

Thermodynamics of polynuclear aromatic molecules

I. Heat capacities and enthalpies of fusion of pyrene, fluoranthene, and triphenylene†

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The heat capacities of three crystalline condensed-ring aromatic substances were studied from 5 to 350 K by adiabatic cryogenic calorimetry and into the liquid phase with the intermediate-range adiabatic calorimeter. The heat capacities, entropies, and enthalpies at 298 K, together with the triple points and enthalpies of melting are:

	C_p cal mol ⁻¹ K ⁻¹	S° cal mol ⁻¹ K ⁻¹	$H^\circ - H_0^\circ$ cal mol ⁻¹	T_m K	ΔH_m cal mol ⁻¹
Pyrene	54.90	53.75	8040	423.81	4148
Fluoranthene	55.03	55.11	8191	383.34	4477
Triphenylene	61.95	60.87	9205	471.01	5914

A gradual transition in pyrene occurs near 120.8 K with an associated enthalpy increment of 68.8 cal mol⁻¹. The nature of the melting process is considered.

1. Introduction

It is generally appreciated that the physicochemical properties of the condensed polynuclear aromatic compounds are closely correlated with the number of either carbon atoms or π -electrons. The linear dependence of electrical conductivity,⁽¹⁾ the enthalpy of sublimation,⁽²⁾ as well as the logarithmic dependence of the reciprocal density⁽³⁾ from benzene through circumanthracene (C₄₀H₁₆), correlate closely with the number of carbon atoms. The densities relate to that of graphite, which may be considered to be the upper bound for this type of molecule. There is also a progressive shift in color with increasing complexity of the molecule. Although some thermochemical data on these substances are reported in the literature, thermal data are not available for compounds of greater complexity than pyrene. Since the heat-capacity determination provides a powerful tool for the study of phase transitions,

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as well as the basic data for chemical thermodynamic functions useful in science and technology, the present study is the first in a series of investigations intended to provide insight into the thermal properties of these interesting molecules. Rather low-precision measurements of the heat capacity of pyrene have been reported⁽⁴⁾ over the region 90 to 300 K. The present investigation reports both low- and intermediate-temperature heat capacities extending through fusion into the liquid phase for pyrene ($C_{16}H_{10}$) fluoranthene ($C_{16}H_{10}$), and triphenylene ($C_{18}H_{12}$) whose structures are shown below.



Pyrene



Fluoranthene



Triphenylene

2. Experimental

PURIFICATION AND CHARACTERIZATION OF THE SAMPLES

Pyrene. Crude, orange-colored material, labelled 98 per cent pure and obtained from Rütgerswerk-Aktiengesellschaft, was fractionally recrystallized eight times from *p*-dioxane. The pale yellow crystals obtained thereby were dried under vacuum at 300 K for several days and fractionally resublimed trap-to-trap in vacuum six times from about 400 to 200 K, with the more volatile impurities removed by a liquid nitrogen trap. The massive crystalline sublimate was shattered into colorless fragments by quenching the Pyrex receiver in liquid nitrogen. Microchemical analyses on the resulting material indicated 95.00 mass per cent of C and 4.99 mass per cent of H (theoretical: 95.02 mass per cent of C and 4.98 mass per cent of H). The mole fraction of the liquid-soluble, solid-insoluble impurity determined by fractional fusion was 0.0003.

Fluoranthene. Fluoranthene, obtained from the Aldrich Chemical Co., Inc., was subjected to five fractional recrystallizations from benzene and four successive gradient sublimations in vacuum. Preliminary measurements were made in the intermediate-temperature calorimeter through fusion at this stage of purification (0.0039 mole fraction impurity) and are designated "Impure Sample I" in subsequent tables. Finally, 15 passes of zone-refining were performed. The final product (Pure Sample II) had a faint yellowish tinge. Microchemical analyses indicated 95.02 mass per cent of C and 4.96 mass per cent of H (theoretical: 95.02 mass per cent of C and 4.98 mass per cent of H). Fractional melting indicated a mole fraction of impurity of 0.00064. Melting temperatures are discussed in the results section.

Triphenylene. A gray-colored, reputedly 99 moles per cent pure sample from K. & K. Laboratories, Inc. was fractionally recrystallized five times from benzene and subjected to four successive gradient sublimations in vacuum. A total of 15 passes of

zone-refining yielded a transparent crystal. Microchemical analyses indicated 94.74 mass per cent of C and 5.28 mass per cent of H (theoretical: 94.70 mass per cent of C and 5.30 mass per cent of H). Fractional fusion studies indicated a mole fraction of impurity of 0.00038 and a triple point temperature for the sample of 471.01 K.

CALORIMETRIC APPARATUS

The cryostats, calorimeters, and designations of the capsule-type platinum-resistance thermometers, together with the sample masses, pressures of helium gas added to facilitate thermal conduction, and the percentages of total heat capacity due to sample, have been summarized in table 1. The Mark II cryostat and the adiabatic technique

TABLE 1. Identification of calorimetric apparatus and quantities; m denotes mass, p pressure of added He, C_s heat capacity, M molar mass, and ρ density.

Compound and temperature range	Cryostat Mark	Calorimeter	Thermometer	$\frac{m(\text{sample})}{\text{g}}$	$\frac{p(\text{He})}{\text{Torr}}$	$100 \frac{C_s(\text{sample})}{C_s(\text{total})}$
Pyrene						
$M = 202.2581 \text{ g mol}^{-1}$						
$\rho = 1.27 \text{ g cm}^{-3}$ ⁽¹¹⁾						
4.7 to 348 K	II	W-28	A-5	55.312	111	94 to 54
279 to 484 K	IV	W-22	A-7	53.664	130	63 to 72
Fluoranthene						
$M = 202.2581 \text{ g mol}^{-1}$						
$\rho = 1.243 \text{ g cm}^{-3}$ ⁽¹²⁾						
Impure Sample (I)						
297 to 457 K	IV	W-22	A-7	91.274	99	
Pure Sample (II)						
4.6 to 348 K	II	W-28	A-5	63.563	133	95 to 60
291 to 427 K	IV	W-22	A-7	79.512	146	74
Triphenylene						
$M = 228.2963 \text{ g mol}^{-1}$						
$\rho = 1.30 \text{ g cm}^{-3}$ ⁽¹³⁾						
4.7 to 339 K	II	W-28	A-5	66.526	145	94 to 60
298 to 514 K	IV	W-22	A-8	66.798	95	70 to 79

