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Phase Transition in 9-Hydroxyphenalenone at 255 K and Crystal Structure of the Ordered Phase at 215 K

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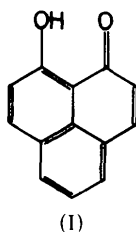
Abstract

9-Hydroxyphenalenone, $C_{13}H_8O_2$, $M_r = 196.205$, monoclinic, space group $P2_1$ below the reversible first-order phase transition at 255 K and space group $P2_1/c$ above. The thermal expansion has been followed from 145 to 360 K by single-crystal X-ray diffractometry. On heating, the a axis decreases sharply in length at the phase transition by 1.7%, the b axis increases smoothly, the c axis increases sharply by 1.5% and the angle β decreases sharply by 2.0%, with the volume expanding abruptly by 0.4%. Corresponding principal linear thermal-expansion coefficients at 145 K are -56 (19), 25 (8) and 192 (19) $\times 10^{-6} K^{-1}$ and at 360 K are -236 (9), 342 (5) and 283 (9) $\times 10^{-6} K^{-1}$. At 215 K $a = 9.091$ (4), $b = 28.581$ (7), $c = 7.011$ (3) Å and $\beta = 100.78$ (8)°, $V = 1789$ (1) Å³, $Z = 8$, $D_x = 1.456$, $D_m = 1.45$ (5) g cm⁻³

(298 K), λ (Mo $K\alpha_1$) = 0.70930 Å, $\mu = 0.89$ cm⁻¹, $F(000) = 816$. Crystal growth from benzene solution. Final $R = 0.0458$ for 5089 unaveraged independent hkl and $h\bar{k}l$ reflections measured at 215 K followed by least-squares refinement with anisotropic C and O, isotropic H-atom thermal amplitudes. Equivalent bond lengths in the four ordered independent molecules do not differ significantly. The average length of the intramolecular asymmetric hydrogen bond O...O is 2.490 (5) Å, with O-H = 1.12 (7) Å. The phase transition is associated with a 35° rotation in the molecular plane for one independent molecule: both this and one other molecule become disordered above the transition by an additional 120° rotation in the molecular plane. The configurational entropy change is calculated as 2.28 J mol⁻¹ K⁻¹, which compares well with the observed entropy change of 2.20(2) J mol⁻¹ K⁻¹.

Introduction

The crystal structure of 9-hydroxyphenalenone (I)



at 298 K was initially studied as part of an investigation into a strong OH...O hydrogen-bond system (Svensson, Abrahams, Bernstein & Haddon, 1979), since potentially symmetric hydrogen bonds in bi-stable molecules may provide information storage media at the molecular level. An ESCA study of the vapor phase indicated the hydrogen bond in (I) to be asymmetric (Brown, Tse, Nakashima & Haddon, 1979) but the X-ray diffraction study showed the O...O hydrogen-bond distance to be 2.486 (4) Å, typical of a symmetric hydrogen bond; the proton, however, was not located. One of the two independent molecules of (I) in the unit cell at 298 K was found to be disordered, and a subsequent heat-capacity study revealed three phase transitions at 254.9, 379.8 and 385.5 K (Abrahams, Bair, Haddon, Stillinger & Svensson, 1981). The measured change in entropy at each transition was fitted by an orientational-disorder model. Rosetti, Haddon & Brus (1980) investigated the fluorescence and fluorescence-excitation spectra for (I) in solid Ar and Ne, from which they calculated a double-minimum potential energy for the phenolic proton ground and excited electronic states. The room-temperature phase has very recently been identified (Svensson & Abrahams, 1984a) as ferroelastic, with large-amplitude molecular and inversion-center displacements under uniaxial stress on the order of 10^5 N m⁻². The present study elucidates the molecular reorientations associated with the order-disorder phase transition at 255 K and provides a further measure of the intramolecular hydrogen bond in 9-hydroxyphenalenone. A preliminary report of the solid-state transformations in (I) has been given by Svensson & Abrahams (1984b).

Experimental, structure solution and refinement

A single crystal of (I), ground to form a sphere of radius 0.14 (1) mm, was mounted on a glass fiber. A CAD-4 diffractometer controlled by a PDP-8a minicomputer under Enraf-Nonius (1983) software, with graphite monochromator [$\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å] and cold N₂ gas-flow cryostat (Danielsson, Grenthe & Oskarsson, 1976), was used to measure both unit-cell dimensions and integrated intensities. The former were determined between 145

and 298 K from accurate measurement of the Bragg angles of 25 reflections with $8^\circ \leq \theta \leq 18^\circ$: the inclusion of some low-angle reflections allowed rapid recovery of the crystal orientation after each temperature change. Two other crystals, mounted within a micro-furnace (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1981) set on the diffractometer, were used in measurement of the unit-cell dimensions between 298 and 370 K. The results are shown in Fig. 1.

