The heat capacity and thermodynamic functions of crystalline and liquid triptycene

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The heat capacity of the propeller-shaped molecule triptycene ($C_{20}H_{14}$) was measured from 5 to 550 K. No anomaly other than melting was apparent, and the sample (99.999 per cent pure, as determined by analysis of the melting curve) melted at 527.18 K ($\Delta_m S = 13.73$ cal mol^{-1} K^{-1}). The crystal density, determined from X-ray measurements, was 1.227 g cm^{-3}. A comparison of the heat capacity of triptycene with that of bicyclo[2.2.2]octane showed that the two were simply related at low temperatures, but that the comparison was not valid beyond 164.25 K where bicyclo-octane has a transition to a restricted-rotor phase. The values of C_p, S° ($H^\circ - H_0^\circ)/T$, and $-(G^\circ - H_0^\circ)/T$ for triptycene at 298.15 K were found to be 67.56, 65.48, 33.23, and -32.25 cal mol^{-1} K^{-1}.

1. Introduction

The hydrocarbon triptycene ($C_{20}H_{14}$; 9,10-*o*-benzeno-9,10-dihydroanthracene) possesses an interesting paddle-wheel structure which was assigned on the basis of chemical,[1] spectroscopic,[2] and n.m.r.[3] evidence. The molecular and crystal structures have been confirmed by X-ray analysis of the 9-β-chloroethyl[4] and 9-bromo[5] derivatives of triptycene and of triptycene itself.[6]

The hub of the structure is akin to that of bicyclo[2.2.2]octane,[7] the thermo-dynamic properties of which have been reported elsewhere;[8] in triptycene the cage of bicyclo-octane is augmented by radially disposed benzene rings as shown below.
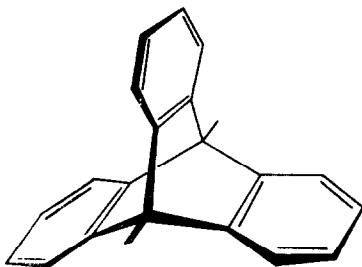
This investigation of the thermal properties of triptycene was undertaken to further our understanding of the thermodynamic properties of molecular crystals composed of symmetrical molecules. It was also hoped that a relationship might be found

between the heat capacity of triptycene and that of the parent bicyclo-octane. Measurement of the density of the material by X-ray diffraction was used to gain insight regarding the packing within the crystal.

2. Experimental

SAMPLE PROVENANCE AND PURIFICATION

The sample of triptycene obtained from Distillation Products, Inc. consisted of small, white, cubical crystals. The sample was purified by zone-refining techniques: about 120 g of material was loaded into a Pyrex tube (13 mm i.d., 70 cm long), which was then placed in a vertical array of seven heaters. After slowly raising the tube through a distance equal to the (constant) spacing between the heaters it was then rapidly returned to the starting position. In this way, 693 zones were passed through the sample mass. At the end of the zone-refining, the sample was transparent and colorless save for a 2 to 3 cm portion at each end of the tube, which was cut off and discarded.

PURITY DETERMINATION

The purity of the sample was determined from observations of the melting behavior. A plot of the melting temperature against the reciprocal of the fraction melted was analyzed according to the method of Mastrangelo and Dornte,[9] and the results are discussed in detail later in this paper.

SPACE GROUP AND DENSITY DETERMINATION

A small, well-formed, crystal was chosen from a number grown from the vapor phase, and was mounted on a goniometer. X-ray diffraction photographs were taken of the 0kl, h0l, hK0, 1kl, H1l, and hk1 reciprocal lattice nets using a Buerger precession camera equipped with a Polaroid film holder. Copper K_α radiation was employed, and the dimensions of the unit cell were calculated from direct measurements of the precession photographs.

CALORIMETRY

The heat capacity of triptycene was determined over two temperature ranges. That from 300 to 550 K was measured first in the Mark IV intermediate temperature thermostat.[10] The sample was loaded into the high temperature calorimeter by vacuum fusion through a glass frit, which removed any glass chips introduced in the trimming of the zone-melting tube. At the completion of the high temperature measurements, the sample was unloaded by vacuum fusion. Subsequently, it was loaded mechanically into the calorimeter for cryogenic measurements which were made in the Mark II cryostat.[11] Both sets of apparatus employ vacuum techniques to isolate the calorimeter, and use three channels of automatic electronic apparatus (equipped with proportional, rate, and reset action) to control the temperature of the adiabatic shield. The Mark IV thermostat also includes an automatically controlled guard shield. The high temperature calorimeter (laboratory designation W-22N, internal