employed for cryogenic calorimetry (4 to 350 K) have been described,⁽⁵⁾ as have the intermediate-temperature Mark IV thermostat and the adjuvant techniques.⁽⁶⁾ Calorimeter W-28 has a soldered closure similar to that described elsewhere;⁽⁷⁾ calorimeter W-22, provided with a gold-gasketed seal, has been detailed.⁽⁶⁾ To avoid exposure of the sample to air, the calorimeters were loaded in a nitrogen-atmosphere anhydrous chamber. Each calorimeter was then connected to a high-vacuum line, highly evacuated, degassed and sealed either by soldering or by remote mechanical closure of the gasketed screw-cap after adding the conduction helium to enhance thermal contact between calorimeter and sample. Where necessary in the cryogenic calorimetry, the amounts of Apiezon-T grease, Cerroseal solder, and helium gas were adjusted to correspond to the quantities present during the separate heat-capacity determinations on the empty calorimeter + heater + thermometer assembly.

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 maintain the null thermal head between calorimeter and shield within 0.001 K.

Accuracy is assured by ultimately referring all determinations of mass, 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

HEAT CAPACITIES

The experimental values of the molar heat capacities of these three substances are summarized in table 2 and presented graphically in figure 1. All data in this and subsequent tables are derived in terms of the defined thermochemical calorie equal to 4.184 J and an ice point of 273.15 K. The heat capacities are listed in chronological

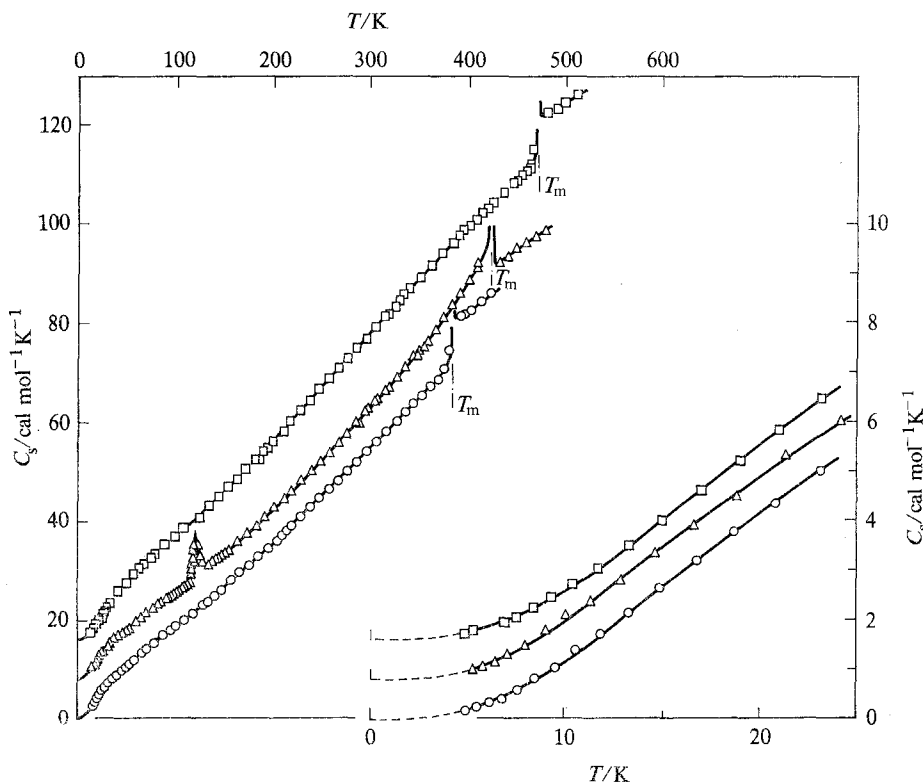


FIGURE 1. The heat capacities of pyrene Δ , fluoranthene \circ , and triphenylene \square . The ordinates for each curve other than that of fluoranthene are successively displaced by $8 \text{ cal mol}^{-1} \text{ K}^{-1}$ for each curve on the left and by $0.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ for the enlarged-scale curves on the right. The points indicated represent the experimental determinations.

