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Thermodynamic Studies of Orientational Disorder in π-π Molecular Compounds: 1. Heat Capacities of Naphthalene-Tetracyanobenzene

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Thermodynamic Studies of Orientational Disorder in π-π Molecular Compounds

I. Heat Capacities of Naphthalene-Tetracyanobenzene†

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The heat capacity of the π-π molecular compound naphthalene-tetracyanobenzene has been determined from 5 to 300 K. A small anomaly was observed in the heat capacity near 75 K with an entropy of transition of 0.71 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$. It is believed to arise from an order-disorder transition involving the reorientation of the naphthalene molecules. The smoothed thermodynamic functions have been reported at selected temperatures over the region from 5 to 300 K.

INTRODUCTION

Solid state, π-π molecular compounds formed from the interaction of planar aromatic hydrocarbons with various electron acceptors have been the subject of much research. The results of a large number of X-ray crystallographic studies on these compounds have been described in two excellent review articles[1,2] while the author of a third review article[3] discussed the high level of molecular motion observed in many of these compounds.

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In view of the widespread interest in these compounds, it is somewhat surprising to note that to date, heat-capacity measurements in the region from 5 to 300 K have been reported on only two crystalline charge-transfer compounds, pyrene-pyromellitic dianhydride[4] and pyrene-tetracyanobenzene.[5] The present paper reports the investigation of the heat capacity of naphthalene-tetracyanobenzene from 5 to 300 K; succeeding papers will discuss the results of similar studies on other charge-transfer compounds. The results of the heat-capacity measurements have been used in conjunction with those from other types of studies to resolve some unanswered questions about the presence of orientational disorder in these compounds.

In many of the X-ray diffraction studies made on π-π molecular compounds, the refinement of the structure was hindered by the presence of diffuse reflections in the X-ray patterns. Very often, the conclusion was reached that one of the components, usually the donor moiety, possessed anomalously large thermal motion. The results of these studies have been reinterpreted and it is now thought that many of these crystals are disordered.[1]

Solid state, nuclear magnetic resonance (n.m.r.) techniques[6-8] have established that in many of the pyrene and naphthalene compounds believed to be disordered there is indeed considerable freedom of motion of the aromatic hydrocarbon. In both naphthalene-tetracyanobenzene and pyrene-pyromellitic dianhydride X-ray diffraction evidence for disorder[9,10] can be substantiated by wide-line[6,7] and pulsed n.m.r. results.[8] On the other hand, for naphthalene-tetracyanoethylene, naphthalene-pyromellitic dianhydride and other compounds where the X-ray diffraction results are less reliable and where the two allowed orientations for the donor molecule are believed to be separated by only a small angle, two interpretations of the n.m.r. results are possible. In these compounds, it becomes difficult to distinguish between a motion which consists of rapid jumps between two distinct orientations and one in which the hydrocarbon moiety undergoes a large in-plane libration about a single equilibrium position.

If the observed motion is reorientational in nature with the molecules jumping back and forth between distinguishable orientations, the crystal is disordered. The onset of a disordering process is usually accompanied by the appearance of an anomaly in the heat capacity. The transitional entropy associated with this anomaly is often on the order of R ln N where N is the number of distinguishable orientations in the disordered high-temperature phase for one mole of complex. If, on the other hand, each donor moiety occupies a single orientation and undergoes a large amplitude libration about that equilibrium position, no disorder is present and no transition will be observed in the heat-capacity curve.

It is considered that heat-capacity measurements on these π-π molecular compounds are valuable in studying the molecular motion in these solids both in compounds like naphthalene-tetracyanobenzene (N-TCNB) where claims for disorder can be tested and in others where the nature of the motion is not so clear.

EXPERIMENTAL

Sample preparation and characterization

The sample of naphthalene-tetracyanobenzene was prepared at the University of Guelph by a preparation reported in the literature.[9] Naphthalene and tetracyanobenzene were purified by sublimation and the complex prepared by cooling a hot ethanol solution containing equimolar amounts of the two components. The light yellow crystals were dried overnight under vacuum. Analysis of this material by a commercial analytical laboratory in Ann Arbor gave 78.35 per cent C (theoretical 78.42), 3.32 per cent H (theoretical 3.29) and 18.27 per cent N (theoretical 18.29).