The integrated intensity of each reflection within a hemisphere of reciprocal space, with $(\sin \theta)/\lambda \leq 0.60$ Å⁻¹ and $-10 \leq h \leq 10$, $-33 \leq k \leq 33$, $0 \leq l \leq 8$, was measured at 215 K from the spherical crystal by an ω - 2θ -scan technique, for $\Delta\omega = 0.6^\circ + 0.5^\circ \tan \theta$. The maximum measurement time was 120s, with a counting-statistic objective of $\sigma_c(I)/I \leq 0.03$. Three standard reflections measured every 2h showed no systematic variation. Of the total 6655 reflections,

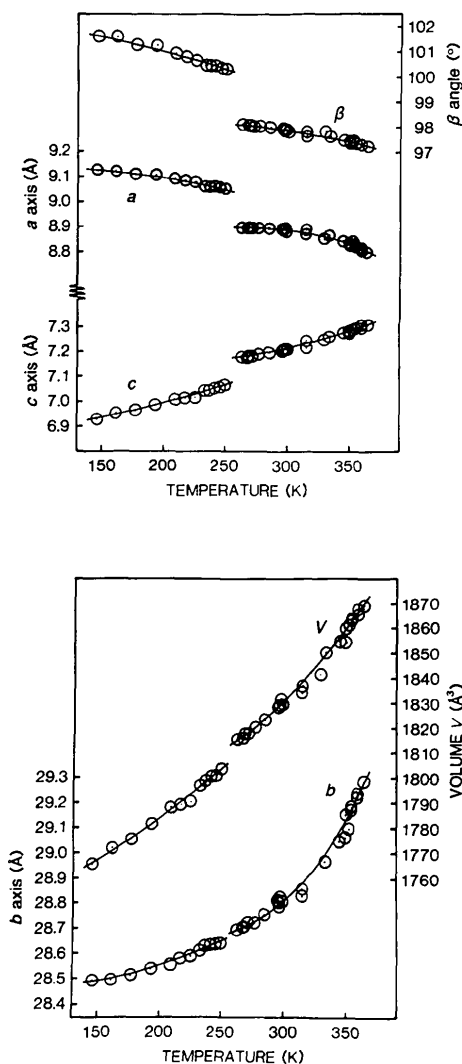


Fig. 1. Unit-cell dimensions vs temperature for 9-hydroxyphenalenone.

1566 were excluded from the refinement procedure: the latter group included 1464 reflections which were considered to be unobserved [$I < 3\sigma_c(I)$]. A subgroup of 52 of these 'unobserved' reflections had highly asymmetric backgrounds caused by strong neighbors resulting from the long b axis, with an average right-to-left background ratio of 4.7 and a maximum background ratio of 19.2: all were later found to have $F_c \geq 5$, see the deposited structure factor lists.* A further group of 102 'observed' reflections, with average background ratio of 2.8 and maximum ratio of 8.7, was similarly excluded from the refinement and each such reflection is also individually identified.* Lorentz, polarization and absorption ($\mu R = 0.013$) corrections were made on the remaining 5089 integrated intensities. Bijvoet pairs were not averaged, although differences due to anomalous scattering are small with $R_{\text{int}}(I) = 0.023$. The structure at 215 K was solved directly with *MULTAN* (Germain, Main & Woolfson, 1971), although it was already known at 298 K. All four independent molecules were located after recycling the molecular fragments. The origin was chosen at $0y\frac{1}{4}$, with respect to a 2_1 axis, to simplify comparison with the 298 K structure determination. Following least-squares refinement of the C and O atomic parameters, using scattering factors from *International Tables for X-ray Crystallography* (1974), the H atoms were located from electron density difference maps. The isotropic-extinction factor g refined to the value $0.13(12) \times 10^4$, based on absorption-weighted mean path lengths (Flack & Vincent, 1978), and resulted in a maximum correction of 2%. All C and O atoms were assigned anisotropic temperature factors in the final least-squares refinement while the H atoms were taken as vibrating isotropically. The 669 parameters were refined simultaneously in a full-matrix program (Lundgren, 1982) until all shifts ($\Delta\xi$) were less than $0.10\sigma(\xi)$: weights were taken as $wF_m = 1/[\sigma^2(F_m) + (0.06F_m)^2 + 0.1]$. The largest correlation coefficient was 0.65: all coefficients greater than 0.5 occur between y coordinates. Final agreement factors are $R = 0.0458$, $wR = 0.0620$ and $S = 0.913$.* The polar axis sense is indeterminate in this experiment as a consequence of the small anomalous-dispersion corrections for Mo $K\alpha$ radiation, hence the relationship between structural chirality and macroscopic polar properties has not been investigated. The maximum positive and negative features in the final difference electron density are $(\Delta\rho)_{\text{max}} = 0.24$,

$(\Delta\rho)_{\text{min}} = -0.21 \text{ e}\text{\AA}^{-3}$. Final atomic position coordinates and equivalent isotropic thermal parameters are listed in Table 1. A view of the atomic thermal ellipsoids in the four independent molecules is illustrated in Fig. 2 and the bond lengths and angles are given in Fig. 3.