TABLE 2. Heat capacities of pyrene, fluoranthene, and triphenylene

$\langle T \rangle$ K	C_s cal mol ⁻¹ K ⁻¹	$\langle T \rangle$ K	C_s cal mol ⁻¹ K ⁻¹	$\langle T \rangle$ K	C_s cal mol ⁻¹ K ⁻¹	$\langle T \rangle$ K	C_s cal mol ⁻¹ K ⁻¹
Pyrene (C ₁₆ H ₁₀)							
Results using Mark II cryostat							
Series I		Series III		115.39	20.48	122.81	23.49
5.27	0.173	93.88	17.06	116.16	20.91	124.82	34.35
5.78	0.235	100.93	18.06	116.77	21.22	127.99	29.05
6.40	0.319	107.60	19.07	117.37	21.68		
7.08	0.454	112.11	19.78	117.97	22.15	Series VIII	
7.99	0.646	114.60	20.18	118.56	21.98	ΔH _t Run A	
9.01	0.939	117.03	21.30	119.15	21.60	119.41	25.90
10.10	1.254	119.14	32.56	119.73	23.97	121.60	31.44
11.37	1.548	121.01	30.80	120.33	21.44	123.73	28.16
12.90	1.987	123.08	23.29	120.92	22.62	126.24	27.47
14.63	2.512	126.81	25.72	121.50	23.98	129.53	23.92
16.60	3.089	132.63	23.72	122.08	21.85	133.69	23.60
18.83	3.727	139.27	24.19	122.70	21.44	138.63	24.09
21.30	4.411	146.02	25.28	123.29	21.52		
24.25	5.192	152.94	26.39	124.28	23.80		
27.97	6.111					Series IX	
31.73	6.978	Series IV				116.35	19.85
35.32	7.761	151.35	26.13	Series VI		117.69	20.71
39.66	8.625	161.37	27.89	107.63	19.11	118.74	20.85
44.21	9.468	171.04	29.62	114.45	20.22	119.78	20.95
48.29	10.17	180.32	31.29	116.00	20.69	120.82	21.20
52.87	10.93	189.46	32.97	117.50	22.35	121.85	21.32
		198.95	34.73	118.92	25.35	122.87	21.49
		208.59	36.58	119.90	21.91	123.89	21.61
Series II		218.05	38.42	120.86	27.08	124.90	21.82
33.06	7.268	227.49	40.26			125.90	22.08
38.54	8.401	236.75	42.16			126.90	22.14
44.06	9.453	245.93	44.01	Series VII		127.89	22.39
48.80	10.27	255.23	45.86	82.07	15.36	128.87	22.49
52.69	10.90	264.63	47.82	90.44	16.62	129.85	22.61
56.72	11.54	274.08	49.82	99.27	17.85	131.50	22.85
62.17	12.42	283.66	51.79	107.20	19.02	134.19	23.36
68.10	13.30	293.63	54.02	113.84	20.11	138.43	24.02
74.37	14.18	303.72	56.16	117.81	21.40	143.93	24.96
81.74	15.30	313.50	58.36	118.83	20.89	150.04	25.93
89.63	16.49			119.42	21.24		
93.88	17.06	Series V		120.00	21.15	Series X	
104.65	18.67	101.40	18.19	120.80	23.09	ΔH _t Run B	
111.55	19.70	114.15	20.24	121.81	23.90		
Results using Mark IV thermostat							
Series XI		Series XII		334.91	63.10	391.35	77.64
414.06	86.19	284.75	51.71	343.97	65.18	400.65	80.68
421.15	178.8	294.70	54.11	353.21	67.18	409.82	83.97
423.74	12700	304.34	56.32	362.26	69.75	416.61	87.84
423.77	38600	313.74	58.55	371.28	72.15	421.65	168.5
423.79	23400	316.98	59.07	380.50	74.70	423.62	4600
426.31	180.5	326.05	61.22	389.78	77.43	423.72	15000

TABLE 2—continued

$\frac{\langle T \rangle}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\langle T \rangle}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\langle T \rangle}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\langle T \rangle}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$
Pure Sample II—results using Mark IV calorimetric thermostat							
Series XII		Series XIII		380.14	74.45	ΔH_f Run A	
296.53	54.33	295.98	54.20	382.55	752.9		
304.76	56.45	304.91	56.47	383.18	9734		
313.93	58.59	314.41	58.46	383.25	21590	Series XV	
323.37	60.45	323.97	60.39	383.28	35270	365.22	68.41
332.92	62.26	333.39	62.20	383.31	36390	374.39	71.17
342.45	64.02	342.73	64.06	387.01	98.44	ΔH_f Run B	
351.95	66.25	352.02	65.89	394.97	81.52	393.69	81.39
361.39	68.06	361.27	67.50	Series XIV		403.27	82.69
370.85	69.96	369.55	69.29	ΔH Run		412.97	84.15
		375.76	70.67			422.57	85.88
Triphenylene ($C_{18}H_{12}$)							
Results using Mark II calorimetric cryostat							
Series I		333.61	69.74	Series III		29.13	6.695
182.01	36.75			4.88	0.104	32.89	7.804
190.83	38.57	Series II		5.32	0.135	37.15	8.999
199.80	40.44	78.89	17.75	5.98	0.202		
209.05	42.37	89.30	19.64	6.80	0.300	Series IV	
218.65	44.43	98.52	21.16	7.59	0.429	37.27	9.030
228.37	46.55	107.16	22.65	8.40	0.603	41.50	10.11
237.98	48.62	116.19	24.25	9.32	0.836	46.20	11.25
247.47	50.70	125.33	25.91	10.41	1.105	51.20	12.38
257.05	52.86	134.42	27.60	11.75	1.419	56.43	13.49
266.72	54.96	143.79	29.35	13.36	1.873	62.28	14.69
276.10	57.05	152.99	31.04	15.11	2.394		
285.42	59.12	162.21	32.85	16.98	2.962	Series V	
295.07	61.28	171.46	34.69	19.02	3.591	60.70	14.37
304.77	63.44	180.75	36.58	21.05	4.223	67.62	15.70
314.42	65.58	190.04	38.46	23.22	4.896	74.96	17.00
324.00	67.68			25.90	5.722		
Results using Mark IV calorimetric thermostat							
Series VI		Series VII		473.14	264.3	Series IX	
316.59	65.90	391.77	81.71			451.81	92.92
328.06	68.48	403.20	83.84	Series VIII		460.22	94.62
339.22	70.84	414.38	86.10	458.88	94.25	ΔH_f Run A	
350.55	73.25	425.33	88.21	466.41	99.53		
362.03	75.69	436.06	90.27	470.47	1222	Series X	
373.23	78.11	446.58	92.46	470.88	14950	463.14	95.05
384.18	80.15	456.93	94.18	470.93	26250	ΔH_f Run B	
395.34	82.44	466.44	115.3	470.96	66790	481.02	106.5
406.71	84.52	470.87	8019	470.97	68680	490.27	107.5
418.01	86.93	470.94	17770	470.98	1306000	499.78	108.7
		470.98	20730	473.32	173.6	509.55	110.4

