organic papers

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

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Key indicators

Single-crystal X-ray study
$T = 296$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.046
wR factor = 0.167
Data-to-parameter ratio = 14.2

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

The title compound, $C_{23}H_{22}O$, is composed of molecules bonded into linear one-dimensional chains through O—H···π(fluorene) hydrogen bonds, each molecule being both H-atom donor and acceptor. No O—H···O—H hydrogen bonding is exhibited, despite the reasonable donor–acceptor proximity [2.849 (3) Å]. The melted crystals failed to recrystallize on cooling, but solution NMR showed that no decomposition had occurred during the melting.

Comment

We recently reported the crystal structure of 9-(*para-tert*-butylphenyl)-9-fluorenol, (II) (McLean *et al.*, 2003), and compared it with that of its isomeric 9-(*ortho-tert*-butylphenyl)-9-fluorenol, (III) (Robinson *et al.*, 1998; see also Meyers *et al.*, 1999), whose NMR spectrum shows it to be rotationally restricted at the 9-position in solution. The similarities and differences between isomers (II) and (III) prompted us to study the crystal structure of the third isomer, 9-(*meta-tert*-butylphenyl)-9-fluorenol, (I), which is freely rotating in solution, like (II), but, like (III), could exhibit conformational preferences in its crystalline structure.
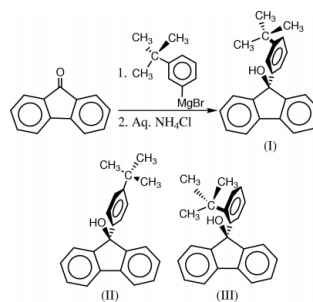
The structure of (I) with atom numbering is shown in Fig. 1. No unusual geometric parameters were noted. The angle between the fluorene least-squares plane and that of the substituted phenyl ring is 84.10 (12)°. Although the *meta-tert*-butylphenyl group of (I) is freely rotating in solution, it crystallizes in an *sp* conformation, like its *ortho-tert*-butylphenyl isomer (III), in which this conformation is thermodynamically preferred over the *ap* conformation because of rotational and steric restrictions. Presumably, the favorability of the *sp* conformation of (I) is associated with its molecular packing. While the *para* isomer (II) and *ortho* isomer (III) each crystallized in two somewhat different molecular conformations, crystalline (I) is composed of a single molecular conformation. The latter molecules are linked into linear one-dimensional chains through O—H···π(fluorene) hydrogen bonds, each molecule being both an H-atom donor and acceptor. The
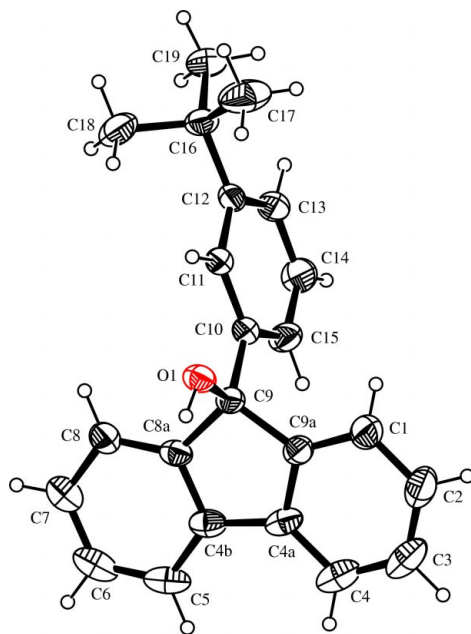
Figure 1
The molecular structure and atom numbering scheme for (I) with displacement ellipsoids at the 30% probablilty level.

Figure 3
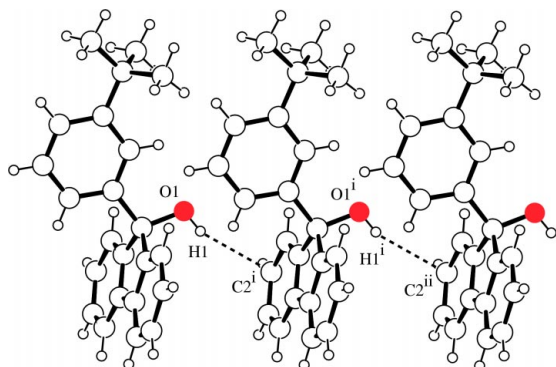The molecular packing in (I), as viewed down the *a* axis.

