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Thermodynamic Studies of Orientational Disorder in π-Molecular Compounds

III. Heat Capacities of Naphthalene-Pyromellitic Dianhydride and Pyrene-Pyromellitic Dianhydride†

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The heat capacities and thermodynamic functions from 5 to 300 K for naphthalene-pyromellitic dianhydride (N-PMDA) and pyrene-pyromellitic dianhydride (P-PMDA) are reported. From the featureless heat-capacity curve of N-PMDA, it has been concluded that the naphthalene moieties executed anharmonic librations in a thermodynamically-ordered crystal and not reorientational motion in a disordered crystal. Two minor anomalies have been observed in the heat capacity of P-PMDA. A small peak near 155 K may arise from the disordering of the PMDA molecules while an irreproducible transition observed near 250 K has been tentatively ascribed to a disordering motion of the pyrene molecules. The agreement of the P-PMDA heat capacity results of this study with previously-published data is discussed.

INTRODUCTION

This paper is the third in a series of investigations of the heat capacities of π-molecular compounds. Previous studies from this laboratory have reported on the heat capacities of naphthalene-tetracyanobenzene[1] (N-TCNB) and naphthalene-tetracyanoethylene[2] (N-TCNE). The thermophysical measurements on these compounds have been used to characterize the nature of the molecular motion observed by n.m.r.[3,4] techniques.

The compounds of interest here, naphthalene-pyromellitic dianhydride (N-PMDA) and pyrene-pyromellitic dianhydride (P-PMDA), have also

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been studied by n.m.r. solid-state methods.[3–5] Like N-TCNE, motion of naphthalene molecules was detected at 77 K in N-PMDA but its nature was unclear. Reorientations between two distinguishable sites or large-amplitude librations about a single site were the possibilities proposed for the motion. Heat-capacity measurements have been performed on N-PMDA to resolve this uncertainty. According to the authors of the n.m.r. studies[4,5] P-PMDA is rigid (on an n.m.r. timescale, at least) to about 250 K. At this temperature, the pyrene and perhaps the PMDA molecules begin to execute in-plane reorientations. Although the heat capacity of P-PMDA has been reported previously,[6] the results of that study were not in good agreement with the conclusions drawn from a well-known X-ray diffraction study of this compound.[7] Since P-PMDA is one of the few π-molecular compounds known to show orientational disorder in both compounds, it was deemed worthwhile to re-measure the heat capacity of this compound, but on a new sample.

EXPERIMENTAL

Sample preparation and characterization

The samples were prepared for us by Professor C. A. Fyfe of the University of Guelph, Guelph, Ontario, Canada, by the same methods of sample preparation used in the n.m.r. studies.[3,5] N-PMDA was crystallized as yellow needles from glacial acetic acid and P-PMDA as red-orange needles from methyl ethyl ketone. The results of elemental analyses of the samples by Spang Microanalytical Laboratory, Eagle Harbor, MI are given in Table I.

TABLE I

Analysis of samples[a] and calorimeter loading data

	wt. % C		wt. % H		wt. % 0	
Sample	Expl.	Theo.	Expl.	Theo.	Expl.	Theo.
N-PMDA	69.28	69.37	2.86	2.91	27.86	27.72
P-PMDA	74.42	74.29	3.06	2.88	22.49	22.83

		M[b]	m (vacuo)	ρ	Helium mass $\times 10^4$
Sample	Calorimeter	g mol^{-1}	g	g cm^{-3}	g
N-PMDA	W-52	346.30	35.83481[c]	1.45	3.67
P-PMDA	W-54	420.38	58.01265	1.47	2.09

[a] Spang Microanalytical Laboratories, Eagle Harbor, Michigan.
[b] Based on 1975 IUPAC table of atomic weights.
[c] Corrected for presence of solvent, see text.

Calorimetric methods

The heat-capacity measurements were performed in the Mark II adiabatic cryostat described elsewhere.[8] Approximately 35.8 g of N-PMDA were loaded into a gold-plated copper calorimeter (laboratory designation W–52) while a similar calorimeter (designation W–54) was used with 58.0 g of P-PMDA. Both calorimeters were of the gold-gasket screw-closure type. The calorimeters were evacuated quickly and small amounts of high-purity helium gas were added to ensure good thermal contact and rapid equilibration. The sealed calorimeters were loaded into the cryostat, heated to about 310 K, and then cooled. Temperatures were measured with a platinum-resistance, capsule-type thermometer (laboratory designation A–5) inserted into a central well in the calorimeters. 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 capacities of the empty calorimeters, determined in separate sets of experiments, represented between 10 and 40 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 correct 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