TABLE 3. Thermodynamic properties of pyrene, fluoranthene, and triphenylene

T K	C_s cal mol ⁻¹ K ⁻¹	S° cal mol ⁻¹ K ⁻¹	$H^\circ - H_0^\circ$ cal mol ⁻¹	$-(G^\circ - H_0^\circ)/T$ cal mol ⁻¹ K ⁻¹
Crystal II phase		Pyrene (C ₁₆ H ₁₀)		
5	0.159	0.054	0.202	0.014
10	1.163	0.413	3.085	0.105
15	2.618	1.157	12.51	0.324
20	4.053	2.109	29.22	0.648
25	5.383	3.159	52.86	1.044
30	6.587	4.248	82.84	1.487
35	7.687	5.348	118.6	1.960
40	8.688	6.441	159.5	2.452
45	9.593	7.517	205.3	2.955
50	10.46	8.572	255.4	3.464
60	12.07	10.62	368.2	4.488
70	13.57	12.60	496.4	5.506
80	15.05	14.51	639.4	6.512
90	16.53	16.36	797.4	7.504
100	17.96	18.18	969.8	8.481
110	19.46	19.96	1157	9.444
Transition region				
115	20.45	20.84	1257	9.91
120	27.20	21.79	1369	10.38
120.75	33.30	21.98	1392	10.45
125	26.58	23.01	1517	10.87
130	24.08	23.99	1643	11.35
135	23.67	24.89	1762	11.84
Crystal I phase				
140	24.28	25.76	1881	12.32
150	25.97	27.49	2133	13.27
160	27.68	29.22	2400	14.22
170	29.41	30.95	2686	15.15
180	31.19	32.68	2989	16.08
190	33.01	34.42	3310	17.00
200	34.89	36.16	3650	17.91
210	36.81	37.91	4008	18.82
220	38.78	39.66	4386	19.73
230	40.78	41.43	4784	20.63
240	42.81	43.21	5202	21.54
250	44.86	45.00	5640	22.44
260	46.92	46.80	6099	23.34
270	48.99	48.61	6578	24.24
273.15	49.65	49.18	6734	24.53
280	51.07	50.43	7079	25.15
290	53.17	52.26	7600	26.05
298.15	54.90	53.75	8040	26.79
300	55.30	54.10	8142	26.95
310	57.46	55.94	8706	27.86
320	59.66	57.80	9291	28.77
330	61.92	59.67	9899	29.67
340	64.24	61.56	10530	30.58
350	66.63	63.45	11180	31.50
360	69.09	65.36	11860	32.41

TABLE 3—continued

$\frac{T}{K}$	C_s cal mol ⁻¹ K ⁻¹	S° cal mol ⁻¹ K ⁻¹	$\frac{H^\circ - H_0^\circ}{\text{cal mol}^{-1}}$	$\frac{-(G^\circ - H_0^\circ)/T}{\text{cal mol}^{-1} \text{K}^{-1}}$
Crystal I Phase—continued				
370	71.65	67.29	12570	33.33
380	74.33	69.24	13300	34.25
390	77.20	71.20	14050	35.17
400	80.35	73.20	14840	36.09
410	83.96	75.22	15660	37.02
423.81 ^a	(88.93)	78.08	16850	38.32
Liquid phase				
423.81 ^a	(83.34)	87.87	21000	38.32
430	84.16	89.17	21560	39.04
440	85.56	91.12	22400	40.20
450	86.89	93.06	23270	41.36
460	88.19	94.98	24140	42.50
470	89.52	96.89	25030	43.64
480	90.95	98.79	25930	44.77
Fluoranthene (C ₁₆ H ₁₀)				
Crystal I phase				
5	0.162	0.056	0.211	0.014
10	1.219	0.436	3.255	0.110
15	2.663	1.202	12.94	0.339
20	4.107	2.166	29.88	0.672
25	5.488	3.233	53.91	1.076
30	6.750	4.347	84.55	1.528
35	7.935	5.477	121.3	2.012
40	9.040	6.610	163.8	2.516
45	10.08	7.74	211.6	3.033
50	11.06	8.85	264.4	3.559
60	12.88	11.03	384.2	4.623
70	14.55	13.14	521.5	5.690
80	16.12	15.19	674.9	6.749
90	17.63	17.17	843.7	7.798
100	19.10	19.11	1027	8.832
110	20.60	21.00	1226	9.852
120	22.13	22.85	1439	10.86
130	23.70	24.69	1669	11.85
140	25.33	26.50	1914	12.83
150	27.00	28.31	2175	13.80
160	28.70	30.10	2454	14.77
170	30.43	31.89	2749	15.72
180	32.19	33.68	3062	16.67
190	34.00	35.47	3393	17.61
200	35.84	37.26	3742	18.55
210	37.72	39.06	4110	19.48
220	39.63	40.86	4497	20.41
230	41.57	42.66	4903	21.34
240	43.52	44.47	5328	22.27
250	45.47	46.29	5773	23.19

TABLE 3—continued

T K	C_p cal mol ⁻¹ K ⁻¹	S° cal mol ⁻¹ K ⁻¹	$H^\circ - H_0^\circ$ cal mol ⁻¹	$-(G^\circ - H_0^\circ)/T$ cal mol ⁻¹ K ⁻¹
Crystal I phase—continued				
260	47.43	48.11	6238	24.12
270	49.39	49.93	6722	25.04
273.15	50.02	50.51	6878	25.33
280	51.38	51.77	7226	25.96
290	53.38	53.60	7749	26.88
298.15	55.03	55.11	8191	27.63
300	55.40	55.45	8293	27.80
310	57.42	57.30	8857	28.73
320	59.43	59.15	9442	29.65
330	61.42	61.01	10046	30.57
340	63.40	62.87	10670	31.49
350	65.37	64.74	11314	32.42
360	67.34	66.61	11980	33.34
370	69.38	68.48	12660	34.26
380	71.42	70.36	13370	35.19
383.36 ^a	(72.08)	70.92	13580	35.50
Liquid phase				
383.36 ^a	(79.97)	82.61	18057	35.50
390	80.83	84.06	18620	36.32
400	82.21	86.12	19430	37.54
410	83.74	88.17	20260	38.75
420	85.42	90.21	21110	39.95
Triphenylene (C ₁₈ H ₁₀)				
Crystal I phase				
5	0.113	0.038	0.142	0.010
10	0.979	0.327	2.474	0.079
15	2.364	0.978	10.74	0.262
20	3.890	1.865	26.34	0.548
25	5.449	2.901	49.69	0.913
30	6.958	4.029	80.74	1.337
35	8.398	5.210	119.2	1.806
40	9.732	6.421	164.6	2.307
45	10.97	7.639	216.3	2.832
50	12.12	8.855	274.1	3.373
60	14.23	11.26	406.1	4.488
70	16.14	13.59	558.1	5.622
80	17.93	15.87	728.5	6.762
90	19.69	18.08	916.6	7.897
100	21.43	20.25	1122	9.024
110	23.19	22.37	1345	10.14
120	24.96	24.46	1586	11.25
130	26.76	26.53	1845	12.34
140	28.60	28.58	2121	13.43
150	30.48	30.62	2417	14.51
160	32.41	32.65	2731	15.58
170	34.39	34.67	3065	16.64
180	36.40	36.70	3419	17.70
190	38.44	38.72	3793	18.75

