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Thermodynamics of Polynuclear Aromatic Molecules: II. Low-Temperature Thermal Properties of Perylene, Coronene, and Naphthacene

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Thermodynamics of Polynuclear Aromatic Molecules

II. Low-temperature Thermal Properties of Perylene, Coronene, and Naphthacene†

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(Received February 12, 1980)

The heat capacities of crystalline coronene and naphthacene have been determined by adiabatic calorimetry from 5 to 350 K; that of perylene was likewise measured from 5 K into the liquid phase (578 K). Values at 298.15 K of the thermodynamic properties/cal_{th} K⁻¹ mol⁻¹ are:

	C_p	S_p^0	$-\{G_p^0 - H_p^0(0)\}/T$
Perylene	65.71	63.23	30.96
Coronene	74.99	67.13	31.57
Naphthacene	56.54	51.48	24.80

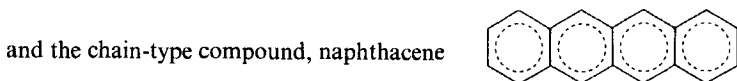
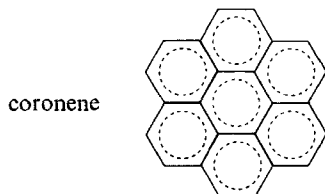
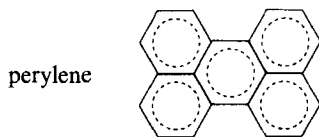
The enthalpy of fusion for perylene is 7618 cal_{th} mol⁻¹ at the triple-point temperature, 550.9 K. A rather irreproducible, broad thermal anomaly occurs in coronene near 230 K. A previously reported transition in naphthacene was not found. The trends of the entropy against the number of carbon atoms for disc-type and chain-type polynuclear aromatic compounds are discussed.

† The studies were abstracted in part from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree from the Horace H. Rackam School of Graduate Studies at the University of Michigan and initiated under a project supported by the Division of Research, U.S. Atomic Energy Commission and completed under the support of the Structural Chemistry and Chemical Thermodynamics Program, Chemistry Division, National Science Foundation under Contract No. CHE-77-10049. The preceding paper in this series is reference 1.

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1 INTRODUCTION

The previous endeavor¹ which provides basic thermal and thermochemical data on three condensed polynuclear aromatic compounds is here extended to include the disc-type compounds:



Because of the higher melting points encountered, data through fusion and into the liquid region have been obtained on only the first mentioned of these compounds. Trends in the dependence of the entropy and other properties on the size of the compounds are considered for all disc- and chain-type polynuclear aromatic hydrocarbons on which data are available.

2 EXPERIMENTAL

Purification and characterization of samples

Perylene Perylene obtained from Hi Laboratory, Inc. was recrystallized three times from a solution of benzene in glacial acetic acid and repeatedly sublimed in vacuum by the gradient method. The yellow crystals thereby obtained were transferred into a glass tube (1.2 cm inner diameter and 100 cm long) for zone-refining. The sample was heated under high vacuum for two days to absorb any air and then sealed off under 6.6 kPa of pure helium gas. After about 15 passes of a 1.5 cm molten zone moving downward at a rate of 2 cm/h, the lower 5 cm of material were discarded and the pure, transparent, colorless sample stored under vacuum in the dark. Microchemical analysis indicated the presence of 95.09 per cent C and 4.81 per cent H (theoretical: 95.21 per cent C, 4.79 per cent H). Fractional fusion studies

indicated 0.0003 mole fraction of liquid-soluble, solid-insoluble impurity and a melting temperature of 550.95 K. Previously reported melting points are the following: 546,² 534,³ 542,⁴ 547,⁵ and $(553.85 \pm 0.3 \text{ K})$.⁶

Coronene A reputedly 99 per cent pure, dark green sample, obtained from Rütgerswerke-Aktiegesellschaft was recrystallized six times from benzene solution, subjected to two sublimations in vacuum and to 15 passes of zone-melting. The purified sample thereby obtained consisted of pale yellow acicular crystals. Microchemical analyses indicated the presence of 95.96 per cent C and 4.04 per cent H (theoretical: 95.97 per cent C, 4.03 per cent H). Because of the reportedly high melting temperature (712 K)⁷ of this material, fractional fusion studies have not been attempted.

Naphthacene A commercial product from Chemical Procurement Laboratories was recrystallized from a solution of benzene in glacial acetic acid and the middle portion of the sample was sublimed four times in vacuum by the gradient method. Microchemical analysis of the orange-colored product showed 94.55 per cent C and 5.27 per cent H (theoretical: 94.70 per cent C, 5.30 per cent H). The high melting point (630 K)⁷ precluded fractional fusion studies.

