

The low-temperature phase transition of 9-methylfluoren-9-ol: comparison of the crystal structures at 100 and 200 K

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Crystals of 9-methylfluoren-9-ol, C₁₄H₁₂O, undergo a reversible phase transition at 176 (2) K. The structure of the high-temperature α form at 200 K is compared with that of the low-temperature β form at 100 K. Both polymorphs crystallize in space group $P\bar{1}$ with $Z = 4$ and contain discrete hydrogen-bonded $R_4^4(8)$ ring tetramers arranged around crystallographic inversion centres. The most obvious changes observed on cooling the crystals to below 176 K are an abrupt increase of *ca* 0.5 Å in the shortest lattice translation, and a thermal transition with $\Delta H = 1 \text{ kJ mol}^{-1}$.

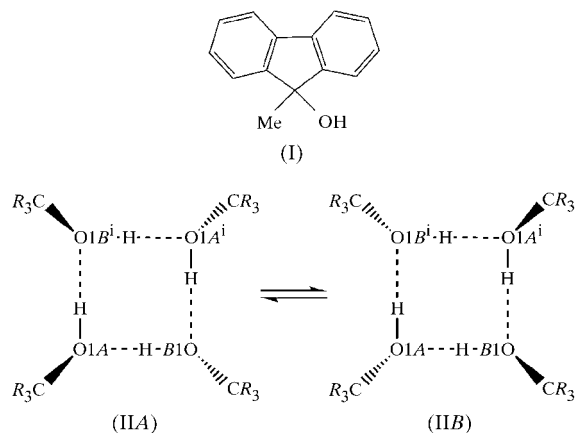
Comment

Our interest in derivatives of fluoren-9-one (Morris *et al.*, 2000) and in the hydrogen-bonding patterns displayed by tertiary monoalcohols (Morris *et al.*, 2001) led us to examine the crystal structure of 9-methylfluoren-9-ol, (I), at 100 K (Fig. 1).

At room temperature, (I) crystallizes as a centrosymmetric cyclic tetramer in space group $P\bar{1}$ with $Z = 4$ (Csöregi *et al.*, 1993; hereinafter CCW93). At 293 K, our sample of (I) gave cell dimensions virtually identical to those reported in CCW93. However, we found that the crystals frequently, though not invariably, shattered on cooling. Further crystallographic investigation established that (I) undergoes a reversible phase transition at *ca* 173–176 K. We compare here the crystal structures adopted by (I) at 100 K (the β form) and at 200 K (the α form). The latter structure is, in essence, that described in CCW93 when allowance is made for the difference in temperature. Attempts to define the temperature of the phase transition crystallographically and by differential scanning calorimetry (DSC) are also described.

Cooling a crystal of (I) from ambient temperature to 100 K does not alter its space group. At 100 K, the triclinic unit cell again contains four molecules linked into a ring by cooperative hydrogen bonding. Indeed, the crystal structure of

the β polymorph is very similar to that of the α form, as can be seen from a comparison of their packing diagrams (Fig. 2). This similarity is emphasized here in two ways, as follows.



First, for the β form, the unit cell has been chosen so that its axes correspond to those of the reduced cell used here and in CCW93 for the α form. The cell used for the β form can be transformed by the matrix (100/101/0–10) to give the reduced cell $a = 9.2540$ (2), $b = 11.3720$ (3) and $c = 11.4154$ (4) Å, and $\alpha = 77.009$ (1), $\beta = 72.892$ (1) and $\gamma = 69.243$ (1) $^\circ$. In the following discussion, the a axis is therefore always the shortest lattice translation for each structure. When (I) is cooled to below 173 K, the a axis increases abruptly by *ca* 0.5 Å and the cell angle β by 13 $^\circ$. The changes in the other cell parameters are less dramatic and there is no obvious discontinuity in the plot of unit-cell volume with temperature. A comparison of the diffractometer orientation matrices at 200 and 100 K establishes that, in the indexing we have chosen for the α and β forms, the directions of the crystallographic b and c axes change by no more than 2 $^\circ$ during the phase transition, whereas the change in magnitude of the a axis is accompanied by a change in direction of 12 $^\circ$.

Secondly, the same atom-numbering system is used for the two independent molecules, A and B , in each of the two forms, so that corresponding atoms occupying similar positions in the respective unit cells have the same identifier (Fig. 2). This is possible because the positions and orientations of the molecules relative to the cell axes differ only slightly in the two forms. Indeed, the coordinates of the β form can be used

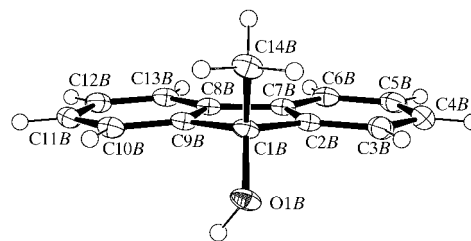


Figure 1

A view of molecule B of the β form of (I) at 100 K, showing 50% probability displacement ellipsoids. The same numbering scheme is used for each molecule in each form. Drawings of both molecules in both forms have been deposited.

successfully as a starting point for refining the α structure; this refinement correctly repositions the atoms of molecule *B*, but the new position of atom C1A must be found from a difference synthesis and the other atoms of molecule *A* have to be renumbered to correspond with the scheme shown in Fig. 1.