TABLE 3—continued

$\frac{T}{K}$	C_s cal mol ⁻¹ K ⁻¹	S° cal mol ⁻¹ K ⁻¹	$H^\circ - H_0^\circ$ cal mol ⁻¹	$-(G^\circ - H_0^\circ)/T$ cal mol ⁻¹ K ⁻¹
Crystal I phase—continued				
200	40.50	40.74	4188	19.80
210	42.59	42.77	4603	20.85
220	44.70	44.80	5040	21.89
230	46.86	46.83	5497	22.93
240	49.04	48.87	5977	23.97
250	51.26	50.92	6478	25.01
260	53.50	52.97	7002	26.04
270	55.73	55.03	7548	27.08
273.15	56.43	55.69	7725	27.40
280	57.96	57.10	8117	28.11
290	60.16	59.17	8707	29.15
298.15	61.95	60.87	9205	29.99
300	62.36	61.25	9320	30.18
310	64.54	63.33	9955	31.22
320	66.72	65.41	10611	32.26
330	68.90	67.50	11290	33.29
340	71.08	69.59	11990	34.33
350	73.23	71.68	12710	35.37
360	75.33	73.77	13450	36.40
370	77.36	75.87	14220	37.44
380	79.35	77.96	15000	38.48
390	81.31	80.04	15800	39.52
400	83.28	82.13	16630	40.56
410	85.27	84.21	17470	41.60
420	87.23	86.29	18330	42.64
430	89.11	88.36	19210	43.68
440	90.90	90.43	20110	44.72
450	92.69	92.49	21030	45.75
460	94.56	94.55	21970	46.79
470	96.44	96.60	22920	47.83
471.01 ^a	(96.64)	96.81	23020	47.95
Liquid phase				
471.01 ^a	(105.4)	109.38	28930	47.95
480	106.5	111.38	29890	49.12
490	107.6	113.6	30960	50.41
500	108.7	115.8	32040	51.70

^a Assuming melting to be truly isothermal.

sequence so that the approximate temperature increments employed in the measurements may usually be deduced from the 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 to the differential relation. Vaporization corrections are insignificant.

It is believed that the precision of these results is reflected by probable errors decreasing from 5 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 results and are presented in table 3 at selected temperatures, together with the entropy S° , enthalpy increment $(H^\circ - H_0^\circ)$, and Gibbs energy function $-(G^\circ - H_0^\circ)/T$. These properties were obtained by fitting a polynomial through the results 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 3 are considered to be less than 0.1 per cent above 100 K. Nuclear spin and isotopic mixing effects have not been incorporated in the evaluation of the entropy and Gibbs energy function so that these values are practical for use in chemical equilibrium calculations.

PYRENE—TRANSITION

The heat capacity of pyrene was previously reported by Jacobs and Parks⁽⁴⁾ from 90 to 300 K with an assigned "estimated reliability of ± 1 per cent." Their points do indeed scatter over most of the common region by approximately this amount from the present results, except above 260 K where, as may be noted in figure 2, they are about 1.5 per cent higher than the present result.

In the present measurements, a thermal anomaly is found with a maximum at 120.8 K, a temperature slightly higher than the value (116 K) at which Jacobs and Parks noted a hump in the heat capacity. The cause of the anomaly has been attributed to a slight change in the lattice structure. Powder photographs taken at room temperature and at liquid-air temperature⁽¹¹⁾ are interpreted as indicating the

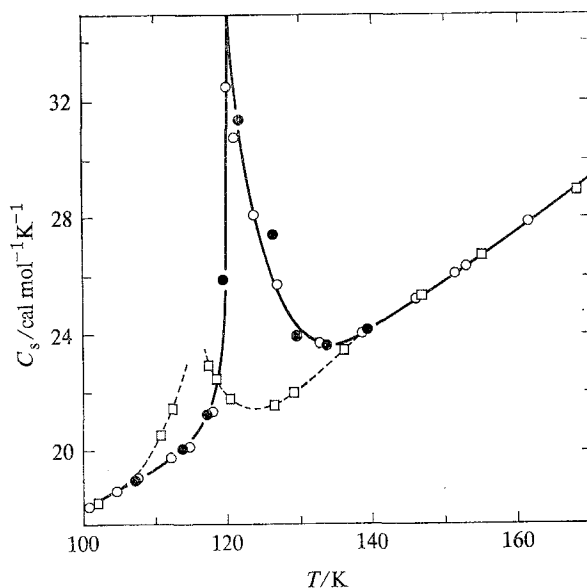


FIGURE 2. The heat capacity of pyrene in the transition region. The points and curves indicated —○—●— are from the present research; those shown ---□--- are from Jacobs and Parks.⁽⁷⁾

TABLE 4. Enthalpy increments of transition and melting for pyrene and for melting of fluoranthene and triphenylene

Source of data	Number of runs	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{H(T_2) - H(T_1)}{\text{cal mol}^{-1}}$	$\frac{H(140 K) - H(110 K)}{\text{cal mol}^{-1}}$
Pyrene transition					
Series III	9	110.85	142.71	774	724
Series V	17	89.42	124.98	687	682 ^a
Series VII	10	110.61	129.66	481	725
Series VIII	8	85.19	141.28	1196	727
Series IX	18	115.54	146.75	713	656 ^a
Series X	1	109.16	137.64	683	724
Average value:					725 ± 1
Graphical integration:					725
Lattice contribution:					656
$\Delta H_v/\text{cal mol}^{-1}$:					69 ± 1
$\Delta S_v/\text{cal mol}^{-1} \text{K}^{-1}$:					0.55
T_v/K :					120.8
<hr/>					
Source of data	Number of runs	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{H(T_2) - H(T_1)}{\text{cal mol}^{-1}}$	$\frac{H(430 K) - H(410 K)}{\text{cal mol}^{-1}}$
Pyrene melting					
Series XI	6	409.52	428.84	5842	5900
Series XII	8	413.47	429.13	5555	5896
Series XV	1	413.94	431.60	5694	5894
Series XVI	1	420.78	425.55	4581	5894
Average value:					5896 ± 1
Graphical integration:					5894
Lattice contribution:					1746
$\Delta H_m/\text{cal mol}^{-1}$:					4150 ± 1
$\Delta S_m/\text{cal mol}^{-1} \text{K}^{-1}$:					9.79
T_m/K :					423.81
<hr/>					
Source of data	Number of runs	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{H(T_2) - H(T_1)}{\text{cal mol}^{-1}}$	$\frac{H(385 K) - H(370 K)}{\text{cal mol}^{-1}}$
Impure fluoranthene (Sample I) melting					
Series X	6	377.62	386.64	5078	5513
Series XII	7	373.64	389.12	5607	5536
Series XIII	1	370.79	389.68	5852	5531
Series XIV	1	378.42	391.15	5384	5520
Series XV	1	374.66	384.91	5179	5523
Average value:					5525 ± 4
Lattice contribution:					1067
$\Delta H_m(\text{impure})/\text{cal mol}^{-1}$:					4458 ± 4

