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Polymorphism in Bicyclo[3.3.1]nonan-9-one: A Molecular Solid that Can Exist in Both Its Ordered and Its Disordered Phases at Room Temperature

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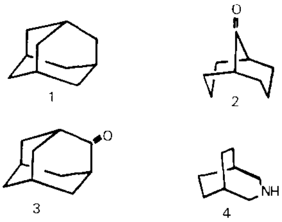
The heat capacity of the polycyclic molecular solid bicyclo[3.3.1]nonan-9-one has been determined from 35 to 306 K by adiabatic calorimetry. There is one solid–solid phase transformation to a high-temperature orientationally disordered phase: T_{tr} = 300.5 ± 0.2 K, $\Delta_{tr}H$ = 14110 ± 30 J mol^{-1}, $\Delta_{tr}S$ = 46.99 ± 0.08 J $K^{-1}mol^{-1}$ (=5.652 ± 0.009 R). The hysteresis of this transformation permits, by suitable thermal treatment, the preparation of either the ordered or the disordered phase at room temperature.

Introduction

It has long been known that molecules of high symmetry and near spherical shape have intermolecular forces with only weak orientational dependences. If the temperature is sufficiently high, the barrier to reorientation is easily surmounted and the material can exist in a high-temperature orientationally disordered phase. As the temperature is lowered this barrier is not so easily overcome and the solid usually transforms to an orientationally ordered phase. Because these molecular solids are held together by weak van der Waals interactions, they have relatively low melting points, in comparison with, for example, ionic solids. The internal vibrational modes of these "globular" molecules are usually of sufficiently high frequency (several times k_BT at the melting point) that the rigid molecule approach to understanding molecular motion is valid.



SCHEME 1

Because of the high symmetry of polycyclic hydrocarbons, they can exhibit polymorphism due to high-temperature orientationally disordered solid phases. Adamantane, **1**, can be considered to be the archetypal polycyclic hydrocarbon: it transforms on heating to an orientationally disor-

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dered phase at 208.6 K (*1*). Studies of substituted adamantanes (*2, 3*) have shown the effects of making the intermolecular potential slightly anisotropic through chemical modification. Indeed, it is interesting to investigate just how extreme the molecular anisotropy (and hence intermolecular potential) can be without preventing an orientationally disordered phase.

An investigation of the slightly polar molecular solid bicyclo[3.3.1]nonan-9-one ($C_9H_{14}O$; **2**) by ^{13}C NMR has shown (*4*) that this molecule is in an orientationally disordered solid phase at 315 K. Furthermore, the molecule adopts the chair–chair conformation in the solid state (as shown in **2**), and the molecules are reorienting more rapidly than the corresponding adamantane analogue (adamantanone, $C_{10}H_{14}O$; **3**). Although this reorientational motion should freeze out at lower temperatures, there appears to be no further information in the literature concerning the physical properties of bicyclo[3.3.1]nonan-9-one. Our goal was to investigate polymorphism in this compound through the measurement of its heat capacity by adiabatic calorimetry.

Experimental

Bicyclo[3.3.1]nonan-9-one (99%, m.p. 428–430 K) was obtained from Aldrich Chemicals. The purity of the sample was checked by gas chromatography with flame ionization detection; only one impurity, corresponding to 0.62% of the total area of the chromatograph, was detected. The sample was used without further purification.

The heat capacity of 1.5862 g of bicyclo[3.3.1]nonan-9-one was determined in the temperature range from 35 to 306 K. The measurements were carried out in an adiabatic dc heat pulse calorimeter that had been previously tested with Calorimetry Conference standard benzoic acid, giving results that agreed with the literature to within 0.5%. The calorimeter is described in detail elsewhere (*5*). One of the features of this calorimeter is that it has a wide opening to allow introduction of samples of various morphologies. The calorimetric vessel is then sealed in a helium-atmosphere glove box. The purpose of the helium is to facilitate thermal equilibrium within the sample during the calorimetric experiments. Although it is our practice with this calorimeter to first evacuate the dead space in the calorimeter above the sample before making the seal, in this case we initially chose not to pump on it, in order to prevent loss of our (potentially volatile) sample. As will become evident, this procedure allowed some air to remain inside the calorimeter.