volume 83.7 cm^3, tare mass including screw closure 94.75 g) was of silver; that used for the low temperature measurements was made of gold-plated copper (laboratory designation W-42, internal volume 93.0 cm^3, tare mass including screw closure 44.88 g). Both calorimeters were equipped with entrant wells into which 25 Ω platinum resistance thermometers were fitted. The heaters were wound on copper sleeves around the thermometers. Thermal contact between the calorimeter and the thermometer–heater assembly was assured by screw pressure (Mark IV), or by use of a small quantity of Apiezon T grease (Mark II). Both calorimeters were sealed with screw closures fitted with gold gaskets. Both platinum resistance thermometers (A-8 in Mark IV, and A-5 in Mark II) had been calibrated by the National Bureau of Standards. All potential differences were measured with a Rubicon six-dial, micro-volt, double potentiometer, and all measurements of potential difference, resistance, mass, and time were referred to calibrations or standardizations performed by the National Bureau of Standards.

Heat capacity measurements were made by the quasi-adiabatic technique,[12] corrections being applied for the small departures from adiabatic conditions. The heat capacity of the empty calorimeter together with the thermometer–heater assembly was measured in a separate series of experiments. Small quantities of helium (0.68 mg for the Mark IV series, 0.76 mg for the Mark II series) were sealed within the calori-meters to assist in the rapid attainment of thermal equilibrium, and corrections were applied for the difference in helium content between the calorimeters when run empty and when run with triptycene.

The calorimetric sample of triptycene had a mass of 70.755 g for the Mark IV series, and 66.275 g for the Mark II series. A density of 1.227 g cm^{-3} (obtained from the X-ray measurements) was used to calculate the masses from the weighings.

3. Results

HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS

The heat capacity results are reported in chronological sequence in table 1. Through-out this paper the molar mass of triptycene, $C_{20}H_{14}$, is taken as 254.33 g mol^{-1} (according to the 1961 atomic weights[13]), cal = 4.184 J, and the ice temperature is taken as 273.15 K. The results have been corrected for the "curvature" occasioned by the finite temperature increments necessarily employed in the heat capacity deter-minations.[12] These temperature increments may be, in general, inferred from the difference between the mean temperatures of adjacent determinations. Above 50 K the results are considered to have a probable error of a few hundredths of a per cent. Below this temperature, the results are less precise and 1 per cent may be claimed near 10 K. These estimates are confirmed by comparisons of results taken in these cryo-stats on standard reference materials[12] with those taken in other laboratories. The heat capacity measurements on triptycene are presented in figure 1, which combines results from both apparatuses. No thermal anomaly other than that occasioned by fusion is evident in the heat capacity results. Enthalpy Runs A and B covering the temperature interval from 429 to 519 K, agreed within ±0.01 per cent with the in-tegral along the smooth curve through the heat capacities.

TABLE 1. Experimental heat capacity of triptycene

$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal K}^{-1}\text{mol}^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal K}^{-1}\text{mol}^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal K}^{-1}\text{mol}^{-1}}$
		Measurements in the mark IV thermostat			
	Series I	490.26	112.07	529.22	275.4
295.64	66.95	497.32	113.62	533.81	130.94
298.63	67.74	504.31	114.94		
305.97	69.83	507.33	115.16		Series III
309.00	70.41	514.21	116.88	518.65	117.72
316.49	72.49	520.92	118.26	522.06	118.51
325.29	74.72	525.69	268.1	525.39	123.81
334.37	76.89	527.17	110×10^3	527.08	291.2
343.75	79.27	527.18	160×10^3		$\Delta_m H$ Run C
353.43	81.62	527.18	528×10^3		$\Delta_m H$ Run D
362.89	83.92	527.18	200×10^3	528.59	145.47
372.16	85.97	527.18	100×10^3		
378.78	87.65	527.18	100×10^3		Series IV
388.21	90.22	527.19	57×10^3	520.07	117.77
397.95	92.23	528.94	234.5		$\Delta_m H$ Run E
407.48	94.36	532.50	131.01		
416.81	96.48	536.12	131.60		Series V
425.13	98.39				$\Delta_m H$ Run F
432.51	99.89		Series II		
439.81	101.50		Enthalpy Run A		Series VI
442.99	102.13		Enthalpy Run B	527.18	36×10^3
450.11	104.43	521.74	118.41	535.36	131.29
457.18	105.34	525.67	374.3	538.59	131.46
464.14	106.84	527.18	480×10^3	542.01	132.14
471.01	108.27	527.18	1100×10^3	545.42	132.51
477.51	109.62	527.18	840×10^3	548.81	133.23
483.67	111.09	527.18	2600×10^3		
		Measurements in the mark II cryostat			
	Series VII	129.27	28.47	15.83	2.82
214.46	46.54	138.51	30.28	17.38	3.33
219.35	47.96	147.88	32.14	19.12	3.98
226.95	49.55	157.28	34.05	21.02	4.67
235.97	51.88	166.40	35.98	23.19	5.46
246.14	54.36	175.46	37.92	25.79	6.36
255.94	56.79	184.57	39.90	28.78	7.34
265.39	59.18	193.69	41.89	31.66	8.25
274.53	61.46	202.86	43.99	34.71	9.18
283.38	63.70	212.05	46.16	38.54	10.27
292.59	66.06	221.17	48.34		
302.15	68.46	230.58	50.60		Series X
311.43	70.84	239.87	52.91	34.93	9.24
320.44	73.07			38.95	10.37
330.13	75.46		Series IX	42.97	11.42
340.45	77.97	5.71	0.12	47.34	12.53
347.34	79.46	6.56	0.20	52.03	13.64
		7.50	0.32	57.09	14.75
	Series VIII	8.42	0.48	62.62	15.95
95.11	22.12	9.41	0.74	68.77	17.18
102.88	23.49	10.52	1.03	75.66	18.47
111.37	25.04	11.78	1.36	83.32	19.98
120.24	26.73	13.17	1.80	91.69	21.52
		14.51	2.22	100.77	23.11