Naphthalene-pyromellitic dianhydride

The results of the heat-capacity measurements on N-PMDA are listed in Table II and are given for one mole of π-molecular compound which is taken to be one mole of naphthalene and one mole of PMDA molecules. They are reported in chronological order so that, within a series, the temperature increment of a measurement can usually be inferred from the temperature differences between adjacent determinations. The heat-capacity curve obtained from these measurements is shown in Figure 1. In the region from 285 to 288 K, as indicated by the dashed line in Figure 1, a very small anomaly was observed and has been attributed to the fusion of a minute amount of acetic acid. The experimental points at these temperatures have been omitted from the curve and the dashed line was obtained by the interpolation of the data above and below this region. From the reported value

TABLE II

Experimental heat capacity of N-PMDA (1 cal = 4.184 J)

T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}
Series I		123.17	42.50	253.88	79.52	8.02	0.681
58.88	24.51[a]	132.82	45.02	263.45	82.63	8.97	0.952
61.66	25.17	142.26	47.49	273.13	85.73	9.99	1.310
66.04	26.67	151.86	50.03	282.80	89.51[b]	11.09	1.690
71.75	28.44	161.55	52.60	292.34	91.98	12.22	2.178
77.49	30.19	171.12	55.22	298.92	94.13	13.361	2.709
		180.60	57.81			14.65	3.375
Series II				*Series VI*		16.16	4.143
53.65	22.24	*Series IV*		267.92	83.96	17.75	5.008
58.81	24.15	170.02	54.92	272.50	85.46	19.40	5.920
64.22	26.06	179.41	57.48	276.11	86.70	21.27	6.984
70.14	27.95	189.10	60.18	279.69	87.88[b]	23.39	8.171
76.42	29.86	198.90	62.96	283.22	89.34[b]	25.55	9.353
83.20	31.98	208.72	65.78	286.72	91.26[b]	28.36	10.87
91.06	34.22	218.54	68.73	290.18	91.23	31.79	12.67
99.66	36.40	228.33	71.66	293.62	92.34	35.09	14.33
108.55	38.70	238.09	74.63			38.39	15.88
118.00	41.17	247.84	77.62	*Series VII*		41.58	17.29
				4.89	0.136	45.39	18.93
Series III		*Series V*		5.58	0.224	50.32	20.95
103.88	37.48	234.83	73.60	6.35	0.331	55.85	23.05
113.37	39.94	244.35	76.53	7.16	0.485	61.35	25.05

[a] This point was excluded from final fit.
[b] See text.

of ΔH^0 (fusion) of acetic acid[9] and the excess enthalpy under the peak, it was estimated that the sample contained about 0.01 g of acetic acid which was less than 0.03 mass per cent of the total sample. Heat-capacity corrections for this small amount of acetic acid were negligible except in the fusion region.

The experimental results of Table II have been fitted to a series of orthogonal polynomials from which the thermodynamic functions have been generated. These functions have been tabulated at even temperatures in Table III. The $[H^0\ (5\ K)-H^0\ (0\ K)]$ and $[S^0\ (5\ K)-S^0\ (0\ K)]$ increments were obtained assuming Debye-T^3 behavior.

Pyrene-pyromellitic dianhydride

In Table IV are listed the experimental results of our heat-capacity determinations on P-PMDA. The thermodynamic functions generated by the computer-fitting of these data are summarized in Table V. The heat-capacity curve

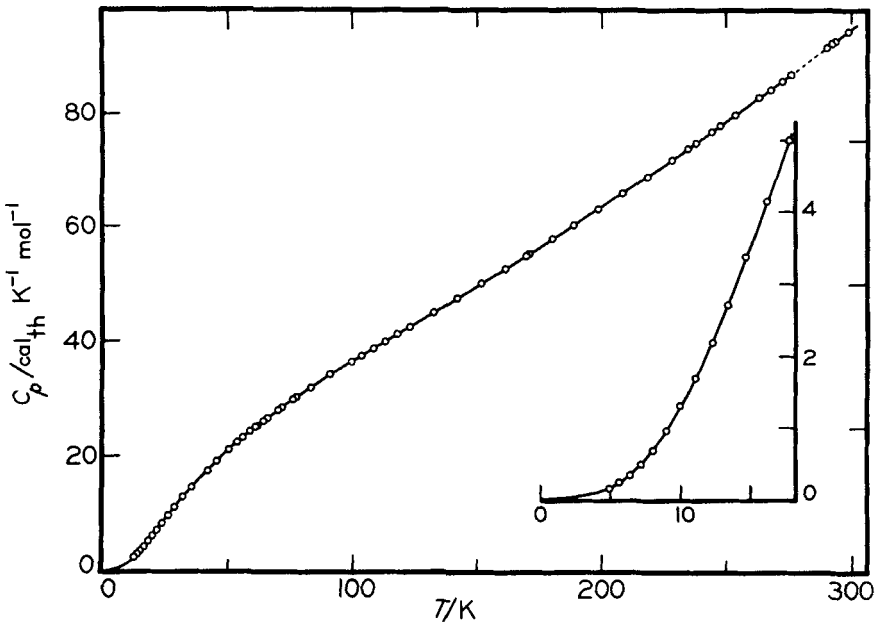

FIGURE 1 Experimental heat capacity of N-PMDA. The dashed line indicates the region in which the melting of acetic acid was observed.

showing the experimental points is given in Figure 2. Our results are in qualitative agreement with those reported earlier by Dunn *et al.*;[6] a plot of the deviation of their data from our smoothed curve is shown in Figure 3. In this figure, ΔC_p is defined as C_p (Reference 6)–C_p (this study), and the circles represent the deviations of their experimental points while the triangles mark the deviation of their smoothed heat-capacity curve from ours. The details of the enthalpy determinations made in the region of excess heat capacity from 125 K to 160 K are shown in Table VI.