Calorimetric apparatus

The Mark II and Mark III adiabatic cryostats and adjuvant techniques employed for cryogenic calorimetry (4 to 350 K) have been described,⁸ as have those for the intermediate temperature Mark IV thermostat.⁹ Automatic adiabatic shield control is used in both instruments and consists of three separate channels of recording circuitry provided with proportional, rate, and reset actions which usually maintain the thermal head between calorimeter and shield within a millidegree. Prototype calorimeters, similar to the gold-plated copper calorimeters employed in the cryogenic measurements⁸ and to the silver calorimeter for higher temperatures,⁹ have been detailed. The cryogenic determinations on perylene and naphthacene were made in the gold-plated copper calorimeter (laboratory designation W-42) which has a threaded, vacuum-tight closure with a 1.25 cm diameter aperture and an annealed gold gasket between the stainless-steel screw cap and the circular, sharp, sealing edge of monel metal. Cryogenic measurements on coronene were made in a 1.2 cm diameter calorimeter of similar design with respect to the entrant thermometer-heater well, etc., but of only 4 cm³ volume and with a soldered closure. Table I summarizes the cryostats, temperature ranges, calorimeters, and platinum-resistance thermometers, molecular mass, sample mass (in vacuum), densities, pressures of helium

TABLE I
Identification of calorimetric apparatus and quantities^a

Compound and T range	K	Cryostat	Calorimeter	Thermometer	M g mol ⁻¹	m g	ρ g cm ⁻³	He(g) kPa	C_p (sample) per cent
Perylene 5.2-345 297-575		Mark II	W-42	A-5	252.3186	61.194	1.35	12	94-62
		Mark IV	W-22	A-8		60.299		14	66-77
Coronene 5.2-349		Mark III	W-38	A-3	300.3632	7.875	1.37	10	75-30
Naphthacene 4.5-349		Mark II	W-42	A-5	228.2963	60.887	1.35	11	91-52

^a The quantities symbolized in the headings are designated in the text.

gas, and percentages of total heat capacities due to samples. To avoid direct exposure of the samples to air, the calorimeters were loaded with the samples in a nitrogen-atmosphere, dry box. They were placed in a loading chamber connected to a high vacuum line, evacuated, degassed, and sealed either by soldering or by remote mechanical closure of the screw cap after adding the helium to enhance thermal contact between calorimeter and sample. Where necessary, adjustments were made for differences in amounts of Apiezon-T grease, Cerroalloy (In-Sn) solder, and helium present during the separate heat-capacity determinations on the empty calorimeter-heater-thermometer assembly and during the measurements on the sample. Accuracy is assured by ultimately referring all determinations of mass, time, temperature, resistance, and potential to calibrations and standardizations performed by the National Bureau of Standards and to test measurements on heat-capacity standards established by the Calorimetry Conference.

3 RESULTS

Thermal data

The experimental values of the molal heat capacity of these three substances are summarized in Table II and are depicted in Figures 1 and 2 in conjunction with those of related substances. All the data in the tables are stated in terms of the defined thermochemical calorie.† The heat capacities are listed in chronological sequence so that the approximate temperature increments employed in the measurements may usually be deduced from differences in the adjacent mean temperatures. Where appropriate, the values have been corrected for curvature, i.e., for the difference between the ratio of finite increments and the derivative. Corrections for vaporization are negligible.

It is believed that the precision of these data are reflected by a standard deviation decreasing from 7 per cent at 5 K to 1 per cent at 15 K and to less than 0.1 per cent at higher temperatures. Values of the smooth heat capacities at saturation (C_s) obtained from digital-computer fits, agree well with those read from large-scale plots of the data and are presented in Table III at selected temperatures together with the entropy (S^0), enthalpy increment $\{H^0 - H^0(0)\}$, and tempered Gibbs energy $\{[G^0 - H^0(0)]/T\}$. These properties were obtained by fitting a polynomial through the data points by the method of least-squares and integrating the resulting functions. Below 5 K, the functions were estimated from the Debye T^3 -limiting law by plotting C_s/T against T^2 . The probable errors of the values in Table III are considered

† Throughout this paper $\text{cal}_{\text{th}} = 4.184 \text{ J}$.

TABLE II (continued)

\bar{T}	C_s	\bar{T}	C_s	\bar{T}	C_s	\bar{T}	C_s
K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹
Mark IV Calorimetric Thermostat							
Series III				420.00	92.07	553.10	321.2
301.48	65.96	429.60	94.14	557.21	123.2	Series VI	
310.33	68.08	439.55	96.41	Series V		525.40	112.2
319.40	70.23	449.53	98.26	Series VII		534.66	114.6
328.83	72.53	459.44	100.2	540.59	114.6	543.59	123.0
338.61	74.75	469.38	102.2	543.67	116.9	ΔH_f Detn. B	
348.50	77.14	479.36	103.9	546.82	121.3	Series VII	
358.50	79.21	489.40	105.8	549.56	406.5	527.89	113.1
368.57	81.38	499.48	107.7	550.81	11500	536.20	116.0
378.49	83.57	509.85	112.9	550.87	37700	544.19	125.2
388.37	85.78	520.02	115.0	550.88	750000	ΔH_f Detn. B	
398.23	87.97	530.99	226	550.90	32200	554.43	123.9
407.93	89.87	540.92	21800	550.92	680000	559.09	123.4
Series IV				550.93	73200	563.74	124.8
417.79	91.76	550.96	26800	552.23	375.7	568.39	124.9
		550.97	65300			573.04	125.2
			55200				

TABLE II (continued)

