Heat Capacity and Thermodynamic Properties of Benzothiazole from 5° to 320° K.

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The low-temperature heat capacity of benzothiazole was determined by adiabatic calorimetry. The heat capacity (C_p), entropy ($S°$), and Gibbs function, ($(G° - H_0°)/T$), of the liquid phase at 298.15° K. are: 45.30, 50.15, and −20.58 cal. per mole ° K. The stable form melts at 275.65° K. with an entropy of melting of 11.09 cal. per mole ° K. The heat capacity showed only normal sigmate behavior.

LOW-TEMPERATURE thermal measurements have been made on benzothiazole as an extension of the researches of Metzger (*1, 15, 20*) in Marseilles on the structural properties of thiazole bases, and of this laboratory on the thermal properties of rigid aromatic molecules (*7, 8, 23*). Neither the interesting thermal behavior of thiazole (*8*) nor the transitions characteristic of benzothiophene (*4*) were found in this study. A metastable form which occurred upon crystallization from the melt was detected; but in contrast to those observed for 2-methylthiazole (*7*) and for benzothiophene, it could not be isolated in the calorimeter for thermal investigation.

EXPERIMENTAL

Measurements were made at temperatures between 5° and 320° K. entirely by adiabatic calorimetry, using the previously described (*21*) Mark III cryostat. The gold-plated copper calorimeter provided with horizontal radial vanes (laboratory designation W-24A) has a capacity of 90.4 cc. Precise electrical energy additions to the calorimeter provided temperature increments (of about 10% of the temperature, but not in excess of 10° K.) carefully monitored by a capsule-type, strain-free platinum resistance thermometer (laboratory designation A-3) located within the entrant well of the calorimeter. This permits determination of $\Delta H/\Delta T$, which in the limit (as ΔT approaches zero) may be interpreted as the heat capacity. During these determinations automatic adiabatic shield control provided with proportional, rate, and reset control actions reduces energy exchange between calorimeter and surroundings so that it is negligible in comparison with other sources of error. All measurements of mass, temperature, resistance, potential, and time are referred to standardizations and calibrations performed by the National Bureau of Standards.

The mass of the calorimetric sample was in vacuo 67.7107 grams. Its heat capacity ranged from 88% of the total at 10° K. to 80% at 100° K. and gradually decreased to 70% at 310° K. Buoyancy corrections were made using a sample density of 1.2384 grams per cc. (*1*). Helium at a pressure of 112 torr at 300° K. was used to facilitate thermal equilibration in the sample space.

Preparation and Characterization of Sample. Benzothiazole was synthesized at Marseilles (*13*) by standard procedures, purified by fractional crystallization and low-pressure distillation (T_b = 120° C. at 20 torr), and stored in evacuated glass ampoules. The sample was characterized by its infrared spectrum. The amount of liquid-soluble, solid-insoluble impurity was estimated from a plot of the apparent melting temperature *vs.* the reciprocal of the fraction melted, $1/F$, using the data given in Table IV. The mole fraction of impurity, N_2, was evaluated from the formula:

$$N_2 = \Delta Hm\ (T_0 - T_1)/RT_0^2$$

in which ΔHm is the enthalpy of melting; T_0 and T_1 are the triple point temperatures of the pure substance and of the present sample, and are the temperatures corresponding to $1/F = 0$ and $1/F = 1$, respectively. Values of T_0, T_1, and N_2 so found are 275.65° K., 275.60° K., and 0.0010, respectively. Meyer (*14*) reported T_0 = 275.98° K. and ΔHm = 3182 cal. per mole from cryometric measurements.

RESULTS AND DISCUSSION

Thermodynamic Properties. The heat capacity at the mean temperature of each determination is listed in Table I. These data have been adjusted for curvature and are given in terms of the defined thermochemical calorie of 4.1840 joules, an ice point of 273.15° K., and a molar mass of 135.189 grams. The probable errors of the heat capacity measurements are considered to be 0.2% above 25° K. and increase to 5% at 5° K. The determinations designated ΔHm in Table I refer to enthalpy of melting measurements (detailed in Table III); those designated ΔH refer to enthalpy increment runs spanning too great a range of temperature to provide heat capacity values. However, the latter provide the basis for a check, upon comparison with the integrated heat capacity curve. ΔH determinations, D, E, F, and I, accord within ±0.08% with the integrals over the temperature range. The smoothed heat capacity and the thermodynamic functions derived from these data are given at selected temperatures in Table II. The heat capacity was extrapolated below 6° K. by the Debye T^3 limiting law. The functions were calculated by a high speed digital computer, using programs previously described (*9*). The entropy and the Gibbs function have not been adjusted for nuclear spin and isotopic mixing contributions and hence are practical values for use in chemical thermodynamic calculations.

