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Heat Capacity and Thermodynamic Properties of p'-Substituted p-n-Hexyloxybenzylideneaniline. I. p-n-Hexyloxybenzylideneamno-p'-Benzonitrile (HBAB)

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Heat Capacity and Thermodynamic Properties of *p*′-Substituted *p*-n-Hexyloxybenzylideneaniline. I. *p*-n-Hexyloxybenzylideneamino-*p*′-Benzonitrile (HBAB)†

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The heat capacity of the nematogenic liquid crystal, HBAB, has been measured between 15 K and 385 K by using an adiabatic calorimeter. The crystal-crystal phase transition has been discovered at 27 K below the crystal-nematic phase transition temperature. The transition temperatures, the enthalpies and the entropies of the three phase transitions have been determined: $T_t = 306.98$ K, $\Delta H_t = 5.11$ kJ mol^{-1}, $\Delta S_t = 16.7$ J K^{-1}; $T_m = 334.05$ K, $\Delta H_m = 23.77$ kJ mol^{-1}, $\Delta S_m = 71.2$ J K^{-1} mol^{-1}; and $T_c = 375.10$ K, $\Delta H_c = 1.75$ kJ mol^{-1}, $\Delta S_c = 3.2$ J K^{-1} mol^{-1}, respectively. The thermodynamic functions of HBAB from 0 K to 385 K have been determined from the heat capacity data and the enthalpies of the transitions. Two crystal modifications, one yellow and granular form and the other white and needle-like form, have been obtained during the course of the preparation of the sample. It turned out that the yellow form was the stable crystal and the white the metastable modification. The crystal-crystal phase transition has been discussed as an onset of partial melting from the entropy consideration. In this connection the total entropies of the transitions, 91.1 J K^{-1} mol^{-1} has been proposed to be an important measure of melting.

1 INTRODUCTION

Many compounds which exhibit the liquid crystalline state can be classified into several basic forms according to their chemical formulas.[1] A number of studies of liquid crystals were generally carried out as a function of carbon

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number in an homologous series of these specific systems. Variation of the melting temperature, the heat of fusion, or the transition entropy of the homologous series of liquid crystal are usually presented.[2] In general, only one nematic state exists in short-chain compounds under ordinary pressure. And the smectic as well as the nematic state appears with increasing chain length. On further increasing the chain length, the nematic state merged into the smectic state. This trend of appearance is sometimes called a phase diagram. In other words the chain length is the important factor which describes the phase diagram of an homologous series.

Theoretical work was also carried out.[3–6] McMillan has proposed a general formulation of the phase transitions between the smectic, the nematic, and the isotropic states.[3,7,8] In his papers the alkyl chain length plays an essential role. These sorts of the studies seem, however, to have some weak points in them. When one mthylene group is added to an homolog of liquid crystal, the molecule will be lengthened and the strength of the intermolecular force will be altered. This change of the strength of the intermolecular force will induce a different kind of mesogenic state. An introduction of the methylene group will also increase the intramolecular freedom of motion. These internal motions of the molecule may affect the state of aggregation of this material. The result is the change of the molecular length and the increase of the internal motions of the molecule which will induce inevitably another mesogenic state for this compound.

In order to elucidate a relation between the kind of mesogenic state and the intermolecular force, it is necessary to compare systems which are composed of molecules having possibly similar dimensions and chemical formulas. For instance, if two materials exhibit a different kind of mesogenic state in spite of the same chemical formula and the same molecular dimension, except for only an end substituent, its difference will be attributed reasonably to the difference of polarity of the substituents.[9–10] The replacement of this kind of substituent may induce a different type of electrostatic force from that of the previous molecule. This helps to clarify a relationship of the appearance of the mesogenic state to the intermolecular force. Thermodynamic measurements of these materials will provide a quantitative explanation of the interrelation.

Since Kelker and Scheule synthesized MBBA and some of its homolog,[12] this group has been extensively studied by many workers[13–17] because of the facility of the experiments due to their low melting points. In the present study, Shiff's bases were selected as the basic form on account of these facts. General chemical formula of these homologs is represented as $C_nH_{2n+1}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C_mH_{2m+1}$ or abbreviated as nOm, where m and n are integers. For these homologs, Smith *et al.*[15,17] have carried out a systematic investigation by use of differential scanning calorimetry (DSC) and thermomicroscopy. They have reported that the smectic state together with nematics existed in the compounds of *n* being 4, 5, and 6 irrespective of any *m* values. Accordingly, these compounds denoted as 6Om were considered as the upper limit materials at which they had exhibited the smectic state together with nematics in this homologous system. Based on these findings, 60m was selected as a starting chemical formula of our study and alkyl group "*m*" will be replaced by other substituents.