\bar{T}	C_p	\bar{T}	C_p	\bar{T}	C_p	\bar{T}	C_p
K	cal _h K ⁻¹ mol ⁻¹	K	cal _h K ⁻¹ mol ⁻¹	K	cal _h K ⁻¹ mol ⁻¹	K	cal _h K ⁻¹ mol ⁻¹
Coronene (C ₂₄ H ₁₂)							
Mark III Calorimetric Cryostat							
Series I							
79.32	17.54	233.03	60.30	44.73	10.49	223.77	58.12
90.29	19.92	241.99	61.67	49.68	11.59	225.56	57.72
99.93	21.90	251.05	63.35	54.64	12.62	227.34	57.67
109.49	24.01	260.07	65.24	60.11	13.73	229.70	58.45
119.02	26.24	Series IV		66.42	14.99	232.89	59.46
				73.62	16.28	236.88	59.94
						241.79	61.11
128.84	28.62	ΔH Detn. 1		Series VI		247.20	62.25
138.70	31.03	210.54	49.84	ΔH Detn. A		Series X	
148.37	33.48	215.09	51.69	Series VII		ΔH Detn. 5	
157.67	35.86	218.40	56.35	Series VIII		213.13	50.84
167.07	38.33	221.62	58.89	ΔH Detn. B		ΔH Detn. C	
176.85	40.83	224.79	58.93	206.77		Series XI	
186.69	43.49	227.97	58.58	ΔH Detn. 2		ΔH Detn. 6	
196.40	46.21	231.13	58.73	Series VIII		ΔH Detn. D	
205.91	48.76	234.28	58.80	210.55		264.79	68.72
215.33	53.76	237.42	59.46	212.63		Series XII	
224.66	63.51	240.53	59.56	214.80			
234.49	62.79	243.62	60.41				
245.20	62.72	246.69	60.89				
256.01	64.08	249.73	61.59				
265.23	65.55						

TABLE II (continued)

\bar{T}	C_s	\bar{T}	C_s	\bar{T}	C_s	\bar{T}	C_s
K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹	K	cal _{th} K ⁻¹ mol ⁻¹
Series II							
258.51	63.38	Series V					
268.93	66.55	5.58	0.1815	216.95	53.14	ΔH Detn. E	
279.07	69.61	6.05	0.2487	219.05	56.09	Series XIII	
288.94	72.39	6.76	0.2769	221.10	57.98	47.90	
298.56	75.22	8.18	0.5717	223.14	58.48	212.74	50.67
308.05	77.79	9.49	0.9331	225.17	58.44	222.17	57.07
315.13	79.70	10.82	1.311	227.19	58.25	231.68	59.06
324.97	82.65	12.19	1.665	Series IX			
334.77	85.73	13.63	2.186	ΔH Detn. 3			
344.37	88.64	15.15	2.657	ΔH Detn. 4			
Series III							
187.15	43.51	16.78	3.132	190.75	44.58	Series XIV	
196.62	46.09	18.57	3.689	198.85	46.75	48.94	
205.73	48.59	20.53	4.261	206.73	48.84	206.86	52.24
215.07	52.26	22.71	4.912	212.88	50.71	216.43	52.24
224.17	59.78	25.11	5.576	216.46	51.58	226.38	58.56
Series IV							
187.15	43.51	27.64	6.265	218.33	53.00	235.99	60.34
196.62	46.09	30.22	6.971	220.17	56.04	245.84	62.39
205.73	48.59	33.04	7.713	221.98	57.85	255.46	64.93
215.07	52.26	36.35	8.551	Series XV			
224.17	59.78	40.16	9.460	48.94			

TABLE II (continued)

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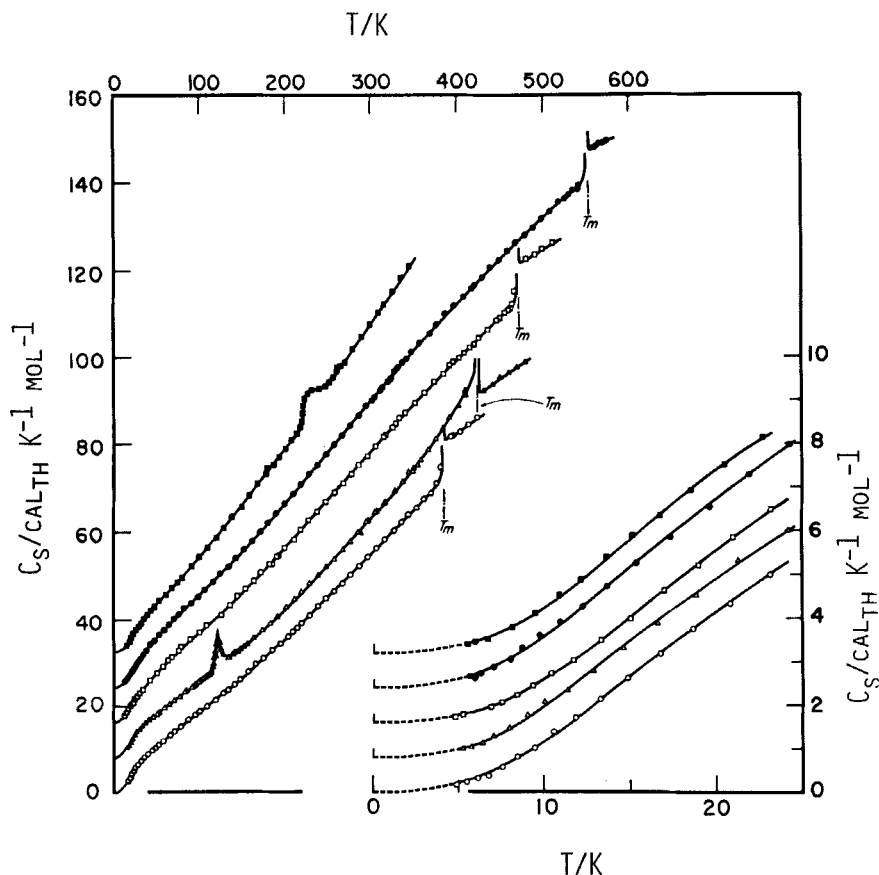


