3865.
(82) Gupta, A.; Hammond, G. S. *J. Am. Chem. Soc.* **1976,** *98,* 1218–1223.
(83) Arnold, D. R.; Morchat, R. M. *Can. J. Chem.* **1977,** *55,* 393–406.
(84) Weller, A.; Zachariasse, K. "Molecular Luminescence", Lim, E. C., Ed.; W. A. Benjamin: New York, 1969; pp 895–920. Grellman, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972,** *76,* 3132–3137. Schomburg, H.; Staerk, H.; Weller, A. *Chem. Phys. Lett.* **1973,** *22,* 1–7.
(85) Carrathers, R. A.; Crellin, R. A.; Ledwith, A. *Chem. Commun.* **1969,** 252. Crellin, R. H.; Lambert, M. C.; Ledwith, A. *Ibid.* **1970,** 682–683. Ledwith, A. *Acc. Chem. Res.* **1972,** *5,* 133–139.
(86) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973,** *95,* 4080–4081.
(87) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973,** 677–678.
(88) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975,** 53–54, 56–57.
(89) All melting points and boiling points are uncorrected. Elemental analyses were performed by Altantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc lamp.
(90) Koelsch, C. F.; Johnson, P. R. *J. Am. Chem. Soc.* **1943,** *65,* 567–573.
(91) Zimmerman, H. E. *J. Am. Chem. Soc.* **1956,** *78,* 1168–1173.
(92) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972,** *94,* 7178–7179.
(93) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969,** *1,* 245–252.
(94) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1974,** *96,* 3668–3670.

Crystal Structure of 9-Hydroxyphenalenone: a Very Short Intramolecular Hydrogen Bond System

C. Svensson,[1] S. C. Abrahams,* J. L. Bernstein, and R. C. Haddon

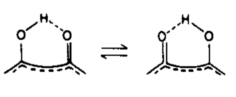
Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.

Received March 1, 1979

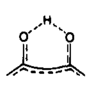
Abstract: 9-Hydroxyphenalenone ($C_{13}H_8O_2$) crystallizes in the monoclinic system with lattice constant a = 8.8941 (2) Å, b = 28.8159 (4) Å, c = 7.2117 (2) Å, β = 97.937 (1)°, and eight molecules in the unit cell. The space group is $P2_1/c$. The structure was solved by direct methods and refined by the method of least squares. The final indicator R = 0.068 for the 2270 reflections with $|F_{obsd}|^2 > 3\sigma|F_{obsd}|^2$. One of the two independent molecules is disordered leading to reduced dimensional accuracy. The other molecule has effective *mm*2 symmetry. The intramolecular O···O distance is 2.486 (4) Å; all dimensions in this molecule are consistent with a symmetric hydrogen bond or a situation in which the hydrogen is undergoing exchange between two closely spaced equilibrium positions. The disordered molecule equally occupies two major orientations, approximately related by a 120° rotation in the molecular plane. Diffuse X-ray scattering indicates appreciable short-range correlations between the orientations of the disordered molecule. Two phase transitions have been detected: one is at 252 K, the other occurs in the range 330–395 K.

Introduction

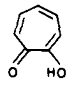
Hydrogen bonding in solids continues to attract considerable attention, with particular emphasis being placed on systems involving potentially symmetric intramolecular hydrogen bonds. Most investigations have focused on molecules incorporating the hydroxy ketone unit (**1**). Such bistable molecules are of general interest for possible information storage at the molecular level, in photochemical hole burning,[2] and for the possible involvement of proton tunneling in the primary event of vision.[3] Compounds involving the unit **1** fused to a conjugated ring system, for which crystallographic information is available, fall into two categories: (i) nonalternant π-electron systems with a single hydrogen bond, e.g., tropolone (**2**)[4a] and 6-hydroxy-2-formylfulvene (**3**);[4b] and (ii) dihydroxyquinones with two sets of hydrogen bonds attached to benzenoid ring systems, e.g., naphthazarin (**4**)[5a] and 1,5-dihydroxyanthraquinone (**5**).[5b] In category i, the bonding hydrogen atom is required to be part of a five- or seven-membered ring, whereas ii requires a six-membered ring.



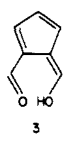
1a 1b



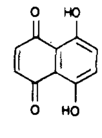
1c



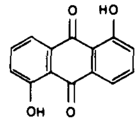
2



3

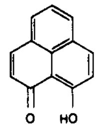


4



5

The present work reports a compound which combines some features of both categories. 9-Hydroxyphenalenone (**6**)[6] is benzenoid and incorporates a single hydrogen bond as part of a six-membered ring. The compound is known to possess a very strong hydrogen bond:[6] an IR study[7] found no evidence for an absorption due to the O–H stretching vibration. Very recent ESCA[8] (gas phase) and DQR[9] (solution phase) studies indicate that 9-hydroxyphenalenone possesses *m* rather than *mm*2 ground-state symmetry (i.e., **1a–1b** rather than **1c**). 9-Hydroxyphenalenone in the condensed state is shown vide infra to contain one of the shortest O···O distances, <2.5 Å, documented in a neutral intramolecularly hydrogen-bonded molecule.