On completing the solution and refinement of the 9-hydroxyphenalenone structure at 215 K, the possibility of an ordered structure at room temperature in space group $P2_1$ arose, as an alternative to the published results (Svensson *et al.*, 1979), and was investigated. A hemisphere of reciprocal space was thereupon measured at 295 K as above, with a crystal having natural faces and approximate dimensions $0.27 \times 0.22 \times 0.37$ mm: the scan angle was $0.8^\circ + 0.5^\circ \tan \theta$. The resulting 6832 reflections recorded were reduced to 3895 observations, excluding $I < 3\sigma_c(I)$, and Lorentz, polarization and absorption corrections were applied. A single reflection $I(303) = 5.4\sigma_c(I)$ was the only apparent violation of the previous space-group assignment (Svensson *et al.*, 1979), $P2_1/c$. Refinement proceeded in space group $P2_1$, with molecules (Ia), (Ib) and (IIa) oriented as in the low-temperature phase but with molecule (IIb) rotated about 35° in the molecular plane. The presence of disorder in molecules (IIa) and (IIb) soon became apparent, each having an additional orientation state corresponding to a further molecular rotation of 120° , resulting in a total of 675 variable parameters. The occupancy factors for the two orientation states were

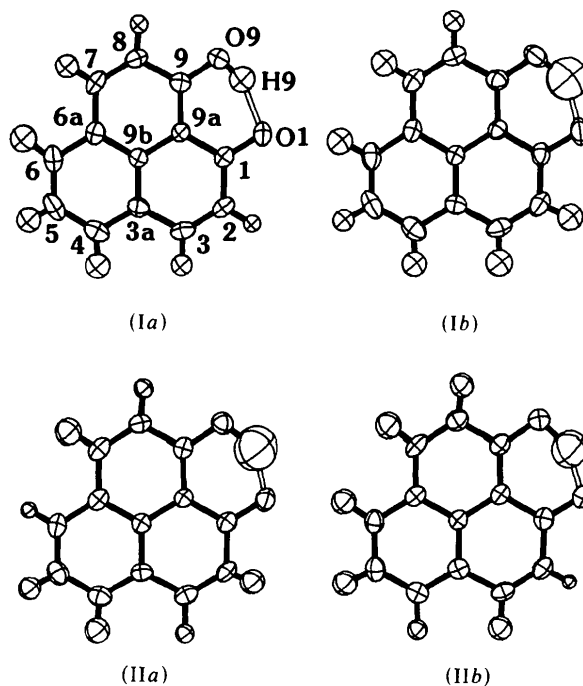


Fig. 2. Plots of the four independent molecules in solid 9-hydroxyphenalenone at 215 K with the thermal ellipsoids scaled to include 50% probability and atomic numbering only on (Ia).

* Lists of structure factors, anisotropic thermal parameters and equations of best planes through the four independent molecules, with deviations of each atom from the molecular plane, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42672 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0.55 (1) and 0.45 (1) for molecule (IIa), 0.51 (1) and 0.49 (1) for molecule (IIb). The maximum isotropic extinction correction was 23% for $F(\bar{1}12)$, with $R = 0.0431$, $wR = 0.0553$ and $S = 0.545$ for $w^{-1} = \sigma_c^2(F_m) + (0.05F_m)^2 + 1.0$. The resulting structural model corresponded very closely to the previous results reported in $P2_1/c$, hence refinement was continued in the centrosymmetric space group with 338 variable parameters after averaging (Ia, b) and (IIa, b). Final occupancy factors for the two orientation states of molecule (II) became 0.530 (4) and 0.470 (4), with $R = 0.0647$, $wR = 0.0860$ and $S =$

0.814: all other structural parameters are equivalent to and confirm those given earlier by Svensson *et al.* (1979).