In the present paper, the cyano group was selected as the substituent. The cyano group has a strong nematogen-forming tendency[2] and in fact HBAB is known as a nematic liquid crystal.[18] This substituent is considered to be rigid, coplanar with the benzene ring, and has a strong polarity. Some of the nematogenic properties of HBAB were already studied by several workers.[10,11,18–20] However, a precise thermodynamic experiment had not yet been reported.[21]

As to the precise heat capacity measurement on liquid crystals we refer to a series of work by Arnold *et al.* in the nineteen sixties.[22] The first thermodynamic investigation from 14 K to 370 K on a well-characterized liquid crystal sample (purity 99.39%) was performed by Sorai and Seki on N-(*o*-hydroxy - *p* - ethoxybenzylidene) - *p′* - butylaniline.[23] Then, Andrews and Bacon[24] reported the results of heat capacity measurement from 300 K to 550 K on di - (*p* - methoxyphenyl) - *trans* - cyclohexane - 1,4 - dicarboxylate (DMC).[24] In the present paper we have measured the heat capacity of HBAB between 15 and 385 K by using an adiabatic calorimeter. We will report the results of the experiments in the following two sections and will discuss the thermodynamic properties of HBAB in the final section.

2 EXPERIMENTAL

Sample preparation

The sample was synthesized by the azeotropic dehydration reaction of *p*-n-hexyloxybenzaldehyde (Tokyo Kasei Co.,) and *p*-aminobenzonitrile (Kodak). Quarter moles of both reagents were dissolved in ca. 300 ml. benzene. Reflux for four hours and remove the water and then remove the solvent by evaporation. This procedure was repeated twice. Then the reaction mixture was cooled to precipitate the product and filtered. The crystal obtained was recrystallized twice from ethanol and was purified twice by molecular distillation under vacuum (~1 Pa). The yield of final product was about 20 g. The results of the elemental analyses agreed well with calculated values.

The distilled sample was lumpy and bulky. A sample was fused in the sample cell so as to fill the cell completely and then it was outgassed at about 80°C under vacuum (~1 Pa).

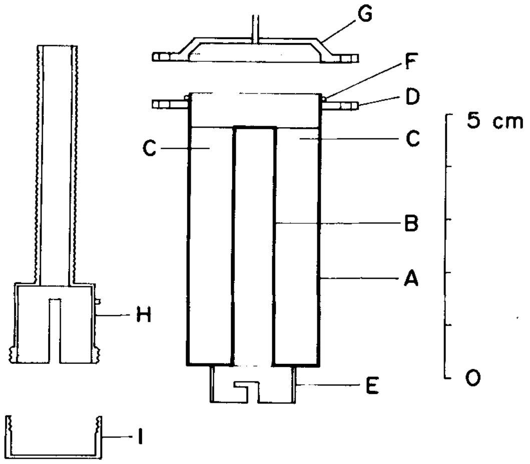

FIGURE 1 Schematic drawings of the sample cell. (A) cell cylinder, (B) thermometer well, (C) vanes, (D) frange, (E) guard ring, (F) Indium wire, (G) lid, (H) sheath for a thermometer, (I) lid.

The sample is yellow in color and granular in shape. In the course of recrystallization, however, a white needle-like crystal was sometimes obtained. Stability of the crystals will be discussed later.

Differential thermal analysis (DTA)

Prior to the heat capacity measurements, the thermal behavior of the sample, especially below room temperature was studied by use of DTA apparatus.[25] Above room temperature DTA (Du Pont Thermal Analyzer 990) was employed.

Heat capacity measurements

The sample cell used for the heat capacity measurements is shown in Figure 1. The cylinder "A" was made of 20 karat gold and the thermometer well "B" and four vanes "C" were made of platinum. The flange "D" and the lid "G" were gold-plated copper and were drilled eight holes for screwing small bolts and nuts. Indium wire of 0.5 mm diameter "F" was used for vacuum seal. A copper tube of 1 mm diameter was soldered on the lid for evacuation or for exchange of the inner atmosphere by helium gas. This copper tube was pinched off above the lid before use. The platinum resistance thermometer with the sheath "H" was inserted into the thermometer well. Around this sheath, "KARMA" wire (Driver Harris) was wound to be about 100Ω for the cell heater. The thermometer and the sheath were covered with the lid "I". Thermal contact among the sample cell, the sheath with the heater, the thermometer, and the lid were realized

