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Citation: *The Journal of Chemical Physics* **74**, 644 (1981); doi: 10.1063/1.440822

View online: <http://dx.doi.org/10.1063/1.440822>

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# Order-disorder phase transitions in 9-hydroxyphenalenone

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(Received 22 July 1980; accepted 8 September 1980)

A heat capacity study of 9-hydroxyphenalenone reveals three phase transitions at 254.9, 379.8, and 385.5 K, followed by melting at 475.5 K. The observed entropy change at each transition can be fitted by an orientational disorder model. The broad transition at 379.8 K is ascribed to the onset of multiple disorder in both symmetry-independent molecules. Complete deuteration of the hydroxyl groups increases the lower phase transition temperature by 7.6 K, decreases that of both upper phase transitions by 2.4 K and decreases the melting point by 2.3 K. The effect of deuteration on the transition temperatures appears to be linearly dependent on the extent of isotopic replacement.

9-Hydroxyphenalenone has been shown in a recent crystallographic study<sup>1</sup> to contain an intramolecular O...O bond of 2.486(4) Å, which is among the shortest known in a neutral molecule. One of the two symmetry-independent molecules in the monoclinic unit cell<sup>2</sup> at room temperature is disordered such that the two positions it primarily occupies are related, in a first approximation, by a rotation of the molecule through 120° in the molecular plane. The benzenoid molecule is represented in Fig. 1. The rotational disorder at 298 K corresponds to equal occupancy of the given orientation and another in which the molecular vector *ab* is superposed on *ad*. A third orientation was also detected, with an occupancy estimated at about 5%,<sup>1</sup> in which the vector *ab* is superposed on *ac*. The probability that the disorder is temperature dependent led to the present study of the heat capacity of 9-hydroxyphenalenone.

Measurement of the specific heat  $C_p$  was made on an 8 mg sample of crystalline 9-hydroxyphenalenone using a Perkin-Elmer differential scanning calorimeter, Model DSC-2. The sample was encapsulated in an aluminum pan and maintained under nitrogen (flow rate of 20 cm<sup>3</sup>/min). The melting of four standards was used to calibrate the DSC-2 for temperature: *m*-xylene (225.2 K), *p*-xylene (286.4 K), indium (429.8 K) and tin (505.1 K). Energy calibration was based on the fusion ( $\Delta H_f$ ) of indium ( $6.80 \pm 0.03$  cal g<sup>-1</sup>). Continuous determination of  $C_p$  was made in four temperature ranges: 230–290 K, 285–360 K, 320–405 K, and 400–500 K at a heating rate of 20 K min<sup>-1</sup>. Use of a Scanning Auto Zero accessory gave a baseline that was essentially flat from 230 to 500 K.

Heat capacity calculations were carried out on a Tektronix 31 interfaced with the DSC-2. Data points were collected at 3 s intervals. Values of  $C_p$  for a synthetic sapphire sample determined in the same temperature range were found to be within 1% of the reported values.<sup>3</sup> The volatility of 9-hydroxyphenalenone was thermogravimetrically examined in the temperature range 295–625 K with a Perkin-Elmer Autobalance Model AR-2. Weight loss initiates at 430 K and becomes rapid above 480 K. Prior to the  $C_p$  run between 400 and 500 K, the

sample was hermetically sealed in an aluminum container. It is necessary to ensure that the sample is free from water or solvate, because we have observed that shifts of 6°–7° in transition temperatures can result if such volatile components are present.

The heat capacity of 9-hydroxyphenalenone in the temperature range 230–500 K is shown in Fig. 2. The major peak at 475.5 K (see Table I) corresponds to melting. The remaining three peaks represent reversible and reproducible solid-state phase transitions. It is possible to fit the entropy change associated with each transition on the basis of a simple model that extends the observation<sup>1</sup> of orientational disorder observed at 298 K.

In the model, it is assumed that the volume of the unit cell remains approximately constant between 230 and 500 K, and that an integral number of distinguishable orientations for the eight molecules within each unit cell may be identified for each temperature range between phase transitions. The observed entropies of transition may then be rationalized on the basis of a change in this number at each phase transition.