TABLE 4—continued

Source of data	Number of runs	T_1 K	T_2 K	$\frac{H(T_2) - H(T_1)}{\text{cal mol}^{-1}}$	$\frac{H(385 \text{ K}) - H(375 \text{ K})}{\text{cal mol}^{-1}}$
Pure fluoranthene (Sample II) melting					
Series VI	8	373.20	390.70	5865	5203
Series VII	1	375.79	391.37	5666	5207
Series VIII	1	378.89	388.99	5247	5202
			Average value:		5204 \pm 2
			Graphical integration:		5205
			Lattice contribution:		728
			$\Delta H_m/\text{cal mol}^{-1}$:		4476 \pm 2
			$\Delta S_m/\text{cal mol}^{-1} \text{ K}^{-1}$:		11.68
			T_m/K :		383.33
Triphenylene melting					
Series VII	6	462.06	475.29	7219	6910
Series VIII	8	462.71	475.65	7242	6914
Series IX	1	464.39	472.79	6740	6915
Series X	1	467.34	476.38	6834	6912
			Average value:		6913 \pm 1
			Graphical integration:		6914
			Lattice contribution:		999
			$\Delta H_m/\text{cal mol}^{-1}$:		5914 \pm 1
			$\Delta S_m/\text{cal mol}^{-1} \text{ K}^{-1}$:		12.57
			T_m/K :		471.01

^a Excluded from the average because rapidity of cooling obviously occasioned some undercooling of the Crystal I phase.

presence of such a phase transformation at an intermediate temperature. Seven sets of heat-capacity and enthalpy-type determinations (summarized in table 4) were made through the anomalous region, and the excess enthalpy (of transformation) was obtained by subtracting the interpolated lattice contribution from the total. The entropy contribution was integrated from a smooth curve drawn through points from several series of heat-capacity determinations through the anomalous region and constrained to give the proper total enthalpy. As shown in table 4, the corresponding values are 68.8 cal mol⁻¹ for the enthalpy increment, compared with 24 cal mol⁻¹ obtained in the previous study.⁽⁴⁾ These differences are attributed to the higher purity of the present sample, since Jacobs and Parks purified their pyrene only by recrystallization from benzene and obtained light yellow-colored crystals. The transformational excess entropy is estimated to be 0.55 cal mol⁻¹ K⁻¹.

PYRENE—MELTING

The four sets of determinations made through the melting region are also summarized in table 4. Removal of the extrapolated contributions of the crystalline and liquid phases yield a value for the enthalpy of melting, $\Delta H_m = 4148.9 \text{ cal mol}^{-1}$ and a corresponding entropy of melting, $\Delta S_m = 9.79 \text{ cal mol}^{-1} \text{ K}^{-1}$. The amount of solid-soluble, liquid-soluble impurity was estimated from the fractional melting results of table 5. The triple point of the experimental sample was found to be 423.78 K and that of the pure substance to be 423.81 K. Previously reported melting temperatures are 148 °C⁽¹²⁾ and 151 °C.⁽¹³⁾ The slope of the fractional fusion curve corresponds to 0.0003 mole fraction of liquid-soluble, solid-soluble impurity on the basis of the van't Hoff equation.

FLUORANTHENE—HEAT CAPACITY AND MELTING

The initial measurements were made on Impure Sample I which had been sublimed but not zone-melted. A distinct pre-melting effect and an excess slope of the melting curve were found. The curvature of the plot of T against $1/F$ suggested that impurity was present also in solid solution. Applications of the treatment of Mastrangelo and Dornte⁽¹⁴⁾ for solid-soluble, liquid-soluble contaminants indicated 0.0039 mole fraction of impurity and a ratio of solubility between the solid and liquid phases of 0.0883. The triple point of the pure compound was extrapolated as 383.34 K. After zone-refining the material, the new Pure Sample II (on which the definitive measurements were made) exhibited sharper melting.

Results through the melting region are presented in table 4 for three series of measurements on Sample I and for five series of measurements on Sample II, including one and two series of fractional melting results respectively. Because the sample is now sufficiently pure (0.00064 mole fraction impurity), the melting temperature may be treated in terms of the van't Hoff equation and yields extrapolated triple points of 383.29 K for Sample II and 383.33 K for the pure substance. The latter is in good agreement with the previous value on the impure material and with the reported value of 110 °C.⁽¹⁵⁾ No significant differences in the heat capacity are observed from 300 to 350 K (within 33 K of melting) between the two samples.

In the evaluation of the enthalpies of melting, the same extrapolations were used to represent the lattice and liquid heat capacities for both samples. The mean ΔH_m of 4477 cal mol⁻¹ was calculated from the excess enthalpy of Sample II. The corresponding entropy increment of melting is 11.68 cal mol⁻¹ K⁻¹. A value of 4457 cal mol⁻¹ was obtained for ΔH_m on Sample I. If the value for the enthalpy of melting of Sample I is multiplied by the factor 1/0.99611 to correct for the presence of only 0.99611 mole fraction of pure compound in this sample, the result is 4475 cal mol⁻¹, in good accord with that found for the purer sample.