TABLE 2. Thermodynamic functions of triptycene

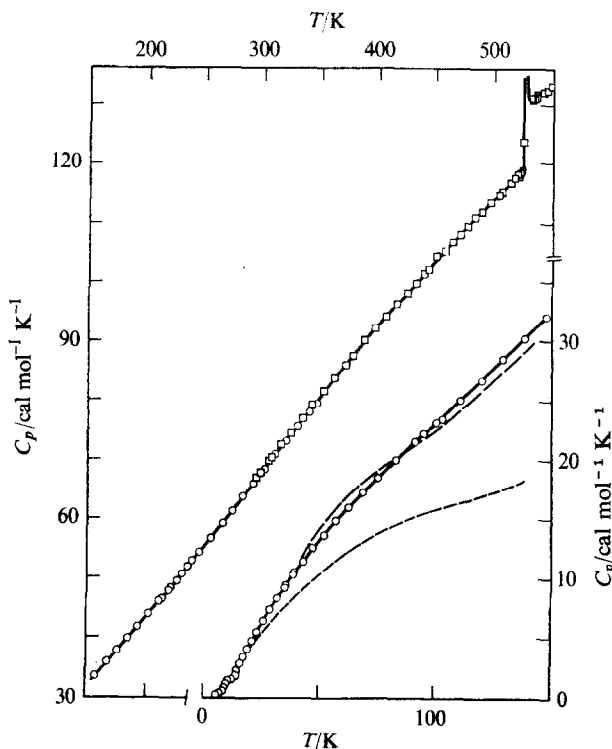| $\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal mol}^{-1}\,K^{-1}}$	$\dfrac{S^\circ}{\text{cal mol}^{-1}\,K^{-1}}$	$\dfrac{(H^\circ - H_0^\circ)/T}{\text{cal mol}^{-1}\,K^{-1}}$	$\dfrac{-(G^\circ - H_0^\circ)/T}{\text{cal mol}^{-1}\,K^{-1}}$
10	0.863	0.266	2.02	0.064
20	4.303	1.859	26.99	0.510
30	7.731	4.272	87.65	1.350
40	10.649	6.907	179.96	2.408
50	13.17	9.561	299.3	3.574
60	15.40	12.163	442.4	4.790
70	17.43	14.691	606.7	6.025
80	19.33	17.144	790.5	7.262
90	21.16	19.526	993.0	8.493
100	22.98	21.85	1213.8	9.712
110	24.81	24.13	1452.7	10.92
120	26.67	26.36	1710	12.11
130	28.58	28.57	1986	13.30
140	30.55	30.76	2282	14.46
150	32.56	32.94	2597	15.62
160	34.63	35.11	2933	16.77
170	36.75	37.27	3290	17.92
180	38.91	39.43	3668	19.05
190	41.12	41.59	4068	20.18
200	43.37	43.76	4491	21.31
210	45.67	45.93	4936	22.43
220	48.01	48.11	5404	23.54
230	50.40	50.30	5897	24.66
240	52.83	52.49	6413	25.77
250	55.29	54.70	6953	26.89
260	57.79	56.92	7519	28.00
270	60.33	59.15	8109	29.11
273.15	61.13	59.85	8300	29.46
280	62.88	61.39	8725	30.22
290	65.46	63.63	9367	31.34
298.15	67.56	65.48	9909	32.25
300	68.03	65.90	10034	32.45
310	70.60	68.17	10728	33.57
320	73.16	70.45	11446	34.68
330	75.70	72.74	12191	35.80
340	78.20	75.04	12960	36.92
350	80.67	77.34	13755	38.05
400	92.53	88.90	18090	43.68
450	103.85	100.46	23000	49.35
500	113.98	111.94	28453	55.03
527.18	(119.38)	118.11	31620	58.12
Liquid				
527.18	(130.86)	131.84	38856	58.12
530	130.90	132.53	39229	58.51
540	131.56	134.98	40541	59.90
550	133.45	137.41	41865	61.29