6

Experimental Section

X-ray Study. Transparent amber-colored crystals with dimensions as large as 5 mm were grown by slow cooling of saturated 9-hydroxyphenalenone in benzene solution, using a sealed container: (010) formed the principal platelet face. A sphere of radius 0.24 (1) mm was ground and mounted,[10] in random orientation, on a Pyrex capillary. Integrated intensity measurements were made on a PDP 11/40-8e computer-controlled Enraf-Nonius CAD-4 diffractometer, using

0002-7863/79/1501-5759$01.00/0

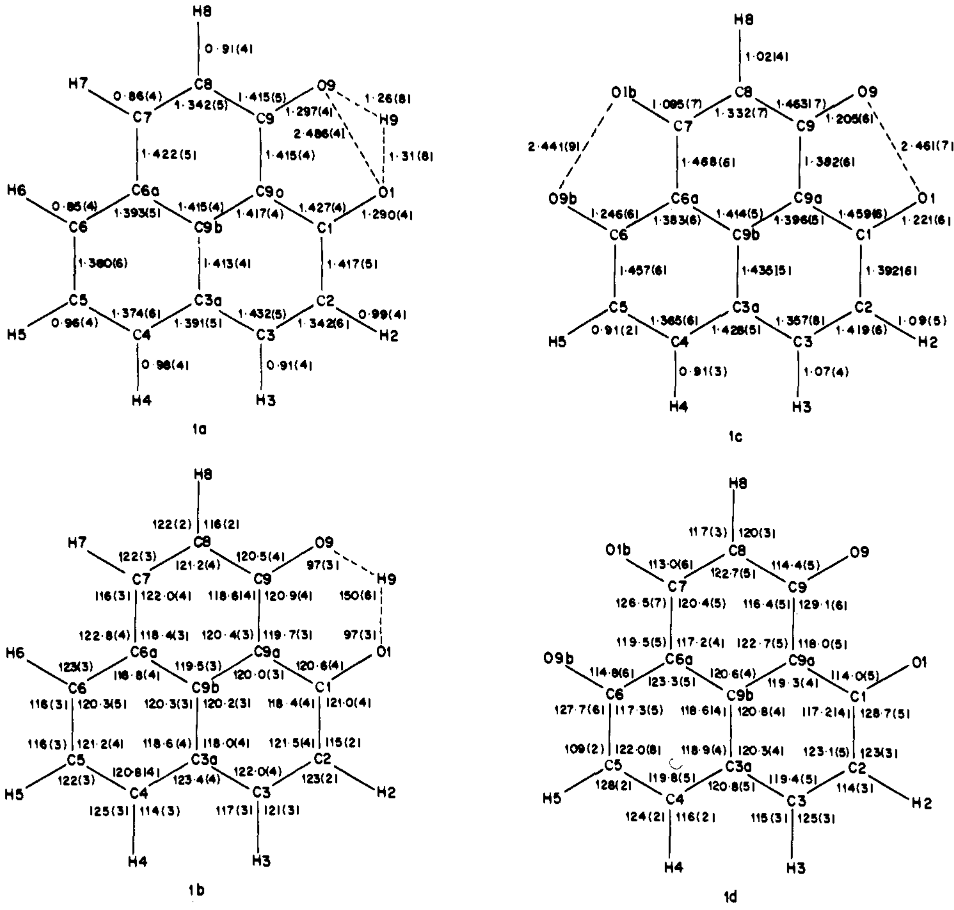


Figure 1. (a) Interatomic bond lengths, with esd's in parentheses, in molecule I. (b) Corresponding bond angles in molecule I. (c) Interatomic bond lengths in molecule II. (d) Corresponding bond angles in molecule II.

Table I. Crystal Data for 9-Hydroxyphenalenone[a]

Laue symmetry: $2/m$	
space group: $P2_1/c$	
$a = 8.8941$ (2) Å	formula: $C_{13}H_8O_2$
$b = 28.8159$ (4) Å	mol wt 196.20
$c = 7.2117$ (2) Å	$Z = 8$
$\beta = 97.937$ (1)°	$D_{measd} = 1.45$ (5) mg mm^{-3}
$V = 1830.6$ (4) Å^3	$D_{calcd} = 1.426$ mg mm^{-3}
λ (Cu Kα_1) = 1.54062 Å	$\mu = 0.93$ mm^{-1}
$T = 298$ K	mp 473-474 K
packing coefficient:	0.74[b]
systematic absences:	$h0l$ (l odd), $0k0$ (k odd)

[a] Reference 10. [b] Given by $Z \times V_0/V$, where V_0 is the molecular volume: taken from A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964), and A. I. Kitaigorodsky, "Molecular Crystals and Molecules", Academic Press, New York, 1973.