FIGURE 1 Heat capacities: \triangle , pyrene; \circ , fluoranthene; \square , triphenylene; \bullet , perylene; \blacksquare , coronene. The curves are displaced in increments of 10 and 1 $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$. The first three compounds are from Ref. 1.

to be less than 0.1 per cent above 100 K. Nuclear spin and isotopic mixing effects have been neglected in the evaluation of the entropy and Gibbs energy function so that these values are practical for use in chemical thermodynamic calculations.

Perylene—melting

No transitions other than melting were observed. Table IV, which summarizes measurements made in the melting region, shows that melting occurs with an enthalpy increment of $7618 \text{ cal}_{\text{th}} \text{mol}^{-1}$ and a corresponding entropy

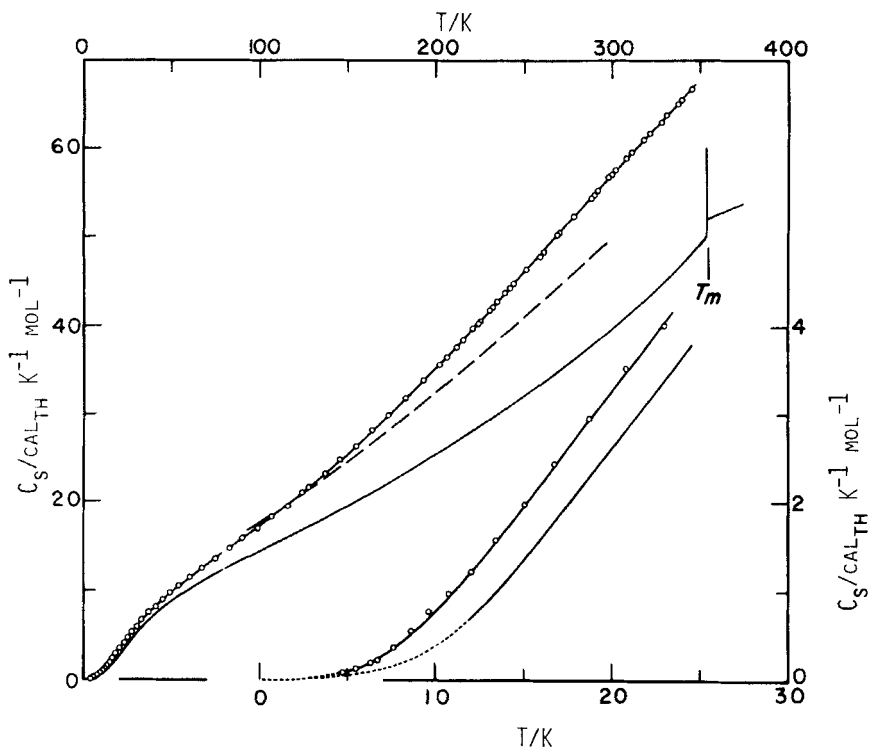


FIGURE 2 Heat capacities: —○—, naphthacene; ----, anthracene;¹⁰ —, naphthalene.¹¹

increment of $13.84 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. A plot of the reciprocal fraction melted against temperature (data of Table V) indicates the solid-insoluble, liquid-soluble impurities of the sample to be 0.0003 mole fraction. The triple point of the pure substance is extrapolated thereby as 550.95 K and that of the calorimetric sample as 550.93 K. A d.s.c. measurement of ΔH_m has been reported as $(7.59 \pm 0.14) \text{ kcal mol}^{-1}$ in good accord with the more precise value reported above.

Coronene—heat capacity and transition

Because only about 8 g of purified coronene were available for the measurements, a special small calorimeter was employed. In spite of this, the heat capacity of the sample decreased from 75 per cent of the total observed at 10 K to a minimum of 30 per cent at 90 K and steadily increased to about 51 per cent at 350 K. The precision is, therefore, reflected by probable errors