In the β form, the two independent molecules, *A* and *B*, are structurally nearly indistinguishable at 100 K; the r.m.s. difference is 0.019 Å when the C and O atoms of molecule *A* are fitted to the corresponding atoms of molecule *B* transformed by the inversion operation (i) [Table 3; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. Each molecule shows almost exact C_s symmetry; the non-crystallographic mirror plane passes through atoms C1, C14 and O1, and the midpoint of the C7—C8 bond. The central five-membered ring adopts a very shallow envelope conformation, with atom C1 at the flap and the OH moiety equatorial, as may be seen from the endocyclic torsion angles (Table 3). The six-membered rings in each molecule are planar to within 0.008 Å and bend away from atom C14, so as to define dihedral angles of 3.7 (1) and 4.3 (1)° with one another in molecules *A* and *B*, respectively. The most

obvious difference between the two molecules is in the orientation of the hydroxyl groups [C14—C1—O1—H1 = 175 (2) and 146 (2)° in molecules *A* and *B*, respectively]. Each molecule appears to vibrate as a rigid body, since the atomic U^{ij} values are tolerably well reproduced by a TLS analysis (Schomaker & Trueblood, 1968), with $R_2 = (\Sigma \Delta U^2 / \Sigma U^2)^{1/2} = 0.068$ and 0.066 for molecules *A* and *B*, respectively. The worst discrepancy in the Hirshfeld (1976) rigid-bond test is $\Delta U = 0.003(1_2)$ Å².

The molecules in the α form at 200 K are almost indistinguishable, both from one another (r.m.s. difference 0.036 Å) and from those in the β polymorph. The two most striking differences in molecular structure between the α and β forms (Table 3) are that, in the α form, first the central rings are flatter, particularly those of molecule *A*, where the largest endocyclic torsion angle is only 1.3 (1)°, and secondly, the hydroxyl groups in the two independent molecules are no longer oriented differently [C14—C1—O1—H1 = 170 (1) and 166 (1)°]. The U^{ij} values at 200 K are roughly double those for the β form at 100 K and do not pass the rigid-bond test [worst ΔU 0.021 (2) Å² for C4A—C5A], although the R_2 values for the TLS fit are 0.075 and 0.049.

Bond lengths and angles in both α and β forms agree with standard values (Orpen *et al.*, 1992) and require no discussion.

The α and β forms of (I) both contain hydrogen-bonded cyclic tetramers which belong to the graph set $R_4^4(8)$ (Etter, 1990). This is not surprising; half of the 45 C_{sp^3} —C—OH tertiary monoalcohol crystal structures in the Cambridge Structural Database (Version 5.22, 245 391 entries; Allen & Kennard, 1993) also contain this hydrogen-bond motif, and no other motif is as common for this class of compound (Morris & Muir, 2002). The individual molecules of (I) in the α and β forms have structures which can barely be distinguished from one another, the hydrogen bonds that connect them (Tables 1 and 2) involve nearly identical O···O distances, and in both tetramers, the four O atoms are exactly coplanar.

It follows that the two forms differ only in the disposition of the four molecules relative to the plane of the O atoms and in the packing of the tetrameric units. These differences are small enough not to be obvious when the packing diagrams (Fig. 2) are compared; they only become apparent when the orientations of the molecular mirror planes relative to the plane defined by atoms O1A, O1B, O1Aⁱ and O1Bⁱ are considered (Fig. 3). The hydroxyl-substituted C1 atoms lie on different sides of the plane of the four O atoms in the two forms. The relevant torsion angles in the α and β forms consequently differ in sign (Table 3); the largest difference in magnitude is 17° between corresponding C1A—O1A···O1B—C1B angles [71.0 (2) and -53.6 (2)°]. There are also significant differences between the O···O···O···O angles at O1A and O1B (86 and 94° in the β form, but 82 and 98° in the α form). Evidently, the β and α forms of (I) contain similar but not identical cyclic tetramers. A simplified description of the β -to- α transition in terms of the conversion of (2A) to (2B) is shown in the Scheme.