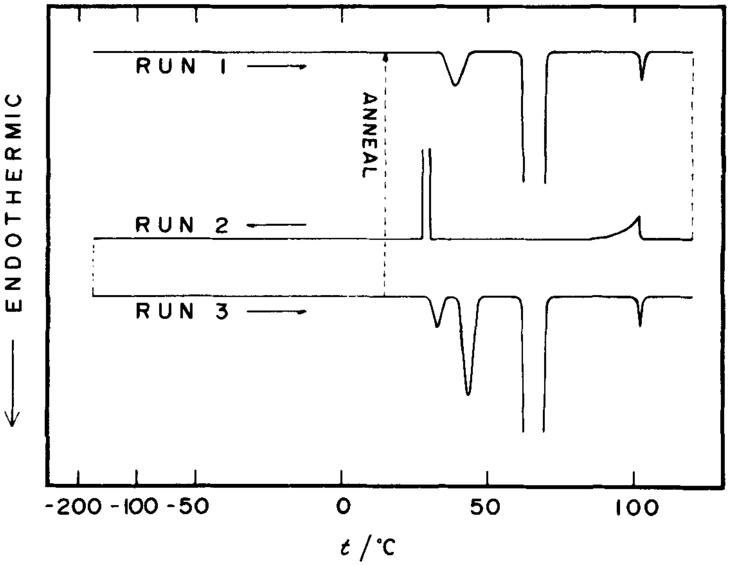

FIGURE 2 DTA curves of HBAB.

partly by mechanical contact and partly by GE-7031 adhesive. The heat capacity at 273.15 K was found to be 23.901 JK^{-1} mol^{-1}.

The calorimeter was of a standard-adiabatic type and had two cans for refrigerant. The lower one provides a mechanical thermal switch for cooling the sample cell. An arbitrary temperature from 2 K to 390 K is able to be realized by a standard cryogenic technique. Adiabatic temperature control was carried out by four-channels automatic temperature-controller.

The platinum resistance thermometer (Leeds & Northrup, CAT-8164) and the Mueller Bridge (Leeds & Northrup, G-2) were used for temperature measurements. The temperature scale was based on IPTS-68. Electric energy supplied to the sample cell was measured by use of the digital multimeter (Keithley, TR-5766). Data were processed by the standard methods.[26] Overall precision of the measured value was less than 0.2 %.

3 RESULTS

DTA DTA curves of HBAB are shown in Figure 2. Run 1 shows the heating curve after cooling the sample down to liquid nitrogen temperature with the average rate of 2°C/min. Three endothermic peaks were observed. The lowest temperature peak was found at about 35°C. The second large peak found at about 61°C corresponding to the known crystal-nematic phase transition. The third peak was due to the nematic-isotropic liquid phase transition. On the cooling curve, Run 2, only two exothermic peaks were

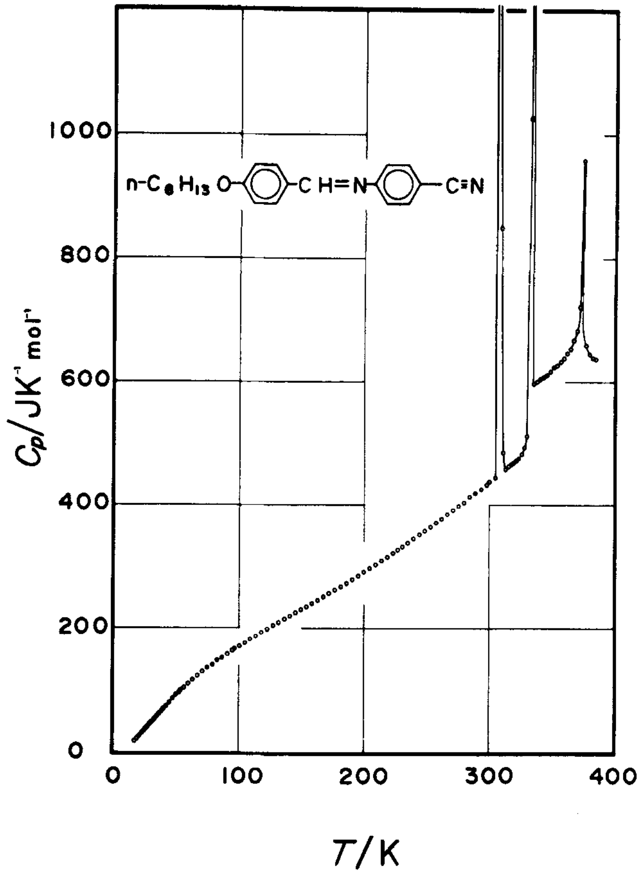

FIGURE 3 Heat capacity curve of HBAB. Whole view.

observed. In contrast with the cooling curve, the second heating curve, Run 3, showed four phase transitions. Sometimes a small exothermic peak at around 0°C was observed in this heating curve. However, the same DTA curve as the Run 1 was obtained by annealing the sample for several hours at around ambient temperature. Therefore it was concluded that these peaks observed in Run 3 except the highest temperature one were due to the phase transitions occurring within the metastable state of HBAB.