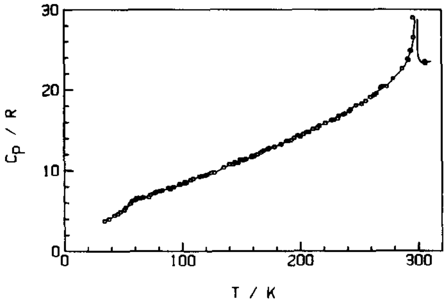

FIG. 1. The experimental heat capacity, C_p, of bicyclo[3.3.1]nonan-9-one as a function of temperature.

Results and Discussion

The heat capacity of the sample comprised about 20% of the total heat capacity of the calorimetric assembly below 260 K, considerably more at higher temperatures. The heat capacities measured were reproducible, and showed no thermal history effects. The results of the heat capacity measurements for bicyclo[3.3.1]nonan-9-one are given in Table I and illustrated in Fig. 1.

Immediately apparent from Fig. 1 are two thermal anomalies—one at about 60 K and the other at about 300 K. The lower temperature anomaly is an experimental artifact, due to the sublimation of residual air in the

TABLE I

THE EXPERIMENTALLY DETERMINED VALUES OF THE MOLAR HEAT CAPACITY, C_p, OF BICYCLO[3.3.1]NONAN-9-ONE. R = 8.3145 J K^{-1} mol^{-1}

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
34.20	3.84	145.06	11.07	262.85	19.38
38.02	4.07	146.93	11.02	263.00	19.53
42.47	4.52	149.45	11.45	264.59	19.61
45.51	4.70	151.15	11.36	268.19	20.33
47.63	4.98	152.74	11.45	269.55	20.51
50.96	5.20	154.31	11.49	273.39	20.51
50.99	5.25	159.04	11.75	278.60	21.43
51.96	5.52[a] 5.24[b]	159.18	11.89	283.75	22.60
55.81	5.97[a] 5.58[b]	161.12	11.95	286.29	22.74
55.97	6.03[a] 5.60[b]	161.21	11.86	288.67	24.02
57.55	6.29[a] 5.68[b]	164.03	12.11	291.31	23.95
60.00	6.43[a] 5.90[b]	166.95	12.34	292.28	23.79
60.91	6.58[a] 5.96[b]	168.90	12.54	293.81	24.99
61.01	6.64[a] 5.96[b]	172.67	12.71	294.28	24.94
62.31	6.68[a] 6.08[b]	173.71	12.85	296.08	29.10
64.54	6.67[a] 6.20[b]	178.29	13.01	297.81	44.17
66.59	6.76[a] 6.44[b]	178.61	13.04	298.23	90.08
66.71	6.76[a] 6.44[b]	183.88	13.36	298.96	140.0
71.66	6.78	184.29	13.34	299.29	322.4
72.89	7.08	188.36	13.76	299.64	351.4
76.38	7.30	189.45	13.76	299.77	567.4
77.10	7.35	192.77	13.87	299.97	766.7
77.95	7.44	194.94	14.12	300.11	819.7
81.18	7.54	198.16	14.42	300.15	1105.
82.89	7.60	200.20	14.26	300.35	1192.
87.92	7.91	200.37	14.37	300.53	1609.
89.76	7.78	203.06	14.60	300.68	1450.
92.07	8.04	205.71	14.81	300.74	664.1
92.91	8.04	207.40	14.85	301.05	335.5
97.61	8.40	210.99	15.25	302.41	36.85
98.10	8.32	214.51	15.36	304.91	26.65
101.78	8.49	216.26	15.63	305.96	23.62
102.29	8.68	221.45	15.96	305.98	23.36
103.47	8.59	221.47	15.97		
106.94	8.89	226.59	16.34		
109.27	9.08	228.26	16.37		
114.52	9.34	231.66	16.54		
116.34	9.37	232.75	16.86		
119.62	9.51	236.68	17.05		
121.02	9.59	237.91	17.14		
124.56	9.82	241.56	17.47		
127.17	9.81	242.86	17.67		
135.00	10.45	247.30	18.16		
139.75	10.86	252.13	18.36		
142.79	10.86	255.65	18.72		
144.60	11.09	259.59	19.21		

[a] Uncorrected.

[b] Corrected for air sublimation (see text).