TABLE III

Thermodynamic properties of perylene, coronene, and naphthacene ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T	C_p	$\{S^0(T) - S^0(0)\}$	$\{H^0(T) - H^0(0)\}$	$-\{G^0(T) - H^0(0)\}/T$
K	$\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$\text{cal}_{\text{th}} \text{ mol}^{-1}$	$\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$
Perylene ($\text{C}_{20}\text{H}_{12}$)				
Crystal I Phase				
5	0.197	0.056		0.014
10	1.226	0.439		0.112
15	2.694	1.211	13.04	0.342
20	4.240	2.197	30.36	0.679
25	5.724	3.303	55.30	1.091
30	7.139	4.473	87.49	1.557
35	8.474	5.675	126.6	2.059
40	9.728	6.889	372.1	2.587
45	10.91	8.104	223.7	3.133
50	12.03	9.311	281.07	3.690
60	14.12	11.69	411.9	4.826
70	16.09	14.02	563.0	5.974
80	18.01	16.29	733.5	7.122
90	19.90	18.52	923.1	8.265
100	21.78	20.71	1131	9.400
110	23.66	22.88	1359	10.53
120	25.58	25.02	1605	11.65
130	27.54	27.14	1870	12.76
140	29.55	29.26	2156	13.86
150	31.63	31.37	2462	14.96
160	33.76	33.48	2789	16.05
170	35.94	35.59	3137	17.14
180	38.14	37.71	3507	18.22
190	40.37	39.83	3900	19.30
200	42.61	41.95	4315	20.38
210	44.88	44.09	4752	21.46
220	47.17	46.23	5213	22.54
230	49.49	48.38	5696	23.61
240	51.84	50.53	6202	24.69
250	54.23	52.70	6733	25.77
260	56.63	54.87	7287	26.84
270	59.04	57.05	7865	27.92
273.15	59.79	57.74	8052	28.26
280	61.43	59.24	8468	29.00
290	63.80	61.44	9094	30.08
298.15	65.71	63.23	9622	30.96

TABLE III (continued)

<i>T</i>	<i>C_p</i>	{ <i>S</i> ⁰ (<i>T</i>) − <i>S</i> ⁰ (0)}	{ <i>H</i> ⁰ (<i>T</i>) − <i>H</i> ⁰ (0)}	−{ <i>G</i> ⁰ (<i>T</i>) − <i>H</i> ⁰ (0)}/ <i>T</i>
K	cal _{th} K ^{−1} mol ^{−1}	cal _{th} K ^{−1} mol ^{−1}	cal _{th} mol ^{−1}	cal _{th} K ^{−1} mol ^{−1}
300	66.14	63.64	9744	31.16
310	68.44	65.85	10416	32.25
320	70.71	68.06	11112	33.33
330	72.96	70.27	11830	34.42
340	75.20	72.48	12571	35.51
350	77.42	74.69	13334	36.59
360	79.63	76.90	14120	37.68
370	81.81	79.12	14927	38.77
380	83.96	81.33	15756	39.86
390	86.06	83.53	16606	40.95
400	88.14	85.74	17477	42.05
410	90.20	87.94	18369	43.14
420	92.25	90.14	19281	44.23
430	94.30	92.33	20214	45.32
440	96.36	94.53	21167	46.42
450	98.39	96.71	22141	47.51
460	100.4	98.90	23134	48.60
470	102.3	101.1	24148	49.70
480	104.1	103.2	25180	50.79
490	105.9	105.4	26230	51.88
500	107.8	107.6	27298	52.98
510	109.8	109.7	28386	54.07
520	111.6	111.9	29493	55.16
530	113.0	114.0	30616	56.25
540	114.4	116.1	31753	57.34
550.95 ^a	(116.4)	118.4	33007	58.49
Liquid Phase				
550.95 ^a	(123.7)	132.2	40625	58.49
555	124.0	133.2	41136	59.09
565	124.7	135.4	42379	60.42
575	125.4	137.6	43629	61.74
Coronene (C ₂₄ H ₁₂)				
Crystalline Phase				
5	0.166	0.050	0.19	0.013
10	1.049	0.351	2.61	0.090
15	2.600	1.066	11.69	0.287
20	4.114	2.024	28.52	0.598
25	5.539	3.096	52.68	0.989
30	6.911	4.228	83.82	1.434
35	8.217	5.392	121.7	1.916
40	9.428	6.570	165.8	2.424
45	10.56	7.746	215.8	2.950
50	11.65	8.915	271.3	3.488

<i>T</i>	<i>C_p</i>	{ <i>S</i> ⁰ (<i>T</i>) – <i>S</i> ⁰ (0)}	{ <i>H</i> ⁰ (<i>T</i>) – <i>H</i> ⁰ (0)}	– { <i>G</i> ⁰ (<i>T</i>) – <i>H</i> ⁰ (0)}/ <i>T</i>
K	cal _{th} K ^{–1} mol ^{–1}	cal _{th} K ^{–1} mol ^{–1}	cal _{th} mol ^{–1}	cal _{th} K ^{–1} mol ^{–1}
60	13.73	11.23	398.4	4.586
70	15.68	13.49	545.5	5.697
80	17.65	15.71	712.0	6.810
90	19.71	17.91	898.7	7.921
100	21.90	20.10	1107	9.029
110	24.18	22.29	1337	10.14
120	26.53	24.49	1591	11.24
130	28.91	26.71	1868	12.34
140	31.34	28.94	2169	13.45
150	33.84	31.19	2495	14.56
160	36.42	33.45	2846	15.67
170	39.08	35.74	3223	16.78
180	41.77	38.05	3628	17.90
190	44.43	40.38	4059	19.02
200	47.03	42.73	4516	20.15
210	49.78	45.09	5000	21.28
Anomaly Region				
220	55.60	47.51	5518	22.43
230	60.10	50.12	6109	23.56
240	60.20	52.68	6709	24.72
250	61.85	55.17	7319	25.89
260	64.10	57.63	7947	27.06
270	66.94	60.10	8604	28.23
273.15	67.86	60.88	8816	28.61
280	69.83	62.59	9287	29.42
290	72.68	65.09	10000	30.60
298.15	74.99	67.13	10600	31.57
300	75.51	67.60	10740	31.80
310	78.35	70.12	11510	32.99
320	81.24	72.65	12310	34.19
330	84.20	75.20	13140	35.39
340	87.27	77.76	13990	36.60
350	90.47	80.33	14880	37.82
Naphthacene (C ₁₈ H ₁₂)				
Crystalline Phase				
5	0.095	0.033	0.12	0.008
10	0.806	0.270	2.05	0.067
15	1.973	0.811	8.90	0.218
20	3.288	1.557	22.02	0.456
25	4.614	2.434	41.80	0.762