Table 1. Atomic coordinates ($\times 10^5$ for non-hydrogen, $\times 10^4$ for hydrogen atoms) and U_{eq} ($\text{\AA}^2 \times 10^2$) for 9-hydroxyphenalenone at 215 K

$$U_{eq} = (1/8\pi^2)(4/3) \text{Tr}(\beta \cdot G).$$

	x	y	z	U_{eq}
Molecule (Ia)				
C(1)	85110 (35)	27794	99455 (45)	3.4 (1)
O(1)	99143 (26)	28673 (14)	104093 (41)	4.9 (1)
C(2)	74311 (40)	31488 (16)	94884 (50)	3.9 (1)
C(3)	59575 (39)	30496 (16)	90052 (48)	4.0 (1)
C(3a)	53845 (36)	25768 (17)	89166 (46)	3.5 (1)
C(4)	38739 (39)	24726 (18)	84129 (52)	4.5 (1)
C(5)	33840 (41)	20114 (19)	83249 (58)	5.1 (1)
C(6)	43749 (39)	16490 (18)	87404 (52)	4.4 (1)
C(6a)	59214 (36)	17405 (16)	92732 (46)	3.5 (1)
C(7)	70091 (39)	13742 (16)	97506 (48)	3.9 (1)
C(8)	84925 (38)	14682 (16)	102704 (52)	3.9 (1)
C(9)	90281 (34)	19375 (15)	103269 (45)	3.5 (1)
O(9)	104626 (26)	20193 (15)	108087 (43)	5.0 (1)
C(9a)	79873 (34)	23058 (16)	98699 (44)	3.0 (1)
C(9b)	64312 (32)	22087 (16)	93509 (42)	3.0 (1)
H(2)	7769 (32)	3465 (12)	9600 (45)	2.4 (7)
H(3)	5186 (38)	3297 (14)	8695 (54)	3.9 (9)
H(4)	3159 (44)	2737 (15)	8107 (60)	5.3 (11)
H(5)	2482 (52)	1938 (15)	8109 (60)	5.0 (11)
H(6)	4104 (43)	1302 (17)	8502 (62)	5.7 (12)
H(7)	6657 (39)	1062 (15)	9759 (54)	4.4 (10)
H(8)	9274 (34)	1234 (12)	10561 (45)	2.8 (8)
H(9)	10595 (48)	2324 (18)	10562 (62)	5.5 (12)
Molecule (Ib)				
C(1)	86414 (34)	22445 (15)	51312 (47)	3.7 (1)
O(1)	100589 (27)	21623 (15)	56132 (43)	5.5 (1)
C(2)	75922 (42)	18674 (17)	48571 (53)	4.4 (1)
C(3)	61153 (43)	19507 (17)	43102 (51)	4.2 (1)
C(3a)	55206 (35)	24094 (16)	40094 (44)	3.3 (1)
C(4)	39862 (41)	24966 (19)	34557 (54)	4.7 (1)
C(5)	34543 (42)	29523 (20)	31792 (59)	5.3 (1)
C(6)	44322 (40)	33257 (19)	34294 (52)	4.8 (1)
C(6a)	59781 (35)	32562 (16)	40337 (44)	3.4 (1)
C(7)	70279 (41)	36309 (18)	43672 (51)	4.2 (1)
C(8)	85378 (41)	35541 (16)	49019 (52)	4.0 (1)
C(9)	90921 (36)	30927 (16)	51591 (47)	3.8 (1)
O(9)	105409 (25)	30230 (15)	56535 (40)	4.9 (1)
C(9a)	80850 (34)	27089 (16)	48571 (42)	3.0 (1)
C(9b)	65287 (33)	27907 (15)	42939 (40)	2.9 (1)
H(2)	8059 (44)	1573 (17)	5183 (63)	5.8 (11)
H(3)	5376 (46)	1681 (16)	4171 (66)	6.1 (12)
H(4)	3267 (43)	2222 (15)	3177 (60)	5.3 (11)
H(5)	2419 (41)	3018 (13)	2952 (54)	3.9 (9)
H(6)	3963 (44)	3645 (16)	3426 (63)	5.6 (12)
H(7)	6649 (45)	3952 (18)	4337 (61)	5.7 (11)
H(8)	9230 (38)	3824 (13)	4965 (50)	3.6 (9)
H(9)	10900 (90)	2645 (29)	5427 (122)	15.4 (29)
Molecule (IIa)				
C(1)	35817 (32)	-1949 (16)	33357 (46)	3.3 (1)
O(1)	42951 (25)	-2681 (14)	19466 (36)	4.3 (1)
C(2)	33696 (39)	-5610 (16)	46502 (56)	3.8 (1)
C(3)	26103 (35)	-4838 (16)	61013 (51)	3.7 (1)
C(3a)	19757 (32)	-335 (16)	63910 (45)	3.2 (1)
C(4)	11735 (36)	500 (17)	78653 (49)	3.9 (1)
C(5)	5795 (38)	4889 (18)	81024 (54)	4.2 (1)
C(6)	8006 (33)	8533 (17)	69062 (51)	3.8 (1)
C(6a)	16014 (31)	7855 (16)	53987 (47)	3.3 (1)
C(7)	18335 (35)	11498 (16)	40962 (50)	3.8 (1)
C(8)	25934 (34)	10807 (16)	26421 (50)	3.7 (1)
C(9)	32077 (31)	6312 (16)	23621 (44)	3.2 (1)
O(9)	39660 (24)	5668 (14)	9664 (35)	4.1 (1)
C(9a)	29857 (29)	2596 (16)	35989 (45)	2.9 (1)
C(9b)	21863 (30)	3378 (16)	51270 (44)	2.9 (1)
H(2)	3734 (46)	-799 (16)	4382 (61)	5.0 (12)
H(3)	2434 (35)	-756 (12)	7143 (47)	3.1 (8)
H(4)	934 (44)	-189 (17)	8764 (59)	5.4 (11)
H(5)	71 (37)	552 (14)	9112 (57)	4.3 (10)
H(6)	359 (31)	1138 (12)	7048 (43)	2.1 (7)
H(7)	1400 (44)	1476 (16)	4319 (63)	5.7 (11)
H(8)	2755 (34)	1314 (13)	1610 (48)	3.0 (8)
H(9)	4530 (83)	184 (29)	1015 (121)	15.7 (29)

