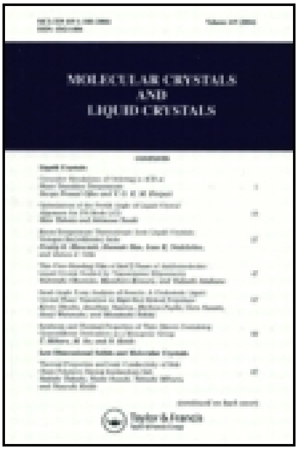

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Thermodynamic Studies of Orientational Disorder in π-Molecular Compounds

Juliana Boerio-goates [a] & Edgar F. Westrum Jr. [a]

[a] Department of Chemistry, University of Michigan, Ann Arbor, Ml, 48109, U.S.A.

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Thermodynamic Studies of Orientational Disorder in π-Molecular Compounds

II. Heat Capacity of Naphthalene-Tetracyanoethylene†

JULIANA BOERIO-GOATES and EDGAR F. WESTRUM, JR.
Department of Chemistry, University of Michigan, Ann Arbor, MI, 48109 U.S.A.

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The heat capacity of naphthalene-tetracyanoethylene was determined from 5 to 300 K and the smoothed thermodynamic functions reported at selected temperatures over the region of measurement. A bifurcated peak was observed in the heat capacity near 160 K. This transition was attributed to the crystal structure change reported elsewhere. A second anomaly overlaps the high-temperature end of the bifurcated peak and extends to 240 K. The nature of this second transition cannot be conclusively determined, but probably arises from the onset of reorientational motion of the naphthalene molecules. From the absence of anomalies below 160 K, it was concluded that the motion observed by solid-state n.m.r. measurements near 77 K is naphthalene libration and not reorientation.

INTRODUCTION

Despite considerable study by X-ray diffraction[1] and solid-state n.m.r. techniques,[2–4] questions still remain concerning the presence of orientational disorder and molecular motion in many crystalline π-molecular compounds. X-ray diffraction studies have been interpreted as revealing either static positional disorder[5] or dynamic librational disorder[6] in these compounds. More recently, n.m.r. measurements[2–4] have confirmed the presence of motion and, in a few compounds, could determine its nature. For example, n.m.r. second-moment studies[3] showed that the naphthalene molecules in naphthalene-tetracyanobenzene (N-TCNB) undergo two types

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of reorientational motion. At low temperatures the hydrocarbon molecules interconvert between two naphthalene sites, related by a 36° in-plane rotation, by jumping over this small angle; at higher temperatures, the interconversion between sites can take place also by a jump over the larger 144° angle separating the orientations. The coupling of 36° and 144° jumping motions results in a complete in-plane reorientation of the naphthalene molecules.

For other compounds, e.g., naphthalene-tetracyanoethylene (N-TCNE), n.m.r. measurements[3,4] cannot distinguish between this type of reorientational motion involving two distinguishable sites and a large-amplitude librational motion about a single site given by the average of the two orientations. Heat-capacity measurements can do so however, because for reorientational motion, the naphthalene molecules alternate between two distinct orientations and the crystal is disordered. For molecules with only librational motion, the crystal is ordered since the molecules occupy a single equilibrium position. On heating the compound at low temperatures, a disordering thermal transition would be expected in the former case but none in the latter.

We have determined the heat capacities of several of these compounds to resolve this uncertainty about the nature of their molecular motion; the measurements[7] on N-TCNB showed an order-disorder transition near 70 K and supported other evidence[8–11] that the motion in this compound is reorientational. In the present paper, measurements of the heat capacity of N-TCNE from 5 to 300 K by adiabatic calorimetric techniques are used to ascertain the nature of the molecular motion observed by other techniques.[3,4]

EXPERIMENTAL

Sample preparation and characterization

The calorimetric sample of N-TCNE was prepared by Dr. Colin Fyfe of the University of Guelph, Guelph, Ontario, Canada. Hot equimolar solutions of naphthalene and tetracyanoethylene in ethyl acetate were mixed together. Purple crystals precipitated as the mixture cooled, were removed by filtration, and dried overnight *in vacuo*.