TABLE III (continued)

T	C_p	$\{S^0(T) - S^0(0)\}$	$\{H^0(T) - H^0(0)\}$	$-\{G^0(T) - H^0(0)\}/T$
K	cal _{th} K ⁻¹ mol ⁻¹	cal _{th} K ⁻¹ mol ⁻¹	cal _{th} mol ⁻¹	cal _{th} K ⁻¹ mol ⁻¹
30	5.846	3.386	68.00	1.119
35	6.963	4.372	100.1	1.513
40	7.992	5.370	137.5	1.933
45	8.917	6.365	179.8	2.370
50	9.786	7.350	226.6	2.819
60	11.37	9.277	332.5	3.736
70	12.83	11.14	453.5	4.661
80	14.25	12.95	588.9	5.584
90	15.69	14.71	738.6	6.500
100	17.16	16.44	902.8	7.408
110	18.66	18.14	1082	8.306
120	20.23	19.83	1276	9.196
130	21.87	21.51	1487	10.08
140	23.61	23.20	1714	10.96
150	25.43	24.89	1959	11.83
160	27.29	26.59	2223	12.70
170	29.19	28.30	2505	13.57
180	31.12	30.02	2807	14.43
190	33.10	31.76	3128	15.30
200	35.14	33.51	3469	16.16
210	37.24	35.27	3831	17.03
220	39.39	37.06	4214	17.90
230	41.56	38.85	4618	18.77
240	43.72	40.67	5045	19.65
250	45.88	42.50	5493	20.53
260	48.05	44.34	5963	21.41
270	50.25	46.19	6454	22.29
273.15	50.96	46.78	6613	22.57
280	52.50	48.06	6968	23.18
290	54.74	49.94	7504	24.07
298.15	56.54	51.48	7957	24.80
300	56.94	51.84	8062	24.96
310	59.12	53.74	8643	25.86
320	61.32	55.65	9245	26.76
330	63.54	57.57	9869	27.66
340	65.62	59.50	10520	28.57
350	68.19	61.43	11180	29.48

^a Assuming melting to be truly isothermal.

TABLE IV

Enthalpy increments of melting for perylene and of transition for coronene ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

Source of Data	Number of Detns.	T_1 K	T_2 K	$\{H^0(T_2) - H^0(T_1)\}$ $\text{cal}_{\text{th}} \text{ mol}^{-1}$	$\{H^0(560) - H^0(540)\}$ $\text{cal}_{\text{th}} \text{ mol}^{-1}$
Perylene Melting					
Series IV	8	534.95	559.18	10479	10004
Series V	11	539.11	553.52	9303	10005
Series VI	2	539.24	558.72	9933	10005
Series VII	4	540.31	561.43	10146	10003
Average value		$\{H^0(560) - H^0(540)\} = 10004 \pm 0.8$			
Graphical integration		$\{H^0(560) - H^0(540)\} = 10004$			
Lattice contribution		$\{H^0(560) - H^0(540)\} = 2386 \pm 10$			
		$\Delta H_m/\text{cal}_{\text{th}} \text{ mol}^{-1} = 7618 \pm 10$			
		$\Delta S_m/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 13.84 \pm 0.02$			
		$T_m/\text{K} = 550.95 \pm 0.02$			
<hr/>					
		$\{H^0(T_2) - H^0(T_1)\}$		$\{H^0(260) - H^0(210)\}$	
		$\text{cal}_{\text{th}} \text{ mol}^{-1}$		$\text{cal}_{\text{th}} \text{ mol}^{-1}$	
<hr/>					
Coronene Transition					
Series I	5	210.59	261.37	3122	3063 ^a
Series III	6	210.37	264.51	3266	2993
Series IV	13	207.68	251.25	2500	2938
Series VI	1	108.88	245.75	5754	2985
Series VII	1	209.25	251.83	2376	2852 ^b
Series IX	13	210.63	249.94	2249	2913
Series XI	1	213.06	259.99	2724	2878 ^b
Series XII	1	214.58	270.48	3297	2840 ^b
Series XIII	5	208.00	255.41	2752	2944
Series XIV	5	211.73	260.21	2856	2930
Average value		$\{H^0(260) - H^0(210)\} = 2951 \pm 13$			
Graphical integration		$\{H^0(260) - H^0(210)\} = 2948$			
Lattice contribution		$\{H^0(260) - H^0(210)\} = 2845 \pm 10$			
		$\Delta H_t/\text{cal}_{\text{th}} \text{ mol}^{-1} = 106 \pm 17$			
		$\Delta S_t/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1} = 0.44 \pm 0.07$			
		$T_t/\text{K} = 225$			

^a Excluded from average because of the irreproducible heat capacity data.
^b Excluded from average because the measurements were made after the rapid cooling.