graphite monochromated Mo Kα radiation. All reflections within a quarter-sphere of reciprocal space with radius $(\sin\theta)/\lambda \leq 0.70$ Å^{-1} were sampled by the ω-2θ scan technique with $\Delta\omega = 0.7° + 0.4° \tan\theta$. The maximum time spent on a reflection was 90 s. Three standard reflections were remeasured hourly: no significant variation in intensity was detected as a function of exposure time except for a discontinuity when the X-ray generator power was inadvertently increased. In consequence, the intensities of about half the 5547 measured reflections were corrected by the factor 1.19. Eleven reflections were rejected due to highly asymmetric backgrounds caused by strong neighboring reflections. The remaining 5536 reflections were corrected for Lorentz and polarization effects: the absorption correction was negligible for $\mu R = 0.223$. An extinction correction[11] was applied during the later stages of structure refinement, but it also proved to be negligible with $g = 0.8$ (8) $\times 10^3$. All calculations were performed on the PDP 11/40 computer.[12]

Crystal Data. The crystal data are presented in Table I. Lattice constants of $a = 8.8899$ (22), $b = 28.8083$ (72), and $c = 7.2059$ (18) Å, and $\beta = 97.886$ (24)° were initially determined from the scattering angles of 50 reflections with 2θ between 6 and 36° on the CAD-4 diffractometer. More accurate values (Table I) were measured on a modified version[13] of Bond's precision lattice constant diffractometer.[14]

Determination and Refinement of the Structure. The structure was solved using the MULTAN program,[12] and both independent molecules were located from the E map. Refinement by the method of least squares of the position and isotropic thermal parameters for all 30 carbon and oxygen atoms resulted in the high R value of 0.27.[15] A difference electron density map contained two prominent peaks which indicated that one of the two independent 9-hydroxyphenalenone molecules was disordered by a rotation of ~120° in the plane of the molecule. Refinement with four oxygen atoms of molecule II having half-occupancy each resulted in approximately equal temperature factors and $R = 0.21$. Further refinement with anisotropic temperature factors for the atoms in molecule I gave $R = 0.13$.

A difference map now revealed most of the hydrogen atom positions. In the final refinement cycles, all carbon and oxygen atoms were assigned anisotropic and the hydrogen atoms isotropic temperature factors. A total of 342 parameters were varied, with 2270 observed structure factors having $|F_{obsd}|^2 > 3\sigma\,|F_{obsd}|^2$. The weights used in the least-squares calculations were derived from the equation $w_i = (4|F_{obsd}|^2{}_i Lp^{-1})/[\sigma^2(I)_i + (0.06I_i)^2]$ for $|F_{obsd}| > 20$, where $\sigma^2(I)_i$ is the standard deviation in the ith intensity due to counting statistics. For $|F_{obsd}| < 20$, $\sigma|F_{obsd}| = \max(0.7, \sigma|F_{obsd}|)$. The resulting agreement indices are $R = 0.068$, $wR = 0.078$, and $S = 1.25$.[15] The corresponding δR plot[16] is almost linear over the entire range. A final difference map revealed a series of peaks with electron density of ~0.5 e Å^{-3}, corresponding to a third orientation of molecule II. These peaks may be fitted by a rotation of 60°, in the plane of the molecule, to a location midway between the positions occupied by the two other major orientations; see Table II. The third orientation is estimated to occur with a frequency of 5% and was not included in the refinement

