

9-(*p*-Methylphenyl)-9-fluorenolPaul D. Robinson,^{a*} Aaron W. McLean^b and Cal Y. Meyers^b

^aDepartment of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA, and ^bMeyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry and the Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA

Correspondence e-mail: robinson@geo.siu.edu

Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.037

wR factor = 0.128

Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{20}\text{H}_{16}\text{O}$, has two molecules in the asymmetric unit, of nearly identical conformations, linked *via* $\text{O}-\text{H}\cdots\text{O}-\text{H}$, as well as $\text{O}-\text{H}\cdots\pi(\text{fluorene})$ intermolecular hydrogen bonds. The 9-aryl and fluorene rings of both molecules deviate substantially from perpendicularity. Although the crystals melt sharply without molecular decomposition, the melt fails to recrystallize when cooled, even after a long period. Similar phenomena are observed with other crystalline 9-alkylphenyl-9-fluorenols that exhibit intermolecular $\pi(\text{arene})$ interactions.

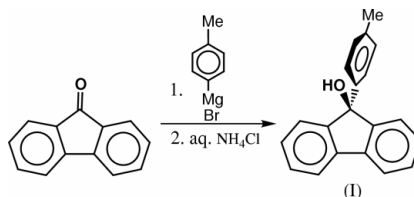
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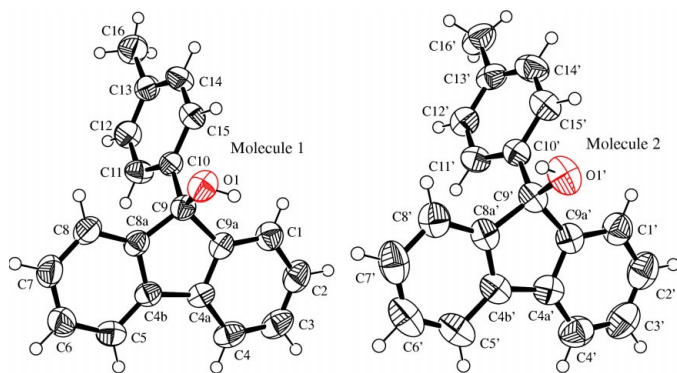
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Comment

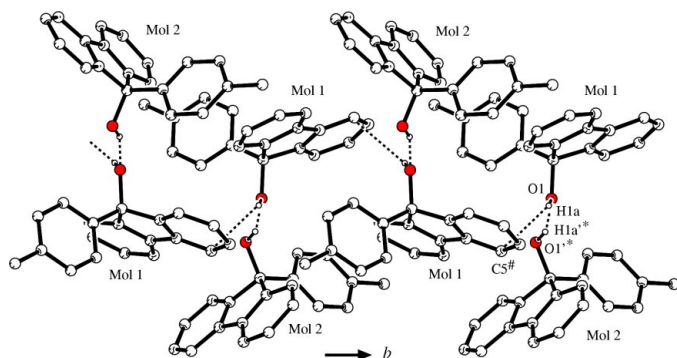
9-(*p*-Methylphenyl)-9-fluorenol, (I), prepared from the reaction of fluorenone with *p*-tolylmagnesium bromide, crystallizes in two nearly identical conformations in the asymmetric unit; these are shown as 1 and 2 in Fig. 1. A comparison of the geometric parameters of the two molecules shows that there are only minor differences, none of which seems to be of significance. Also, no unusual geometric parameters were noted. Molecules of conformation 1 interact with molecules of conformation 2 *via* $\text{O}-\text{H}\cdots\text{O}-\text{H}$ hydrogen bonding, while conformation 1 molecules also interact with each other *via* $\text{O}-\text{H}\cdots\pi(\text{fluorene})$ hydrogen bonds which are directed at the edge of the fluorene ring rather than at a ring centroid. The resultant double chains of hydrogen-bonded molecules propagate in the *b* axial direction. The hydrogen-bonding scheme is shown in Fig. 2, and the geometry is given in Table 1. The molecular packing (Fig. 3) shows two of the hydrogen-bonded molecular chains passing through the unit cell.