FIGURE 1. The heat capacity of triptycene. The circles represent the experimental determinations. The dotted curve is the heat capacity of bicyclo[2.2.2]octane.[8] The dashed curve is the latter incremented by three times the C_{vib} of benzene from spectral data[16] and by the hinged motion of the three vanes, and thus represents a model heat capacity in good accord with the results.

The thermodynamic functions of triptycene have been obtained by integration of a polynomial in reduced temperature fitted to the experimental measurements by least-squares procedures.[14] The resulting functions are considered to have a probable error less than 0.1 per cent above 100 K. They are presented in table 2, together with the heat capacity at rounded temperatures obtained by the expansion of the polynomial.

The extrapolation of the heat capacity below the lowest temperature of the measurements was accomplished with the aid of a C_p/T against T^2 plot.[12] The linearity of this plot indicated that the Debye T^3 law holds well for this material.

THERMODYNAMICS OF MELTING

The enthalpy of melting $\Delta_m H$ was measured in five series of determinations through the melting region. The apparent enthalpy increments were corrected for the lattice (or background) heat capacities of the liquid and crystal phases by the use of linear extrapolations fitted by least-squares to the heat capacities below and above the melting temperature. The enthalpy changes were also corrected for the departure from adiabatic conditions over the duration of long determinations from a knowledge of

the temperature drift and the average heat capacity of the sample. These drift corrections were required only on those sequences which consisted of many small energy inputs, or if a long wait was needed before thermal equilibration was reached. Of the five series, two required large drift corrections, and were therefore excluded from the averaging procedure. The remaining three sequences required only very small corrections.

A summary of the determinations of the melting enthalpy is made in table 3. $\Delta_m S$ was determined by assuming that melting is truly isothermal. In view of the absence of premelting, this is a defensible procedure.

The apparent melting temperature varied as a function of the fraction f of the sample melted (see table 4). A plot of the melting temperature against the reciprocal

TABLE 3. Enthalpy of fusion of triptycene

Series and designation	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{H(T_1) - H(T_2)}{\text{cal mol}^{-1}}$	$\dfrac{\Delta H(\text{lattice})}{\text{cal mol}^{-1}}$	$\dfrac{\Delta_m H^{\,a}}{\text{cal mol}^{-1}}$
1, Points 32 to 41	517.62	530.70	8830.8	1592	7240 [b]
3, $\Delta_m H$ Runs C and D	520.36	530.01	8422.9	1180	7236
4, $\Delta_m H$ Run E	516.42	537.19	9820.3	2584	7236
5, $\Delta_m H$ Run F	522.68	536.55	8998.0	1762	7236

$T_m/K = 527.18$
$\Delta_m S/\text{cal mol}^{-1}\,K^{-1} = 13.73$

Average $\Delta_m H$: 7236

[a] Corrected for "lattice" enthalpy increments between T_1 and T_m, T_m and T_2, and for quasi-adiabatic drifts.
[b] Excluded from the average as thermal equilibrium was not awaited during this series.

of the fraction melted was linear at larger values of $1/f$, but showed significant upward curvature at lower values indicative of solid solution formation between the pure material and its impurity. Analysis of this curve by the method of Mastrangelo and Dornte[9] shows that the sample was 99.999 moles per cent pure and that the distribution coefficient of the impurity between solid and liquid phases was 0.637.