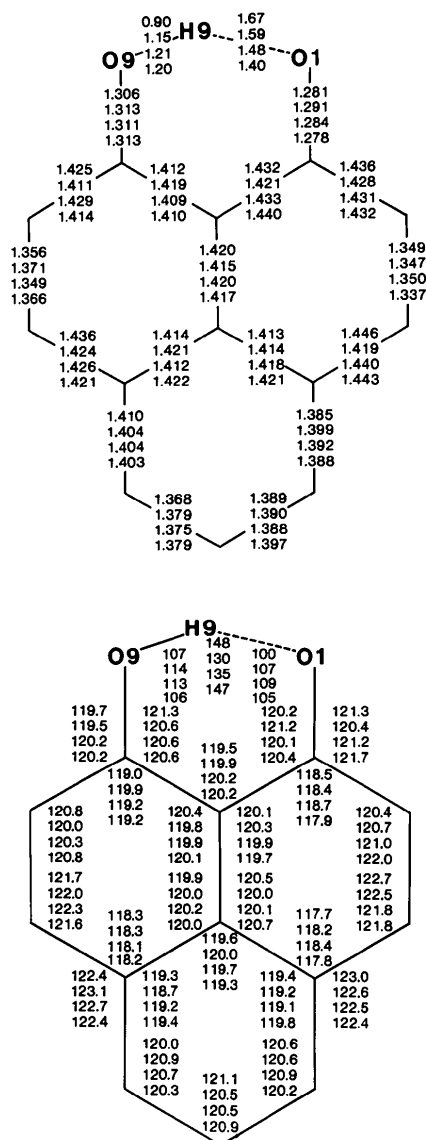


Fig. 3. Bond lengths (\AA) and angles ($^\circ$) at 215 K. Data are given for molecules (Ia), (Ib), (IIa) and (IIb), in that order. The ranges of e.s.d.'s are 0.004–0.006 \AA for bond lengths and 0.1–0.3 $^\circ$ for bond angles at C and O atoms and 0.05–0.08 \AA , 2–6 $^\circ$ for the hydrogen bonds.

Table 1 (*cont.*)

Molecule (IIb)	x	y	z	U_{eq}
C(1)	19333 (33)	52467 (16)	118303 (46)	3.5 (1)
O(1)	13504 (27)	53594 (14)	132888 (37)	4.4 (1)
C(2)	28176 (36)	55701 (17)	109662 (52)	3.8 (1)
C(3)	33903 (34)	54590 (16)	94020 (50)	3.6 (1)
C(3a)	31997 (33)	49999 (17)	85341 (50)	3.4 (9)
C(4)	37891 (35)	48801 (17)	69115 (46)	3.8 (1)
C(5)	35971 (38)	44282 (18)	61450 (53)	4.3 (1)
C(6)	28220 (34)	40942 (17)	69777 (49)	3.9 (1)
C(6a)	22081 (31)	42035 (16)	86155 (45)	3.4 (1)
C(7)	13920 (35)	38723 (16)	95156 (51)	3.8 (1)
C(8)	7722 (35)	39879 (17)	110834 (49)	3.8 (1)
C(9)	9074 (31)	44464 (16)	118553 (46)	3.3 (1)
O(9)	2689 (26)	45566 (14)	133271 (35)	4.2 (1)
C(9a)	17461 (31)	47810 (16)	110365 (42)	3.1 (1)
C(9b)	23880 (30)	46626 (16)	94080 (44)	2.8 (1)
H(2)	2890 (29)	5850 (12)	11457 (42)	1.6 (7)
H(3)	4048 (42)	5675 (14)	8720 (56)	4.7 (10)
H(4)	4418 (37)	5125 (13)	6278 (51)	3.4 (9)
H(5)	3907 (45)	4324 (15)	4946 (64)	5.2 (11)
H(6)	2622 (42)	3750 (15)	6443 (58)	5.2 (11)
H(7)	1224 (44)	3544 (17)	9066 (62)	5.6 (11)
H(8)	145 (43)	3785 (15)	11809 (56)	4.8 (10)
H(9)	533 (66)	4965 (24)	13660 (91)	11.1 (20)