The following results were concluded from the DTA. (1) The specimen had the three phase transitions, that is, the crystal-crystal, the crystal-nematic, and the nematic-isotropic liquid phase transitions. (2) Although the metastable crystal appeared on cooling the melted specimen, it was transformed into the stable modification by annealing of the sample at room

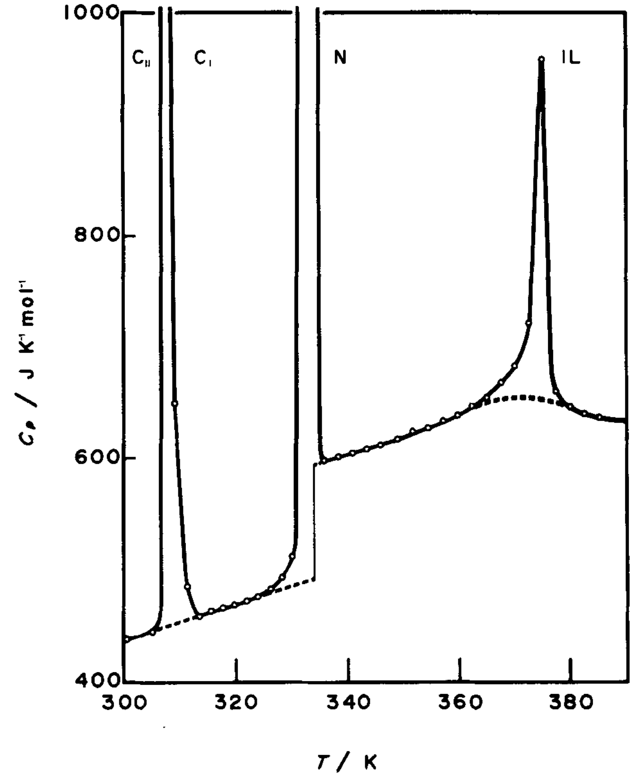

FIGURE 4 Heat capacity curve of HBAB. Enlarged portion of the transition region. Broken lines mean the lattice part of the heat capacity of HBAB.

temperature. We designate hereafter the lower temperature crystalline phase as C_{II} and the higher one as C_I.

Heat Capacity The heat capacity curve of HBAB is shown in Figure 3. In Figure 4, the enlarged portion of the transition region is given. Numerical data are also given in Table I, where the asterisk means the heat capacity of the supercooled form of C_I.

The first anomaly in the heat capacity was observed at about 306 K. The peak temperature in the heat capacity curve, 306.98 K was adopted as the phase transition temperature. This heat capacity anomally corresponded to the lowest temperature peak of DTA, where it was observed at about 308 K. This transition peak had a steep rise and a rather gradual descent and seemed to be somewhat a super-heated one. The rate of this phase transition was so sluggish that more than one day of time was required to attain a thermal equilibrium. The higher temperature crystalline phase C_I easily supercooled