Table II. Atomic Positional Coordinates of 9-Hydroxyphenalenone at 298 K

atom	*x*	*y*	*z*	B_{iso} (Å^2)
		Molecule I		
C-1	0.8430 (5)	0.2787 (2)	0.9948 (5)	
O-1	0.9834 (3)	0.2888 (1)	1.0491 (5)	
C-2	0.7326 (5)	0.3140 (2)	0.9520 (6)	
C-3	0.5864 (5)	0.3038 (2)	0.8944 (6)	
C-3a	0.5331 (4)	0.2569 (2)	0.8765 (5)	
C-4	0.3819 (5)	0.2452 (2)	0.8204 (6)	
C-5	0.3373 (5)	0.1995 (2)	0.8052 (7)	
C-6	0.4407 (5)	0.1639 (2)	0.8452 (6)	
C-6a	0.5931 (4)	0.1738 (2)	0.9047 (5)	
C-7	0.7044 (5)	0.1387 (1)	0.9504 (5)	
C-8	0.8509 (5)	0.1489 (2)	1.0063 (6)	
C-9	0.9020 (4)	0.1954 (2)	1.0213 (5)	
O-9	1.0439 (3)	0.2047 (1)	1.0757 (5)	
C-9a	0.7946 (4)	0.2314 (1)	0.9787 (5)	
C-9b	0.6399 (4)	0.2208 (1)	0.9196 (4)	
H-2	0.772 (4)	0.346 (1)	0.964 (4)	4 (1)
H-3	0.516 (4)	0.327 (2)	0.871 (5)	6 (1)
H-4	0.316 (5)	0.272 (2)	0.789 (6)	8 (1)
H-5	0.234 (4)	0.190 (2)	0.765 (6)	7 (1)
H-6	0.405 (4)	0.136 (5)	0.836 (5)	6 (1)
H-7	0.672 (4)	0.111 (2)	0.940 (5)	6 (1)
H-8	0.921 (4)	0.127 (1)	1.042 (5)	5 (1)
H-9	1.039 (7)	0.247 (3)	1.034 (10)	16 (2)
		Molecule II (Disordered)[a]		
C-1	0.3211 (5)	0.0630 (2)	0.1921 (6)	
O-1	0.3997 (6)	0.0528 (2)	0.0719 (7)	
C-2	0.2531 (5)	0.1054 (2)	0.2223 (6)	
C-3	0.1718 (5)	0 1135 (2)	0.3753 (7)	
C-3a	0.1573 (5)	0.0788 (2)	0.4987 (6)	
C-4	0.0749 (5)	0.0857 (2)	0.6532 (6)	
C-5	0.0610 (5)	0.0502 (2)	0.7749 (6)	
C-6	0.1292 (5)	0.0048 (2)	0.7539 (6)	
O-9b	0.1321 (7)	−0.0291 (2)	0.8616 (7)	
C-6a	0.2064 (5)	−0.0012 (2)	0.6064 (6)	
C-7	0.2786 (5)	−0.0461 (2)	0.5802 (7)	
O-1b	0.2825 (8)	−0.0762 (2)	0.6736 (10)	
C-8	0.3546 (5)	−0.0528 (2)	0.4355 (7)	
C-9	0.3708 (5)	−0.0166 (2)	0.2970 (7)	
O-9	0.4464 (5)	−0.0278 (2)	0.1777 (7)	
C-9a	0.3050 (4)	0.0258 (2)	0.3254 (6)	
C-9b	0.2243 (4)	0.0342 (1)	0.4752 (5)	
H-2	0.258 (6)	0.135 (2)	0.130 (7)	11 (2)
H-3	0.117 (5)	0.145 (2)	0.403 (6)	8 (1)
H-4	0.034 (3)	0.114 (1)	0.662 (4)	3.4 (6)
H-5	0.017 (2)	0.050 (1)	0.881 (3)	−0.5 (3)
H-8	0.407 (4)	−0.084 (2)	0.427 (5)	7 (1)

[a] Equal occupancy is assumed for both orientations of this molecule; see text.

model to avoid the large consequent increase in the number of variables.

The final atomic position coordinates for carbon, oxygen, and hydrogen in both independent molecules are given in Table II, together with isotropic temperature factors for hydrogen. The final anisotropic temperature coefficients for the carbon and oxygen atoms are given in Table III. The magnitudes of the 2270 observed and calculated structure factors, on the final least-squares scale, are listed in Table IV and are available as supplementary material.

Results and Discussions

Molecular Dimensions. The bond distances and angles determined for molecule I are given in Figures 1a and 1b and for molecule II in Figures 1c and 1d. The atomic distribution in molecule I is accurately coplanar, see Table VA. The deviations from planarity listed in Table VB for molecule II would be highly significant in the absence of disorder. However, the two major orientations occupied by molecule II are not crystallographically required to be coplanar. A small misregistration would result in deviations comparable to those given in Table VB and to anomalous bond distances similar to those in Figure 1c. A linear misregistration of ~¼ ångström is compatible with our measurements. The dimensions obtained for molecule I are hence regarded as more representative of 9-hydroxyphenalenone than those obtained for molecule II.

The presence of a second mirror plane of symmetry, normal to that passing through the molecular plane, may be demonstrated without ambiguity by means of probability plot analysis.[16] The 9-hydroxyphenalenone molecule contains 12 pairs of bond lengths and 19 pairs of bond angles that would be equivalent if a mirror existed normal to the plane of **6** and passing through C-9a, C-9b, C-5, and H-5 (Figure 1a). A plot of the order statistic Δ_i/σ_i where Δ_i is the difference corresponding to the *i*th pair and σ_i is the pooled standard deviation in Δ_i, against the expected[17] values of the ranked moduli of 31 normal observations, is linear with slope of 1.1 and zero intercept. Equivalence thus exists, and molecule I hence possesses *mm*2 symmetry. The standard deviations shown in Figures 1a and 1b are shown by the probability plot to be un-