Four of the eight molecules have at least twofold orientational degeneracy at room temperature, resulting in  $2^4 = 16$  configurations.<sup>1</sup> The observed occasional third

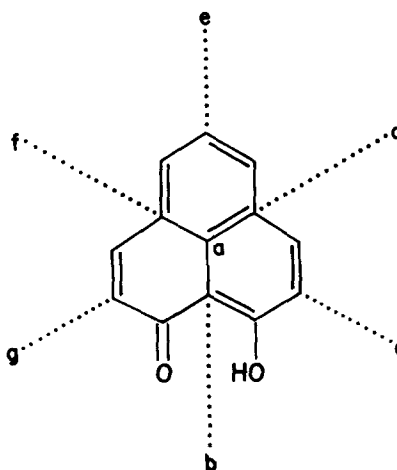


FIG. 1. 9-Hydroxyphenalenone, with six molecular vectors indicated by dotted lines. The rotation axis passes through *a* (see text).

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TABLE I. Enthalpy and entropy changes at the phase transitions in 9-hydroxyphenalenone.

$T(K)^a$	$\Delta H$ (cal mol <sup>-1</sup> ) <sup>b</sup> (observed)	$\Delta S$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) <sup>b</sup> (observed)	$\Delta S$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) (calculated)
254.9	134	0.526	0.532
379.8	577	1.517	1.522
385.5	63	0.163	0.172
475.5	3626	7.62	...

<sup>a</sup>Transition temperatures for 100% deuteration are 262.5, 377.4, and 383.2 K, obtained after melting to eliminate any volatile component (see text). For 50% deuteration, the corresponding temperatures are 258.3, 378.2, and 384.1 K. The mp for 100% deuteration is 473.2 K.

<sup>b</sup>The error in  $\Delta H$  and  $\Delta S$  is estimated to be 2%.

orientation suggests that one more configuration (roughly 5%) is present, for a total of  $2^4 + 1 = 17$  configurations at 298 K. This count is assumed to be valid between the transitions at 254.9 and 379.8 K.

The reduction in entropy observed on cooling through the 254.9 K transition may be accounted for by assuming that the 17 configurations above are reduced to two configurations below this transition, because  $\Delta S = (\frac{1}{8}) R \ln(17/2) = 0.532$  cal mol<sup>-1</sup> K<sup>-1</sup>, which is in excellent agreement with the experimental value in Table I.

The increase in entropy observed on heating through 379.8 K requires not only that the four partially disordered molecules become fully disordered, occupying all six orientations shown in Fig. 1 but, in addition, that the remaining four molecules collectively generate six further configurations. The total number of configurations present on passing through this transition thus becomes  $6^4 \cdot 6$ . The implied entropy change is hence  $\Delta S = (\frac{1}{8}) R \ln(6^5/17) = 1.522$  cal mol<sup>-1</sup> K<sup>-1</sup>, in excellent agreement with the observed value in Table I.

The sharp phase transition at 385.5 K may be accounted for by an increase to  $6^4 \cdot 12$  configurations as

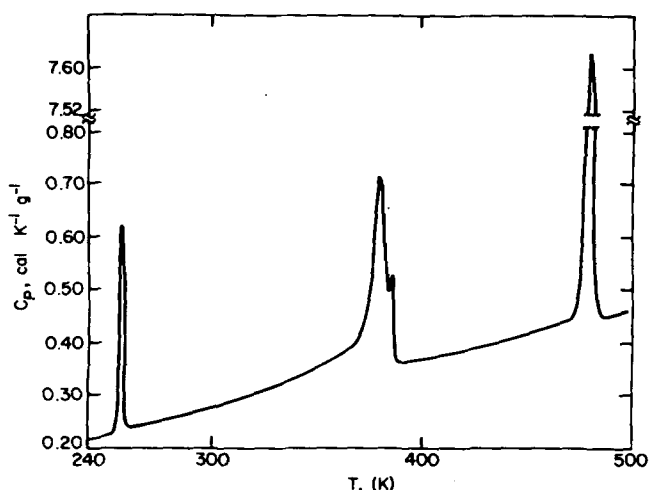


FIG. 2. Heat capacity of 9-hydroxyphenalenone between 240 and 500 K.

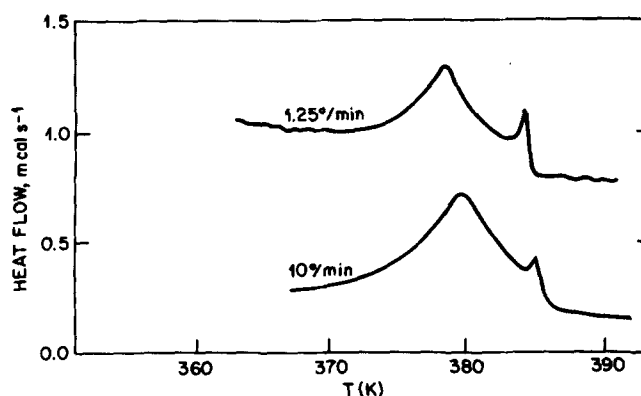


FIG. 3. Expanded heat capacity profile near transitions at 379.8 and 385.5 K.

