 3.2 (2)°, and C9—C10—C11—C16 of 2.1 (2)°, the 9-aryl plane is essentially perpendicular to the fluorene plane. In this *ap* conformation of (I), therefore, the *o*-methyl C atom (C16) is virtually touching the fluorene ring, clearly illustrated in Fig. 1 and by the observed parameters C16···C8a = 3.140 (3) Å (0.26 Å less than the sum of their van der Waals radii) and C16···C9a = 3.182 (3) Å (0.22 Å less than the sum of their van der Waals radii). In spite of these proximities, it must be assumed, therefore, that the *ap* rotamer of (I) affords the greatest rotational thermodynamic favorability. This characteristic may be an intrinsically molecular feature, since it is exhibited by crystalline (I) as well as (I) in solution, the spectrum of the latter also indicating the presence of the *ap* rotamer exclusively, *viz*. the shielded methyl resonance of (I), δ 1.31, compared to that of the related *m*-methyl compound, δ 2.29 (McLean *et al.*, 2003).

Experimental

After a mixture of magnesium (0.36 g, 14.71 mmol), freshly distilled tetrahydrofuran (15 ml) and 1,2-dibromoethane (0.30 ml, 3.48 mmol) was stirred and gently heated under an atmosphere of argon until bubbles appeared on the surface of the magnesium, *o*-bromotoluene (1.90 g, 11.11 mmol) was added and heating was continued until all of the magnesium had been consumed. A solution of fluorenone (1.06 g, 5.89 mmol) in tetrahydrofuran (20 ml) was then added and the reaction mixture, which immediately turned dark brown, was refluxed for 6 h. After being cooled to 298 K, the mixture was diluted with water, then with an excess saturated aqueous ammonium chloride solution, and extracted with ether. The dried extracts (anhydrous $MgSO_4$), concentrated *in vacuo*, yielded a tan-colored oil which solidified after several days (yield 1.41 g, 88.3%). Recrystallization from hexanes provided colorless crystals [m.p. 392–393 K; literature m.p. 394–395 K (Chandross & Sheley, 1968)]. The melted crystals failed to recrystallize on standing for several hours at room temperature, but very slowly crystallized overnight, providing crystals whose melting point was identical to that of the original crystals. The NMR spectra of the crystals and their melt were identical, showing that no decomposition had occurred on melting. ^1H NMR ($CDCl_3$): δ 1.31 (broad *s*, 3H), 2.32 (*s*, 1H), 6.94–6.96 (*m*, 1H), 7.15–7.25 (*m*, 6H), 7.34–7.41 (*m*, 2H), 7.67–7.70 (*m*, 2H), 8.31–8.33 (*m*, 1H); ^{13}C NMR: δ 19.42, 82.66, 120.20, 124.29, 125.67, 126.52, 127.51, 128.55, 129.10, 131.43, 135.12, 139.99, 140.20, 149.31.

Crystal data

$C_{20}H_{16}O$
$M_r = 272.33$
Monoclinic, $P2_1/c$
$a = 7.991$ (3) Å
$b = 14.211$ (3) Å
$c = 13.3274$ (19) Å
$\beta = 105.501$ (17)°
$V = 1458.4$ (7) Å^3
$Z = 4$
$D_x = 1.240$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 17.8$–20.0°
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Prism, colorless
0.43 × 0.33 × 0.21 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
2780 measured reflections
2587 independent reflections
1640 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 25.1°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = -15 \rightarrow 15$
3 standard reflections every 100 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.104$
$S = 1.00$
2587 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.2124P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0150 (18)

Table 1

Shortest intermolecular aryl-H···π(arene) interactions (Å, °).

*Cg*1 and *Cg*2 represent the centroids of rings C10–C15 and C1–C4/C4a/C9a, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···$Cg1^{i}$	0.93	2.84	3.723 (3)	159
C7—H7···$Cg1^{ii}$	0.93	2.81	3.606 (2)	145
C12—H12···$Cg2^{iii}$	0.93	2.68	3.599 (2)	170

Symmetry codes: (i) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$.

The rotational orientations of the methyl and hydroxyl groups were determined by the circular Fourier refinement methods available in *SHELXL*97 (Sheldrick, 1997). The location calculated for the hydroxyl H atom is essentially identical to its initial position, which was easily determined from a difference Fourier synthesis. Thus, we feel confident that this atom is correctly located. All H atoms were treated as riding, with an O—H distance of 0.82 Å, C—H distances in the range 0.93–0.96 Å, and $U_{\rm iso}$(H) values equal to 1.5 (hydroxyl and methyl H atoms) or 1.2 (all other H atoms) times $U_{\rm eq}$ 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: FG1712). Services for accessing these data are described at the back of the journal.

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