Table III. Anisotropic Temperature Coefficients for 9-Hydroxyphenalenone at 298 K[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Molecule I			
C-1	183 (6)	13 (1)	202 (7)	−19 (3)	51 (11)	−2 (3)
O-1	195 (4)	18 (1)	388 (8)	−43 (2)	−20 (10)	6 (3)
C-2	254 (7)	10 (1)	257 (9)	1 (3)	77 (13)	2 (4)
C-3	238 (7)	13 (1)	229 (8)	37 (3)	88 (12)	10 (4)
C-3a	158 (5)	16 (1)	165 (7)	19 (3)	71 (10)	8 (3)
C-4	145 (5)	26 (1)	246 (9)	27 (4)	38 (12)	20 (5)
C-5	140 (6)	29 (1)	286 (10)	−27 (4)	17 (12)	14 (5)
C-6	190 (6)	22 (1)	236 (9)	−48 (3)	53 (12)	10 (4)
C-6a	162 (5)	14 (1)	165 (6)	−16 (3)	66 (9)	3 (3)
C-7	254 (7)	10 (1)	220 (8)	−9 (3)	92 (12)	−4 (3)
C-8	190 (6)	14 (1)	260 (9)	25 (3)	39 (12)	−3 (4)
C-9	149 (5)	15 (1)	218 (7)	10 (3)	78 (10)	3 (4)
O-9	131 (4)	22 (1)	395 (8)	7 (2)	11 (9)	21 (4)
C-9a	140 (4)	11 (1)	164 (6)	−3 (3)	69 (8)	−2 (3)
C-9b	126 (4)	12 (1)	127 (5)	−2 (2)	71 (8)	3 (3)
			Molecule II (Disordered)[b]			
C-1	166 (6)	22 (1)	286 (10)	−46 (3)	10 (13)	19 (5)
O-1	181 (7)	18 (1)	218 (10)	−7 (4)	160 (14)	6 (5)
C-2	185 (6)	21 (1)	253 (9)	−16 (4)	82 (12)	7 (4)
C-3	188 (6)	15 (1)	349 (11)	−4 (4)	−66 (14)	4 (5)
C-3a	151 (5)	16 (1)	282 (9)	−9 (3)	−33 (12)	−14 (4)
C-4	152 (5)	24 (1)	262 (9)	1 (4)	111 (11)	−49 (4)
C-5	207 (7)	18 (1)	316 (11)	6 (4)	25 (15)	−40 (4)
C-6	239 (7)	28 (1)	231 (9)	−64 (4)	−5 (14)	11 (5)
O-9b	241 (9)	17 (1)	232 (11)	−25 (5)	134 (16)	34 (5)
C-6a	164 (6)	20 (1)	260 (9)	−26 (4)	−66 (12)	−11 (4)
C-7	212 (7)	12 (1)	393 (12)	5 (3)	−130 (15)	−27 (4)
O-1b	339 (4)	16 (1)	415 (18)	−8 (6)	68 (26)	13 (7)
C-8	210 (7)	15 (1)	425 (13)	9 (4)	−92 (16)	−30 (5)
C-9	137 (5)	24 (1)	431 (11)	−4 (4)	−3 (14)	−100 (5)
O-9	157 (7)	16 (1)	288 (11)	0 (4)	178 (14)	−28 (5)
C-9a	125 (5)	23 (1)	300 (9)	−6 (3)	12 (12)	−64 (4)
C-9b	102 (4)	11 (1)	200 (7)	−2 (2)	−7 (9)	−17 (3)

[a] Based on the exponential expression $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$. All coefficients have been multipled by 10^4. [b] See footnote *a*, Table II.

Table V. Atomic Deviations from the Molecular Plane[a]

atom	distance from plane, Å	atom	distance from plane, Å
A. Molecule I, $0.3071X - 0.0133Y - 0.9516Z + 4.8665 = 0$			
C-1	0.002 (4)	O-9	0.005 (3)
O-1	−0.004 (3)	C-9a	0.003 (3)
C-2	−0.009 (4)	C-9b	0.003 (3)
C-3	0.005 (4)		
C-3a	0.004 (3)	H-9	0.27 (7)
C-4	−0.006 (4)	H-2	0.01 (3)
C-5	−0.003 (4)	H-3	−0.03 (4)
C-6	0.009 (4)	H-4	0.02 (4)
C-6a	−0.001 (3)	H-5	0.00 (4)
C-7	−0.008 (4)	H-6	−0.01 (4)
C-8	−0.008 (4)	H-7	−0.01 (4)
C-9	0.007 (4)	H-8	−0.06 (3)
B. Molecule II, $0.7695X + 0.3086Y + 0.5592Z - 3.3835 = 0$			
C-1	−0.006 (4)	C-8	−0.020 (5)
O-1	0.052 (5)	C-9	−0.035 (4)
C-2	0.003 (4)	O-9	−0.003 (5)
C-3	0.013 (4)	C-9a	−0.017 (4)
C-3a	0.004 (4)	C-9b	−0.010 (3)
C-4	0.001 (1)		
C-5	−0.016 (4)	H-2	−0.00 (5)
C-6	0.045 (5)	H-3	0.01 (3)
C-6a	−0.023 (4)	H-4	0.00 (3)
C-7	−0.013 (5)	H-5	0.03 (2)
O-1b	0.048 (7)	H-8	0.04 (4)

[a] X, Y, and Z are orthogonal coordinates, defined by $X = xa + zc \cos\beta$, $Y = yb$, $Z = zc \sin\beta$ where x, y, and z are as given in Table II. The angle between the two planes is 72.5°.