DISCUSSION OF THE EXPERIMENTAL RESULTS

Naphthalene-pyromellitic dianhydride

At the time the heat-capacity study of N-PMDA was performed, no detailed X-ray diffraction results were available for this compound. A preliminary structural study had been reported by Boeyens and Herbstein,[10] who showed the possible space groups of the crystal to be C2, Cm, or C2/m. These authors concluded that of the three possibilities, the most probable

TABLE III

Thermodynamic functions of N-PMDA[a] (1 cal = 4.184 J)

T / K	C_p / cal K^{-1} mol^{-1}	$\{S^0(T) - S^0(0)\}$ / cal K^{-1} mol^{-1}	$\{H^0(T) - H^0(0)\}$ / cal mol^{-1}	$-\{G^0(T) - H^0(0)\}/T$ / cal K^{-1} mol^{-1}
5	0.151	0.053	0.200	0.013
10	1.292	0.435	3.271	0.108
15	3.536	1.355	14.998	0.355
20	6.263	2.741	39.409	0.770
25	9.059	4.440	77.75	1.330
30	11.746	6.332	129.82	2.004
35	14.262	8.334	194.92	2.764
40	16.60	10.393	272.15	3.589
45	18.79	12.476	360.69	4.461
50	20.83	14.562	459.78	5.366
60	24.57	18.70	687.1	7.245
70	27.91	22.74	949.8	9.171
80	30.95	26.67	1244.4	11.114
90	33.77	30.48	1568.1	13.055
100	36.47	34.18	1919.4	14.983
110	39.09	37.78	2297.3	16.89
120	41.67	41.29	2701.1	18.78
130	44.28	44.73	3130.9	20.64
140	46.90	48.10	3586.7	22.48
150	49.54	51.43	4068.9	24.30
160	52.20	54.71	4577.6	26.10
170	54.90	57.96	5113	27.88
180	57.64	61.17	5676	29.64
190	60.44	64.36	6266	31.38
200	63.28	67.54	6885	33.11
210	66.18	70.69	7532	34.83
220	69.13	73.84	8208	36.53
230	72.14	76.98	8915	38.22
240	75.20	80.11	9651	39.90
250	78.31	83.25	10419	41.57
260	81.47	86.38	11218	43.23
270	84.68	89.51	12049	44.89
273.15	85.70	90.50	12317	45.41
280	87.93	92.65	12912	46.54
290	91.19	95.80	13807	48.18
298.15	93.86	98.36	14561	49.52
300	94.46	98.94	14736	49.82

[a] One mole of compound is taken to be one mole of naphthalene molecules and one mole of PMDA molecules.

TABLE IV

Experimental heat capacity of P-PMDA (1 cal = 4.184 J)