Melting and Freezing Behavior. The phase equilibria, and consequently the thermal behavior of benzothiazole, are complicated by the existence of both a stable and a metastable crystalline form. The metastable form, observed by cooling-curve studies and on one crystallization in the calorimeter, could not be routinely formed or retained. Nevertheless, these observations confirmed the existence of a metastable form as reported by Meyer and Metzger (*16*), Witschonke (*22*), and Goursot (*6*). The fact that no thermal irregularity was observed on the C_p *vs.* T curve, comparable to the transition noted on the benzothiophene curve, confirms that the introduction of a nitrogen atom in the thiophene ring smoothes the low-temperature thermal behavior. A similar effect has previously been noted for thiazole (*8*) and for 2-methylthiazole (*7*) relative to the corresponding thiophenes. The increasing slope of C_p *vs.* T for benzothiophene was attributed to a probable increase in the number of orientations permitted to the molecule. Introduction of a nitrogen atom into the benzothiophene ring increases the geometrical molecular volume or repulsive

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Table I. Experimental Heat Capacity of Benzothiazole[a]

T	C_p
Series I	
226.85	26.64
ΔHm Detns. A	
Series II	
Melting Detns. B	
279.01	44.26
287.77	44.65
Series III	
223.22	26.27
234.66	27.60
245.72	28.91
256.33	31.31
ΔHm Detns. C	
286.82	44.52
Series IV	
110.80	14.89
120.28	15.73
130.19	16.67
140.57	17.65
151.38	18.67
162.59	19.76
172.96	20.79
183.06	21.84
193.92	22.98
205.02	24.19
215.91	25.38
226.61	26.58
236.98	27.82
Series V	
5.67	0.059
6.54	0.104
7.14	0.135
8.12	0.233
8.98	0.326
9.82	0.456
10.81	0.602
11.97	0.793
Series VI	
5.53	0.066
5.70	0.059
6.78	0.112
7.66	0.189
8.75	0.298
10.03	0.471
13.98	1.202
15.36	1.522
16.78	1.892
18.42	2.321
20.13	2.767
21.99	3.299
24.46	3.927
27.04	4.587
29.84	5.250
33.43	6.050
37.07	6.764
40.35	7.367
44.27	8.014
49.48	8.782
55.80	9.619
62.39	10.398
70.26	11.130
79.32	12.100
88.20	12.962
98.09	13.771
ΔH Detn. D	
125.42	16.20
132.72	16.89
139.79	17.74
149.89	18.52
167.10	20.28
ΔH Detn. E	
215.81	25.40
ΔH Detn. F ΔHm Detns. G	
291.38	44.89
298.49	45.35
305.56	45.66
312.55	46.19
Series VII	
ΔHm Detn. H	
Series VIII	
ΔH Detns. I ΔHm Detns. J	
Series IX	
240.03	28.22
ΔHm Detns. K	
Series X	
ΔHm Detns. L	
Series XI	
243.85	28.59
251.42	30.14
256.11	31.73
260.70	32.37
265.31	33.59
269.57	38.39
273.04	63.59
ΔHm Detn. M	
279.03	50.16
286.15	44.58
Series XII	
282.45	44.32
289.96	44.74
297.42	45.26
304.81	45.74
312.14	46.20
319.41	46.70
Series XIII	
ΔHm Detn. N	

[a] Units. Cal., mole, ° K.

Table II. Thermodynamic Properties of Benzothiazole[a]

T	C_p	$S°$	$H° - H_0°$	$-(G° - H_0°)/T$
		Crystal		
5	0.056	0.018	0.069	0.005
10	0.470	0.142	1.075	0.034
15	1.441	0.500	5.663	0.123
20	2.745	1.089	16.05	0.286
25	4.076	1.846	33.15	0.521
30	5.286	2.698	56.60	0.812
35	6.372	3.597	85.81	1.145
40	7.304	4.510	120.05	1.508
45	8.123	5.418	158.7	1.893
50	8.852	6.313	201.1	2.290
60	10.109	8.041	296.1	3.106
70	11.184	9.682	402.7	3.929
80	12.149	11.239	519.4	4.746
90	13.057	12.723	645.5	5.551
100	13.943	14.145	780.5	6.340
110	14.83	15.515	924.4	7.112
120	15.74	16.844	1077.2	7.868
130	16.66	18.140	1239.1	8.608
140	17.60	19.409	1410.5	9.334
150	18.56	20.656	1591.3	10.048
160	19.53	21.885	1782	10.749
170	20.52	23.099	1982	11.440
180	21.53	24.300	2192	12.121
190	22.56	25.492	2413	12.794
200	23.63	26.676	2644	13.458
210	24.73	27.86	2885	14.12
220	25.86	29.03	3138	14.77
230	27.02	30.21	3403	15.41
240	28.22	31.38	3679	16.05
250	29.80	32.56	3967	16.69
260	32.12	33.73	4266	17.32
275.60[b]	(32.36)	(35.56)	(4757)	18.30
		Liquid		
275.60[b]	(43.88)	46.65	7812	18.30
280	44.16	47.35	8005	18.75
290	44.78	48.91	8450	19.77
298.15	45.30	50.15	8817	20.58
300	45.42	50.44	8901	20.76
310	46.08	51.94	9359	21.75
320	46.73	53.41	9823	22.71
325	47.07	54.14	10057	23.19

[a] Units. Cal., mole, ° K. [b] Assuming completely isothermal melting.

envelope and decreases the pseudosymmetry of the molecule, making it more difficult either to realize such rotation in the crystal or to prevent it fully.