Figure 2
The hydrogen bonding scheme in (I) [symmetry codes: (i) $x, y, 1 + z$; (ii) $x, y, 2 + z$].

hydroxyl H atom most closely approaches the fluorene π-cloud near C2, as depicted in Fig. 2, and the chains propagate in the *c*-axial direction by simple unit translations. The hydrogen bond geometry is given in Table 1. A view of the molecular packing, as viewed down the *a* axis, is shown in Fig. 3, with the previously described molecular chains propagating from right to left. Note that there are two centrosymmetrically related orientations of the chains which form what could be called 'layers' of chains parallel to (010); three such layers are apparent in this figure. Another important difference in the structures of the isomers resides in the fact that, while (II) as well as (III) exhibit both O—H···O—H and O—H···π(fluorene) hydrogen bonding, only the latter is apparent in (I). It is pertinent to note in this context that within the
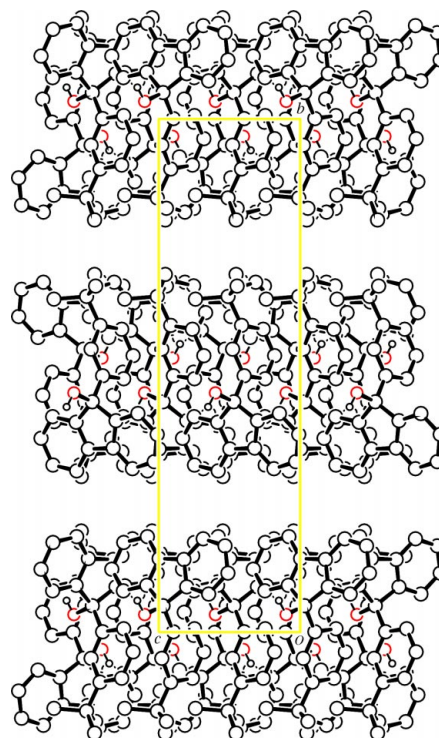
'layers' of (I), adjacent hydroxyl groups are quite intimately associated, with an O···O distance of only 2.849 (3) Å, a respectable donor–acceptor distance. Despite this fact, no O—H···O hydrogen bonds are formed, ostensibly because the hydroxyl H atoms are not in reasonable positions to hydrogen bond with the respective O atoms. It is worth noting that the closely associated hydroxyl groups are related by an inversion center and it may be difficult or impossible for O—H···O—H hydrogen bonding to occur under a symmetry constraint of this type.

We have already pointed out that crystalline fluorenols (II) and (III), respectively, have sharp melting points, but their melts fail to recrystallize, even after prolonged standing, although NMR shows that no decomposition has occurred (McLean *et al.*, 2003). Now we find that fluorenol (I) behaves identically. It appears that in the non-packing melt orientation, the molecules of all three of these isomeric 9-(*tert*-butylphenyl)-9-fluorenols have difficulty reorganizing into the orientation required for their crystalline packing.

Experimental

Freshly distilled tetrahydrofuran (20 ml) and 1,2-dibromoethane (0.30 ml, 3.48 mmol) were added to a flask containing magnesium (0.29 g, 11.82 mmol) and the mixture was gently heated. When bubbles appeared at the surface of the magnesium, *meta-tert*-butylbromobenzene (Czarnik, 1984; Schaefer & Higgins, 1967) (1.85 g, 12.09 mmol) was added and the mixture was gently heated until all of the magnesium was consumed. A solution of 9-fluorenone (1.01 g,

5.62 mmol) in tetrahydrofuran (15 ml) was added and the mixture, which immediately became yellow–brown, was refluxed for 22 h. A saturated aqueous NH_4Cl solution was then added, the mixture was extracted with ether and the combined extracts were dried and concentrated *in vacuo*, leaving a dark yellow oil that solidified on standing; 1.41 g, 79.8% yield. Recrystallization (hexanes) afforded colorless crystals of (I), mp 374.5–376 K. The melt did not recrystallize even on standing for several days, although its ^1H NMR spectrum was identical to that of the crystals, showing that they did not decompose on melting. NMR ($CDCl_3$): ^1H, δ 1.30 (s, 9H), 2.43 (s, 1H), 6.92–6.95 (m, 1H), 7.10–7.38 (m, 8H), 7.64–7.71 (m, 3H); ^{13}C: δ 31.40, 34.81, 83.94, 120.06, 122.33, 122.75, 124.19, 124.81, 127.77, 128.37, 129.00, 139.66, 142.82, 150.57, 151.15.

Crystal data

C₂₃H₂₂O
$M_r = 314.41$
Orthorhombic, $Pccn$
$a = 22.123 (5)$ Å
$b = 24.203 (3)$ Å
$c = 6.676 (4)$ Å
$V = 3575 (2)$ Å^3
$Z = 8$
$D_x = 1.168$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.2–18.8°$
$\mu = 0.07$ mm^{-1}
$T = 296$ K
Prism, colorless
$0.49 \times 0.43 \times 0.22$ mm

Data collection

Rigaku AFC-5S diffractometer
ω scans
Absorption correction: none
3143 measured reflections
3143 independent reflections
1395 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0°$

$h = 0 \rightarrow 26$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 7$
3 standard reflections
    every 100 reflections
    intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.167$
$S = 1.00$
3143 reflections
221 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.4759P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ 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—H1$\cdots$C2^i	0.82	2.75	3.436 (5)	143

Symmetry codes: (i) $x, y, 1 + z$.

The rotational orientations of the methyl H atoms of the *tert*-butyl group and the H atom of the hydroxyl group were refined by the circular Fourier methods available in *SHELXL*97 (Sheldrick, 1997). The hydroxyl H atom was clearly visible in a difference electron density map. All H atoms are riding, with C—H distances ranging from 0.93 to 0.96 Å and 0.82 Å for O—H.

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* (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: *SHELXL*97.

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