TABLE I

Heat capacity of HBAB

T_{av} / K	C_p / J K^{-1} mol^{-1}	T_{av} / K	C_p / J K^{-1} mol^{-1}	T_{av} / K	C_p / J K^{-1} mol^{-1}
16.74	18.73	158.36	240.40	303.82	440.32*
17.52	20.56	162.80	245.84	306.51	445.81*
18.43	22.62	167.31	251.12	309.57	452.03*
19.39	24.70	171.90	256.88	312.60	457.40
20.26	26.61	176.56	262.12	315.60	461.68
21.06	28.49	181.29	267.72	318.59	466.21
21.90	30.34	185.95	273.27	322.56	474.68
22.76	32.38	190.56	278.92	324.50	479.78
23.63	34.21	195.10	284.47	327.41	489.06
24.65	36.79	199.72	290.57	330.26	514.88
25.92	39.63	204.41	296.59	332.58	1026.7
27.27	42.73	209.17	302.32	333.67	6764.5
28.74	45.87	213.98	308.28	333.90	31142
30.43	49.67	218.72	314.42	333.96	63507
32.22	53.95	223.41	320.87	333.99	102310
34.20	58.49	226.95	326.21	334.01	160200
36.19	62.89	230.45	331.15	334.02	275480
38.19	67.27	234.98	337.46	334.03	311250
39.88	71.08	239.53	344.36	344.05	170770
41.97	75.56	244.08	351.33	334.26	5800.7
44.42	80.66	248.57	357.35	335.77	597.52
47.04	85.85	253.01	363.94	338.34	600.98
49.77	91.66	257.52	370.61	340.90	604.53
52.61	97.40	262.11	377.16	343.45	608.00
53.01	98.14	266.65	384.35	345.99	611.64
56.20	104.32	271.13	391.69		
59.47	110.36	275.56	398.10	349.08	616.69
63.00	117.04	279.95	404.63	351.77	624.26
66.82	123.69	284.27	411.24	354.44	627.11
70.76	130.24	288.52	417.75	357.11	633.21
74.69	136.26	292.69	424.30	359.75	638.52
78.65	141.91	295.84	428.99	362.38	646.24
82.62	148.48	298.10	432.43	365.00	654.00
86.60	152.92	300.39	437.53	367.60	667.86
90.62	158.44	302.76	436.94	370.18	682.65
94.68	164.18	305.02	443.99	372.72	721.14
96.44	166.57	306.50	2399.2	375.10	959.06
100.55	171.75	306.98	7252.1	377.51	659.28
104.70	177.26	307.57	1969.3	380.11	645.71
108.91	182.48	309.03	649.31	382.71	639.57
113.16	187.46	311.23	484.62	385.32	636.40
117.74	193.20	313.47	457.45		
122.49	198.38	315.56	462.13		
127.13	204.27	317.65	465.10		
131.67	209.23	319.73	467.79		
136.19	214.73	321.89	471.30		
140.68	219.95	323.95	475.07		
145.09	225.03	326.09	482.01		
149.44	230.06	328.12	429.45		
153.86	235.20	330.12	511.76		

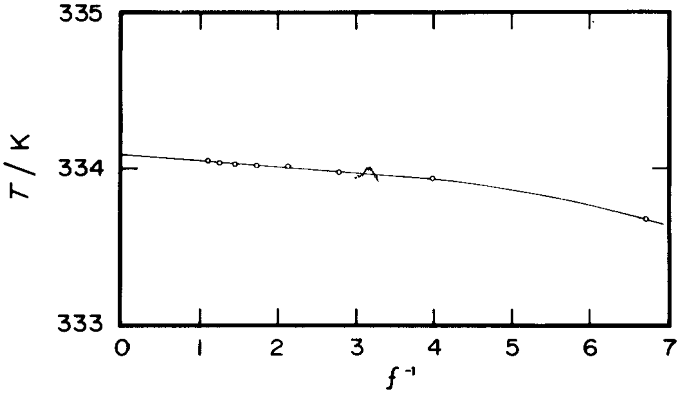

FIGURE 5 Fractional melting of HBAB. Equilibrium temperature vs. reciprocal of fraction melted.

and its heat capacity was able to be measured. The heat capacity curve of supercooled C_I phase coincided with that of the lower temperature phase C_{II}. Therefore the curve was used as a base line in determining the enthalpy and the entropy of this crystal-crystal phase transition.

The C_I-nematic phase transition was found at about 334 K. Accompanying this transition, about 100 J K^{-1} mol^{-1} of the heat capacity jump was observed. The purity of the sample was determined as 99.90 % from the analysis of equilibrium temperature measured as a function of the fraction melted. The melting point of the sample and the triple point of pure HBAB were determined as 334.05 K and 334.088 K, respectively. This melting point was in fairly good agreement with that obtained from DTA. These cryoscopic data are given in Figure 5 and Table II.

The heat capacity curve of the nemaic state increased gradually to the nematic-isotropic phase transition temperature due to the premelting effect. At 375.10 K, the heat capacity curve became maximum. Above the transition

TABLE II
Purity determination of HBAB

$\frac{T}{K}$	$\frac{1}{f}$		
333.671	6.72	enthalpy of melting	23.774 kJ mol^{-1}
333.937	3.99		
333.978	2.78	melting point of sample	334.049 K
334.003	2.13		
334.020	1.73	triple point of pure sample	334.088 K
334.029	1.45		
334.038	1.25	sample purity	99.90 %
334.052	1.10		

TABLE III

Transition temperatures, enthalpies and entropies of transitions of HBAB

	$\frac{T}{\mathrm{K}}$	$\frac{\Delta H_t}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta S_t}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	Reference
$C_{II} \rightarrow C_I$	306.98	5.11	16.7	This work
$C_I \rightarrow N$	334.05	23.77	71.2	This work
	328.15	25.8	77.7	10
	329.65	25.8	78.3	21
$N \rightarrow IL$	375.10	1.75	3.2	This work
	375.15	—	—	10
	375.35	0.64	1.71	21

temperature a post-melting effect was observed. This effect remained even 10 K higher than the transition temperature. Beacause of the high-temperature limit of the calorimeter, the measurement was stopped at 385 K.