Analysis by n.m.r. and mass spectrometry in Guelph indicated that the sample contained no solvent within the limits of detection of these techniques (estimated to be about one percent). However, subsequent to completion of the thermal measurements visual examination as well as microanalysis of the sample by Spang Microanalytical Laboratory, Eagle Harbor, MI suggested that some decomposition had taken place. The results given in mass percent are carbon: 73.56 (theoretical 74.99); hydrogen: 3.24 (theoretical 3.14); and nitrogen: 22.26 (theoretical 21.86). The TCNE/N ratio was about 1.10. (Another commercial analysis reported an essentially stoichiometric composition for the sample, see Ref. 13 for details.) The sample decomposition probably occurred by napthalene subliming from the molecular compound leaving behind an excess of TCNE. Such behavior has been observed for another naphthalene compound: naphthalene-1,3,5-trinitrobenzene.[12]

Calorimetric methods

The Mark II adiabatic cryostat described previously[14] was used for the calorimetric measurements. Approximately 35 g of N-TCNE crystals were loaded into a gold-plated copper calorimeter (laboratory designation W-54) with a gold-gasketed screw-type closure. The calorimeter was then evacuated and a small amount of helium gas (0.00027 g) was added to facilitate rapid thermal equilibration. A capsule-type, platinum-resistance thermometer (laboratory designation A-5) was used to measure the temperature of the sample-filled calorimeter over the entire temperature region. The thermometer has been calibrated by the U.S. National Bureau of Standards (NBS) against the textual revision of the International Practical Temperature Scale of 1948[15] for temperatures above 90 K, against the NBS provisional scale from 10 to 90 K, and against a provisional scale of Chang[16] below 10 K. Temperatures are judged to correspond to the thermodynamic temperature scale to within 0.03 K from 10 to 90 K and to 0.04 K above 90 K. Mass, current, and time determinations are also referred to calibrations performed at NBS. The heat capacity of the empty calorimeter containing a small amount of helium gas and Apiezon T grease was determined prior to the calorimetric experiments with N-TCNE. The experimental (sample + calorimeter) data has been corrected using the results of the measurements on the empty calorimeter to yield the heat capacity of N-TCNE. In these measurements, the heat capacity of the sample represented between 65 to 88 per cent of the total heat capacity.

RESULTS

The experimental results for the heat capacity from 5 to 300 K for N-TCNE are presented in Table I. These are given on a molar basis assuming a 1:1 molar ratio of the components and taking a mole of complex as one mole each of donor and acceptor molecules. Throughout this paper, 1 cal = 4.184 J.

TABLE I

Experimental Heat Capacities of N-TCNE (cal = 4.184 J)