TABLE 4. Fractional melting of triptycene

$\dfrac{\langle T \rangle}{K}$	$\dfrac{C_p}{\text{cal mol}^{-1}\,K^{-1}}$	$\dfrac{\Delta H}{\text{cal mol}^{-1}}$	$\dfrac{\Delta H_{\text{excess}}}{\text{cal mol}^{-1}}$	f^{-1}	$\dfrac{T_{\text{final}}}{K}$
525.67	374.28	1125.36	766.96	9.43	527.1745
527.18	480×10^3	1086.16	1085.89	3.91	527.1767
527.18	1150×10^3	1880.31	1880.11	1.94	527.1784
527.18	840×10^3	1489.08	1488.86	1.39	527.1802
527.18	2600×10^3	1487.18	1487.18	1.08	527.1807
529.22	275.41	1125.52	590.19		

$\Sigma \Delta H_{\text{excess}} = 7236.2$

Triple point of sample: $T_m/K = 527.181$; triple point of pure compound: $T_m^0/K = 527.184$.
Mole fraction of impurity: 5×10^{-6} by method of Mastrangelo and Dornte.[9]

SPACE GROUP AND DENSITY OF THE CRYSTAL

Examination of the reciprocal lattice nets obtained with the precession camera showed that three point groups had to be considered: mmm, $mm2$, 222. The crystal was therefore orthorhombic. No general absences were to be seen, but special absences of the type $h00$, $0k0$, $00l$ were seen where h, k, l were odd. These absences are those due to three 2_1 screw axes parallel to the crystal axes, and the space group may therefore be unambiguously determined as $P2_12_12_1$. This space group has four general positions in the unit cell[15] which do not have special symmetry (point symmetry 1). Since the unit cell contains four formula units (as determined from molecular weight and cell volume), it is not possible to draw any conclusions as to the molecular symmetry from the space group. Measurement of the reciprocal lattice parameters shows that the dimensions of the unit cell are 0.826, 2.055, and 0.811 nm. For four formula units per cell, the density is $1.227 \, g \, cm^{-3}$. This crystallographic information is in good agreement with unpublished X-ray data of Neuman and Knox[6] and the apparent density in the zone melting tube.

4. Discussion

The similarities between the molecular structures of triptycene and bicyclo-octane encouraged attempts to relate the heat capacity of these two compounds. The molecule of triptycene may be regarded as a central hub of bicyclo-octane around which three benzene rings are arranged somewhat like the vanes (or blades) of a paddle wheel. This model obviously introduces some atoms and bonds that are not present in the molecule of triptycene and the comparison ought not to be carried to high temperatures where these "extra" components contribute significantly to the heat capacity. At low temperatures, however, the vibrations associated with these groups should not be greatly excited, and comparison may be attempted. The contributions of the benzene rings to the heat capacity are occasioned by the internal vibration of the benzene molecule and the bending motions of the rigid vanes with respect to the hub. The first contribution may be calculated from the vibrational frequency assignment of Calloman, Dunn, and Mills;[16] the second, from the bending modes, might be estimated by comparison with the as yet unknown bending mode in dihydroanthracene.

Figure 1 demonstrates the applicability of this model. Here, the heat capacity of bicyclo-octane[8] plus three times the vibrational heat capacity of benzene[16] is taken to represent all contributions for the model except that from the bending modes. The difference between this sum and the heat capacity of triptycene is related to the heat capacity of the bending mode and may be represented by three Einstein terms with characteristic temperatures of 144 K ($\hat{=} \, 100 \, cm^{-1}$). This implies that the wavenumber of the normal mode best describing this bending lies at $100 \, cm^{-1}$. In the absence of experimental results, calculated force constants for this mode are in substantial accord with force constants for similar bending listed by Herzberg.[17] The model shows good agreement with the heat capacity of triptycene until bicyclo-octane undergoes transition to a restricted-rotor phase at 164.25 K. Triptycene, however, is tightly packed into the lattice and is apparently unable to reorient. This model of the behavior of triptycene appears to have validity at low temperatures, but at higher

temperatures it is likely that the "extra" bonds and atoms introduced contribute to the heat capacity.

The difference in heat capacity between the crystal and liquid phases may be calculated (from the intercepts at the melting temperature of the linear extrapolations fitted to the data above and below this temperature) as $11.48 \, cal \, mol^{-1} \, K^{-1}$ or $5.8 \, R$. This large difference suggests that the molecules are held rigidly in the crystal lattice, and acquire significant motion only upon passing into the liquid phase.

If the molecules, rigidly held in the lattice, acquire free rotational and translational ability on melting, then the new motions will add $R/2$ for each degree of freedom of the motion, or $3R$ in all. Restricted motions can add up to R for each degree of freedom, or $6R$ in all. The experimental heat capacity difference, $5.8 \, R$, suggests that the motions of the molecules in the liquid immediately above the melting point are restricted. Al Mahdi and Ubbelohde[18] concluded (from volumetric studies) that this must be the case for many organic molecules.

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