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The Heat Capacity of 1,2,4,5-Tetracyanobenzene and of its 1 : 1 Charge-Transfer Complex with Pyrene from 10 K to 300 K.

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The heat capacity of 1,2,4,5-tetracyanobenzene and of its 1 : 1 complex with pyrene has been measured from ~ 10 K to ~ 300 K. There is a transition in the complex which appears as an approximately symmetrical anomaly in the heat capacity-temperature curve between ~ 220 K and 250 K, but the heat capacity is not reproducible in this region even if the sample is subjected to the same preliminary thermal treatment. Moreover, the room-temperature form can be undercooled at least down to 150 K. In the two runs in which the heat capacity anomaly was most prominent. C_p reached its maximum at 232 ± 1 K. The largest measured value of the entropy of transition was 9.2 JK^{-1} mol^{-1}. This value is compatible with, but does not prove, the existence of static disorder above the transition, with one of the components (pyrene, in the light of the structural information) having at least two distinguishable orientations. At all temperatures in the range covered (apart from the transition region), the heat capacity of the complex is less than the sum of that of the pure components, and possible reasons for this are briefly discussed.

INTRODUCTION

A considerable amount of structural work has been carried out on charge-transfer molecular complexes in which the electron donor is a molecule such as naphthalene or pyrene, and the acceptor a molecule like pyromellitic-dianhydride, tetracyanoethylene (TCNE), or 1,2,4,5-tetracyanobenzene (TCNB). In such complexes, of which the subject of this paper is a typical example, the donor and acceptor molecules are stacked alternately in columns. The diffraction investigations have shown that sometimes one or both of the constituent molecules is disordered in the molecular plane, the disorder taking the form either of dynamic disorder, that is of large and no doubt somewhat anharmonic torsional oscillations, or of static disorder

between two possible orientations. In the pyrene–TCNE complex, for example, even at 105 K the TCNE molecules are disordered between two orientations. These are not energetically equivalent, one of them being occupied to the extent of only 7 per cent.[1] The structure of the 1 : 1 pyrene–TCNB complex has been determined by Prout *et al.*[2] Their study established that the two kinds of molecule are not quite parallel in a stack, the planes of adjacent molecules being inclined at 4.4° to each other, and that they are displaced somewhat from a centre-upon-centre superposition. Furthermore, whereas the atoms in the TCNB molecule have reasonably well-defined positions, the pyrene molecules are undergoing a large in-plane libration. This might be due to static disorder, or to oscillation in a relatively wide and flat-bottomed potential well. Prout *et al.* determined the structure of the complex at 178 K as well as at 290 K. The structure at the lower temperature remains essentially the same, with no change in space group, but the in-plane motion of the pyrene molecules is considerably reduced. The comparison of the diffraction results at 290 K and 178 K was regarded as favouring dynamic rather than static disorder of the pyrene molecules.

At Dr. Prout's suggestion, we have measured the heat capacity of the complex from $\sim$10 K to 300 K, with the primary object of finding out whether there are any transitions or thermal anomalies in the heat capacity curve. However, a very considerable contribution can be made to the heat capacity of the complex from the numerous internal degrees of freedom of the two molecules, this contribution increasing considerably with rising temperature, and accordingly a protracted but nevertheless significant thermal anomaly might be rather hard to detect. For example, an effect in the heat capacity—temperature curve due to a change in occupancy with temperature of two energetically nonequivalent energy levels might well be obscured. In such a case, the analysis of the heat capacity of the complex can be simplified by comparing this heat capacity with the sum of the heat capacities of the two components. The heat capacity of pyrene had already been determined,[3] but not that of TCNB, and we have accordingly measured C_p for TCNB from 10 K to 300 K. In comparing the heat capacity of the complex with the sum of that of the components, it is reasonable to assume that the contribution from the intramolecular vibrations of each constituent which involve bond stretching is approximately the same whether it is in the complex or in its own crystal, since the structural work showed that the bond lengths are unchanged within experimental error.