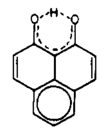
Table VI. O···O Distances in Some Hydrogen-Bonded Hydroxy Ketones Fused to a Cyclic π-Electron System

compd[a]	distance, Å	ref
5	2.62	5b
4 (modification C)	2.619, 2.576	5a
4 (modification A)	2.574	5a
2	2.553	4a
3	2.550[b]	4b
6	2.486	this work

[a] See text for formulas. [b] Neutron diffraction study; all others by X-ray diffraction.

derestimated by at least 10%. The mean C—O distance in molecule I is 1.293 (3) and C—C ranges from 1.342 (4) to 1.427 (4) and C—H from 0.89 (3) to 0.96 (4) with overall mean of 0.93 (2) Å.

The short C-2—C-3 and C-7—C-8 bonds which are of equal length, together with the relatively long and equal C—O distances, show that the resonance form **7** makes an important contribution to the electronic structure of the molecule (see below for discussion of the hydrogen atom position).



7

Short Intramolecular Hydrogen Bond. The O···O distance of 2.486 (4) Å (Figure 1a) is among the shortest reported

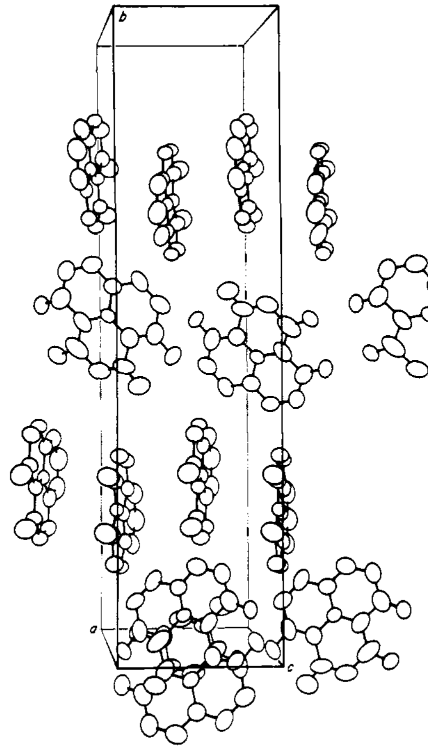
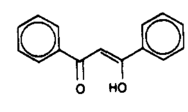
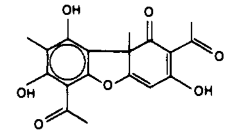


Figure 2. View of molecular packing in 9-hydroxyphenalenone along a axis.

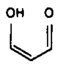
within a neutral molecule. Examination of Table VI shows that this O···O approach is very short indeed for compounds containing the hydroxy ketone unit **1** fused to a cyclic π-electron system. Nevertheless, this bond length is not the shortest O···O separation among neutral molecules containing the hydroxy ketone function. The smallest reported separations occur in compounds which do not possess extended π-electron systems directly fused to the hydroxy ketone backbone **1**. Thus, we note the distances 2.468 (5) in dibenzoylmethane (**8**)[18] and 2.41 Å (esd not stated) reported in usnic acid (**9**).[19] Semiempirical and ab initio calculations[20] on malonaldehyde suggest that the symmetry of **10** is m with C—O distances of 1.256 and 1.340 Å and C—C distances of 1.430 and 1.341 Å: if the symmetry is constrained to be $mm2$, the C—O bond lengths are calculated to be 1.292 and the C—C lengths 1.402 Å. Our experimental C—O distance of 1.293 Å is clearly consistent with $mm2$ symmetry for **6**, but we cannot rule out the possibility of m symmetry with two closely spaced equilibrium positions for the hydrogen atom. The calculations[20] also suggest that, for O···O separations >2.32 Å, the ground state for **9** corresponds to the asymmetric structure **1a–1b**.



8



9



10

A correlation[21] between O—H and O···O distances suggests that, for O···O = 2.486 Å, O—H = 1.09 Å for an asymmetric O—H···O bond and ~1.25 Å for a symmetric hydrogen bond. The O—H distance in 9-hydroxyphenalenone of 1.28_5 Å is consistent with a hydrogen bond that is effectively symmetric under the conditions of our experiment. O···H bonds as short as 1.28_5 Å are generally associated with O—H···O angles close to 180°, although none of those reviewed[22] occurs within neutral molecules. The present evidence thus favors a symmetric intramolecular hydrogen bond, or a situation in which the hydrogen atom undergoes rapid exchange between two closely spaced equilibrium positions. Assuming a ground-state O—H bond length of 1.09 Å, the separation of these two positions would be ~0.4 Å.