T	C_p	T	C_p	T	C_p	T	C_p
K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}	K	cal K^{-1} mol^{-1}
Series I[a]		158.56	91.95	5.62	0.178	159.13	51.24
118.66	39.46[b]	159.95	71.28	6.32	0.244	159.25	50.87
126.24	41.42	161.65	52.99	7.24	0.358	159.37	50.76
134.94	43.55	163.51	51.98	8.23	0.521		
143.52	45.68	165.36	52.84	9.15	0.696	*Series XIII*[a]	
151.95	47.97	168.57	53.92	10.01	0.888	154.13	49.20
158.99	78.86	173.91	55.04	10.98	1.134	155.70	52.16
165.73	52.92	ΔH Detn. F		12.06	1.463	156.60	66.99
173.29	55.02	201.38	63.07	13.26	1.842	157.22	77.28
181.37	57.56	205.81	64.44	14.56	2.330	157.64	88.88
190.18	59.99	208.88	65.39	15.89	2.865	157.90	86.00
		210.62	65.99	17.41	3.531	158.18	78.72
Series II[a]		212.34	66.54	19.14	4.335	158.47	76.58
181.83	57.27	214.06	67.14	21.02	5.260	158.76	77.32
190.74	59.78	215.76	67.70	23.18	6.370	159.05	79.77
199.55	62.41	217.45	68.43	25.41	7.540	159.33	84.66
208.36	65.11	219.12	68.81	27.49	8.641	159.59	88.95
217.18	68.04	220.80	69.14	30.30	10.12	159.85	93.03
226.06	65.54	222.47	68.73	33.68	11.88	160.10	92.70
235.36	65.21			37.10	13.62	160.36	86.84
		Series VIII[a]		40.92	15.47	160.64	79.49
Series III[a]		ΔH Detn. G		45.06	17.34	160.93	70.72
228.35	64.40	219.25	68.92	49.66	19.32	161.41	59.75
238.02	65.70	220.72	69.14	55.07	21.45	161.96	55.44
247.66	67.71	221.21	69.19			162.35	53.61
257.35	69.70	221.70	69.03	*Series XI*[c]		162.74	52.82
267.04	71.77	222.44	68.80	153.34	48.40	163.13	52.22
276.62	73.85	223.69	66.93	154.88	49.36	163.53	52.30
		225.21	64.26	155.82	51.41	163.93	52.45
Series IV[a]		227.28	63.94	156.52	66.99	164.52	52.53
146.58	46.44	230.66	64.43	157.11	84.66	165.31	52.62
ΔH Detn. A		ΔH Detn. H		157.61	96.21	166.90	53.17
176.82	55.84	282.88	75.17	158.09	92.21		
		292.22	77.22	158.59	85.19	*Series XIV*[a]	
Series V[a]		301.52	79.34	159.11	84.85	ΔH Detn. I	
146.77	46.57			159.62	87.68	155.79	54.88
ΔH Detn. B		*Series IX*		160.13	85.15	156.85	70.43
ΔH Detn. C		51.60	20.13	160.68	72.28	157.14	80.95
236.40	65.40	54.09	21.11	161.37	59.45	157.41	86.56
		58.65	22.81	162.06	54.13	157.68	84.07
Series VI[a]		64.78	24.99	162.64	52.59	157.95	78.26
146.78	46.52	71.72	27.16	163.22	52.24	158.25	78.07
ΔH Detn. D		80.02	29.67	163.95	52.38	158.56	74.82
ΔH Detn. E		88.46	32.09	164.82	52.53	158.84	81.14
236.25	65.36	96.84	34.20			159.23	91.68
		105.94	36.39	*Series XII*[a]		159.60	93.60
Series VII[a]		115.45	38.76	158.10	51.17	159.84	99.21
150.58	47.59	124.74	41.03	158.40	50.87	160.08	93.96
154.06	49.25			158.70	50.94	161.34	63.77
155.88	60.09	*Series X*		158.90	50.80	ΔH Detn. J	
157.34	96.03	5.01	0.134	159.02	50.57		

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[a] Detns. in the transition region from 150 to 240 K are not included in the curve fitting.

[b] Not included in the curve fitting (unreliable shield control).

[c] These Detns. were made without complete thermal equilibrations of the sample and were not used in drawing the final heat-capacity curve.