EXPERIMENTAL

The sample of TCNB was prepared by the method of Bailey, Henn and Langdon.[4] The crude product was purified by crystallization from glacial

acetic acid, followed by recrystallization from methyl ethyl ketone and finally from glacial acetic acid. This procedure yielded large, thin, translucent white plates whose infrared spectrum (hexachlorobutadiene mull) showed the proper absorption bands and the absence of the amide impurity present in the crude product. Analysis gave 67.6 per cent C (theory 67.4), 31.4 per cent *N* (theory 31.5), and 0.98 per cent *H* (theory 1.13). Due to the low density of the bulk crystals, the mass of the calorimetric sample was only ~12.7 g. The complex was kindly prepared for us from purified reagents by Dr. A. S. Bailey, as described by Bailey *et al.* The mass of the calorimetric sample was ~23.4 g.

All heat capacity measurements were made in the smaller of the two calorimeters described by Waterfield and Staveley.[5] A pressure of 8 Torr of helium was used to facilitate thermal equilibrium. Temperatures were measured on the IPTS-68 scale.

RESULTS

The C_p results for TCNB are recorded in Table I. They show no sign of any transition or anomaly. The experimental C_p values for the 1 : 1 TCNB–pyrene complex are given in Table II. There is only one region of temperature in which the heat capacity is obviously anomalous, namely that between ~220 K and ~250 K. The results obtained in this range, however, depended on the previous thermal treatment of the sample, and were not necessarily reproducible even when this treatment had been the same. Five series of measurements were made in the transition region, which gave the values shown graphically in Figure 1. The following is a summary of the thermal history of the sample preceding each of these five runs and of the results obtained, presented in the order in which the five series were carried out.

Run 1. The sample was cooled to 77 K, and C_p measured from 77 K to 280 K. This run gave one high C_p point at 220 K, then two "normal" values followed by two slightly high results at 245.8 K and 254.4 K, suggesting two minor, separate anomalies.

Run 2. The sample was cooled to only 150 K, and C_p then measured from 210 K to 233 K. The significant feature of this run is that none of the C_p values was "abnormal".

Run 3. The sample was cooled to 77 K, and C_p measured from 215 K to 245 K. This gave the highest C_p values, with the transition appearing roughly as a cone in the $C_p - T$ plot.

Run 4. A repeat of run 3. This gave results which, while approximately the same as those of series 3, were not identical with them, the transition being displaced to a somewhat higher temperature.

TABLE I

Experimental heat capacities of 1,2,4,5-tetracyanobenzene (TCNB).

T/K	$C_p/JK^{-1}\,mol^{-1}$	T/K	$C_p/JK^{-1}\,mol^{-1}$	T/K	$C_p/JK^{-1}\,mol^{-1}$
5.46	0.29	71.52	75.27	175.74	151.1
5.65	0.33	76.63	79.81	179.94	153.6
7.06	0.66	79.19	82.10	184.33	156.1
9.05	1.44	82.29	84.65	188.67	158.9
10.99	2.94	85.30	87.02	192.96	161.4
13.09	5.21	88.48	89.32	197.20	164.0
15.28	7.85	91.82	92.10	201.40	166.4
17.37	10.36	95.08	94.43	205.55	169.0
19.43	12.95	98.27	96.61	209.97	171.4
21.40	15.55	102.02	99.35	214.54	174.1
23.36	18.31	106.08	102.3	219.07	176.6
25.32	21.10	110.04	105.2	223.62	179.8
27.29	23.81	113.91	108.2	228.08	182.3
29.24	26.49	117.99	111.1	232.74	185.1
31.42	29.66	122.25	114.3	237.70	187.9
33.59	32.73	126.44	117.2	242.56	190.7
35.76	35.62	130.55	120.5	247.37	194.0
38.11	38.94	134.58	123.3	252.13	196.1
40.70	42.31	138.55	126.1	257.07	199.1
43.48	45.80	142.46	129.0	262.19	202.3
46.42	49.40	146.57	131.8	267.49	205.1
49.33	53.20	150.87	134.7	273.04	208.6
52.22	57.05	155.15	137.7	278.50	211.7
55.28	60.54	159.37	140.4	283.89	214.4
58.73	63.87	163.54	143.2	289.17	217.2
62.57	67.41	167.65	145.9	294.46	220.1
66.76	71.14	171.72	148.2	299.73	223.3