T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}	T / K	C_p / cal K^{-1} mol^{-1}
Series I		181.68	65.87	88.65	36.62	61.85	27.22
253.44	90.58	186.84	67.78	93.71	38.17		
260.85	93.36			98.82	39.75	*Series XI*	
268.62	96.03	*Series V*		103.98	41.40	121.03	46.99
		122.93	47.56	109.26	43.07	ΔH Detn. C	
Series II		127.69	49.14	114.59	44.79		
275.12	98.28	132.70	50.86	119.68	46.49	*Series XII*	
282.28	100.9	137.93	52.68	123.65	47.82	252.69	90.65[a]
289.95	103.7	142.16	54.25	ΔH Detn. B		257.77	92.71[a]
297.97	106.6	144.85	55.28	153.71	62.57	263.18	94.88[a]
306.04	109.6	147.07	56.21	154.31	64.08	268.96	96.30
313.93	112.4	148.51	56.91	154.92	64.89	275.14	98.47
321.68	115.2	149.30	57.34	155.55	61.08	281.70	100.96
329.28	118.1	150.19	47.86	159.79	59.05	288.35	103.3
		151.17	58.41			294.90	105.6
Series III		152.30	59.32	*Series IX*			
181.66	65.85	153.50	61.78	179.15	64.96	*Series XIII*	
185.62	67.11	154.72	64.33	182.99	66.25	243.68	87.36
191.12	68.95	155.98	59.77	185.83	67.21	251.10	90.03
197.24	71.01	157.22	58.45	189.56	68.40	258.58	93.28
203.94	73.23	158.53	58.54			266.17	95.34
211.29	75.76	159.87	58.81	*Series X*		273.94	97.90
218.76	78.39	161.44	59.26	5.83	0.422	282.29	101.0
226.30	81.02	163.46	59.90	6.71	0.627	291.03	104.2
233.85	83.63			7.66	0.904		
241.46	86.38	*Series VI*		8.62	1.275	*Series XIV*	
249.15	89.22	122.94	47.59	9.64	1.713	202.13	72.70
256.45	91.74	ΔH Detn. A		10.75	2.251	208.48	74.86
267.38	95.74	171.95	62.62	12.01	2.882	215.84	77.49
275.83	98.66			13.45	3.671	223.49	80.11
284.09	101.7	*Series VI*		14.96	4.586	231.17	82.79
291.58	104.2	52.74	23.67	16.63	5.554	239.02	85.56
		57.02	25.35	18.56	6.757	247.03	88.50
Series IV		61.68	27.17	20.55	7.942	253.35	90.70
133.22	51.00	66.36	28.92	22.89	9.328	258.51	93.33
136.80	52.25	71.16	30.54	25.81	11.01	261.25	93.76
141.62	54.02	76.19	32.26	28.87	12.66	262.33	94.00
146.59	56.00	81.45	34.15	31.75	14.21	263.47	94.38
151.68	59.30	86.77	36.02	34.88	15.79	264.99	94.91
156.63	60.16	92.01	37.67	38.56	17.55	269.21	96.30
161.62	59.36			42.58	19.37		
166.63	60.90	*Series VIII*		46.96	21.29		
171.54	62.54	79.07	33.32	51.71	23.26		
176.67	64.12	83.81	34.99	56.82	25.24		

[a] Experimental points with excess heat capacity. See text.

TABLE V

Thermodynamic functions of P-PMDA (1 cal = 4.184 J)

T / K	C_p / cal K^{-1} mol^{-1}	$\{S^0(T) - S^0(0)\}$ / cal K^{-1} mol^{-1}	$\{H^0(T) - H^0(0)\}$ / cal mol^{-1}	$-\{G^0(T) - H^0(0)\}/T$ / cal K^{-1} mol^{-1}
5	0.265	0.050	0.187	0.012
10	1.875	0.635	4.861	0.149
15	4.598	1.887	20.76	0.503
20	7.617	3.626	51.34	1.059
25	10.54	5.642	96.78	1.770
30	13.29	7.809	156.4	2.595
35	15.84	10.05	229.3	3.499
40	18.22	12.32	314.6	4.460
45	20.44	14.60	411.3	5.460
50	22.55	16.86	518.8	6.487
60	26.51	21.33	764.4	8.590
70	30.14	25.69	1048	10.72
80	33.63	29.94	1367	12.85
90	37.05	34.10	1721	14.98
100	40.12	38.16	2107	17.09
110	43.33	42.14	2523	19.20
120	46.59	46.05	2973	21.28
130	49.94	49.91	3455	23.40
140	53.41	53.74	3972	25.37
150	57.71	57.56	4526	27.39
160	58.84	61.42	5124	29.40
170	61.97	65.08	5728	31.39
180	65.25	68.71	6364	33.36
190	68.58	72.33	7033	35.31
200	71.93	75.93	7736	37.26
210	75.35	79.53	8472	39.18
220	78.83	83.11	9243	41.10
230	82.32	86.69	10050	43.00
240	85.84	90.27	10890	44.90
250	89.41	93.85	11770	46.78
260	93.02	97.42	12680	48.66
270	96.58	101.00	13630	50.53
280	100.1	104.6	14610	52.40
290	103.8	108.15	15630	54.26
300	107.4	111.7	16685	56.12
273.15	97.70	102.1	13930	51.12
298.15	106.7	111.1	16490	55.78

space group was C2/m, the only centrosymmetric one. Their results indicated that like other compounds of this type, the N-PMDA structure consisted of mixed stacks of alternating donor and acceptor molecules with the stack axes along the 001 direction in the crystal.

In a later publication,[11] Herbstein, on the basis of the poor diffraction photographs obtained from the N-PMDA crystals, suggested that the