TABLE V
Fractional melting data for perylene^a ($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T	C_s	ΔT	$\sum \Delta H$	T_{final}	$1/F$
K	$\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	K	$\text{cal}_{\text{th}} \text{ mol}^{-1}$	K	
550.81	12000	0.093	1787	550.86	4.262
550.87	38000	0.028	2856	550.88	2.667
550.88	750000	0.001	3925	550.89	1.941
550.90	32000	0.033	4992	550.92	1.526
550.92	680000	0.002	6060	550.92	1.257
550.93	73000	0.004	7127	550.93	1.066
Triple point of sample/K = 550.93					
Triple point of pure compound/K = 550.95					
Mole fraction impurity = 0.0003					

^a Data from melting detns Series V.

decreasing from 4 per cent at 5 K to 1 per cent at 15 K and 0.2 per cent from 25 K to higher temperatures.

A relatively irreproducible, extended heat-capacity anomaly was found between 215 and 250 K. In the course of the measurements, ten sets of heat-capacity and enthalpy-type determinations were made over the anomalous region. These are listed in Table IV. Prior to Series I, the sample was cooled from 300 to 70 K over a 20 h period. Heat-capacity measurements were begun at this temperature and continued up to 270 K. The anomalous region found in this series was relatively narrow and characterized by larger values of the excess enthalpy of transformation than in all subsequent measurements. Despite a variety of cooling procedures, the original heat-capacity points could not be reproduced. Prior to Series II, the sample had been cooled to 4 K, allowed to warm to 300 K, cooled rapidly to 110 K, heated to 180 K, and heat-capacity measurements were made above this temperature. Prior to Series III, the sample was cooled from 265 to 160 K in 16 h and an enthalpy-type determination was made to heat the sample up to 280 K, followed by a fractional-transition-type heat-capacity series. The time required to reach equilibrium in the anomalous region was approximately the same as in the normal heat-capacity region (i.e., about 10 to 15 min). Prior to Series IV, the sample was cooled from 260 to 5 K and measurements made from 5 K.

Cooling prior to Series V was at maximum rate (from 300 to 200 K over 5 h) and an enthalpy-type determination encompassed the entire anomalous region. The small enthalpy of transition (ΔH_t) observed indicates the sample to have been partially undercooled. In Series VI, the sample was cooled over a period of several d from 300 to 50 K and held for a week prior to the measurements. In Series VII, the sample was cooled rapidly from 250 to 190 K. Prior

to Series VIII, the sample was cooled from 270 to 190 K over 3 h. That no excess enthalpy was found in this series is attributed to the complete quenching of the higher temperature form. In Series IX, the sample was cooled from 270 to 138 K over 65 h and slowly heated to a temperature just below the anomalous region. In Series X, the sample was cooled from 290 to 68 K over 60 h and then heated to 202 K. The excess enthalpy across the anomalous region is considered to be $(106 \pm 13) \text{ cal}_{\text{th}} \text{ mol}^{-1}$ as summarized in table 4, and the corresponding entropy increment is $(0.44 \pm 0.06) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. The mechanism of this heat-capacity anomaly is not yet known, but it is similar in magnitude and general properties to that previously reported for pyrene.¹

It is quite likely that, as in the case of pyrene, impurities significantly alter the shape of the heat capacity curve in the anomalous region for coronene. The extreme difficulties encountered in purifying this material stemming from its high melting point, low vapor pressure, low solubility and high cost, prevented further assessment of this question in the present investigation.

Naphthalene—heat capacity and reported transformation

The heat-capacity curve of naphthalene at low temperatures is of the normal, sigmoid shape expected of compounds which exhibit no thermal anomalies. However, Prikhot'ko and Skorobogat'ko¹² have recently studied the electronic spectra of thin-film single-crystal naphthalene and report that the spectra of loose crystals in a small paper envelope show a discontinuity at 70 K which they interpret as indicating a "phase transition" accompanied by change in the unit cell volume. Crystals which were in optical contact with a quartz substrate did not undergo the "phase transition." No evidence for such a transition was revealed in the heat-capacity measurements. It is presumed that a crystalline phase of material different from that obtained in the present studies might have been deposited in the films. Unless the transformation process is slow for microscopic particles of the size used in the heat-capacity measurements, normal cooling procedures would seem to have been sufficiently gradual to allow a high-temperature form to convert into a stable low-temperature form if indeed one exists.

4 DISCUSSION

A regular relationship exists between the molal entropies of crystalline condensed-linear-chain and disc-shaped series of polynuclear aromatic hydrocarbons and the number of carbon atoms. Except for benzene, for

which the value is obtained by extrapolating the heat-capacity curve from the melting point at 278.6 K to 298.15 K, the other values are obtained from the two papers in this series or from the literature. The plot of the entropy per gram atom of carbon against the number of carbon atoms in the molecule is shown in Figure 3. Except for the first member of the series—which may have molecular reorientational freedom in the crystalline phase¹—both series of (linear-chain and disc) compounds appear to lie on the same curve but data on higher members of the condensed chain series would be of interest. The entropy of graphite¹⁴ appears—as expected—as the asymptotic lower limit of the series.