Run 5. The sample was cooled to helium temperatures, and C_p measured from 10 K to 90 K. It was then heated to 215 K, and C_p determined from 215 K to 250 K. The maximum C_p values recorded in this run were less than in runs 3 and 4.

It would seem that the best estimate of the entropy of transition ΔS_t which can be made is that based on runs 3 and 4, since the transition was most prominent in these. Taking the dotted line in Figure 1 as representing the "normal" heat capacity, graphical integration gave $\Delta S_t = 9.2\,JK^{-1}mol^{-1}$ and $7.3\,JK^{-1}mol^{-1}$ for runs 3 and 4 respectively. The temperature at which C_p reached a maximum in these two runs was 232 ± 1 K. The appearance of the transition in the $C_p - T$ plot as given by runs 3 and 4 is rather reminiscent of the course taken by the heat capacity in a two-dimensional order—disorder transition.

TABLE II

Experimental heat capacities of 1:1 pyrene-TCNB complex

T/K	$C_p/JK^{-1}\,mol^{-1}$	T/K	$C_p/JK^{-1}\,mol^{-1}$	T/K	$C_p/JK^{-1}\,mol^{-1}$
13.20	8.55	71.48	127.4	160.92	253.2
15.41	15.55	78.16	137.3	168.20	261.9
19.52	25.42	83.49	143.5	175.84	272.0
22.66	33.61	87.40	152.2	182.73	281.0
25.08	38.10	92.93	162.3	189.46	291.2
27.18	44.43	98.79	168.9	196.03	299.1
30.00	50.70	102.74	174.3	202.86	307.7
32.12	55.33	108.67	182.2	Transition	
35.73	64.59	116.95	192.5	Region	
41.51	76.82	122.99	200.7	262.97	389.3
49.17	92.42	129.63	211.0	271.19	398.8
55.86	103.6	136.90	220.0	280.76	412.4
61.52	113.7	145.05	231.3	288.04	423.1
66.67	123.2	153.42	242.0	294.99	428.8
		Transition Region			
RUN 1		226.69	340.8	224.52	373.3
211.13	320.2	229.12	344.7	228.75	418.3
220.13	377.2	232.32	350.1	233.14	456.3
228.18	344.4	RUN 3		237.30	436.8
237.15	354.9	217.33	330.4	241.17	427.8
245.84	382.2	221.60	356.9	245.81	418.6
254.37	381.3	225.59	408.2		
RUN 2		231.66	480.3	RUN 5	
216.94	327.5	237.92	443.4	217.47	327.9
218.57	331.1	242.20	413.2	222.65	344.3
220.22	333.1	RUN 4		227.67	363.3
221.86	333.7	211.40	318.3	231.68	387.1
223.47	337.6	216.38	327.1	237.27	427.9
225.09	340.2	220.53	339.9	244.63	421.9
				252.09	409.1

DISCUSSION

The experimental C_p values for TCNB and the complex were smoothed by computer fitting to polynomials. In Table III we give smoothed values at regular temperature intervals, and corresponding values of chemical thermodynamic functions of TCNB and the complex are presented in Table IV. The smoothed C_p values of pyrene given by Wong and Westrum[3] are also recorded in Table III, together with values of the quantity ΔC_p, where

$$\Delta C_p = C_p\,(\text{complex}) - C_p\,(\text{TCNB}) - C_p\,(\text{pyrene}).$$