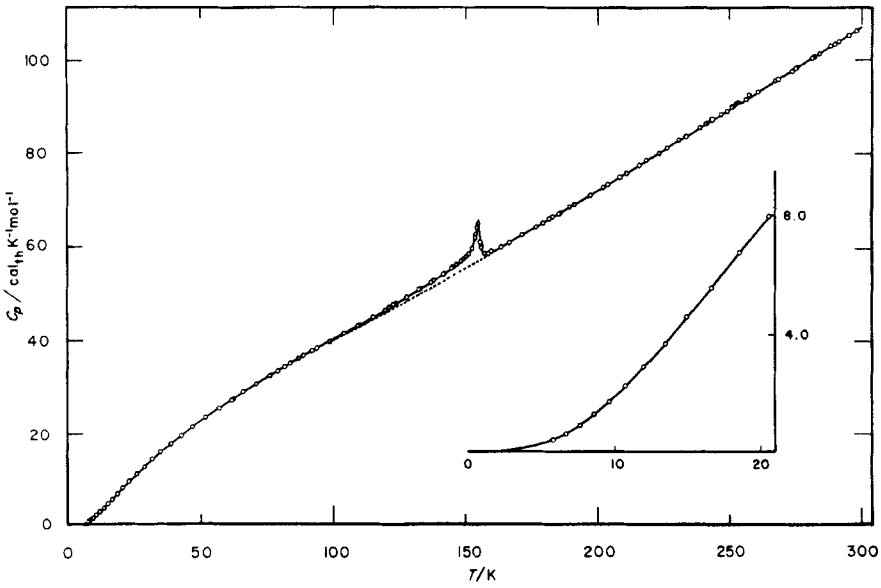

FIGURE 2 Experimental heat-capacity of P-PMDA.

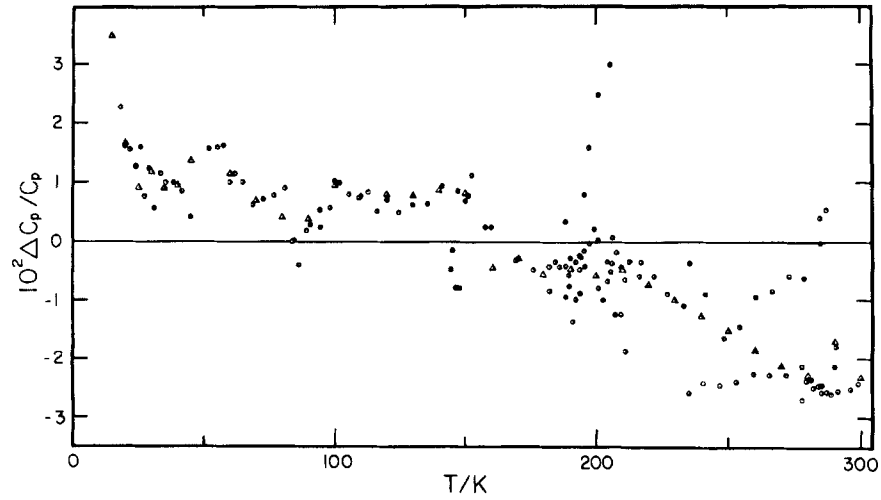

FIGURE 3 Deviation plot of the previously-published heat-capacity data for P-PMDA from the smooth curve obtained in this research. ○ indicates deviations of experimental points; Δ are deviations of the smooth curve from that obtained in this research.

TABLE VI

Enthalpy and entropy of transition of P-PMDA (1 cal = 4.184 J)

Designation	T_1 / K	T_2 / K	$\{H°(T_2) - H°(T_1)\}$ / cal mol^{-1}	$\{H°(165\ K) - H°(80\ K)\}$ / cal mol^{-1}	$\{S°(165\ K) - S°(80\ K)\}$ / cal K^{-1} mol^{-1}
Series IV	132.08	164.15	1810.3	4054.9	—
Series V	125.23	164.57	2175.9	4056.5	—
ΔH_t Detn. A	125.57	168.47	2397.5	4057.1	—
Series VIII	125.16	163.71	2128.6	4057.4	—
ΔH_t Detn. C	124.52	166.91	2354.4	4058.9	—
			Mean value	4057.0 ± 4	
			Numerical integration	4055.6 ± 1	15.27 ± 0.02
			Lattice integration	4004.5 ± 1	14.95 ± 0.02
			ΔH_t =	51.0 ± 5	ΔS_t = 0.32 ± 0.04

crystal was disordered with the occupation of the different naphthalene positions being virtually random at 298 K.

The work of Fyfe[3,4] using various n.m.r. techniques showed that the disorder, if present in N-PMDA, was dynamic rather than static. Both the second moment of the n.m.r. spectrum,[3] $(\Delta H)^2$, and the T_1 and $T_{1\rho}$ spin-lattice relaxation times[4] of N-PMDA showed a temperature dependence indicative of motion. The $(\Delta H)^2$ began to decrease near 200 K and levelled off around 300 K. The lack of a complete structural analysis prevented a rigid-lattice second moment calculation, but the low $(\Delta H)^2$ value found at 77 K suggested that some additional, low-energy motion was present at this temperature. Analysis of the temperature dependence of the spin-lattice relaxation times yielded a value of 9.8 kcal mol^{-1} for the activation energy of the high-temperature motional process. Whether a second, lower energy motion existed could not be determined. The conclusions drawn from these two studies were that at high temperatures the naphthalene molecules underwent a complete in-plane reorientation and that some motion persisted at low temperatures.