To determine the enthalpies and the entropies of the phase transitions, a suitable base line was selected as shown by the broken lines in Figure 4. The thermodynamic quantities associated with the phase transitions were derived by numerical integration of excess heat capacity over the base line. It was very difficult to determine precisely the base line around the nematic-isotropic liquid phase transition region because of pre- and post-melting effects. The values listed in Table III were possibly the minimal ones due to the residual post-melting effect. Table IV gives the smoothed values of the thermodynamic functions at temperatures up to 385 K calculated from the calorimetric data.

Two crystal modifications obtained from recrystallization

As already mentioned, we found two crystal modifications in HBAB. One was yellow colored and granular in shape and the other white or very pale yellow and of needle-like form. When this needle-like form was left at room temperature, it cracked to give the yellow and granular form within a week or so. The DSC curves of these two crystal modifications are shown in Figure 6. Run 1 was for the granular crystal and corresponds to Run 1 in Figure 2. Run 2 was for the needle-like modification and was lacking the C_{II}-C_I phase transition.

4 DISCUSSION

Polymorphism of HBAB

Bernal and Crowfoot studied the crystal structure of *p*-azoxyanisole (PAA).[27] They reported that PAA had two crystal modifications, one was a stable

TABLE IV

Thermodynamic functions of HBAB

T/K	C_p°/J K^{-1} mol^{-1}	S°/J K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$/J K^{-1} mol^{-1}	$-(G^\circ - H^\circ)/T$/J K^{-1} mol^{-1}
10	(6.35)	(3.16)	(2.00)	(1.16)
20	25.97	13.17	8.78	4.39
30	48.83	28.04	18.34	9.70
40	71.25	45.19	28.79	16.40
50	92.09	63.34	39.38	23.96
60	111.34	81.85	49.79	32.06
70	129.00	100.38	59.88	40.50
80	143.82	118.59	69.46	49.13
90	157.66	136.33	78.49	57.84
100	171.18	153.65	87.10	66.55
110	183.76	170.56	95.32	75.24
120	195.63	187.07	103.19	83.88
130	207.34	203.19	110.75	92.44
140	219.11	218.98	118.07	100.91
150	230.70	234.50	125.19	109.31
160	242.44	249.76	132.15	117.61
170	254.46	264.82	138.99	125.83
180	266.22	279.69	145.73	133.96
190	278.30	294.41	152.39	142.02
200	290.90	309.00	159.00	150.00
210	303.18	323.49	165.57	157.92
220	316.12	337.89	172.12	165.77
230	330.50	352.26	178.69	173.57
240	344.92	366.63	185.31	181.32
250	359.50	381.00	191.99	189.01
260	373.99	395.38	198.71	196.67
270	389.76	409.79	205.49	204.30
280	404.72	424.23	212.34	211.89
290	420.00	438.70	219.23	219.47
300	435.50	453.20	226.18	227.02
310	transition	484.10	249.40	234.70
320	468.00	498.95	256.23	242.72
330	transition	513.79	263.07	250.72
340	603.07	601.34	341.39	259.95
350	618.79	619.05	349.07	269.98
360	639.48	636.78	356.86	279.92
370	transition	654.77	364.98	289.79
380	645.90	674.61	374.94	299.67
385	636.68	682.98	378.39	304.59
273.15	394.19	414.34	207.64	206.70
298.15	432.51	450.56	224.89	225.67
373.15	transition	660.73	367.83	292.90

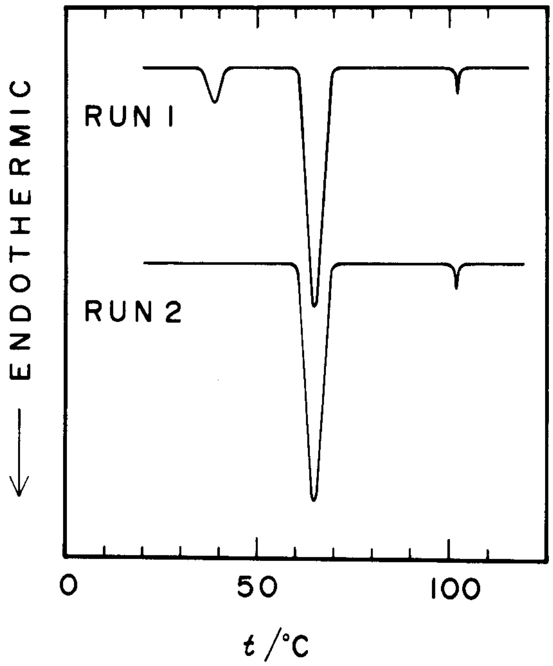

FIGURE 6 DSC curves of two crystalline modifications of HBAB. Run 1: yellow and granular form, Run 2: white and needle-like form.

yellow colored form and the other a white and metastable one. They inferred that these "two crystal modifications differed remarkably little except in habit"[27] of the crystals. They explained also that the molecules might be all parallel and with their benzene rings nearly at right angle in both crystal forms. They did not say anything about why the metastable form was lacking in color.