Repeated unit-cell determinations at different temperatures using a 700 Series Cryostream Cooler (Oxford Cryo-

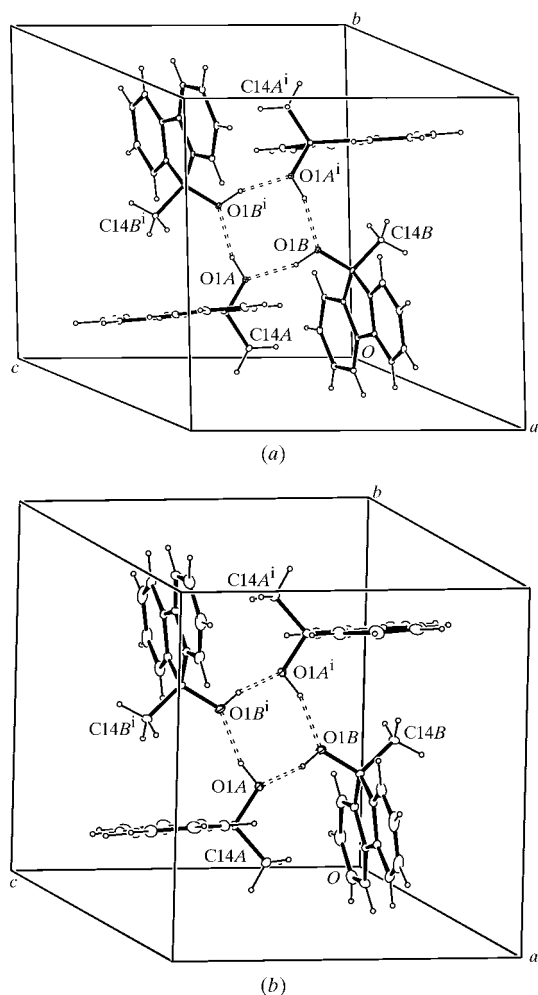
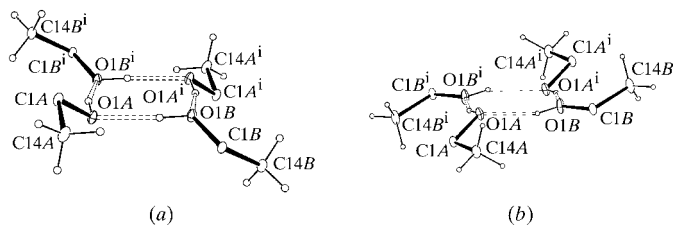


Figure 2

The unit-cell contents of (a) the β form of (I) at 100 K and (b) the α form of (I) at 200 K. In each case, the viewing direction is roughly normal to the plane of the four hydroxyl O atoms. Hydrogen bonds are shown as broken lines [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

**Figure 3**

The orientation of the molecular mirror planes, defined by atoms C1, C14 and O1, relative to the plane of the four hydroxyl O atoms in (a) the β form of (I) at 100 K and (b) the α form of (I) at 200 K. Hydrogen bonds are shown as broken lines [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

systems, 2000) indicated that the mean transition temperature is 174.5 K with a slight hysteresis; on cooling, the α form persists down to 173 K, and on heating it is established at 176 K. The same crystal specimen can sometimes be converted from the α to the β form and back again several times before suffering obvious damage. A DSC experiment indicated that there is a strong thermal transition on heating, starting at 174.2 K, peaking at 177.6 K and finishing at 181.2 K. The enthalpy change for the transition, ΔH , is 1.00 (1) kJ mol⁻¹. On the assumption of thermodynamic reversibility, the entropy change, ΔS , is 5.7 J K⁻¹ mol⁻¹, taking 176 K (the mean defined by the DSC peak and the crystallographic mean value) as the transition temperature. Finally, we note that the crystallographic transition temperature on heating (176 K) agrees to within 2 K with the DSC peak value. The transition, which is easily observed, could be used in the calibration of crystal cryostats.

Experimental

9-Methylfluoren-9-ol was synthesized by reaction of methyl magnesium iodide with fluoren-9-one under nitrogen according to the method of Amyes *et al.* (1992). Recrystallization of the product from toluene gave white crystals of (I) [m.p. 446–447 K; literature values: 447 (Amyes *et al.*, 1992) and 445–447 K (Stiles & Sisti, 1961)]. DSC experiments were performed on a Mettler Toledo DSC 821e. The DSC trace is included in the supplementary material for this paper.