Calorimetric methods

The heat-capacity measurements were made in the Mark II adiabatic cryostat described elsewhere.[11] Approximately 21.9 g of the sample in the form of small yellow needles were loaded into a gold-plated copper calorimeter (laboratory designation W-54). The calorimeter was evacuated and helium gas at a pressure of 2.87 kPa at 300 K was added to ensure good thermal contact and rapid equilibrium. The calorimeter was then sealed, placed in the cryostat and cooled.

Temperatures were measured with a platinum-resistance, capsule-type thermometer (laboratory designation A-5) inserted into a central well in the calorimeter. The thermometer has been calibrated by the U.S. National Bureau of Standards and temperatures are judged to correspond to the IPTS-48 to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 300 K.

The heat capacity of the empty calorimeter was determined in a separate set of experiments. Between 5 and 20 K, the heat capacity of the sample represented 80 per cent of the total heat capacity. Above 25 K, the sample heat capacity was from 50 to 60 per cent of the total.

Small corrections have been made for the differences in the masses of helium exchange gas, Apiezon-T grease, and gold gaskets used in the filled calorimeter and empty calorimeter experiments. No corrections have been applied to the data to account for the vaporization of sample during the measurements or for the heat capacity of sample vapor. Our calculations indicate that such corrections are well within the limits of the accuracy of the data.

RESULTS

The experimental heat capacities are presented in Table I with summaries of the enthalpy determinations given in Table II. The values are given for one mole of complex, where a mole of complex is considered to contain one mole

TABLE I

Experimental heat capacities of N-TCNB[a]
($\mathrm{cal_{th}}$ = 4.184 J)

T	C_p
K	$\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$
Series I	
118.30	43.20
126.24	45.26
137.93	48.45
147.85	51.06
157.39	53.50
166.96	56.01
177.17	58.61
Series II	
165.78	55.65
174.89	58.01
184.34	60.37
193.54	62.69
202.90	65.08
211.29	67.21
220.63	69.53
228.87	71.68
237.37	73.76
Series III	
240.54	74.49
248.78	76.58
257.51	78.62
266.28	80.80
275.53	83.00
285.40	85.34
295.57	87.92
Series IV	
75.09	31.93[b]
81.59	33.39
88.43	35.27
Series V	
77.89	32.33[b]
84.23	34.21
96.18	37.42
102.46	39.14
109.20	40.90
116.80	42.88
Series VI	
75.51	31.84[b]
81.65	33.40
88.64	35.45
96.84	37.56
Series VII[a]	
52.13	23,31
56.19	25.19
60.47	27.37
64.74	29.89
68.93	32.94
73.90	32.11
80.22	32.99
Series VIII[b]	
52.21	23.34
ΔH_t Detn. A	
75.92	31.88
Series IX[b]	
52.24	23.39
ΔH_t Detn. B	
79.42	32.75
Series X	
52.12	23.32
ΔH_t Detn. C	
80.09	32.91
Series XI	
50.25	22.36
51.97	23.21
53.88	24.03
ΔH_t Detn. D	
80.03	32.84
Series XII	
52.66	23.54
ΔH_t Detn. E	
80.08	32.90
Series XIII	
4.94	0.136
5.59	0.218
6.32	0.317
7.14	0.438
8.04	0.598
8.90	0.797
9.78	1.043
10.70	1.353
11.66	1.678
12.54	2.008
13.53	2.451
14.71	3.026
15.98	3.658
17.48	4.441
19.11	5.322
21.13	6.473
23.51	7.859
25.86	9.243
28.39	10.72
31.76	12.65
36.02	15.07
40.24	17.31
44.08	19.32
48.07	21.35
52.43	23.41
ΔH Detn. F	
Series XIV[b]	
56.04	25.09
58.11	26.13
60.13	27.21
63.02	28.83
66.78	31.48
69.73	33.30
71.67	33.47
73.17	31.62
74.50	31.48
75.16	31.77
77.12	32.05
Series XV[b]	
67.45	32.12
68.74	33.18
69.63	33.42[c]
70.24	33.31[c]
70.86	33.29[c]
71.47	33.67[c]
72.08	33.42
72.70	31.96

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[a] One mole of complex is taken to be one mole of naphthalene molecules and one mole of tetracyanobenzene molecules.

[b] Detns. with mean temperatures from 50 to 80 K were not included in the final curve fitting.

[c] These Detns. were not included in the curve because of poor adiabatic shield control.