Unfortunately, we have no crystallographic data for the two crystal modifications of HBAB. In general, however, in the conjugated system such as HBAB the higher the temperature, the more the coplanarity of the benzene planes which results in the deeper color of the materials.[28] Lack of color in the needle-like form suggests that the two benzene planes of HBAB will not be coplanar.

On the other hand, the needle-like modification was proven to be a metastable form at room temperature. The DSC experiments revealed that the needle-like form lacked the crystal-crystal phase transition. These facts strongly suggest that the needle-like modification is a supercooled form of the higher temperature phase. However, this idea seems to contradict the the idea of the color of the crystal. In this respect X-ray structural analyses of these two modifications are strongly desired.

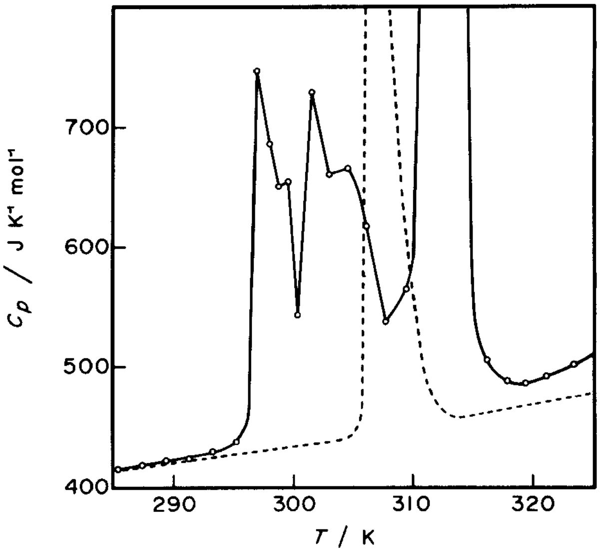

FIGURE 7 Heat capacity curve of HBAB. Crystal-crystal phase transition region. O—O: earlier measurement (Ref. 34), ----: this measurement.

Entrophies of phase transitions

The temperatures and the enthalpies of the phase transitions of several homologs of HBAB were reported by Billard *et al.*[10] and by Smith;[21] both of them obtained their data by using DSC. Since they did not give the transition entropies, we calculated these quantities by the relation $\Delta S_t = \Delta H_t/T_t$. These data are also listed in Table III.

Three nematic-isotropic liquid phase transition temperatures are in fairly good agreement with each other. However, the transition entropy given by Smith is 1.5 J K^{-1} mol^{-1} smaller than that determined by us. As previously mentioned, extreme pre- and post-melting effects are observed at this phase transition. The DSC method is liable to overlook these phenomena. This is why Smith's datum is about one half smaller than our value. Nematic-isotropic phase transition is extensively studied by many investigators both experimentally and theoretically.[29] According to the results of molecular field theory,[30] this transition entropy is given as a constant 0.429 R or 3.56 J K^{-1} mol^{-1}, where R is the gas constant. On the other hand, it is known that the N-I transition entropy increases with increasing aliphatic carbon number in many homologous systems of liquid crystal.[31,32] Martire pointed out[33] that the melting entropy of the N-I phase transition was ascribed to the conformational change of the aliphatic carbon chain from trans to gaushe form. Since the relative ratio of the trans form to the whole conformation between the nematic and the isotropic liquid states seemed to increase with alkyl chain length the N-I transition entropy increased in such homologous series. The experimental N-I transition entropy of HBAB is 3.2 J K^{-1} mol^{-1} and is in close agreement with the one predicted by the molecular field theory. This suggests that the internal rotation of the aliphatic chain does not contribute to the entropy increase at the N-I phase transition of HBAB.

Billard *et al.* and Smith gave crystal-nematic transition temperatures 5.9 K and 4.4 K lower than those reported by us. On the contrary the entropies are 6.5 J K^{-1} and 7.1 J K^{-1} mol^{-1} higher than our value. The C-N transition temperature, 60.9°C, obtained by us is the highest value so far reported and this suggests that the purity of our specimen is much higher. Formerly, our first measurement of heat capacity of HBAB was made on the specimen kindly supplied by the courtesy of Professor Takeda. The sample was found to melt at 329 K and its calculated purity was found to be 98 % from our calorimetric data.[34] The heat capacity peak corresponding to the present C_{II}-C_{I} transition was preceded and complicated by two rather small peaks, each having a shoulder as shown in Figure 7. One year later the present sample was quite newly synthesized from the purer starting materials. As mentioned above, this sample was purified by molecular distillation. The melting point was raised by 5 K and the purity was found to be 99.90 %. We should like to stress here that the small difference (1.9 %) at the stage of highest purity causes a striking effect on the mesogenic behavior.