TRIPHENYLENE—MELTING

Apart from fusion, no thermal anomaly is found in the solid phase. The four series of measurements through the melting region are summarized in table 4. The triple point of the pure material occurs at 471.01 K and at 470.98 K for the calorimetric

TABLE 5. Fractional melting studies of pyrene, fluoranthene, and triphenylene

$\frac{T}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\Delta T}{K}$	$\frac{\sum \Delta H}{\text{cal mol}^{-1}}$	$\frac{T_{\text{final}}}{K}$	$1/F$
Pyrene ^a					
421.65	169	0.164	1044	423.70	3.974
423.72	4600	0.050	1801	423.75	2.304
423.75	15000	0.005	2559	423.76	1.621
423.77	150000	0.023	3317	423.78	1.250
423.78	34000	0.006	4075	423.78	1.018
				Triple point of sample:	423.78 K
				Triple point of pure compound:	423.81 K
				Mole fraction of impurity:	0.0003
$\frac{T}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\Delta T}{K}$	$\frac{\sum \Delta H}{\text{cal mol}^{-1}}$	$\frac{T_{\text{final}}}{K}$	$1/F \quad \{K(1-K)^{-1} + F\}^{-1}$
Fluoranthene (Impure Sample I) ^b					
381.71	460	1.770	815	382.59	5.469
382.73	2960	0.287	1638	382.88	2.721
382.95	6200	0.137	2488	383.01	1.791
383.04	14000	0.060	3339	383.07	1.335
383.10	17000	0.049	4189	383.12	1.064
				Triple point of sample:	383.114 K
				Triple point of pure compound:	383.344 K
				Mole fraction of impurity:	0.00389
				Partition coefficient K :	0.0883
$\frac{T}{K}$	$\frac{C_s}{\text{cal mol}^{-1} \text{K}^{-1}}$	$\frac{\Delta T}{K}$	$\frac{\sum \Delta H}{\text{cal mol}^{-1}}$	$\frac{T_{\text{final}}}{K}$	$1/F$
Fluoranthene (Pure Sample II) ^c					
382.55	753	0.094	1003	383.14	4.462
383.18	9700	0.042	1918	383.23	2.334
383.25	22000	0.026	2825	383.27	1.585
383.28	35000	0.025	3728	383.28	1.201
				Triple point of sample:	383.290 K
				Triple point of pure compound:	383.332 K
				Mole fraction of impurity:	0.00064
Triphenylene ^d					
470.88	15000	0.064	1835	470.91	3.223
470.93	26000	0.036	2888	470.95	2.122
470.96	67000	0.014	3740	470.96	1.582
470.97	69000	0.014	4692	470.98	1.261
470.98	1300000	0.001	5643	470.98	1.048
				Triple point of sample:	470.979 K
				Triple point of pure compound:	471.008 K
				Mole fraction of impurity:	0.00038

^a Values from melting runs Series XII.^b Values from melting runs Series XII.^c Values from melting runs Series VI.^d Values from melting runs Series VIII.

sample. Bachmann and Clarke⁽¹⁶⁾ report a melting temperature of 199 °C. The fractional melting data of table 5 indicate a solid-insoluble, liquid-soluble impurity of 0.00038 mole fraction. Melting occurs with a ΔH_m of 5913 cal mol⁻¹ and an entropy increment of 12.57 cal mol⁻¹ K⁻¹.

4. Discussion

THE MECHANISM OF MELTING

Although the main qualitative distinction between crystalline and liquid phases has long been attributed to the disappearance of the long-range order of the crystalline structure, as yet few theories are able to give satisfactory semi-quantitative descriptions of the thermodynamic changes involved.⁽¹⁷⁾ Presumably, positional, orientational (for non-spherically-symmetrical molecules), and configurational types of disorder are involved. In addition, increases in vibrational entropy appear to make significant contributions to the total entropy of fusion in certain crystal structures, such as those containing rigid polyatomic molecules of high anisotropy.

Hitherto, melting studies have been available only for the simplest condensed polynuclear hydrocarbons; e.g. benzene,⁽¹⁸⁾ naphthalene,⁽¹⁹⁾ anthracene, and phenanthrene.⁽²⁰⁾ The results of this study together with data on perylene⁽²¹⁾ provided entropies of fusion for four additional substances which are incorporated into table 6.

Since fused aromatic rings may be regarded as having an approximately planar repulsion envelope, they provide a useful range of shapes as a basis for the investigation of the structure of melts. For example, Ubbelohde and his collaborators^(11, 22-24) calculated the volume required for free rotation about principal axes for some condensed aromatic compounds on the basis of their van der Waals repulsion envelopes and compared these with the observed molar volumes. They concluded that most of the molecules studied do not have sufficient room to rotate freely (see table 6). However, Frank⁽²⁵⁾ suggested that even when the volume per molecule in the liquid phase does not provide adequate space for rotation of individual molecules independently of their neighbors, two molecules may rotate "in gear" with each other. More than half of the rotational entropy survives because the effective combined rotator has twice the moment of inertia. Unless orientational disordering has already occurred in the crystals below T_m , it is highly probable that orientational disordering will make important contributions to the total entropy of fusion. Generally, the expansion in volume on melting lowers the potential barriers opposing rotation.

Vibrational entropy changes upon fusion may also make a substantial contribution to the total entropy of melting of condensed polynuclear aromatic compounds. In the simplest theory for the vibrational entropy of a crystal containing $3N$ vibrators, all having the same characteristic frequency ν_c , the increment on melting is $\Delta S_{\text{vib}} = 3R \ln(\nu_c/\nu_l)$ if $h\nu_c \gg kT$, and the melt (l) can be treated as quasi-crystalline. The rigid planar molecules in these crystals may have significantly greater vibrational freedom in the liquid with values of ν_l considerably lower than ν_c . Part of the total