TABLE II

Enthalpy and entropy of transition of N-TCNB[b]

Designation	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\{H^\circ(T_2) - H^\circ(T_1)\}$ cal$_{\text{th}}$ mol^{-1}	$\{H^\circ(80\text{ K}) - H^\circ(30\text{ K})\}$ cal$_{\text{th}}$ mol^{-1}	$\{S^\circ(80\text{ K}) - S^\circ(30\text{ K})\}$ cal$_{\text{th}}$ K^{-1} mol^{-1}
Series VII	50.17	83.65	991.1	1215.4	—
ΔH_t Detn. A	54.53	72.85	544.9	1222.2	—
ΔH_t Detn. B	54.44	76.12	658.6	1228.6	—
ΔH_t Detn. C	54.04	76.71	672.9	1214.6	—
Series XI	49.73	84.12	1015.1	1213.6	—
ΔH_t Detn. E	54.84	76.66	650.9	1214.8	—
ΔH_t Detn. F	54.66	78.08	718.0	1231.9	—
Series XIV	54.97	77.76	682.8	1212.4	—
			Mean value:	1219 ± 5	
			Graphical integration:	1215 ± 1	(22.03 ± 0.02)[a]
			Lattice integration:	1173 ± 1	21.32 ± 0.02
				$\Delta H_t = 46 \pm 5$	$\Delta S_t = 0.71 \pm 0.07$

[a] The entropy reported here results from a slight adjustment of the value obtained from graphical integration to correct for the small difference between the experimental enthalpy increment and the graphical integration value.

[b] 1 cal$_{\text{th}}$ = 4.184 J. One mole of complex is taken to be one mole of naphthalene molecules and one mole of tetracyanobenzene molecules.

of naphthalene molecules and one mole of tetracyanobenzene molecules. The results are given in chronological sequence so that the temperature increments used in the measurements may be estimated from the temperature differences between the mean temperatures of adjacent determinations. The experimental results with the small anomaly found in the heat capacity near 75 K are shown in Figure 1. Some experimental results have been omitted from the curve at the top of the transition for the sake of clarity. The transition region is shown in greater detail in Figure 2.

The heat capacities in the region from 5 to 10 K were reproducible to 1 per cent, from 10 to 50 K to about 0.2 per cent, and from 80 to 300 K to about 0.1 per cent. Measurements in the transition region from 50 to 80 K are slightly less precise because of the use of smaller temperature increments for each measurement and the longer time necessary to reach equilibrium between adjacent measurements. The enthalpy increments across the transition (50 K to 80 K) were not completely reproducible and ranged from 872.2 to 889.5 cal$_{\text{th}}$ mol^{-1}. There did not appear to be any correlation of ΔH_t with the rate of cooling, nor was ΔH_t reproducible when identical cooling procedures were used.

The heat-capacity measurements except for the region from 50 to 80 K have been corrected for curvature and computer fitted to polynomials in temperature. The polynomials were integrated to give the thermodynamic functions at various temperatures. A plot of the data from 5 to 8 K as Cp/T

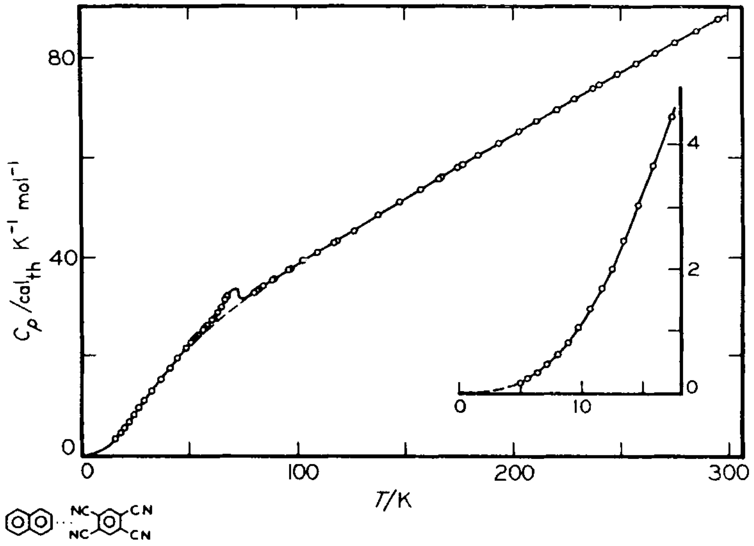

FIGURE 1 Heat capacity of N-TCNB from 5 to 300 K. (Experimental results in the transition region have been omitted for clarity.) The dashed line represents the lattice contribution.