Herbstein's conclusion that disorder was present in the crystal,[11] and the n.m.r. studies[3,4] indicating that motion was still occurred in the crystal at 77 K, would lead one to expect an ordering transition somewhere below 77 K. However, it is evident from Figure 1 that no transition is observed in this compound except for the fusion of the acetic acid impurity. While the possibility that a phase transition had been undercooled cannot be completely eliminated on the basis of the heat-capacity measurements, the lack of a transition most strongly indicated that the low-temperature motion should be interpreted as arising from large amplitude librations about the normal to the molecular plane and not from a reorientational motion between distinct sites in the lattice.

This interpretation is supported by the results of a recent Raman spectroscopic study[12] and a complete X-ray diffraction study on N-PMDA by Le Bars-Combe *et al.*[13] which appeared in the literature after the completion of our measurements. The lack of an abrupt change of the low-frequency Raman spectral parameters of N-PMDA with temperature led Macfarlane and Ushioda[12] to conclude that librational motion of ordered naphthalene molecules was responsible for the narrowing of the n.m.r. linewidth at low temperatures.

Le Bars-Combe *et al.* noted in their diffraction study[13] that two forms of N-PMDA could be prepared. Yellow-colored crystals are synthesized by slow cooling of a hot solution of the components in a mixture of petroleum ether and methyl ethyl ketone. These crystals were ordered and formed in the C2/m space group proposed by Boeyens and Herbstein.[10] However, orange-colored crystals prepared in a Bridgman furnace were found to be

disordered at room temperature and to have the space group, $P2_1/c$. In the disordered crystal, unequal occupation of two naphthalene orientations which differ by a 40° in-plane rotation occurs. A reversible transition at 183 K was observed in the differential thermal analysis trace of the orange crystals; it is believed to arise from an order-disorder transition.

The Raman,[12] X-ray diffraction,[10] n.m.r.[3,4] and heat-capacity studies have all been performed on the yellow form of N-PMDA. Therefore, our concern about undercooling a transition in the heat-capacity measurements can now be eliminated. Clearly the N-PMDA compound is ordered and the motion observed at low temperatures is librational only.

Pyrene-pyromellitic dianhydride

A small but reproducible anomaly was observed in the heat capacity of P-PMDA near 155 K. The location and appearance of this peak are in good agreement with previously published results.[6] However, the excess heat capacity reported near 280 K in this earlier study was not found. Instead a region with a slight excess heat capacity was observed near 250 K. We did experience, however, the same difficulty in reproducing this second transition which was reported in the earlier study.[6]

The thermal history of this compound appears to affect the extent to which this transition occurs. Three sets of measurements (Table IV, Series I–III) were made in this region in which the sample was not allowed to cool below the 155 K transition. In these measurements, a smooth curve was obtained and no evidence for a phase transition was observed. However, in the three sets of measurements (Table IV, Series XII–XIV) in which the sample was cooled to at least 50 K and then warmed through the 155 K transition, several of the runs gave a slightly higher heat capacity than the smooth curve defined from the earlier measurements. (These runs are marked with a superscript, *b*, in Table IV.) The remainder of the points in Series XII–XIV fit very well on the original curve.

The irreproducibility of this high-temperature transition is in direct contrast with the observed for the transition at 155 K. The results of the enthalpy determinations made over the region from 125 to 160 K are given in Table V and the agreement among them is quite good. There did not appear to be a significant correlation of the observed enthalpy with the cooling procedures used prior to the measurements.

The lattice heat capacity was estimated by interpolating the experimental heat capacity curves from above and below the transition region. The resultant curve, shown as the dashed line in Figure 2, was found to approximately parallel the heat-capacity of N-PMDA in this region. The results of numerical integration of the lattice heat-capacity curve were used to determine the

enthalpy and entropy of transition, ΔH_t and ΔS_t, respectively, as detailed in Table V. A value of 53 cal mol^{-1} was obtained for ΔH_t while ΔS_t was found to be 0.32 cal K^{-1} mol^{-1}. The earlier data[6] have not been evaluated in this manner and no direct comparisons can be made for the enthalpy and entropy of transition.

The comparison of the two heat-capacity curves shown by the deviation plot in Figure 3 illustrates that below the transition at 155 K, the data of Dunn *et al.*[6] lie above our smooth curve, while at temperatures greater than 155 K, where the two curves intersect, our data are higher. The few points with positive deviation at 300 K arise from the fusion of a small amount of acetic anhydride in their sample.

Because it is difficult to prepare these compounds without either altering the sample composition from exact stoichiometry, or retaining solvent, it is possible that differences in sample composition may be responsible for the heat-capacity deviations. The abrupt change in the sign of the deviation near the transition at 155 K suggests, however, that sample composition is not the only explanation; otherwise, one might expect to see a consistent, or at least only a gradual, change in the deviation. Possibly a difference in the degree of transformation to the intermediate phase between the two sets of measurements exists. If the original sample had been transformed to a greater extent than ours, it might be expected that our heat capacity would be higher since it would contain a larger proportion of the high-temperature phase.