Thermal expansion of 9-hydroxyphenalenone between 145 and 360 K

The dependence of the unit-cell dimensions on temperature in the range 145 to 360 K is shown in Fig. 1. The sharp break at 255 K in the *a* and *c* axes of about 1.7 and 1.5% respectively, and in the monoclinic angle β of about 2%, corresponds very closely to the 254.9 K first-order phase-transition temperature previously found (Abrahams *et al.*, 1981). It is noteworthy that the length of the *b* axis varies continuously throughout the temperature range. The volume changes sharply by about 0.4% at 255 K. The unit-cell dimensions below the phase transition may be fitted by multiple linear-regression analysis to a second-order polynomial of the form:

$$a_i^T = a_i^{145} [1 + \alpha_i \Delta T + \beta_i (\Delta T)^2],$$

where $\Delta T = T - 145$ K, with $\alpha_1 = -37$ (15), $\alpha_2 = 25$ (8) and $\alpha_3 = 139$ (16) $\times 10^{-6}$ K $^{-1}$, $\beta_1 = -37$ (13), $\beta_2 = 26$ (7) and $\beta_3 = 40$ (14) $\times 10^{-8}$ K $^{-2}$ and $a = 9.130$ (4), $b = 28.494$ (5), $c = 6.928$ (3) Å and $\beta = 101.58$ (8)° at 145 K. The corresponding coefficients above the phase transition, for $\Delta T = T - 298$ K, are $\alpha_1 = -52$ (3), $\alpha_2 = 136$ (3) and $\alpha_3 = 153$ (5) $\times 10^{-6}$ K $^{-1}$, $\beta_1 = -139$ (6), $\beta_2 = 170$ (6) and $\beta_3 = 79$ (12) $\times 10^{-8}$ K $^{-2}$. It is noted that the thermal-expansion tensors are not represented by an ellipsoid, since α_1 is negative. Values of the principal linear thermal-expansion coefficients at 145 and 360 K are given in the *Abstract*. Unit-cell dimensions at 298 K are $a = 8.8941$ (2), $b = 28.8159$ (4), $c = 7.2117$ (2) Å, $\beta = 97.937$ (1)° (Svensson *et al.*, 1979) and at 360 K are $a = 8.820$ (2), $b = 29.226$ (6), $c = 7.295$ (4) Å and $\beta = 97.33$ (2)°. The thermal-expansion coefficients are large and become even larger as the temperature approaches

Table 2. Average bond lengths (Å) in 9-hydroxyphenalenone at 215 K

The e.s.d. of the average, based on $n = 4$ independent lengths for each bond, is given by $\{1/[n(n-1)] \sum_{r=1}^n (d_r - \bar{d})^2\}^{1/2}$ [see, for example, Stout & Jensen (1968)].

C(9)-O(9)	1.311 (2)	C(1)-O(1)	1.284 (3)
C(9)-C(9a)	1.413 (2)	C(1)-C(9a)	1.432 (4)
C(9a)-C(9b)	1.418 (1)	C(9b)-C(3a)	1.417 (2)
C(9b)-C(6a)	1.417 (3)	C(3a)-C(3)	1.438 (6)
C(6a)-C(7)	1.427 (3)	C(3)-C(2)	1.346 (3)
C(7)-C(8)	1.361 (5)	C(2)-C(1)	1.432 (2)
C(8)-C(9)	1.420 (4)	C(6)-C(5)	1.375 (3)
C(6a)-C(6)	1.405 (2)	C(5)-C(4)	1.391 (2)
O(9)···O(1)	2.490 (5)	C(4)-C(3a)	1.391 (3)
O(9)-H(9)	1.12 (7)	H(9)···O(1)	1.54 (6)

the further phase transitions beginning at 379.8 K (Abrahams *et al.*, 1981). The largest principal coefficient makes an angle of 27.5° with the *c* axis at 145 K [*i.e.* close to (201)], becoming about 12° closer by 360 K.