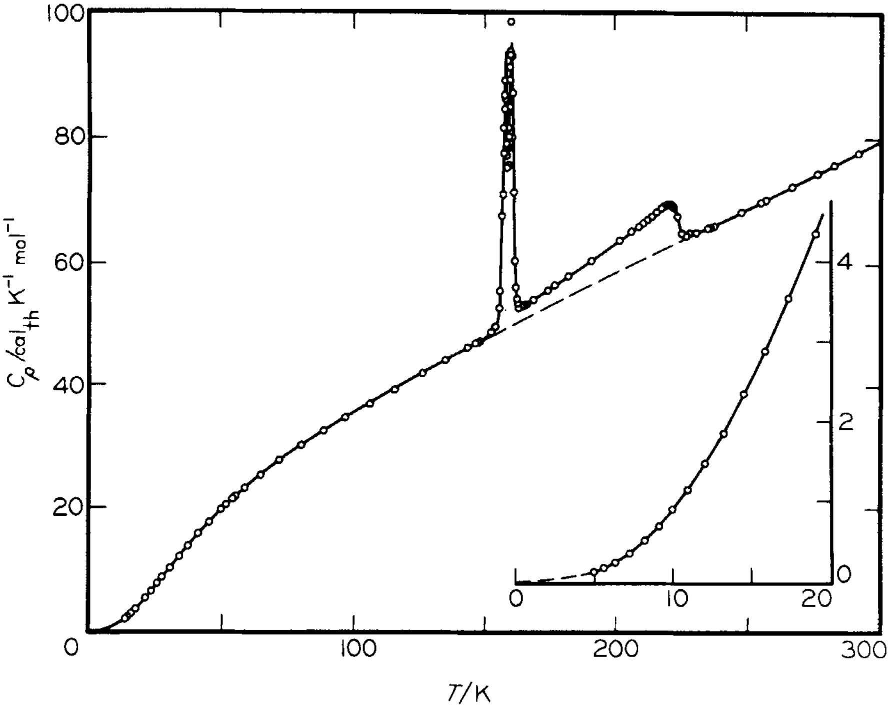

FIGURE 1 Experimental heat capacity of N-TCNE. The dashed line represents the lattice heat-capacity curve.

The results are arranged in chronological order so that approximate temperature increments used in each measurement usually can be inferred from the difference between mean temperatures of adjacent determinations. These results are shown graphically in Figure 1. The smoothed heat capacity and thermodynamic functions obtained from polynomial-fitting of the experimental heat capacities are listed in Table II for selected temperatures. Two interesting features are evident in the curve: a bifurcated peak near 160 K and a long, sloping anomaly culminating near 230 K. The region of the bifurcated peak has been enlarged and shown in greater detail in Figure 2. The open circles represent the results of a set of measurements made with small temperature increments (see Series XIII in Table I). The closed circles are from measurements (Series XIV) made after cooling the sample in exactly the same manner as the previous series of measurements. While the total enthalpy increment through the transition region is the same for both sets of measurements, the curves defined by them are not coincident since the relative heights of the two peaks and the depth of the valley differ.

TABLE II

Thermodynamic Functions for N-TCNE

$\frac{T}{K}$	$\frac{C_p}{\text{cal K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T) - S^\circ(0)\}}{\text{cal K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T) - H^\circ(0)\}}{\text{cal mol}^{-1}}$	$\frac{\{G^\circ(T) - H^\circ(0)\}/T}{\text{cal K}^{-1}\text{ mol}^{-1}}$
5	0.129	0.042	0.159	0.011
10	0.887	0.316	2.341	0.082
15	2.499	0.953	10.474	0.255
20	4.754	1.970	28.405	0.549
25	7.324	3.303	58.503	0.962
30	9.955	4.872	101.75	1.480
35	12.52	6.600	157.95	2.087
40	14.98	8.434	226.77	2.765
45	17.31	10.334	307.55	3.500
50	19.47	12.271	399.57	4.280
60	23.34	16.17	614.1	5.937
70	26.66	20.03	864.5	7.675
80	29.58	23.78	1145.9	9.455
90	32.28	27.42	1455.4	11.250
100	34.87	30.96	1791.2	13.044
110	37.41	34.40	2152.7	14.830
120	39.91	37.76	2539.3	16.60
130	42.34	41.05	2950.7	18.36
140	44.80	44.28	3386.3	20.09
150	47.41	47.45	3847.0	21.80
157.74[a]	92.63	50.16	4265.5	23.12
159.98[a]	94.93	51.34	4451.5	23.51
160	94.53	51.35	4452.4	23.52
170	53.96	54.79	5019.6	25.26
180	56.73	57.95	5626.8	26.69
190	59.56	61.10	6208.3	28.42
200	62.61	64.23	6818.9	30.14
210	65.80	67.36	7460.9	31.83
220	69.03	70.50	8135.8	33.52
222.24[a]	68.81	71.20	8290.5	33.90
230	64.23	73.43	8795.1	35.19
240	66.12	76.21	9397	37.06
250	68.19	78.97	10069	38.70
260	70.28	81.69	10761	40.30
270	72.40	84.38	11474	41.88
273.15	73.08	85.22	11704	42.38
280	74.56	87.05	12209	43.45
290	76.75	89.71	12966	45.00
298.15	78.57	91.86	13599	46.25
300	78.99	92.35	13744	46.53