Compound (I), β form

Crystal data

C₁₄H₁₂O
 $M_r = 196.24$
 Triclinic, $P\bar{1}$
 $a = 9.2540$ (2) Å
 $b = 11.4154$ (4) Å
 $c = 11.8476$ (4) Å
 $\alpha = 89.198$ (1)°
 $\beta = 116.162$ (1)°
 $\gamma = 107.108$ (1)°
 $V = 1063.82$ (6) Å³
 $Z = 4$
 $D_x = 1.225$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3212 reflections
 $\theta = 1.0$ – 27.5 °
 $\mu = 0.08$ mm⁻¹
 $T = 100$ (2) K
 Plate, colourless
 $0.41 \times 0.32 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans, thick slices
 10 069 measured reflections
 4749 independent reflections
 3507 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.4$ °
 $h = -11 \rightarrow 10$
 $k = -13 \rightarrow 14$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R(F) = 0.049$
 $wR(F^2) = 0.127$
 $S = 1.03$
 4749 reflections
 281 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.33P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$$

Table 1

Hydrogen-bonding geometry (Å, °) for (I), β form.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1A—H1A \cdots O1B ⁱ	0.92 (3)	1.84 (3)	2.725 (2)	163 (2)
O1B—H1B \cdots O1A	0.92 (2)	1.85 (2)	2.740 (2)	163 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (I), α form

Crystal data

C₁₄H₁₂O
 $M_r = 196.24$
 Triclinic, $P\bar{1}$
 $a = 8.7380$ (2) Å
 $b = 11.4571$ (3) Å
 $c = 11.7097$ (4) Å
 $\alpha = 90.952$ (2)°
 $\beta = 103.462$ (1)°
 $\gamma = 106.225$ (1)°
 $V = 1090.47$ (5) Å³
 $Z = 4$
 $D_x = 1.195$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5786 reflections
 $\theta = 1.0$ – 30.0 °
 $\mu = 0.07$ mm⁻¹
 $T = 200$ (2) K
 Plate, colourless
 $0.52 \times 0.49 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans, thick slices
 11 636 measured reflections
 6338 independent reflections
 4662 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 30.1$ °
 $h = -12 \rightarrow 11$
 $k = -16 \rightarrow 16$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R(F) = 0.058$
 $wR(F^2) = 0.156$
 $S = 1.05$
 6338 reflections
 281 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.25P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$$

Table 2

Hydrogen-bonding geometry (Å, °) for (I), α form.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1A—H1A \cdots O1B ⁱ	0.91 (2)	1.84 (2)	2.728 (1)	162 (2)
O1B—H1B \cdots O1A	0.85 (2)	1.91 (2)	2.736 (1)	161 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

A riding model was used for all H atoms attached to C atoms, with C—H distances of 0.95 and 0.98 Å for C(aromatic)—H and C(methyl)—H, respectively. H atoms attached to O atoms were freely refined. A single orientation parameter was refined for each methyl group.

Table 3

Comparison of selected bond and torsion angles in the β and α forms of (I) ($^{\circ}$).

Angle	β form (100 K)	α form (200 K)
O1B \cdots O1A \cdots O1B ⁱ	86.28 (4)	81.83 (4)
O1B \cdots O1A—C1A	129.38 (9)	140.35 (8)
O1B ⁱ \cdots O1A—C1A	122.15 (8)	120.89 (8)
O1A \cdots O1B \cdots O1A ⁱ	93.72 (5)	98.17 (5)
O1A ⁱ \cdots O1B—C1B	140.87 (9)	143.02 (9)
O1A \cdots O1B—C1B	120.13 (9)	118.67 (9)
C1A—O1A \cdots O1B—C1B	71.0 (2)	−53.6 (2)
C1A—O1A \cdots O1B \cdots O1A ⁱ	−129.5 (1)	129.8 (1)
C1A—O1A \cdots O1B ⁱ \cdots O1A ⁱ	135.3 (1)	−145.1 (1)
O1B ⁱ \cdots O1A—C1A—C14A	177.5 (1)	166.5 (1)
C9A—C1A—C2A—C7A	−4.0 (2)	−1.0 (1)
C1A—C2A—C7A—C8A	3.3 (2)	0.4 (1)
C2A—C7A—C8A—C9A	−1.1 (2)	0.5 (1)
C7A—C8A—C9A—C1A	−1.6 (2)	−1.2 (1)
C2A—C1A—C9A—C8A	3.4 (2)	1.3 (1)
C1A ⁱ —O1A ⁱ \cdots O1B—C1B	16.0 (2)	−30.0 (2)
O1B ⁱ \cdots O1A \cdots O1B—C1B	−159.5 (1)	176.7 (1)
O1B ⁱ \cdots O1A ⁱ \cdots O1B—C1B	151.3 (1)	−175.1 (2)
O1A \cdots O1B—C1B—C14B	139.9 (1)	−155.8 (1)
C9B—C1B—C2B—C7B	5.1 (2)	3.0 (1)
C1B—C2B—C7B—C8B	−3.5 (2)	−1.7 (1)
C2B—C7B—C8B—C9B	0.3 (2)	−0.4 (1)
C7B—C8B—C9B—C1B	3.1 (2)	2.4 (1)
C2B—C1B—C9B—C8B	−4.9 (2)	−3.2 (1)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

For both forms of (I), data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990, 1998) and *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1524). Additional figures are also available. Services for accessing these data are described at the back of the journal.

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