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ap-9-(*o*-Methylphenyl)-9-fluorenol, a structure exhibiting several aryl-H $\cdots \pi$ (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- $H\cdots\pi(arene)$ interactions, resulting in planar molecular arrays in which each molecule interacts with six adjacent molecules. Surprisingly, there were no $O-H\cdots O-H$ or $O-H\cdots \pi(arene)$ 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 atomnumbering in Fig. 1, which was also its exclusive conformation



in solution, determined by NMR resonance. Several intermolecular aryl- $H \cdot \cdot \cdot \pi$ (arene) interactions were observed (Table 1), resulting in planar molecular arrays in which each molecule interacts with six adjacent molecules, shown in Fig. 2.



Figure 1

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

Surprisingly, there were no $O-H \cdot \cdot \cdot O-H$ or O-H $H \cdot \cdot \pi$ (arene) interactions within hydrogen-bonding distances, the only remote possibility being the latter, in which a near interaction with an $H1\cdots C2^{ii}$ distance of 3.02 Å, an $O1\cdots C2^{ii}$ distance of 3.783 (3) Å, and an O1−H1····C2ⁱⁱ 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 $\cdots \pi$ (arene) interactions in the absence of stronger interactions involving O- $H \cdots O - H$ 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 $O-H \cdot \cdot \pi$ (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 $O-H \cdot \cdot \pi$ (fluorene) intermolecular hydrogen bonding in the absence of stronger O- $H \cdots O - H$ 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- $H \cdots O - H$ as well as $O - H \cdots \pi$ (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).



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. Cg1 and Cg2 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 $-177.60(14)^{\circ}$, O1-C9-C10-C15 of $3.2(2)^{\circ}$, 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 $C16 \cdot \cdot \cdot C8a = 3.140(3) \text{ Å} (0.26 \text{ Å} \text{ less})$ than the sum of their van der Waals radii) and $C16 \cdot \cdot \cdot C9a =$ 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 MgSO₄), concentrated in vacuo, yielded a tan-colored oil which

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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 (CDCl₃): 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); ¹³C NMR: $\delta \ 19.42, \ 82.66, \ 120.20, \ 124.29, \ 125.67, \ 126.52, \ 127.51, \ 128.55, \ 129.10,$ 131.43, 135.12, 139.99, 140.20, 149.31.

Crystal data

| C ₂₀ H ₁₆ O | $D_x = 1.240 \text{ Mg m}^{-3}$ |
|-----------------------------------|---|
| $M_r = 272.33$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 25 |
| a = 7.991 (3) Å | reflections |
| b = 14.211 (3) Å | $\theta = 17.8 - 20.0^{\circ}$ |
| c = 13.3274 (19) Å | $\mu = 0.08 \text{ mm}^{-1}$ |
| $\beta = 105.501 (17)^{\circ}$ | T = 296 K |
| V = 1458.4 (7) Å ³ | Prism, colorless |
| Z = 4 | $0.43 \times 0.33 \times 0.21 \text{ mm}$ |
| Data collection | |

Rigaku AFC-5S diffractometer (i) scans 2780 measured reflections 2587 independent reflections 1640 reflections with $I > 2\sigma(I)$ $R_{\rm int} = 0.013$ $\theta_{\rm max} = 25.1^{\circ}$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.104$ S = 1.002587 reflections 193 parameters H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0479P)^2$ + 0.2124P] where $P = (F_0^2 + 2F_c^2)/3$

 $h = 0 \rightarrow 9$ $k = 0 \rightarrow 16$ $l = -15 \rightarrow 15$ 3 standard reflections every 100 reflections intensity decay: 0.7%

 $(\Delta/\sigma)_{\rm max} < 0.001$ $\Delta \rho_{\rm max} = 0.15 \text{ e } \text{\AA}^{-3}$ $\Delta \rho_{\rm min} = -0.15 \text{ e} \text{ Å}^{-3}$ Extinction correction: SHELXL97 Extinction coefficient: 0.0150 (18)

Table 1

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

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Cg1 and Cg2 represent the centroids of rings C10-C15 and C1-C4/C4a/C9a,
respectively.
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| $D - H \cdots A$ | D-H | $H \cdot \cdot \cdot A$ | $D \cdots A$ | $D - \mathbf{H} \cdots A$ |
|--------------------------------------|------|-------------------------|--------------|---------------------------|
| $C3-H3\cdots Cg1^{i}$ | 0.93 | 2.84 | 3.723 (3) | 159 |
| $C7 - H7 \cdot \cdot \cdot Cg1^{ii}$ | 0.93 | 2.81 | 3.606 (2) | 145 |
| $C12 - H12 \cdots Cg2^{iii}$ | 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 SHELXL97 (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 $U_{iso}(H)$ values equal to 1.5 (hydroxyl and 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*.

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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.