9-(*para-tert*-Butylphenyl)-9-fluorenol

Aaron W. McLean,ᵃ Cal Y. Meyersᵃ and Paul D. Robinsonᵇ*

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

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

The title compound, $C_{23}H_{22}O$, is composed of two slightly different molecular conformations in its asymmetric unit, one conformation hydrogen bonded to the other *via* their OH groups. The two molecular conformers are reproduced by an inversion center and hydrogen bonded through an O—H···π(fluorene) bond, thus producing groups of four hydrogen-bonded molecules. The cooled melted crystals failed to recrystallize, but solution NMR showed that no chemical decomposition had occurred during the melting.

Comment

We previously reported the crystal structure of *sp*-9-(*ortho-tert*-butylphenyl)-9-fluorenol (Robinson *et al.*, 1998; see also Meyers *et al.*, 1999) as well as that of 9-(*ortho*-isopropyl-phenyl)-9-fluorenol (Hou *et al.*, 1999). We wished to compare the crystal structure of the title compound, (I), with that of its *ortho-tert*-butyl isomer. The structure of (I), with the atom numbering, is shown in Fig. 1.
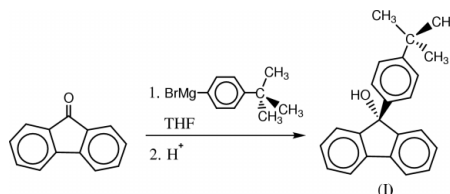
As illustrated, compound (I) crystallizes in two slightly different conformations in the asymmetric unit, molecules numbered 1 and 2. Fig. 2 shows that molecule 1 is hydrogen bonded to molecule 2 *via* a conventional O—H···O interaction, the O atom of molecule 2 being the donor, and the O atom of molecule 1 being the acceptor. In addition, there appears to be a strong interaction between the hydroxyl H atom of molecule 1 and the π-electrons nearest to C4 of the fluorene ring of a centrosymmetrically-related molecule 1, an interaction which may be interpreted as an O—H···π(arene) bond (Ferguson *et al.*, 1994). The end result is a cluster of four hydrogen-bonded molecules situated about an inversion center, denoted by a plus sign at the center of Fig. 2. Details of the hydrogen-bonding geometry are given in Table 1. Since the inversion center is located at the cell origin, each cell corner will be surrounded by an identical group of four molecules, thereby defining the molecular packing of the structure, shown in Fig. 3. It is interesting to note that the related 9-(*ortho-tert*-butylphenyl)-9-fluorenol (Robinson *et al.*, 1998) likewise crystallizes in two different molecular conformations, and also shows the same type of intermolecular O—H···O—H
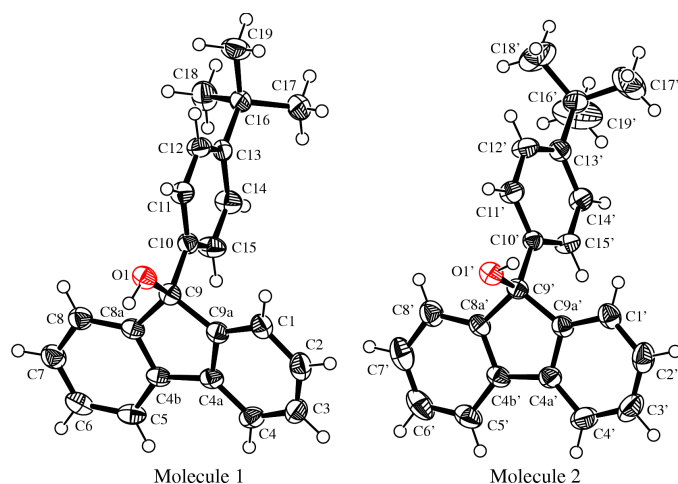
Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level. The two molecules in the asymmetric unit are shown in approximately the same orientation for ease of comparison and do not represent their actual juxtaposition in the structure.
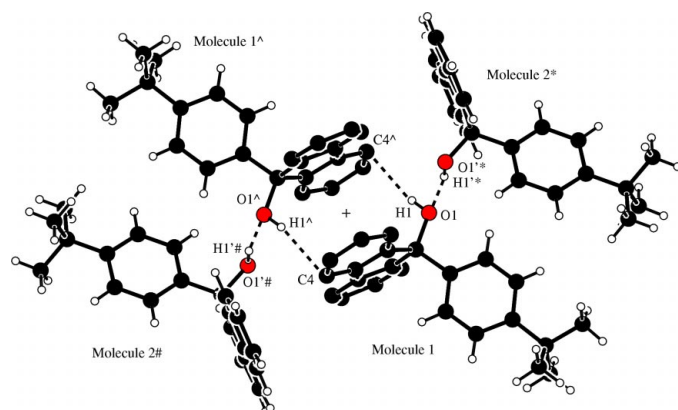

Figure 2
Hydrogen bonding in (I). The two crystallographically distinct hydrogen bonds produce groups of four hydrogen-bonded molecules around the inversion centers located at the corners of the unit cell. Atoms or molecules marked with an asterisk (*), hash (#), or caret (^) are at the symmetry positions $(x, y - 1, z)$, $(-x, 1 - y, 2 - z)$, and $(-x, -y, 2 - z)$, respectively; the plus (+) represents an inversion center.