the remaining four molecules become slightly further disordered, corresponding to an entropy change  $\Delta S = (\frac{1}{8}) R \ln(6^5 \cdot 2/6^5) = 0.172$  cal mol<sup>-1</sup> K<sup>-1</sup>, in good agreement with the experimental value in Table I. The expanded profile of the phase transitions at 379.8 and 385.5 K given in Fig. 3 illustrates the multiple nature of the lower temperature transition. The width and shape of this profile is independent both of heating rate and sense in the range 1.25–10 K min<sup>-1</sup>. A range in the transition temperature as the number of configurations increases from 17 to  $6^5$  is to be expected.

Full orientational freedom corresponding to  $6^8$  configurations can evidently set in only at or above the melting temperature. The entropy of melting contains a contribution from such an increase, but is probably dominated by translational components to which the present elementary model is not relevant.

The postulated presence of two distinct configurations below the lowest observed transition at 254.9 K raises the possibility that a further low temperature phase transition might occur at a still lower temperature, with  $\Delta S = (\frac{1}{8}) R \ln 2 = 0.172$  cal mol<sup>-1</sup> K<sup>-1</sup>. No such transition was observed in an experiment which carried the range of observations to 103 K; the remaining low temperature range has yet to be studied.

The deuterium isotope effect on the transition temperatures was investigated by full and 50% replacement of the H atom indicated in Fig. 1. No significant difference was observed in the enthalpy change at any of the three transitions. For complete replacement, the phase transition temperature at 254.9 K increased by 7.6 K, whereas those at 379.8 and 385.5 K both decreased by about 2.4 K (see Table I). For 50% deuteration, the lower transition temperature increased by 3.4 K, whereas the higher transition temperatures both decreased by about 1.5 K. The magnitude of this isotope effect, which is comparable to that reported for the hydrogen and deuterium halides, sulfides and selenides,<sup>4</sup> indicates that the molecular dipole or weak intermolecular C...O interactions of 3.22 Å or longer in this crystal<sup>1</sup> make an important contribution to the crystal packing forces. The results for 9-hydroxyphenalenone suggest a linear dependence on the extent of deuteration.

Analogous changes, with both increases and decreases in transition temperatures, have been reported.<sup>5,6</sup>

Confirmation of the proposed orientational disorder model for 9-hydroxyphenalenone<sup>7</sup> must await crystallographic investigation of the phases stable above 385.5 K and below 254.9 K.

*Note added in proof:* A single crystal x-ray diffraction study between 100 and 300 K, still in progress, shows small discontinuities in the lattice parameters  $a$ ,  $b$ ,  $c$ , and  $\beta$  at the 254.9 K phase transition. The volume of the unit cell increases by 0.4% on heating through the transition. The low temperature space group is  $P2_1$  with eight molecules per unit cell, of which four are crystallographically independent (cf. Ref. 2, with two independent molecules per unit cell at room temperature). X-ray intensity data collected at 190 K are being used to refine the structure model by the method of least squares. No evidence for the low temperature orientational dis-

order implied by the model discussed in the text has been detected at the present stage of analysis.

<sup>1</sup>C. Svensson, S. C. Abrahams, J. L. Bernstein, and R. C. Haddon, *J. Am. Chem. Soc.* **101**, 5759 (1979).

<sup>2</sup>Lattice constants at 298 K:  $a = 8.8941(2)$ ,  $b = 28.8159(4)$ ,  $c = 7.2117(2)$  Å,  $\beta = 97.937(1)^\circ$ . Space group  $P2_1/c$ , with eight molecules per unit cell (Ref. 1).

<sup>3</sup>D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.* **75**, 522 (1953).

<sup>4</sup>See, for example, N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Clarendon, Oxford, 1978), Chap. 9.

<sup>5</sup>G. M. Loiacono, J. F. Balascio, and W. Osborne, *Appl. Phys. Lett.* **24**, 455 (1974).

<sup>6</sup>N. S. Dalal, J. A. Ripmeester, A. H. Reddoch, and D. F. Williams, *Mol. Cryst. Liq. Cryst.* **49**, 55 (1978).

<sup>7</sup>Alternative models that give almost as good a fit to the observed entropy changes at the three phase transitions as the present model, but that avoid the postulated disorder below 254.9 K, have also been considered.