ΔC_p is negative for the whole temperature region covered, except between ~220 K and 250 K. There is no evidence at all of a gradual rise in the heat

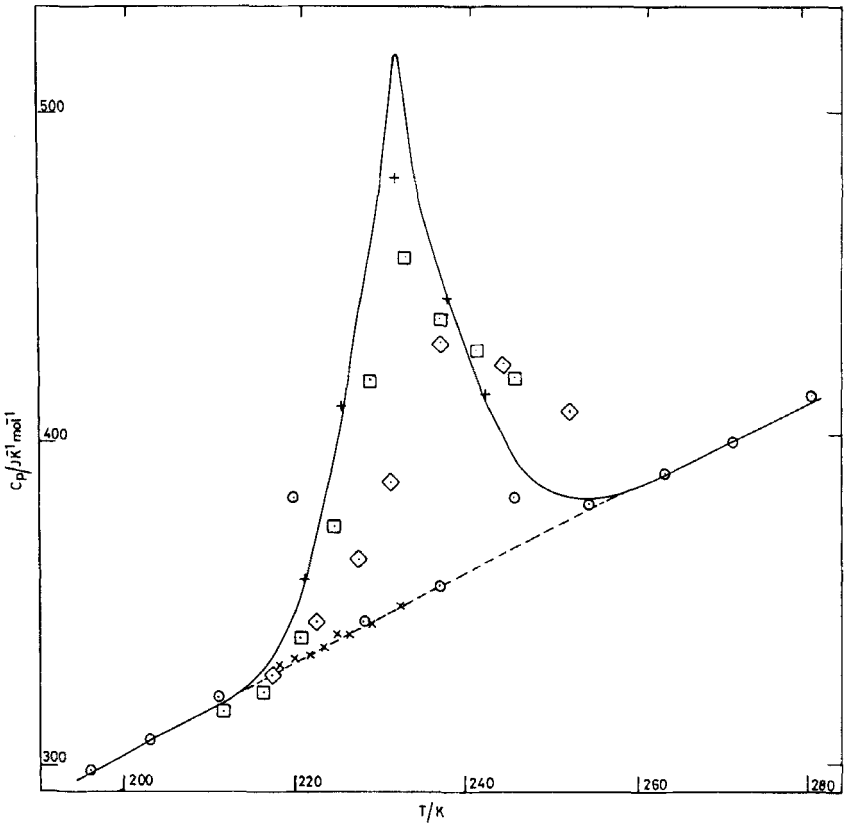

FIGURE 1 Heat capacity of the 1:1 pyrene-TCNB complex in the transition region. ⊙, run 1 (see text); ×, run 2; +, run 3; ⊡, run 4; ◇, run 5. The full curve has been drawn through the points of run 3, which gave the most pronounced peak.

capacity on approaching the transition such as is frequently found in an order–disorder transformation. There is admittedly a slight increase in ΔC_p between 70 K and 110 K, but this happens well below the transition and the increase is very small anyway. It should be noted that pyrene itself has a minor transition at 121 K, which may have some influence on ΔC_p.

Prout and his coworkers reported that crystals of the complex shatter reproducibly at 171 K, and that at the same temperature there is a colour change on cooling from orange to yellow. Our sample was loaded into the calorimeter as large, needle-like crystals. When finally removed, it was in the form of an orange dust. There is, however, no sign at all in our heat capacity results of any transition or even a small thermal anomaly at or near 171 K. On the other hand, our observations of undercooling (series 2) imply that a phase change does occur, but not until the sample has been

TABLE III

Smoothed values of C_p for TCNB, pyrene and the 1 : 1 complex, together with values of $\Delta C_p = C_p$ (complex) $- C_p$ (TCNB) $- C_p$ (pyrene).