Neither our results nor those of Dunn *et al.*[6] can be easily reconciled with the conclusions drawn from a temperature dependent X-ray diffraction study of Herbstein and Snyman.[7] From the behaviour of a series of oscillation photographs taken during the cooling of P-PMDA crystals, these authors concluded that a transformation took place between 170 and 200 K. Detailed analysis of the diffraction patterns at 300 K and 110 K revealed that the phase change was an order-disorder transition involving both the pyrene and the PMDA molecules. In the ordered $P2_1/n$ structure, two independent pyrene molecules, differing in position by a 12° in-plane rotation, are observed; the PMDA molecules all have the same orientation, but alternate molecules have their centers displaced in opposite directions from the $\frac{1}{4}$ and $\frac{3}{4}$ special positions on the c axis. In the disordered $P2_1/a$ form, the pyrene molecules can occupy randomly either of the two allowed positions. It appears that the PMDA molecules are also randomly distributed over two orientations separated by an in-plane rotation of about 12°. Hence, the anomaly in the heat capacity would be expected between 170 and 200 K. Our heat-capacity measurements show a transition region between 125 and 160 K with a maximum at 155 K. The X-ray transformation temperatures were obtained from the behavior of the crystal on cooling, which does not always accurately

reproduce the equilibrium transformation temperature, *i.e.*, the temperature of a heat-capacity anomaly. The effect of such hysteresis usually results in undercooling, so that the transition appears to take place at a temperature lower than that indicated by the heat-capacity measurements. This suggests that the transition observed in the heat-capacity measurements near 250 K may be responsible for the variation of the spot intensity seen in the diffraction photographs. In fact, the heat-capacity measurements indicate that the transition is easily undercooled.

Because many π-molecular compounds are known in which only one component is disordered, it seems possible that when disorder involves both components, the ordering transition for one component may take place independently of the other. Therefore, in such a compound the two transitions may be observed in very different temperature regions, as was observed in the heat capacity of P-PMDA. Since a transition has been observed near 240 K in P-TCNB,[14,15] where disorder, if it exists, involves only the pyrene molecules it is tempting to assign the high-temperature transition in P-PMDA to the ordering process of pyrene molecules. Another piece of evidence linking this transition to the pyrene moiety is the irreproducibility observed in both the high-temperature P-PMDA and the P-TCNB transitions.[14] Hence, the well-behaved transition near 155 K may arise from the ordering of the PMDA molecules.

Objection can be made to this tentative explanation of the two anomalies observed in the heat capacity on the grounds that a transition involving the disorder of the pyrene molecules should have greater thermodynamic consequences than are evident from the heat-capacity curve near 250 K. However, there is no evidence that the heat-capacity measurements reflect the thermodynamic consequences of *fully*-disordered pyrene molecules. The poor reproducibility of the transition indicates difficulty in transforming the sample to the low-temperature phase, and hence, the small excess heat capacity may indicate that the sample has never been transformed to a completely-ordered state. Second, it has been proposed[6,14] that if an order-disorder transition in a π-molecular compound is very gradual, which appears to be so for both transitions in P-PMDA, the effects of the transition may be obscured by the large lattice heat capacity. Of the four compounds we have studied, P-PMDA has the largest lattice heat capacity, since it has the greatest number of intramolecular vibrations. Therefore, it would be the most likely compound in which loss of the effects of disorder in the background heat capacity might be suspected.

The interpretation given by Dunn *et al.*[6] also suggests that two disordering processes take place. These authors concluded, however, that one component was completely disordered and the other partially so by 160 K. The disorder was claimed to begin at very low temperatures

These conclusions were reached using an approach proposed in the heat-capacity study of P-TCNB[14] in which a quantity called ΔC_p is defined as

$$\Delta C_p = C_p\,(\text{compound}) - \{C_p\,(\text{donor}) + C_p\,(\text{acceptor})\}.$$

It is assumed that when only normal lattice and intramolecular vibrations contribute to the heat capacity of the molecular compound, ΔC_p, referred to as ΔC_p (normal), will be negative, and hence that a positive ΔC_p is an indication of configurational or orientational contributions to the heat capacity of the molecular compound. A configurational entropy term could then be extracted from the appropriate integration of the ΔC_p in excess of some estimated ΔC_p(normal). The observed temperature dependence of the corresponding entropy term, designated ΔS, was the basis of the conclusions proposed by these authors.