TABLE 6. Thermodynamics of melting of polynuclear aromatic hydrocarbons

Compound	Formula	ΔS_m^a	$\Delta C_{P,m}^b$	$V(c)/V_{min}^c$	$V(l)/V_{min}^{c,d}$
		cal mol ⁻¹ K ⁻¹	cal mol ⁻¹ K ⁻¹	at T_m	at T_m
Benzene	C ₆ H ₆	8.5 ^e	0.7	0.94	1.06
Naphthalene	C ₁₀ H ₈	12.8 ^f	≈ 2	0.89	1.05
Acenaphthene	C ₁₂ H ₁₀	13.3 ^g	—	1.02	1.14
Anthracene	C ₁₄ H ₁₀	14.4 ^h	≈ 2	0.67	0.78
Phenanthrene	C ₁₄ H ₁₀	12.1 ⁱ	—	0.68	0.74
Pyrene	C ₁₆ H ₁₀	9.8 ^j	≈ 0	0.90	1.00
Fluoranthene	C ₁₆ H ₁₀	11.7	≈ 7	0.93	1.03
Triphenylene	C ₁₈ H ₁₂	12.6	≈ 8	0.98	1.12
Chrysene	C ₁₈ H ₁₂	(14.9) ^k	—	0.69	0.77
Perylene	C ₂₀ H ₁₂	13.8	≈ 5	—	—

^a Values in parentheses have been evaluated by cryoscopic measurements.

^b Observed from C_P against T plots.

^c $V(c)$ is the observed molecular volume of the crystal at T_m ; V_{min} is that required for molecular rotation on the basis of the smallest envelope of rotation; see references 14, 25, 26, and 27.

^d $V(l)$ is the molecular volume of the melt.

^e Reference 21.

^f Reference 22.

^g Reference 29.

^h Reference 30.

ⁱ Reference 31.

^j $\Delta S_t = 0.6$ cal mol⁻¹ K⁻¹ for transition at 116 K.

^k Reference 32.

entropy of fusion would thus have a vibrational origin. Hence, spectroscopic study of solid and melt near the melting temperature are obvious desiderata.

Since reorientation is facilitated by a high degree of isotropy in the plane of the molecule, the nearly circular symmetry of coronene, for example, would be conducive to rotation of the molecule. Coronene does indeed have a thermal anomaly between 215 and 250 K which appears to be a motional transition in n.m.r. measurements whereas triphenylene and perylene are rigidly positioned in the lattice.⁽³⁰⁾

Attempts to correlate melting parameters of these condensed polynuclear hydrocarbons with their molecular structures, molecular symmetries, etc., were disappointing. The entropy of melting of benzene (8.5 cal mol⁻¹ K⁻¹) is comparable to that of less-symmetrical, single-ring compounds such as thiazole, $\Delta S_m = 9.6$ cal mol⁻¹ K⁻¹,⁽³¹⁾ pyridine, $\Delta S_m = 8.5$ cal mol⁻¹ K⁻¹,⁽³²⁾ furane, $\Delta S_m = 4.8$ and $\Delta S_t = 3.7$ cal mol⁻¹ K⁻¹,⁽³³⁾ thiophene, $\Delta S_m = 5.1$ and $\Delta S_t = 4.9$ cal mol⁻¹ K⁻¹,⁽³⁴⁾ aniline, $\Delta S_m = 9.4$ cal mol⁻¹ K⁻¹,⁽³⁵⁾ and toluene, $\Delta S_m = 9.2$ cal mol⁻¹ K⁻¹,⁽³⁶⁾ where ΔS_t is the entropy of transition. Likewise, the value for naphthalene $\Delta S_m = 12.8$ cal mol⁻¹ K⁻¹ is comparable with that of benzothiazole (11.1 cal mol⁻¹ K⁻¹)⁽³⁷⁾ and of benzothiophene ($\Delta S_m = 9.2$ and $\Delta S_t = 2.4$ cal mol⁻¹ K⁻¹)⁽³⁸⁾ under the same conditions. Due caution should be applied to values not based on direct calorimetric determination. However, as may be noted from the third column of table 6, the molar entropy of fusion divided by the number of carbon atoms per molecule decreases rapidly at first and then more gradually with increasing number of carbon atoms and may reach an asymptote at 0.5 to 0.6 cal mol⁻¹ K⁻¹.

Although harder to evaluate experimentally because of premelting effects, $\Delta C_{p,m} = \{C_p(l) - C_p(c)\}$ for the melting process tends to approach zero for the two substances with unusually small values of ΔS_m . Likewise, the experimental volume increments on melting ΔV_m are also relatively small for these two substances.

A further not unrelated and tantalizing question concerns the molecular freedom of these planar molecules in the crystalline phase. Nuclear magnetic resonance⁽³⁹⁾ and low-frequency Raman spectral data⁽⁴⁰⁾ indicate that although benzene begins to reorient rotationally about its hexad axis just below fusion, naphthalene and anthracene do not do so about any axis. Raman spectra confirm, moreover, that torsional oscillations about the axis perpendicular to the plane are the least inhibited for benzene. Yet benzothiophene has been interpreted as doing so about all three axes.⁽⁴¹⁾ Of the three molecules studied in this paper, only pyrene shows a small thermal anomaly of unexplained origin accompanied by a slight change in lattice structure at 120.8 K. The n.m.r. behavior over the range 255 to 285 K has been attributed by Fyfe *et al.*⁽⁴²⁾ to the onset of reorientation of pyrene molecules about the axis perpendicular to the molecular plane with an activation energy of about 13.7 kcal mol⁻¹. Camerman and Trotter⁽⁴³⁾ found approximately 4° angular amplitudes of oscillation about the long axis and about that perpendicular to the molecular plane but no evidence of statistical disorder. However, the presence of a disordered structure above 400 K has been reported.⁽⁴⁴⁾ The above thermal data and other observations are considered evidence for the assertion that both the benzene and pyrene molecules, in contrast to other substances in table 6, are rotationally reorienting in the crystalline phase.

These conclusions differ somewhat from those of Ubbelohde *et al.*^(11,22-24) who consider that only acenaphthene and triphenylene may have sufficient volume to reorient in the crystal and that in addition to these, benzene, naphthalene, pyrene, and fluoranthene, have room for "free rotation" only in the melt. Phenanthrene and chrysene, in principle, do not have room for such rotation even in the melt. In these two instances at least, vibrational entropy changes on melting may make substantial contributions to the entropies of melting. Phenanthrene⁽⁴⁵⁾ also has recently been reported to show a small thermal anomaly of as yet unexplained origin near 342 K. As previously noted, thermal data on the melting of coronene would also be of special interest.

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