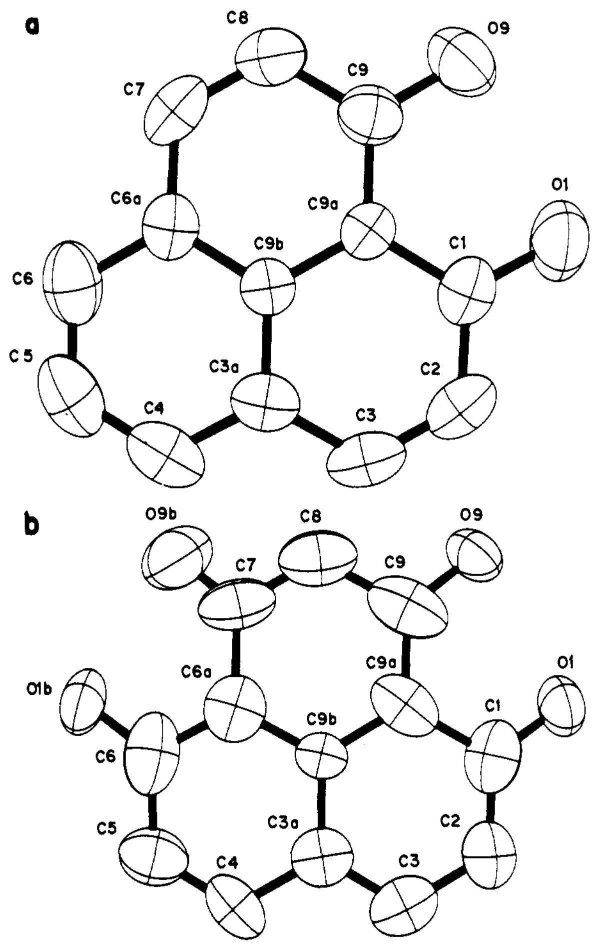


Figure 3. (a) Thermal vibration ellipsoids in molecule I. (b) Thermal vibration ellipsoids in molecule II.

Intermolecular Distances. The 9-hydroxyphenalenone crystal is composed of sheets of molecules perpendicular to the b axis. Sheets of molecule I alternate with sheets of molecule II, as shown in Figure 2. The angle between planes of molecules I and II is 72.5°. The closest contacts between pairs of molecules I are 3.57 Å for C···C and 3.44 Å for C···O; between pairs of molecules II they are 3.36 Å for C···C, 3.29 Å for C···O, and 3.22 Å for O···O. The only short intermolecular contacts between adjacent molecules I and II are 3.29 Å for C-2 (I)···O-9b (II), 3.50 Å for O-9 (I)···C-2 (II), 3.49 Å for O-9 (I)···C-3 (II), and 3.47 Å for O-9 (I)···C-5 (II). An apparent approach of 2.51 Å between O-1 (II) and O-9 (II) in neighboring pairs of disordered molecules need not imply that hydrogen-bonded dimers exist in the crystal. Pairs of molecules II may occur in four different orientations, three of which exclude the possibility of a short approach. It is unlikely that a dimer with very strong hydrogen bonding is formed by the disordered molecule; further, the C—O···O angles required in such a short approach would be 176–179°, whereas the expected angular range is 100–150°.

Thermal Vibrations. It may be seen from the orientation of the thermal vibration ellipsoids in Figure 3 that the largest root-mean-square (RMS) amplitudes, typically ~0.32 Å, lie along the circumference of the molecule, with almost isotropic vibrations for the central C-9b atom. The average of the RMS amplitudes along the two other axes of the ellipsoids of the outer atoms is 0.24 Å. A major component of the thermal motion is hence associated with molecular libration, as a rigid body, about axes perpendicular to the molecular planes. Corrections have not been made to the bond distances and angles in Figure 1 for the dimensional changes that result from such libration.

Disorder in the Room-Temperature Solid. The diffuse X-ray scattering at room temperature provides additional information on the thermal vibrations of both crystallographically independent molecules and on the disorder associated with molecule II. Precession photography reveals prominent diffuse scattering normal to (010) and to the scattering vectors through the reciprocal lattice points 201, $10\bar{2}$, $10\bar{4}$ and $20\bar{4}$. The scattering extends from these points at least through 241, $13\bar{2}$, $12\bar{4}$ and $22\bar{4}$, respectively: it may be noted that the long *b* axis results in a close spacing of reciprocal layers normal to [010]. The interplanar spacing between molecules in direct space is ~3.6 Å. The minimum vector between planes of molecule I corresponds in reciprocal space to the location 0.8, 0.1, −2.0, which is close to $10\bar{2}$. The second order of this vector is also clearly visible on precession photographs around $10\bar{4}$ and $20\bar{4}$. The corresponding vector between planes of molecules II terminates at 1.9, 2.4, 0.9, which is close to 221 and 231. The molecular librations of pairs of symmetry related molecules hence give rise to the diffuse scattering centered at these strong reflections.

Additional continuous diffuse bands of X-ray scattering appear between $\bar{2}00$ and the forbidden 001, between 001 and 202, and between $\bar{2}01$ and 002. The direction normal to these bands corresponds to the orientation of planes composed of molecules II, which form layers throughout the crystal (see Figure 2). The spacing of these diffuse bands is consistent with the intermolecular center-to-center distance of 9.2 Å. The diffuse bands may be interpreted as arising from short range order caused by the correlated orientations of molecules II. Such correlation is necessary to avoid the formation of short intermolecular O···O contacts.

Heat Capacity. The likelihood that the disorder associated with molecule II is temperature dependent, and the possibility of a phase transition occurring if ordering took place, led to a preliminary study of the heat capacity.[23] A first-order phase transition was detected at 252 K; a second transition starts at 330 K and is not complete until 395 K, on heating. Both transitions are reversible and reproducible. Further investigation of these transitions has been undertaken.