Crystal and molecular structure at 215 K

The bond lengths and angles determined in the four independent molecules of (I) in the unit cell at 215 K are collected in Fig. 3, and the average values in Table 2. A full-normal probability plot of the ordered *i*th individual deviates Δ_i/σ_i (Abrahams & Keve, 1971), from the averages in Table 2, has a slope of 0.90 (1) and intercept of -0.02 (1) with correlation coefficient of 0.994. The average bond lengths in Table 2 may hence be taken as representative of (I) at 215 K. The short intramolecular O(9)···O(1) hydrogen bond is asymmetric, see Fig. 3, as shown both by the location of the H(9) atom and the resulting overall departure from C_{2v} molecular symmetry. The deviations from this symmetry are small but significant if the e.s.d.'s from the variance-covariance matrix are accepted: an alternating pattern of shorter and longer bonds may be noted along the perimeter of the molecule, see Fig. 3. Small deviations from planarity are found in each molecule, with r.m.s. deviations of 0.008, 0.014, 0.014 and 0.028 Å respectively in molecules (Ia), (Ib), (IIa) and (IIb). The largest atomic deviation is 0.049 Å for O(9) (IIb), see deposition footnote.

Symmetric O···O bond lengths have been reported throughout the range 2.4 to 2.6 Å, with asymmetric bonds extending in length from 2.4 to 3.0 Å (Ichikawa, 1978). The O···O bond length of 2.490 (5) Å in (I) at 215 K is, however, clearly that of an asymmetric bond with O(9)-H(9) = 1.12 (7) Å and H(9)···O(1) = 1.54 (6) Å, see Table 2. The experimental value for the O(9)-H(9) bond distance does not depart significantly from Ichikawa's average correlation curve.

The molecules pack to form alternating layers parallel to (010), the normals to molecules (Ia), (Ib) lying in the plane and those to molecules (IIa), (IIb)

inclined 15° out of the plane. Molecules (Ia) and (Ib) are approximately parallel, as are molecules (IIa) and (IIb), with interplanar distances of 3.6 \AA . Neighboring molecules (Ia) and (Ib) are related by rotations of about 21° , molecules (IIa) and (IIb) by rotations of about 24° , within the molecular plane.

Structural and entropy change at 255 K phase transition

Molecules (Ia) and (Ib) in space group $P2_1$ below 255 K are related by a pseudoglide plane with translation along [001], as may be seen by examination of the atomic coordinates in Table 1, and correspond closely to the location of molecule (I) in space group $P2_1/c$ at 298 K (Svensson *et al.*, 1979), see Fig. 4. The r.m.s. deviation of corresponding atoms in molecules (Ia) and (Ib), after application of the pseudosymmetry operation, is 0.22 \AA . Molecule (IIa) at 215 K also corresponds, although less closely, to one of the two orientations found for disordered molecule (II) at 298 K. Molecule (IIb), however, has an orientation that differs from any found at 298 K. The origin along the polar b axis in space group $P2_1$ has been chosen to give comparable y coordinates for each of the four independent C(9b) atoms, which lie approximately at the molecular centroids, above and below the phase-transition temperature. Some

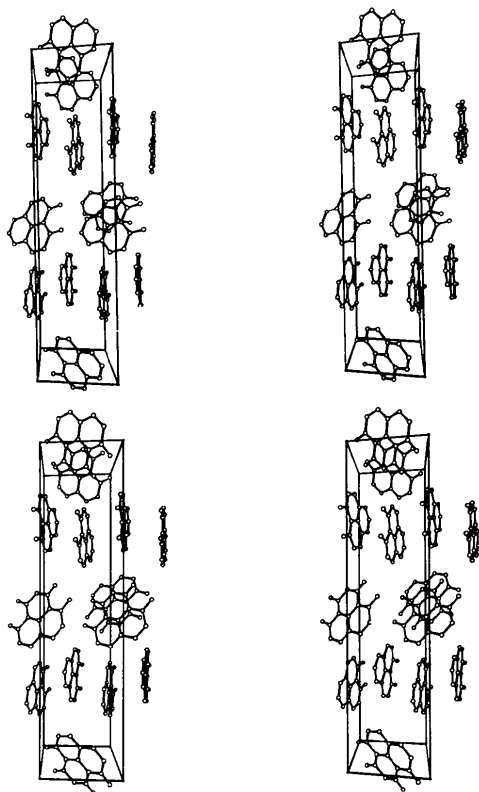


Fig. 4. Molecular arrangement in 9-hydroxyphenalenone at 215 K (upper) and 298 K (lower). The origin is at the lower left-hand corner in each cell, with the a axis pointing into the page and the c axis approximately in the plane of the page.

Table 3. Selected differences in atomic position between 215 and 298 K

Values are based on averaged unit-cell dimensions, with root-mean-square difference ($\Delta_{r.m.s.}$) calculated for the 15 C and O atoms in each molecule. Orientations involving the least differences are given for molecules (IIa) and (IIb). Difference e.s.d.'s less than 0.01 \AA .