The crystal-crystal phase transition of HBAB was first reported by Tsuji *et al.*[34] Both Billard *et al.* and Smith overlooked this phase transition. The crystal-crystal phase transition of liquid crystalline material from the calorimetric point of view was reported by Andrews and Bacon for DMC[24]. This phase transition was observed about 4.5 K below the C-N phase transition temperature of DMC. They inferred that this phase transition was of an order-disorder type due to the orientation of two methoxy groups based on its transition entropy which is close to R ln 4. If C_{II}-C_{I} phase transition of HBAB is of an order-disorder type, its transition entropy 16.7 J K^{-1} mol^{-1} is compared to the value R ln 8 or 17.2 J K^{-1} mol^{-1}. At the present stage it is difficult to account for the eight degeneracy from a molecular basis.

Here we should like to discuss this transition entropy from another possible point of view. Figure 8 shows the C-N transition entropies of HBAB obtained by Billard *et al.*[10] and Smith[21] as a function of alkyl carbon number C_n. We can recognize two straight lines; one is fitting to the members below C_6 and the other above C_7. These straight lines suggest that the entropy increment is expressed as a linear function of C_n. This means that the increment of the entropy of melting in the homologs of HBAB is ascribed only to the additional methylene group.

The order of magnitude of the entropy of melting in these compounds seems to depend on the length of the alkyl chain.[35] The entropy of melting

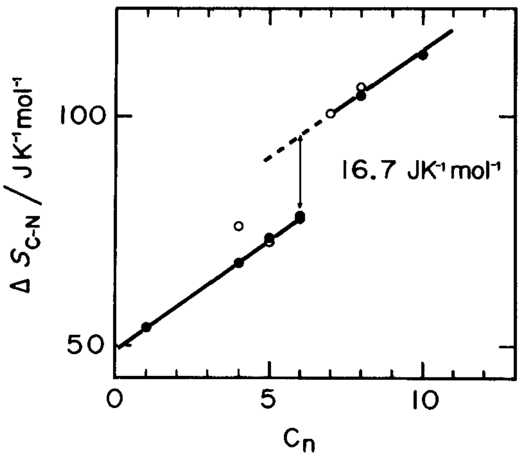

FIGURE 8 Crystal-nematic phase transition entropy vs. carbon number of homologs of HBAB. ●: Billard *et al.*'s data, ○: Smith's data.

of n-hexane is about 73.5 J K^{-1} mol^{-1} [36] and is in close agreement with that of the C–N transition of HBAB. This fact supports the idea that the C–N transition of HBAB is due to the melting of the n-hexyl group. In general, besides the melting entropy of the alkyl chain, an additional entropy such as due to the overall rotation of the molecule along its major axis or an excitation of the freedom of motion of the molecule other than the alkyl chain may contribute to the total entropy increment at the C-N transition.

The entropy of melting of n-heptane is about 76.9 J K^{-1} mol^{-1} [36] and is much smaller than that of the C_7 homolog, 100.7 J K^{-1} mol^{-1}. Accordingly there must exist an additional contribution to the entropy of the C–N transition of the C_7 homolog. On the other hand, we add the entropy of C_{II}-C_I transition to that of the C_6 homolog in Figure 8, their sum, of about 94.7 J K^{-1} mol^{-1} falls just on the extrapolation of the upper straight line. This fact suggests that in the members lower than the C_7 homolog the freedom of the molecule corresponding to the C_{II}-C_I transition of HBAB may be acquired at their crystal-crystal phase transition in contrast to the higher ones, which may acquire it at their C–N transition together with the entropy due to the melting of the aliphatic chain. Of course, the C_{II}-C_I transition may be looked upon as a kind of partial melting in spite of the fact that its behavior does not completely resemble the normal fusion phenomenon. Accordingly the total transition entropy from the crystal C_{II} to the isotropic liquid for HBAB corresponds to the normal fusion process and may be looked upon as 91.1 JK^{-1} mol^{-1} (16.7 ± 74.4).

This explanation will be confirmed by the comparison of the total transition entropy of HBAB with that of other compounds for example, the chloro- or the fluoro-substituted compounds. Directly we may confirm this point by measuring the melting entropy of *p-n*-hexyloxybenzylideneaniline which has no mesogenic state. These comparisons will be reported in the near future.

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