The 9-aryl and fluorene rings of (I) deviate substantially from perpendicularity, as evidenced from the angle between the least-squares planes of the substituted phenyl and fluorene rings, *viz.* $76.18(8)^\circ$ for molecule 1, and $74.77(9)^\circ$ for molecule 2. This conformational geometry is similar to that of other 9-aryl-9-fluorenols. It adds credence to our earlier report that the unexpected *ap* conformation of isomeric 9-(*o*-methylphenyl)-9-fluorenol exhibiting perpendicularity of its 9-aryl and fluorene rings, in which the methyl group is

**Figure 1**

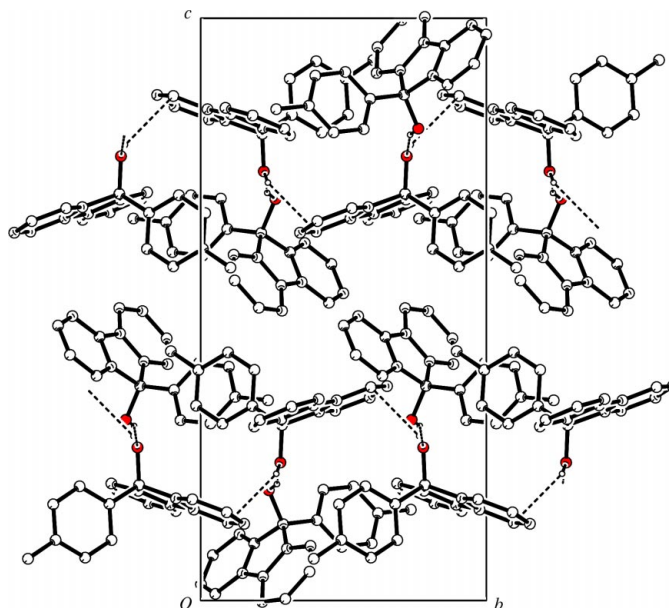
The molecular structure and atom-numbering scheme for the asymmetric unit of (I), with displacement ellipsoids at the 50% probability level. The two molecules in the asymmetric unit are shown in approximately the same orientation for ease of comparison and do not represent their actual juxtaposition in the structure.

**Figure 2**

Hydrogen bonding in (I). Both O—H...O and O—H... π (fluorene) bonds link the molecules into double chains which propagate in the *b* direction. [Symmetry codes: (*) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (#) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

essentially protruding into the fluorene plane in the crystalline state as well as in solution (Meyers, Robinson & McLean, 2003), is thermodynamically optimal for that 9-aryl-9-fluorenol.

While crystalline (I) melts sharply, the melt fails to recrystallize even after a long period of cooling, although its NMR spectrum is identical to that of the crystals, indicating that no molecular decomposition occurs on melting. This phenomenon may be associated with the O—H...O—H and O—H... π (fluorene) intermolecular hydrogen bonding. We have found similar recrystallization failure after melting to be displayed by the five other crystalline 9-aryl-9-fluorenols that we have studied, all of them also displaying O—H...O—H and/or O—H... π (fluorene) intermolecular hydrogen bonding: *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol (Robinson *et al.*, 1998), *ap*-9-(*o*-isopropylphenyl)-9-fluorenol (Hou *et al.*, 1999), *sp*-9-(*m*-*tert*-butylphenyl)-9-fluorenol (Meyers, McLean & Robinson, 2003), *sp*-9-(*p*-*tert*-butylphenyl)-9-fluorenol (McLean *et al.*, 2003a), and *sp*-9-(*m*-methylphenyl)-9-fluorenol (McLean *et al.*, 2003b). In addition, 9-(*o*-methylphenyl)-9-fluorenol (Meyers, Robinson & McLean, 2003) likewise fails to recrystallize at room temperature after melting, and