[a] Peak of transition.

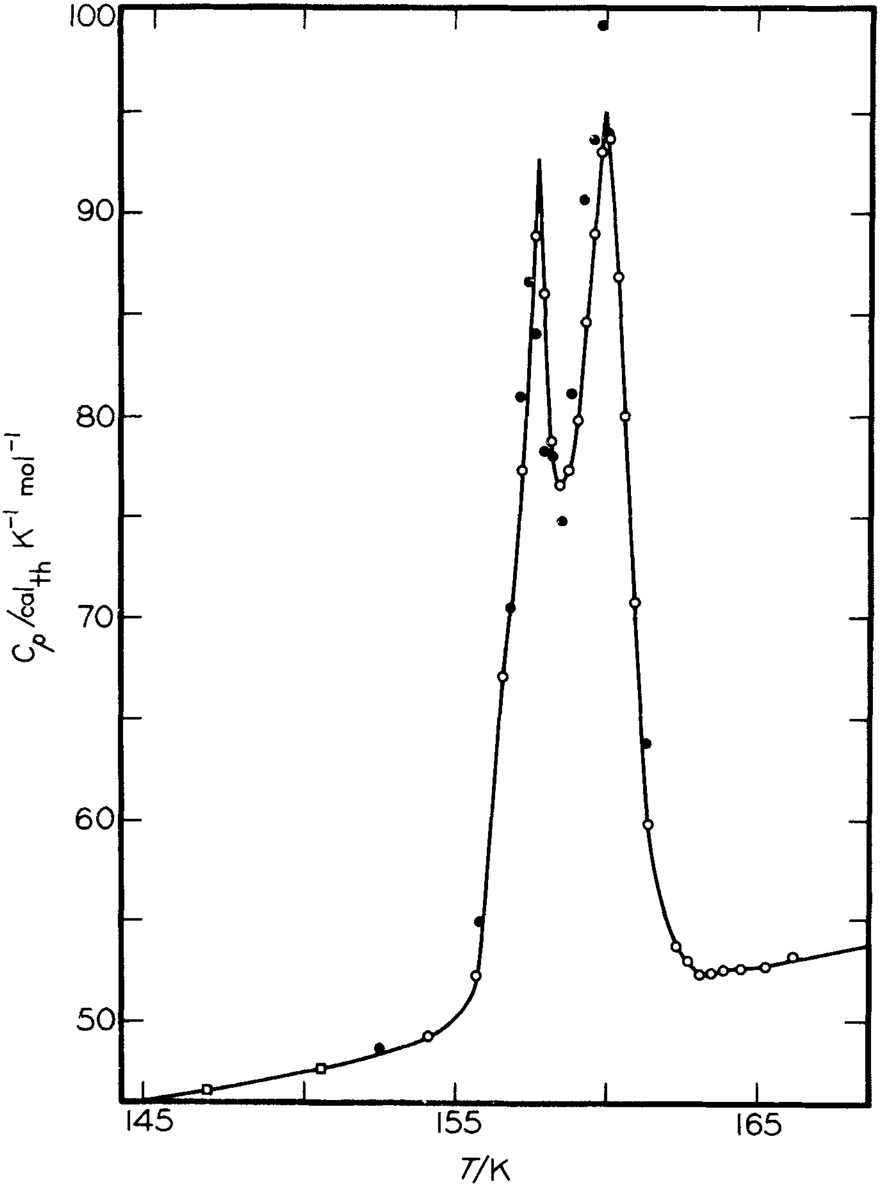

FIGURE 2 Details of the bifurcated peak in N-TCNE showing experimental points. ○ and ● indicate experimental data from different series.

TABLE III

Enthalpies and entropies of transition of N-TCNE

Designation	T_1/K	T_2/K	$\{H°(T_2) - H°(T_1)\}$ / cal mol^{-1}	$\{H°(172.5\ K) - H°(135\ K)\}$ / cal mol^{-1}	$\{S°(172.5\ K) - S°(135\ K)\}$ / cal K^{-1} mol^{-1}
Region from 150 to 172.5 K					
ΔH_t Detn. A	150.02	172.39	1306.6	1995.3	—
ΔH_t Detn. B	150.09	172.86	1328.6	1994.9	—
ΔH_t Detn. D	150.02	172.52	1315.1	1996.7	—
Series VII	153.08	170.85	1075.4	1994.5	—
Series XIII	153.13	168.10	919.3	1989.1[a]	—
			Mean value:	1995.6 ± 1	—
			Graphical Integration:	1991 ± 2	(12.94 ± 0.02)[b]
			Lattice Integration:	1799 ± 1	11.71 ± 0.02
			$\Delta H_t =$	196.6 + 1	$\Delta S_t =$ 1.22 ± 0.03
				$\{H°(240\ K) - H°(172.5\ K)\}$ / cal mol^{-1}	$\{S°(240\ K) - S°(172.5\ K)\}$ / cal K^{-1} mol^{-1}
Region from 172.5 to 240 K					
ΔH_t Detn. C	172.86	231.75	3681.7	4239.9	—
ΔH_t Detn. E	172.52	231.52	3688.4	4239.3	—
Series VII & Series VIII	177.37	232.75	3494.7	4240.2	—
			Mean value:	4240 ± 1	—
			Graphical Integration:	4238 ± 1	20.62 ± 0.02
			Lattice Integration:	3994 ± 4	19.42 ± 0.02
			$\Delta H_t =$	246 ± 5	$\Delta S_t =$ 1.20 ± 0.04

[a] Excluded from determination of the mean.

[b] The entropy increment obtained by graphical integration has been adjusted to take into account the difference between the experimental enthalpy increment and that obtained by integration of the heat capacity curve.

Two sets of measurements made through the region of the bifurcated peak are not shown in Figure 2. The results of Series XI have been excluded because it is believed that the sample did not reach thermal equilibrium between successive energy inputs. The measurements of Series XII have been ignored because the sample was not cooled far enough below the transition to cause complete conversion to the low-temperature phase to take place.

The enthalpy determinations made through the transition regions are summarized in Table III. Because there was no clearcut separation of the two transition regions, 172.5 K was chosen as the endpoint for the integration of the first transition and the starting point for the second. The reproducibility of the enthalpy increments of the two transition was quite good and did not appear to be significantly affected by cooling procedures provided the sample had been cooled below 140 K.