Deviation between the entropies of the condensed-chain and the disc-shaped series might have been expected. The melting point increases more rapidly with increasing molecular weight in the condensed-chain series. For example, the melting point of anthracene is not only higher than that of phenanthrene, which has the same number of aromatic rings, but is also higher than that of pyrene with an even greater number of aromatic rings. Naph-

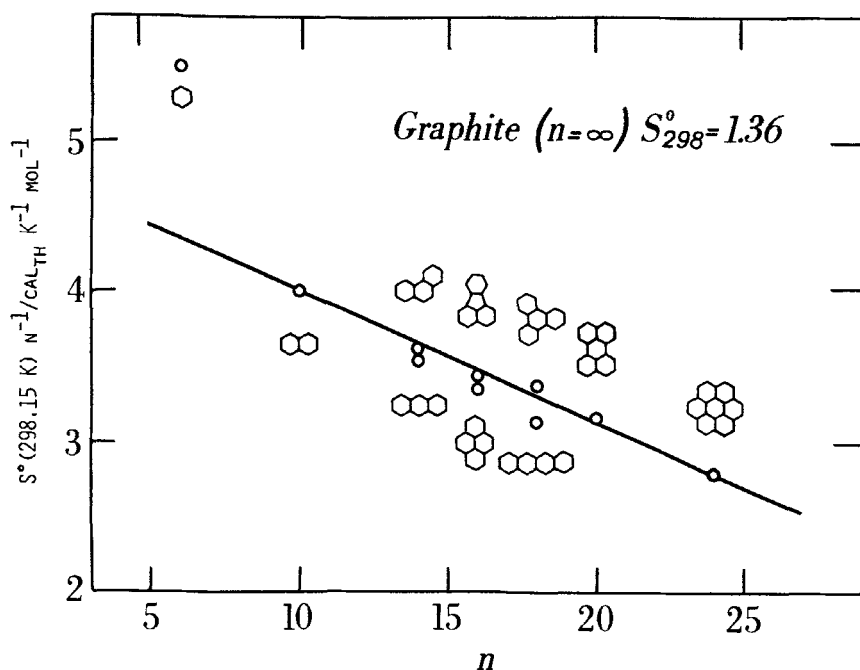


FIGURE 3 Molal entropy divided by the number of carbon atoms as a function of the number of carbon atoms. Data for those not discussed in this paper are from Refs. 1, 10, 11, and 13.

thacene with its four aromatic rings has a melting point higher than the five-ring, disc-shaped, compound perylene. A progressive shift of light absorption from the ultraviolet toward the visible occurs with increasing number of aromatic rings in both series; however, the condensed-chain series shifts much faster than the other. In the former series, the color of naphthacene is orange-red, pentacene is blue, hexacene is blue-green, and heptacene is green-black, while in the disc-shaped series, pyrene and triphenylene are colorless, anthanthrene ($C_{22}H_{12}$) is orange, and coronene is yellow. The chemical reactivity of this series also shows the same tendency. Upon irradiation in carbon disulphide solution in the presence of oxygen, anthracene gives a transannular photo-oxide. Naphthacene and pentacene are photooxidized even more readily. With hexacene, the reaction occurs so rapidly that its solutions are almost instantaneously photooxidized when exposed to light and air. Members of the disc-shaped series are invariably less reactive than the corresponding condensed-chain series. For example, pyrene can be exposed to air in the molten state for more than an hour with no visible reaction, and perylene reacts with air only at high temperatures.¹⁵

Other physico-chemical properties of condensed polynuclear aromatic compounds also correlate closely with the number of carbon atoms comprising the molecule. Additivity in the molecular enthalpy of sublimation for benzene, naphthalene, and anthracene has been demonstrated.^{16,17} The enthalpy of sublimation for compounds of higher molecular weight is a linear function of the number of carbon atoms with an average increment of $1.5 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ per carbon atom.^{10,21} Moreover, the electrical conductivity of these compounds in the crystalline state increases with the number of π -electrons (or the conjugated π -electron bonds).¹⁹ The reciprocal density divided by the number of carbon atoms has a logarithmic correlation with the number of carbon atoms from benzene (C_6H_6) to circumanthracene ($C_{40}H_{16}$) and with the density of graphite,¹⁴ which can be considered to result from the successive fusion of benzene nuclei of polynuclear aromatic compounds. The intercarbon distance of 1.42 \AA within the graphite network is considerably less than the distance of 1.54 \AA in diamond and is slightly greater than the distance 1.39 \AA found in benzene but approximates the average distance which occurs in the larger aromatic molecules.²⁰ Resonance in the covalent linkage gives each carbon bond 33 per cent double-bond character in graphite, in comparison with 50 per cent in benzene and an average 40 per cent in coronene.

Extension of thermal data for naphthacene through the melting region is of particular interest because this is one of the molecules for which rotation about the long molecular axis in the crystal is expected on the basis of comparisons of the experimental crystal volume and that calculated from considerations of closest packing of the calculated repulsion envelope.²¹

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