Acknowledgments. It is a pleasure to thank F. H. Stillinger for stimulating our interest in 9-hydroxyphenalenone and H. E. Bair for the heat capacity study; one of us (C.S.) thanks the Swedish Natural Sciences Research Council, the Swedish Directory for Technical Development, and the Fulbright Exchange Program for grants.

Supplementary Material Available: A listing of the measured and calculated structure factors for 9-hydroxyphenalenone (Table IV) (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Inorganic Chemistry 2, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden
(2) (a) S. Voelker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, *J. Chem. Phys.*, **67**, 1759 (1977); (b) F. Graf, H.-K. Hong, A. Nazzal, and D. Haarer, *J. Phys. Chem.*, submitted for publication; (c) see also J. Goodman and L. E. Brus, *J. Am. Chem. Soc.*, **100**, 7472 (1978).
(3) K. Peters, M. L. Applebury, and P. M. Rentzepis, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3119 (1977).
(4) (a) H. Shimanouchi and Y. Sasada, *Acta Crystallogr., Sect. B*, **29**, 81 (1973); (b) H. Fuess and H. J. Linder, *Chem. Ber.*, **108**, 3096 (1975).
(5) (a) P. D. Cradwick and D. Hall, *Acta Crystallogr., Sect. B*, **27**, 1990 (1971); (b) D. Hall and C. L. Nobbs, *ibid.*, **21**, 927 (1966).
(6) (a) C. F. Koelsch and J. A. Anthes, *J. Org. Chem.*, **6**, 558 (1941); (b) R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, R. E. Cais, and F. B. Bramwell, *J. Am. Chem. Soc.*, **100**, 7629 (1978).
(7) Y. Demura, T. Kawato, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Jpn.*, **48**, 2820 (1975).
(8) R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 3157 (1979).
(9) L. M. Jackman, J. C. Trewella, and R. C. Haddon, unpublished work.
(10) Error values here and elsewhere in this paper in parentheses correspond to the least significant digits in the function value.
(11) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).
(12) Enraf-Nonius Structure Determination Package, B. Frenz and Y. Okaya, Eds., Molecular Structure Corporation, College Station, Texas, 1977.
(13) R. L. Barns, *Mater. Res. Bull.*, **2**, 273 (1967).
(14) W. L. Bond, *Acta Crystallogr.*, **13**, 814 (1960).
(15) See, for example, S. C. Abrahams, J. L. Bernstein, and E. T. Keve, *J. Appl. Crystallogr.*, **4**, 284 (1971), for definitions of *R*, *wR*, and *S*.
(16) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).
(17) W. C. Hamilton and S. C. Abrahams, *Acta Crystallogr., Sect. A*, **28**, 215 (1972).
(18) I.-N. Hsu and B. M. Craven, *Acta Crystallogr., Sect. B*, **30**, 843 (1974).
(19) D. E. Williams, *Acta Crystallogr.*, **21**, 340 (1966).
(20) J. Catalán, M. Yáñez, and J. I. Fernández-Alonso, *J. Am. Chem. Soc.*, **100**, 6917 (1978), and references therein.
(21) M. Ichikawa, *Acta Crystallogr., Sect. B*, **34**, 2074 (1978).
(22) I. D. Brown, *Acta Crystallogr., Sect. A*, **32**, 24 (1976).
(23) H. E. Bair, private communication.

Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate in Benzene Catalyzed by Crown Ethers and Their Polymers

Johannes Smid,* Anjani J. Varma, and Shailesh C. Shah

Contribution from the Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210.

Received February 17, 1979

Abstract: Rate constants and activation parameters of decarboxylation of potassium 6-nitrobenzisoxazole-3-carboxylate (I) were measured in benzene in the presence of 4′-methylbenzo-18-crown-6, 18-crown-6, cryptand 2.2.2, and the homopolymer (P18C6) and styrene copolymers of 4′-vinylbenzo-18-crown-6. The crown-complexed ion pairs of I decompose with rate constants in the order of 0.1–1.0 s^{-1} at 25 °C, depending on the crown compound. The rate constant for the cryptated ion pair (4.78 s^{-1} at 25 °C) is nearly identical with that found for the decarboxylation of I in dimethyl sulfoxide and more than a thousand times higher than previously found for the tetramethylguanidinium salt of I in benzene. The crown ethers are believed to be externally complexed to the tight potassium carboxylate ion pair. For polymers with a high content of crown ligands, the rate constant of decarboxylation increases, probably as a result of an enlargement in the interionic distance of the crown complexed ion pair.

We recently reported[1,2] that poly(4′-vinylbenzo-18-crown-6), abbreviated in this paper as P18C6, catalyzes the decomposition of 6-nitrobenzisoxazole-3-carboxylate (I) in water. The decarboxylation, a unimolecular, concerted, in-

0002-7863/79/1501-5764$01.00/0