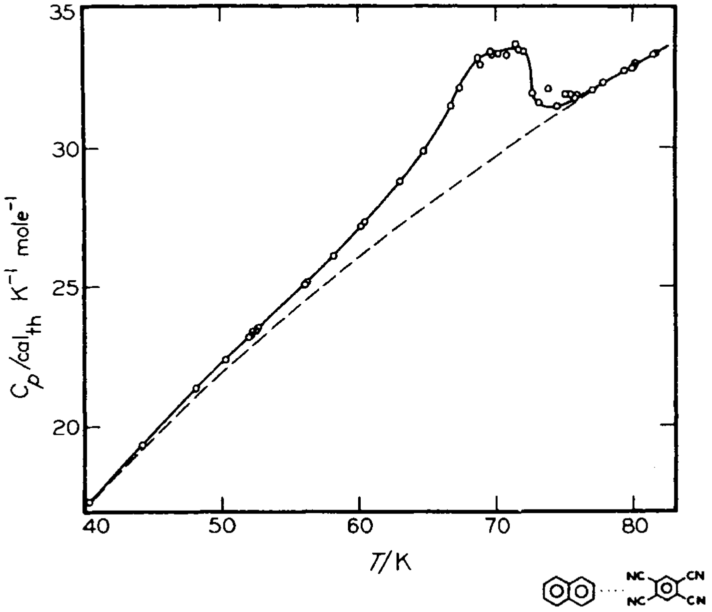

FIGURE 2 The heat capacity of N-TCNB in the transition region. The dashed line represents the lattice contribution.

TABLE III

Thermodynamic functions of N-TCNB[a]

T / K	C_p / $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	$\{S^\circ(T) - S^\circ(0)\}$ / $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	$\{H^\circ(T) - H^\circ(0)\}$ / $\mathrm{cal_{th}\ mol^{-1}}$	$-\{G^\circ(T) - H^\circ(0)\}/T$ / $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$
5	0.150	0.051	0.191	0.013
10	1.112	0.391	2.909	0.100
15	3.152	1.195	13.166	0.317
20	5.835	2.461	35.497	0.686
25	8.735	4.072	71.86	1.197
30	11.656	5.923	122.86	1.828
35	14.485	7.934	188.26	2.555
40	17.20	10.047	267.52	3.359
45	19.80	12.22	360.05	4.222
50	22.28	14.44	465.29	5.133
60	27.13	18.92	711.77	7.057
70	33.40	23.67	1016.4	9.100
71.6	33.50	24.37	1069.9	9.427
80	32.93	27.95	1342.1	11.177
90	35.76	32.00	1685.7	13.267
100	38.44	35.90	2056.8	15.34
110	41.07	39.69	2454.4	17.38
120	43.70	43.38	2878.3	19.39
130	46.35	46.98	3328.5	21.38
140	48.99	50.51	3805.2	23.33
150	51.61	53.98	4308.1	25.26
160	54.19	57.39	4837.2	27.16
170	56.75	60.76	5392	29.04
180	59.29	64.07	5972	30.08
190	61.82	67.35	6578	32.73
200	64.35	70.58	7209	34.54
210	66.88	73.78	7865	36.33
220	69.41	76.95	8546	38.11
230	71.92	80.09	9253	39.86
240	74.40	83.21	9984	41.60
250	76.85	86.29	10741	43.33
260	79.26	89.35	11521	45.04
270	81.66	92.39	12326	46.74
273.15	82.42	93.34	12584	47.27
280	84.08	95.40	13155	48.42
290	86.52	98.40	14008	50.10
298.15	88.51	100.82	14721	51.45
300	88.95	101.37	14885	51.75

[a] One mole of complex is taken to be one mole of naphthalene molecules and one mole of tetracyanobenzene molecules.

versus T^2 yielded a straight line passing through the origin. The slope obtained from a least-squares fit of this line was used to estimate the contributions to the thermodynamic functions from 0 to 5 K. In the region from 50 to 80 K the heat capacity was read at small temperature intervals from a large-scale plot and the thermodynamic functions were obtained by numerical integration. The smoothed heat capacity and the thermodynamic functions are listed in Table III at selected temperatures.