To evaluate the ΔH_t and ΔS_t for the two regions, a lattice heat capacity had to be estimated. Because no spectroscopic data are available for this compound and the region of excess heat capacity spans 100 K, the choice of a lattice heat capacity was somewhat arbitrary. A continuous lattice heat-capacity curve extending over the entire region from 135 to 240 K was used. It is shown as a dashed line in both figures. The lattice and experimental heat-capacity curves were numerically integrated to give the values indicated in Table III and ΔH_t and ΔS_t (obtained as the difference) yield values of 196.6 cal K^{-1} mol^{-1} and 1.20 cal K^{-1} mol^{-1} for the region from 172.5 to 240 K. The entropies of transition of the two regions are equal, within the estimated experimental error, and are close to $R \ln 2$, (1.38 cal K^{-1} mol^{-1}) the value expected for an order-disorder transition involving two distinct sites in the high-temperature phase.

DISCUSSION

Herbstein[1] has reported that cooling of the N-TCNE crystals to about 150 K causes them to change from the high-temperature monoclinic phase to a low-temperature triclinic phase. No detailed crystal structure is available for the low-temperature phase since the monoclinic crystals shatter on cooling through the phase transformation. The crystal damage noted by Herbstein was also observed in this study. The sample, which was loaded into the calorimeter as purple needles, was removed as a finely divided, blackish powder after the calorimetric experiments.

The location of the bifurcated peak in the heat capacity is in good agreement with the temperature observed for the monoclinic to triclinic conversion, and the shape of the peak is more suggestive of the first-order character expected for a change in crystal structure than are other transitions observed so far in π-molecular compounds.

The crystal structure of N-TCNE at 300 K was investigated by Williams and Wallwork,[6] who deduced a monoclinic structure in which the naphthalene molecules had a large thermal motion about the axis normal to the molecular plane. Herbstein,[5] through an analysis of the published Debye–Waller factors for naphthalene and TCNE in N-TCNE and an electron-difference synthesis, concluded that the naphthalene molecules were disordered. This conclusion was supported by the constrained refinement study of Shmueli and Goldberg[17] performed using the diffraction data of Williams and Wallwork.[6] The potential energy calculations of Shmueli and Goldberg[18] and of Fyfe *et al.*[4] gave two minima for the rotation of the naphthalene molecules about the axis normal to the molecular plane which also suggested that the naphthalene molecules should occupy two orientations in the N-TCNE crystal.

The temperature-dependence of the linewidth and second moment of the solid-state n.m.r. spectrum of N-TCNE was interpreted by Fyfe[3] as supportive either of a disordered structure (like that observed at low temperatures for N-TCNB) with the naphthalene molecules reorientating between two sites separated by 16–20°, or of a large-amplitude librational motion over the same angle. In the spin-lattice relaxation time measurements of Fyfe *et al.*,[4] only one motional process was observed. It had an activation energy of 13 kcal mol^{-1}, which is close to the 10 kcal mol^{-1} activation barrier for the large-angle jumping motion in N-TCNB, and it has been attributed to an energy barrier for a similar motion in N-TCNE.

If reorientational motion were present in N-TCNE below 77 K as inferred from the n.m.r. measurements,[3,4] a transition similar to the one observed in N-TCNB[7] should have appeared in our results for N-TCNE. The absence of a transition in this region is reason to conclude that the motion detected by the n.m.r. techniques at 77 K should be interpreted as arising from an anharmonic librational motion and not a reorientational motion of the naphthalene molecules.

Since disorder[5,16] (and therefore reorientational motion) is present at 300 K, it is tempting to ascribe the anomaly culminating near 225 K to the onset of reorientational motion with the concurrent introduction of disorder into the crystal. This determination cannot be made solely on the heat-capacity measurements, however, and two other mechanisms for this transition must be considered. The first is that the anomaly is solvent-related. The solvent, ethyl acetate, has a melting point near 189 K so it is not likely that this peak represents the fusion of ethyl acetate. Nevertheless, some form of some solvent-compound interactions cannot be ruled out. Since the analytical results indicated that excess TCNE was present in the sample, the possibility that a solid solution was formed between the compound and the excess component had to be considered. Hence, new samples of N-TCNE were crystallized from different solvents including acetonitrile, methyl ethyl ketone and ethyl acetate. Elemental analyses (see Ref. 13 for details) showed that these samples had different TCNE-N ratios indicating decomposition had occurred by loss of naphthalene.