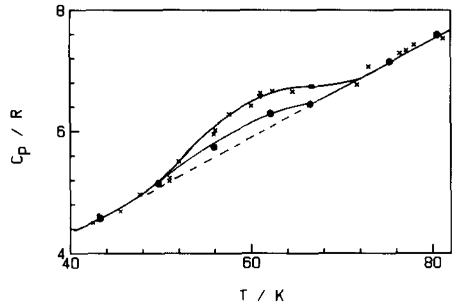

FIG. 2. The experimental heat capacity, C_p, of bicyclo[3.3.1]nonan-9-one as a function of temperature; ×, data from sample sealed without prior evacuation; ●, data from sample evacuated prior to sealing; ---, heat capacity with no air inside calorimeter.

calorimeter. We have proven this by loading the same sample of bicyclo[3.3.1]nonan-9-one in the same calorimeter under conditions identical in all respects except one: the calorimetric vessel was evacuated prior to sealing the calorimeter in a helium-filled glove box. The results, which conclusively show the effect of this pumping procedure, are shown in Fig. 2. Of the total gas pressure within the calorimeter (about 1 atm at room temperature), we estimate the fraction due to air, on the basis of the enthalpy of the observed thermal anomaly and the volume of the dead space, to be 0.5 in the original sample and 0.1 in the pumped sample. The dashed line in Fig. 2 is our estimate of the heat capacity of bicyclo[3.3.1]nonan-9-one without the presence of air in the calorimeter; the values given in Table I have been annotated accordingly.

The thermal anomaly at higher temperatures corresponds to a phase transformation temperature, T_{tr}, of 300.5 ± 0.2 K, as deduced from the maximum in the heat capacity. From direct determination of the enthalpy over the transition we found the transition enthalpy change, $\Delta_{tr}H$, to be 14110 ± 30 J mol^{-1}, and the transition entropy change, $\Delta_{tr}S$, to be 46.99 ± 0.08 J K^{-1} mol^{-1} ($=5.652 \pm 0.009$ *R*). The latter was determined from the integration of the excess enthalpy, and can be considered to consist of an isothermal (first order) contribution and a gradual (higher order) contribution. If the transition were entirely first order this would make $\Delta_{tr}S$ ($=\Delta_{tr}H/T_{tr}$ for a first-order transition) equal to 46.96 J K^{-1} mol^{-1}: clearly, from the thermodynamic evidence, this phase transformation is predominantly first order. Furthermore, the sample showed a minimum cooling rate at about 285 K (corresponding to the temperature of the transition on cooling). In a ^{13}C NMR study of bicyclo[3.3.1]nonan-9-one (*6*), the signal disappeared at 281 K on cooling. This hysteresis is characteristic of a first-order phase transformation, arising from the substantial activation barrier to the transition.

The closest chemical analogue to bicyclo[3.3.1]nonan-9-one for which similar information is available is adamantanone, **3.** However, unlike the transition observed through differential scanning calorimetry studies of adamantanone (**3**), which showed severe effects of thermal treatment on the temperature and thermodynamics of the transformation, we found the transformation to the orientationally disordered phase of bicyclo[3.3.1]nonan-9-one to be reproducible and stable. The entropy change found here for **2** considerably exceeds that of adamantanone: 5.652 *R* vs 4.99 *R* (for the stable transition in adamantanone after many thermal cycles). Given the considerable hysteresis in adamantanone, it is likely that its transition also is strongly first order. The entropy change in a first-order orientationally disordering phase transformation consists of both the configurational entropy change and the volume contribution; it is possible that the difference in the transitional entropies between adamantanone and bicyclo[3.3.1]nonan-9-one is due primarily to differences in the latter. Interestingly, another polycyclic molecule, 3-azabicyclo[2.2.2]octane, **4,** has a phase transition that closely resembles that of **2:** T_{tr} = 297.8 K, $\Delta_{tr}S$ = 5.85 R, first order (*7*). The entropy change involved in the phase transformation found here for bicyclo[3.3.1]nonan-9-one is relatively large (= R ln (285 ± 2)) and certainly is in agreement with the ^{13}CNMR results which show substantial whole-molecule motion in the high-temperature phase.

One final interesting feature of this material stems from the hysteresis of its phase transformation. If a sample of bicyclo[3.3.1]nonan-9-one is cooled, say to 0°C, and the allowed to warm, it will be in the orientationally ordered phase until above 300.5 K. If this same sample is heated above 300.5 K and then cooled, it will remain in the orientationally disordered state until below about 281 K. This means that, depending on the heat treatment, this material can be obtained at *room temperature* in either the orientationally ordered or the disordered state. The phases produced exhibit the mechanical properties so often ascribed: the disordered sample is "sticky" and the ordered one is not. We hope that this unusual polymorphic feature will encourage further investigations of the physical properties of this interesting molecular solid.

Acknowledgments

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