T/K	TCNB C_p/JK^{-1} mol^{-1}	PYRENE C_p/JK^{-1} mol^{-1}	COMPLEX C_p/JK^{-1} mol^{-1}	ΔC_p/JK^{-1} mol^{-1}
5	0.210	0.665	0.522	−0.4
10	2.077	4.866	4.178	−2.8
15	7.506	10.95	13.73	−4.7
20	13.70	16.96	25.88	−4.8
25	20.55	22.52	38.46	−4.6
30	27.61	27.56	50.84	−4.3
35	34.65	32.16	62.63	−4.2
40	41.47	36.35	73.58	−4.2
45	47.96	40.14	83.66	−4.4
50	54.05	43.76	93.02	−4.8
60	64.93	50.50	110.6	−4.9
70	74.31	56.78	126.6	−4.5
80	82.65	62.97	141.6	−4.1
90	90.48	69.16	155.9	−3.7
100	98.03	75.15	169.9	−3.3
110	105.2	81.42	183.6	−3.0
120	112.6	88.10[a]	197.2	−3.5
130	120.0	94.85[a]	210.7	−4.1
140	127.2	101.6	224.2	−4.6
150	134.2	108.7	237.7	−5.2
160	140.9	115.8	251.1	−5.6
170	147.3	123.1	264.6	−5.8
180	153.6	130.5	278.0	−6.0
190	159.6	138.1	291.5	−6.3
200	165.6	146.0	304.9	−6.7
210	171.6	154.0	318.4	−7.1
220	177.5	162.3	~339	−1.0
230	183.4	170.6	~484	+130.0
240	189.3	179.1	~428	+60.0
250	195.2	187.7	~383	0.0
260	201.0	196.3	386.3	−11.0
270	206.7	205.0	399.5	−12.2
280	212.3	213.7	412.1	−13.9
290	217.8	222.5	423.7	−16.6
300	223.3	231.4	433.9	−20.8

[a] These values are interpolated from the "normal" heat capacity of pyrene, which has a transition in this region.

cooled to below 150 K. It therefore seems probable that when Prout *et al.* determined the structure of the complex at 178 K after cooling their specimen to a temperature not below 171 K, they were still investigating the structure of the high-temperature form. From run 3 in which the transition was most in evidence in our work, the entropy gain when the low-temperature form passed into the high-temperature form was ~ Rln 3, which is compatible with the molecules of one of the components, most probably pyrene,

TABLE IV

Thermodynamic functions of 1,2,4,5-tetracyanobenzene (TCNB), and of its 1 : 1 complex with pyrene. The values of $S - S(0)$ and $H - H(0)$ for the complex from 250 K onwards are based on estimates of 9.2 KJ^{-1} mol^{-1} and 2150 J mol^{-1} for the entropy gain and enthalpy gain, respectively, during the transition

	TCNB			Complex		
T/K	$(S - S(0))$ / JK^{-1} mol^{-1}	$(H - H(0))$ / J mol^{-1}	$[-(G - H(0))/T]$ / JK^{-1} mol^{-1}	$(S - S(0))$ / JK^{-1} mol^{-1}	$(H - H(0))$ / J mol^{-1}	$[-(G - H(0))/T]$ / JK^{-1} mol^{-1}
5	0.07	0.3	0.02	0.17	0.7	0.04
10	0.62	4.8	0.15	1.39	10.4	0.35
15	2.42	27.8	0.56	4.69	52.7	1.18
20	5.41	80.6	1.38	10.3	151.0	2.71
25	9.20	166.0	2.55	17.4	312.0	4.92
30	13.6	286.0	4.0	25.5	536.0	7.67
35	18.4	442.0	5.72	34.3	820.0	10.8
40	23.4	632.0	7.61	43.3	1160.0	14.3
45	28.7	856.0	9.66	52.6	1550.0	18.1
50	34.1	1110.0	11.8	61.9	2000.0	22.0
60	44.9	1710.0	16.4	80.4	3020.0	30.2
70	55.6	2410.0	21.3	98.7	4200.0	38.7
80	66.1	3190.0	26.2	116.6	5540.0	47.3