Differential scanning calorimetry (DSC) on these samples as well as on a portion of the adiabatic-calorimetric sample were used to elucidate the heat capacity behavior of N-TCNE over the region from 172 to 240 K. All the samples showed similar peaks in this region. Since the anomaly was observed in samples prepared from different solvents, it is unlikely that the transition is solvent-related. If the transition arose because of the presence of excess TCNE, it might be expected that the temperature at which the transition was complete would be dependent on the amount of excess TCNE. Within the error limits of our DSC temperature measurements, the transition temperatures were the same for all four samples. This suggests that the anomaly from 172 to 240 K is not composition-dependent but rather, intrinsic to the molecular compound.

Since the results of the DSC studies indicate that the transition is neither solvent nor composition dependent, it seems most likely that this anomaly represents the gradual onset of the reorientation of the naphthalene molecules. Because the heat capacity does not return to the lattice value between the two transitions, it would appear that the disordering process may begin once the structural (triclinic-monoclinic) conversion has taken place and becomes complete by 240 K. This conclusion cannot be verified now, but detailed X-ray diffraction studies would be valuable in determining if disorder does indeed set in as the crystal is heated from 160 to 240 K.

Acknowledgements

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References

1. F. H. Herbstein, "Crystalline π-Molecular Compounds: Chemistry, Spectroscopy and Crystallography," in *Perspectives in Structural Chemistry*, Vol. 4, eds., J. D. Dunitz and J. A. Ibers, (John Wiley and Sons, New York, 1971).
2. C. A. Fyfe, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1633 (1974).
3. C. A. Fyfe, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1642 (1974).
4. C. A. Fyfe, D. Harold-Smith and J. Ripmeester, *J. Chem. Soc., Faraday Trans. 2*, **72**, 2269 (1976).
5. F. H. Herbstein and J. A. Snyman, *Phil. Trans. Roy. Soc. (London)*, **A264**, 635 (1969).

6. R. M. Williams and S. C. Wallwork, *Acta Cryst.*, **22**, 899 (1967).
7. J. Boerio-Goates, E. F. Westrum, Jr. and C. A. Fyfe, *Mol. Cryst. Liq. Cryst.*, **48**, 209 (1978).
8. R. M. Macfarlane and S. Ushioda, *J. Chem. Phys.*, **67**, 3214 (1977).
9. H. J. Bernstein, N. S. Dalal, W. F. Murphy, A. H. Reddoch, S. Sunder and D. F. Williams, *Chem. Phys. Lett.*, **57**, 159 (1978).
10. E. Erdle and H. Möhwald, *Chem. Phys.*, **36**, 283 (1979).
11. A. M. Ponte Goncalves and H. M. Vyas, *J. Chem. Phys.*, **70**, 1560 (1979).
12. K. Suzuki and S. Seki, *Bull. Chem. Soc. Japan*, **28**, 417 (1955).
13. J. Boerio-Goates, Ph.D. Thesis, The University of Michigan, Ann Arbor, MI 48109, 1979.
14. E. F. Westrum, Jr, G. T. Furukawa and J. P. McCullough, "Adiabatic Low-Temperature Calorimetry," in *Experimental Thermodynamics*, Vol. 1, eds, J. P. McCullough and D. W. Scott, (Butterworths, London, 1968).
15. H. F. Stimson, *J. Res. Nat'l. Bureau Standards*, **65A**, 139 (1961).
16. F. L. McCrackin and S. S. Chang, *Rev. Sci. Instrum.*, **46**, 550 (1975).
17. U. Shmueli and I. Goldberg, *Acta Cryst.*, **B30**, 573 (1974).
18. U. Shmueli and I. Goldberg, *Acta Cryst.*, **B29**, 2466 (1973).