This approximation has been investigated in detail.[16] The validity of its premises have been considered by looking at the contributions to ΔC_p arising from lattice and intramolecular vibrations and $(C_p - C_v)$ terms. In order for this method to give an accurate picture of the presence of orientational disorder, ΔC_p, when corrected for the effects of complexation on the pure components by using ΔC_p (normal), must contain only a contribution from configurational effects. This is tantamount to asserting (1) that the identities of intramolecular vibrations of components are retained in the complex or perhaps shifted slightly to higher frequencies, (2) that the phonon spectrum of the complex is a superposition of those of the pure components and (3) that $(C_p - C_v)$ for the complex is equal to or less than the sum of these terms for the pure components. Comparative vibrational studies of these compounds show that assertion 1 is probably true over the temperature region of interest. Inspection[16] of the available spectroscopic data on low-frequency vibrations shows that assertion 2, whose effects will be important at low temperatures, is not valid. The contribution to ΔC_p (compound) from differences in the number of molecules per unit cell in complex and component cause differences in the density of lattice vibrational states and intra-charge-transfer modes which are unparalleled in the pure components and cannot be eliminated by estimation of ΔC_p (normal). These effects, in fact, make suspect the claim that ΔC_p (normal) would be expected to be negative. Calculation[16] of the $(C_p - C_v)$ terms from the available volume-expansion and compressibility data suggest that $(C_p - C_v)$ for the complex will be less than the sum of pure component contributions but exceptions may occur for complexes having a large molar volume or thermal coefficient of expansion or a small isothermal compressibility. That in no temperature region are all three assertions valid indicates that the interpretations of disordering processes based upon the ΔC_p approximation may not be accurate.

Experimental evidence which also suggests the inappropriateness of the ΔC_p analysis is obtained using our heat-capacity results for N-PMDA and N-TCNB.[1] These two curves are given in Figure 4; the ○ circles are for N-TCNB while the ● ones refer to N-PMDA. Since ΔC_p (N-PMDA) is positive from 5 to 300 K, the ΔC_p analysis would suggest that this compound has a high degree of orientational disorder even at low temperatures but the absolute heat-capacity, Raman,[12] and X-ray diffraction[13] results show that it is completely ordered. The appearance of ΔC_p (N-TCNB) suggests that

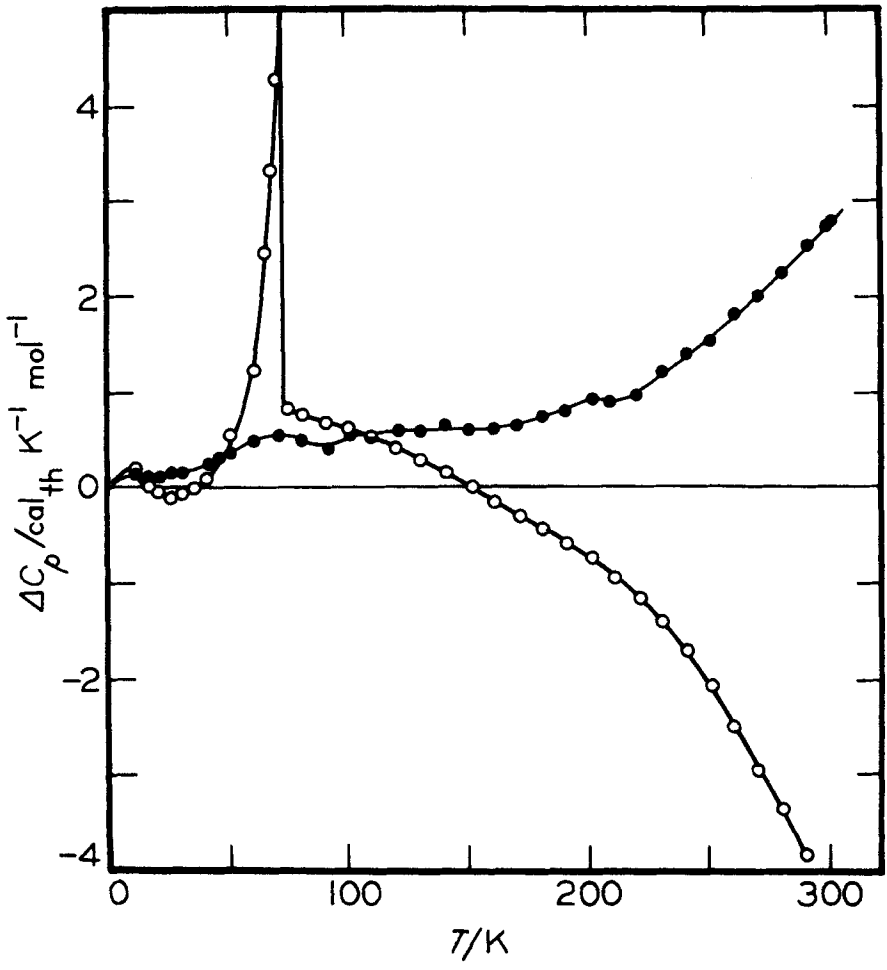

FIGURE 4 ΔC_p curves of N-PMDA and N-TCNB. ●, ΔC_p(N-PMDA); ○, ΔC_p(N-TCNB).

configurational effects remain important to about 150 K while other studies[16] indicate the order-disorder transition is completed by 80 K.

We cannot reconcile either set of heat-capacity results with the behavior of the diffraction patterns on cooling P-PMDA. A more complete X-ray diffraction study of this compound is needed for confirmation or contradiction of the above speculations.

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