90	76.3	4060.0	31.2	134.1	7030.0	56.0
100	86.2	5000.0	36.2	151.3	8660.0	64.6
110	95.9	6020.0	41.2	168.1	10430.0	73.3
120	105.4	7100.0	46.2	184 6	12330.0	81.9
130	114.7	8270.0	51.1	201.0	14370.0	90.4
140	123.8	9500.0	56.0	217.1	16550.0	98.9
150	132.9	10810.0	60.8	233.0	18860.0	107.3
160	141.7	12190.0	65.6	248.8	21300.0	115.6
170	150.5	13630.0	70.3	264.4	23880.0	123.9
180	159.1	15130.0	75.0	279.9	26590.0	132.2
190	167.5	16700.0	79.6	295.3	29440.0	140.4
200	175.9	18320.0	84.2	310.6	32420.0	148.5
210	184.1	20010.0	88.8	325.8	35540.0	156.6
220	192.2	21760.0	93.3	340.9	38790.0	164.6
230	200.2	23560.0	97.8			
240	208.2	25420.0	102.2		Transition region	
250	216.0	27350.0	106.6	395.1	51510.0	189.1
260	223.8	29330.0	111.0	410.0	55310.0	197.3
270	231.5	31370.0	115.3	424.8	59240.0	205.4
280	239.1	33460.0	119.6	439.6	63300.0	213.5
290	246.6	35610.0	123.8	454.3	67480.0	221.6
300	254.1	37820.0	128.1	468.8	71770.0	229.6
298.15	252.7	37400.0	127.3	466.1	70960.0	228.1

having ordered orientations below the transition, while being disordered between at least two orientations above it. Prout *et al.* considered that dynamic disorder of the pyrene molecules (i.e. in-plane librations of large amplitude) is more probable than disorder of the molecules between two equilibrium orientations. Our result for ΔS_t does not, of course, necessarily dispose of the first possibility in favour of the second, since other factors such as a volume change might make an appreciable contribution to ΔS_t. Clark *et al.*[6] have recently suggested that at the transitions in certain organic solids with large entropy increases which lead to so-called plastic crystals, the configurational entropy gain often does not make the major contribution to ΔS_t. The thermodynamic evidence, however, emphasizes the desirability of carrying out further structural work on the complex.

The sign and magnitude of the ΔC_p values merit brief comment. Since the charge-transfer interaction in the complex supplements the other forms of intermolecular attraction, it may be that $(C_p - C_v)$ for the complex is less than the combined $(C_p - C_v)$ values at the same temperature of the separate components. This could account for part, but almost certainly by no means all, of the negative ΔC_p values at higher temperatures, but in view of the trend in $(C_p - C_v)$ as $T \rightarrow 0$, it is highly unlikely that below about 50 K such $(C_p - C_v)$ differences have any significant effect on ΔC_p. It is interesting that ΔC_p attains such considerable negative values at such low temperatures. It will be noted from Table III that below ~ 30 K, C_p for pyrene is larger than C_p for TCNB, but that above 30 K the reverse is true, and that for about 200 K C_p (TCNB) is considerably greater than C_p (pyrene) even though the TCNB molecule has fewer degrees of freedom. It is not until room temperature has almost been reached that the magnitude of the two heat capacities is reversed. It is possible, therefore, that the librational modes of the molecules in pure pyrene have lower frequencies than the corresponding modes of motion for the TCNB molecules (with their polar bonds) in pure TCNB, and that this is responsible for the larger heat capacity of pyrene at the lowest temperatures. In the complex, due to the enhanced intermolecular attraction, these torsional oscillation frequencies may rise. This could lead to a negative ΔC_p. In the long temperature range when C_p (TCNB) > C_p (pyrene), an important contribution to C_p (TCNB) may come from intramolecular bending modes, the frequencies of which may also be increased in the complex, an effect which would likewise produce a negative ΔC_p. Comparative spectroscopic and inelastic neutron scattering studies of the complex and of the pure crystalline components might be informative.

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