In order to obtain values for the enthalpy and entropy of transition, ΔH_t and ΔS_t, respectively, it is necessary to determine a lattice heat capacity which contains all the non-transition-related contributions to the total heat capacity. Because of the complexity of the compound and the lack of spectroscopic data, it was not possible to approximate the lattice heat capacity by a series of Einstein and Debye functions. Instead, a smooth curve was drawn connecting the heat capacity curves below 50 K and above 80 K. In doing so, it became evident that the transition region extended over a larger interval than was originally apparent. The values for ΔH_t and ΔS_t are also given in Table II. The graphical enthalpy and entropy increments were obtained by combining the increments from the 30–50 K curve-fitted region with those from the 50–80 K region using the enthalpy determinations (Table II) and the numerically integrated curve over this region.

DISCUSSION

The variation in the total enthalpy through the transition region is somewhat larger than is usually observed in this laboratory but the results of the two previous studies on crystalline charge-transfer compounds made by Staveley *et al.*[4,5] suggest that the irreproducible nature of the transitions in these compounds may be general.

The crystal structure of N-TCNB determined at 300 K by Kumakura *et al.*[9] shows that the component molecules are arranged in pseudo-1-dimensional chains with an alternating donor-acceptor sequence along the chain axis. The best refinement of the X-ray data was obtained when the naphthalene molecules were assumed to occupy randomly one of two orientations which differ by a rotation of 36° about an axis perpendicular to the molecular plane.

Using the results of this diffraction study, Fyfe was able to calculate values for the second moment of the wide-line n.m.r. spectrum of N-TCNB assuming first a rigid lattice and then various types of motion of the naphthalene molecules.[7] His result for the rigid lattice is considerably larger than the experimental value obtained at 77 K which suggests that there is still some molecular motion present at this temperature. There is a further drop in the second moment centered around 250 K indicating that a new motional process begins to take place. The experimental second moment at 77 K is in good agreement with the value calculated assuming a motion of the naphthalene molecules between the two orientations suggested by the disordered crystal structure. At higher temperatures it appears that the naphthalene molecules become capable of interconverting between the two orientations by jumping over the supplementary angle which separates the orientations. The coupling of the small angle and large angle jumping motions results in the complete in-plane reorientation of the naphthalene molecules.

There is additional evidence for the presence of two distinct motional processes in N-TCNB. The spin-lattice relaxation times, T_1 and $T_1\rho$ obtained from pulsed n.m.r. measurements[8] show minima at different temperatures and values for the activation energies of 10.2 and 2.3 $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$ are obtained by analyses of the curves of ln T_1 or ln $T_1\rho$ versus $1/T$, respectively. More recent measurements[12] have extended the $T_1\rho$ data below 77 K. There is a discontinuity at 72 K indicative of a phase change in agreement with the heat capacity data.

A transition in the region in which molecular motion is thought to begin can be considered to support the claims for disorder put forward by the authors of the diffraction and n.m.r. results. An anomaly will occur only when the motion takes the molecules into distinguishable orientations in the crystal and so the location of the anomaly indicates the temperatures at which a molecular motion begins to introduce disorder. In this situation disorder is introduced at the lowest temperature at which motion is observed but in the case of naphthalene-tetracyanoethylene, to be discussed in a later paper, it is considered that the motion observed by n.m.r. at 77 K may be of a librational nature but that it becomes reorientational above 150 K. There is also supporting evidence for the presence of an order-disorder transition in this region from Raman scattering measurements on the complex.[13,14] The earliest measurements[13] showed large changes at 62 K indicative of motion of the molecules but more recent data place the transition temperature at 69 K.[14]

The value of 0.71 $\text{cal}_{\text{th}}\ \text{K}^{-1}\ \text{mol}^{-1}$ obtained as the entropy of transition is considerably smaller than $R \ln 2$ which might be expected for the entropy of a disordering process involving two allowed orientations but this is not sufficient reason for ascribing the anomaly to a process other than a disordering phenomenon. It is possible that as the temperature is lowered and the motion stops the disorder may gradually freeze in. Differences in the degree of disorder present in the low-temperature phase would also account for the wide spread in the values of ΔH_t obtained from the enthalpy determinations. If the crystal is still somewhat disordered below the transition, the compound should possess residual entropy at 0 K. Unfortunately, the additional information necessary to check for zero point entropy is unavailable for this compound.

The results of the heat-capacity measurements on N-TCNB provide additional evidence for the presence of orientational disorder and suggest that the small angle jumping motion begins near 70 K. The thermodynamic data do not identify the temperature at which the large-angle jumping motion begins, however, because this motion introduces no additional entropy and, consequently, there is not a second transition in the heat capacity.

We think that heat-capacity measurements will continue to be valuable in understanding motion in molecular crystals and are extending our study to several other charge-transfer compounds.

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