hydrogen bonding between the two different molecular conformers. We have recently re-examined the X-ray data of the *ortho-tert*-butyl isomer and feel confident now to suggest that this compound also exhibits O—H···π(arene) bonding but, in this case, it is between the two different molecular conformers. It is interesting to find the hydrogen-bonding similarities exhibited by these two structures, since 9-(*ortho-tert*-butylphenyl)-9-fluorenol has considerable steric and rotational constraints while, in contrast, (I) has no such encumbrances. We therefore must refute the statement that we previously reported for 9-(*ortho-tert*-butylphenyl)-9-fluorenol (Robinson *et al.*, 1998), *viz*. 'It is reasonable to believe that stabilization of the molecular packing is attained *via* the intermolecular H bonding which, because of the large steric effects, is best enabled between structures (1a) and (1b).'
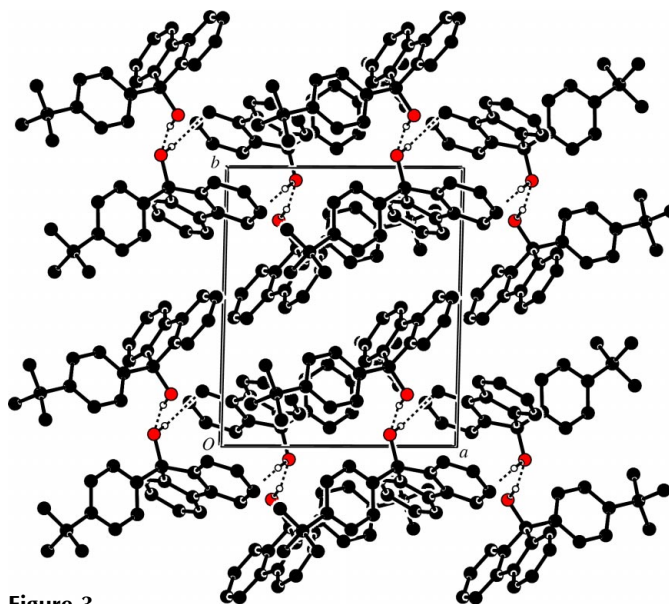

Figure 3
The molecular packing in (I), viewed down the $c*$ axis. Note the groupings of four hydrogen-bonded molecules about each cell corner.

While compound (I) melted quite sharply, the melt failed to crystallize on cooling or even in an ice bath, over several days, although its NMR spectrum was identical to that of crystalline (I). The same phenomenon was exhibited by isomeric 9-(*ortho-tert*-butylphenyl)-9-fluorenol, although its melt did crystallize after standing for several days. It is possible that this phenomenon is associated with the rather complex O—H···O—H and O—H···π(fluorene) hydrogen bonding and resulting molecular packing patterns, which are similar in both compounds. It might be energetically unfavorable for these molecules in the melt to readily reorganize into the complex hydrogen-bonded pattern required for their crystallization, a pattern much more easily attained from a slowly evaporating solution.

Experimental

A mixture of magnesium (0.287 g, 11.78 mmol), freshly distilled tetrahydrofuran (20 ml), and 1,2-dibromoethane (0.30 ml, 3.48 mmol), maintained under argon, was gently heated until bubbles appeared on the magnesium surface. *para*-Bromo-*tert*-butylbenzene (1.77 g, 8.33 mmol) was injected, the mixture was refluxed for 30 min, and a solution of 9-fluorenone (1.00 g, 5.56 mmol) in tetrahydrofuran (15 ml) was added. This mixture was refluxed for 5 h, cooled, diluted with water then $6N$ H_2SO_4 and extracted with ether. The extracts were dried and concentrated to a yellow oil, which was purified by column chromatography (2:1 hexanes–ethyl acetate). Concentration of the major fraction left an oil which, after several days, provided a yellow solid, 1.43 g (84.9% yield), yellow crystals (from hexanes), m.p. 392–395 K (literature m.p. 391–393 K; Weber *et al.*, 1990). The melt failed to crystallize on cooling, even in an ice bath, but its NMR spectrum was identical to that of the crystalline product, showing that no decomposition had occurred on melting. NMR (CDCl$_3$): ^{1}H, δ 1.27 (s, 9H), 2.423 (s, 1H), 7.22–7.38 (m, 9H), 7.64–7.67 (m, 3H); ^{13}C, δ 31.30, 34.39, 83.56, 120.04, 124.81, 125.03, 125.12, 128.35, 128.99, 139.55, 140.06, 149.99, 150.41.

Crystal data

$C_{23}H_{22}O$
$M_r = 314.41$
Triclinic, $P\bar{1}$
$a = 10.2843 (2)$ Å
$b = 12.1135 (2)$ Å
$c = 14.5033 (2)$ Å
$\alpha = 82.915 (1)°$
$\beta = 80.656 (1)°$
$\gamma = 87.563 (1)°$
$V = 1768.75 (5)$ Å^3

$Z = 4$
$D_x = 1.181$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 5098
  reflections
$\theta = 2.3–27.8°$
$\mu = 0.07$ mm^{-1}
$T = 170 (2)$ K
Prism, pale yellow
$0.36 \times 0.33 \times 0.20$ mm

Data collection

Bruker CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: none
20884 measured reflections
6224 independent reflections

4292 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.128$
$S = 1.07$
6224 reflections
438 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2$
  $+ 0.1886P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1$^{\prime i}$—H1$^{\prime i}\cdots$O1	0.82	2.02	2.8276 (17)	167
O1—H1$\cdots$C4^{ii}	0.82	2.40	3.175 (2)	159

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

The rotational orientations of the methyl H atoms in molecule 1 (Fig. 1) were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997); the hydroxyl H atom position for both molecules was determined in a similar manner. The tertiary butyl group of molecule 2 is somewhat rotationally disordered and thus its H atoms were placed in geometrically favorable positions but were not refined. All H atoms are riding with C—H distances ranging from 0.82 to 0.96 Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON*.

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