	Difference in \AA			
	(Ia)	(Ib)	(IIa)	(IIb)
C(1)	0.09	0.23	0.44	1.38
C(9a)	0.06	0.18	0.24	0.58
C(9b)	0.09	0.13	0.29	0.31
O(1)	0.15	0.24	0.19	2.22
O(9)	0.05	0.29	0.19	2.35
$\Delta_{r.m.s.}$	0.14	0.22	0.27	1.59

selected changes in atomic position at temperatures about 40 K above and below the phase transition are presented in Table 3: corresponding molecular translations, as given by displacements of the C(9b) atom, range from 0.1 to 0.3 \AA . Molecular rotations, represented by the displacements of O(1) and O(9), are of similar magnitude except for molecule (IIb). The major structural change on heating through the phase transition, in addition to the development of the c -glide plane, is the 35° in-plane rotation of molecule (IIb) required to assume the second of the two major orientations at 298 K of molecule (II), which has a further in-plane rotation of 120° from the first orientation.

Two interpretations of the structure at 298 K, based on the present low-temperature determination, are possible. In the first, reorientation of molecule (IIb) by a 35° in-plane rotation gives a molecular arrangement in space group $P2_1$ that is rather similar to the original structural description in space group $P2_1/c$ at 298 K. The space-group assignment in this case, however, is incorrect since molecules (IIa) and (IIb) are related only by a pseudo- c -glide plane: the positions of the O atoms are not required to be symmetry related although $h0l$ reflections with $l = 2n + 1$ would be very weak and probably close to the normal limit of detection since they would originate only in the diffraction contribution made by these unrelated O atoms. In the second interpretation, molecule (IIb) rotates 35° at the phase transition as before and both molecules (IIa) and (IIb) undergo further in-plane rotations to give static or dynamic disorder for molecule (II), as originally postulated by Svensson *et al.* (1979), with genuine c -glide-plane development above the transition. A choice between the two interpretations may be made at a confidence level greater than 99% by second-harmonic analysis (Dougherty & Kurtz, 1976). A crystalline solid without inversion centers always generates the second harmonic of an incident coherent beam of light. Demonstration that (I) at 298 K has undetectable second-order nonlinear dielectric susceptibility coefficients (Svensson & Abrahams, 1984b) effectively eliminates the first interpretation.

The observed entropy change at 255 K of $2.20(2) \text{ J mol}^{-1} \text{ K}^{-1}$ was previously fitted by a model in which 17 possible molecular configurations above the transition were assumed to be reduced to two configurations in the low-temperature phase (Abrahams *et al.*, 1981). The configurational entropy change associated with the transition is then $\frac{1}{8}R \ln(17/2) = 2.22 \text{ J mol}^{-1} \text{ K}^{-1}$, in excellent agreement with experiment. The present structure determination shows that molecule (I) is fully ordered below the phase-transition temperature and hence has but a single configuration. At 298 K, however, the disorder associated with each pair of molecules (II) gives rise only to three of the four configurations possible, since one configuration would result in the unacceptably short O...O distance of 2.5 Å. The total number of configurations at 298 K is hence 3^2 , for a corresponding predicted entropy change of $\frac{1}{8}R \ln 9 = 2.28 \text{ J mol}^{-1} \text{ K}^{-1}$.

The dependence of the phase-transition temperature on applied hydrostatic pressure may be estimated from the Clapeyron equation, using the known changes in entropy and unit-cell volume, as about 0.25 K MPa^{-1} .

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Fluorine Nonbonded Potential Parameters Derived from Crystalline Perfluorocarbons

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Abstract

Fluorine-fluorine nonbonded potential-energy functions of the $(\exp - 6 - 1)$ type were derived by least squares from the crystal structures of seven perfluorocarbons. Potential-derived site-charge models for the molecules were obtained using *ab initio* wavefunctions calculated with a 6-31G basis set. The best fit to the calculated molecular electric potential was obtained with a C–F bond-charge model. In addition, extended-charge, net-atomic-charge and no-charge models were considered. The best fits to the crystal structures were also obtained using nonbonded parameters derived using the bond-charge model. A plot of the resulting F...F nonbonded poten-

tial showed that fluorine in perfluorocarbons is as space filling as oxygen in oxohydrocarbons.

Introduction

Nonbonded interatomic potential functions of the $(\exp - 6 - 1)$ type have previously been derived by this research group from the crystal structures of hydrocarbons (Williams & Starr, 1977), azahydrocarbons (Williams & Cox, 1984), oxohydrocarbons (Cox, Hsu & Williams, 1981), perchlorocarbons (Hsu & Williams, 1980), and the noble gases (Williams, 1972a). References and comparisons with the work of other research groups are given in the cited papers.