Ten enthalpy increment determinations were made through the melting region (Table III). The average enthalpy of melting calculated from the excess enthalpy over extrapolated curves drawn to represent the normal crystalline and liquid heat capacities is 3055 cal. per mole. The fractional melting data are summarized in Table IV.

Table V shows that the increments between entropies of melting for pyridine and quinoline, thiazole and benzothiazole, and naphthalene and anthracene are remarkably constant. This fact strongly suggests that the rotational entropy increment upon melting for these pairs of molecules is nearly the same. Probably no significant degree of rotational reorientation is gained by the benzothiazole molecule from 5° K. through melting. ΔSm for naphthalene and ($\Delta Sm + \Delta St$) for benzothiophene are nearly the same, but ΔSm for benzothiazole and quinoline are smaller. These differences may arise from molecular association in the liquid phase for the latter two substances, as suggested by several authors interpreting results of studies in solutions near 300° K. (*1, 12, 16, 17, 19*). This interpretation also accords with Bondi's hypothesis (*3*).

Table III. Enthalpy of Melting of Benzothiazole[a]

Detn. Designation	Energy Increments	T_1	T_2	$H_{T_2}-H_{T_1}$	$H_{280} - H_{240}$
A	5	233.51	287.98	4863.26	4328.0
B	12	248.07	282.38	4172.54	4299.8[b]
C (Series III)	4	240.29	282.74	4434.07	4321.1
G	2	262.73	287.80	3984.61	4332.6
H	2	249.31	288.23	4428.26	4332.3
J	2	251.49	289.88	4435.92	4331.3
K	2	253.56	291.56	4441.58	4325.2
L	2	262.73	278.92	3583.37	4325.4
M (Series XI)	8	249.04	282.45	4170.71	4323.8
N	1	260.78	277.25	3572.28	4322.3

Av. value $H_{280} - H_{240}$ = 4326.9
Lattice contribution $H_{280} - H_{240}$ = 1271.7
$T_m = 275.65°$ K. ΔHm = 3055 ± 9
ΔSm = 11.09 ± 0.04

[a] Units. Cal., mole, ° K. [b] Excluded from average by Chauvenet's criterion.

Table IV. Fractional Melting of Benzothiazole[a]

T	ΔT	C_s	$\Sigma\Delta H$	T_{final}	$1/F$
275.12	0.546	780	604.9	275.39	4.962
275.44	0.102	4000	1010.7	275.49	2.970
275.51	0.032	8400	1272.7	275.52	2.358
275.54	0.022	12100	1531.2	275.55	1.960
275.56	0.012	28900	1877.7	275.56	1.598
275.57	0.013	26600	2223.7	275.58	1.350
275.59	0.004	80700	2570.4	275.59	1.168

Triple point of pure compound = 275.65
Triple point of sample = 275.60
Mole fraction of impurity = 0.0010

[a] Units. Cal., mole, ° K.

Table V. Thermodynamics of Melting of Related Molecules[a]

Substance	Ref.	ΔSm	$\partial(\Delta Sm)$
Pyridine	*(10)*	8.54	1.50
Quinoline	*(18)*	10.04	
Thiazole	*(7)*	9.57	1.52
Benzothiazole		11.09	
Naphthalene	*(11)*	12.80	1.50
Anthracene	*(5)*	14.30	
Benzothiophene	*(4)*	12.82	

[a] Units. Cal., mole, ° K.

ACKNOWLEDGMENT

The authors appreciate the support of the U. S. Atomic Energy Commission in this research endeavor, and that of Le Centre National de la Recherche Scientifique (France) in providing a fellowship for P. Goursot. The cooperation of Soung-Sik Kim in the calculations and measurements is acknowledged with gratitude.

NOMENCLATURE

C_P = heat capacity at constant pressure
F = fraction melted
$G°$ = standard Gibbs energy
ΔH = enthalpy increments
ΔHm = enthalpy of melting
N_2 = mole fraction of liquid-soluble, solid-insoluble impurity
R = gas constant
$S°$ = standard entropy
ΔSt = entropy of transition
T = temperature, ° K.
T_b = boiling temperature

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RECEIVED for review April 29, 1968. Accepted October 11, 1968.