**Figure 3**

The molecular packing in (I), viewed down [100].

although its crystal structure shows no intermolecular hydrogen bonding involving the O—H group, each molecule closely packs with six other molecules *via* aryl-H... π (arene) interactions, perhaps reflecting van der Waals forces. In contrast to this behavior of these 9-fluorenols, all the corresponding crystalline fluorenes that we have studied exhibit no obvious intermolecular bonding or other interactions, and their melts recrystallize rapidly on cooling to room temperature: *sp*-9-(*o*-isopropylphenyl)fluorene (Meyers *et al.*, 1997), *sp*-9-(*o*-*tert*-butylphenyl)fluorene (Robinson *et al.*, 1998), *ap*-9-(*m*-*tert*-butylphenyl)fluorene (Robinson *et al.*, 2003), and 9-(*p*-methylphenyl)fluorene, whose structure determination we have just completed.

Experimental

A mixture of magnesium (0.36 g, 14.61 mmol), tetrahydrofuran (15 ml), and 1,2-dibromoethane (0.30 ml, 3.48 mmol) was stirred and gently heated under argon. When bubbles appeared on the magnesium surface, *p*-bromotoluene (1.92 g, 11.22 mmol) was added and the stirring–heating continued until the magnesium was consumed. A solution of fluorenone (1.03 g, 5.71 mmol) in tetrahydrofuran (20 ml) was then added, the mixture was refluxed for 4 h, then cooled; water was added, followed by saturated aqueous ammonium chloride solution. The mixture was extracted with ether and the extracts were dried (anhydrous MgSO₄) and concentrated *in vacuo*, leaving a tan-colored oil which solidified after a few days and was crystallized from hexanes; m.p. 356–357 K [literature m.p. 357–358 K (Cockerill & Lamper, 1971); 1.40 g, 90.2% yield]. The cooled melt failed to recrystallize even on standing for several days, although ¹H NMR analyses of the melt and crystals were identical, showing that no decomposition had occurred. ¹H NMR (CDCl₃): δ 2.29 (*s*, 3H), 2.41 (*s*, 1H), 7.05–7.08 (*m*, 2H), 7.21–7.38 (*m*, 7H), 7.46–7.48 (*m*, 1H), 7.64–7.67 (*m*, 2H); ¹³C NMR: δ 21.05, 83.53, 120.05, 124.70, 125.28, 126.78, 128.43, 128.92, 129.01, 129.41, 139.53, 150.51.

Crystal data

C₂₀H₁₆O
M_r = 272.33
 Monoclinic, *P*2₁/*n*
a = 12.621 (4) Å
b = 10.778 (4) Å
c = 22.761 (7) Å
 β = 105.14 (3)°
V = 2988.7 (17) Å³
Z = 8

D_x = 1.211 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 16.7–19.6°
 μ = 0.07 mm⁻¹
T = 296 K
 Prism, colorless
 0.44 × 0.33 × 0.27 mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 5546 measured reflections
 5289 independent reflections
 2868 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024

θ_{\max} = 25.1°
h = 0 → 15
k = 0 → 12
l = -27 → 26
 3 standard reflections every 100 reflections
 intensity decay: 1.7%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.037
wR (*F*²) = 0.128
S = 1.01
 5289 reflections
 384 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.2677P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0139 (10)

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 ⁱ —H1A ⁱ ...O1	0.82	2.08	2.863 (2)	161
O1—H1A...C5 ⁱⁱ	0.82	2.65	3.239 (3)	130

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

The rotational orientations of the methyl and hydroxyl groups were determined by the circular Fourier refinement methods available in *SHELXL97* (Sheldrick, 1997). All H atoms were treated as riding, with C—H distances ranging from 0.93 to 0.96 Å and O—H distances of 0.82 Å, and *U*_{iso}(H) values equal to 1.5 (hydroxyl and

methyl H atoms) or 1.2 times (all other H atoms) *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: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*, *SHELXL97*, and *PLATON*.

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