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Heat Capacity and Thermodynamic Properties of p′-Substituted p-n-Hexyloxybenzylideneanilines II. p-n-Hexyloxybenzylidenamino-p′-Chlorobenzene (HBAC)

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Heat Capacity and Thermodynamic Properties of *p*′-Substituted *p*-*n*-Hexyloxybenzylideneanilines II.† *p*-*n*-Hexyloxybenzylideneamino-*p*′-chlorobenzene (HBAC)

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The heat capacity of the smectic liquid crystal, HBAC, has been measured from 15 K to 385 K by using an adiabatic calorimeter. Contrary to the previous experimental results on *p*-*n*-hexyloxybenzylideneamino-*p*′-benzonitrile (HBAB), no solid-solid phase transition was observed in HBAC. However, a new intermediate phase was discovered between the crystal and the smectic B phase. Four phase transitions were found at 327.7 K (crystal-intermediate phase S_3), 330.90 K (S_3–smectic B), 362.98 K (smectic B–smectic A), and 370.38 K (smectic A–isotropic liquid), respectively. The enthalpies and entropies of these transitions were determined to be 10.88 $\mathrm{kJmol^{-1}}$/33.2 $\mathrm{JK^{-1}mol^{-1}}$, 12.35/37.0, 3.39/9.3 and 5.79/15.6, respectively. The standard thermodynamic functions have also been estimated up to 385 K. The total sum of four transition entropies amounts to 95.1 $\mathrm{JK^{-1}mol^{-1}}$ and agrees well with that of three transitions from the crystal II to the isotropic liquid of HBAB.

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1 INTRODUCTION

In the course of our thermodynamic study on a nematogenic liquid crystal,[1] *p-n*-hexyloxybenzylideneamino-*p*′-benzonitrile (HBAB), we perceived that similar studies on the homologues, in which only the CN-group is substituted by halogen, would provide useful information concerning the mechanism of the phase transitions found for HBAB because the internal degrees of freedom are essentially identical among such homologues. A study along this line, however, seems to be not necessarily straightforward because the mesophase sequence strongly depends on the substituted moieties; i.e., the Cl- and Br-homologues exhibit only smectic phases[2-4] while the F-homologue shows nematic as well as smecti phases.[5] Although the apparent phenomena are quite complicated, we thought that a unified interpretation concerning the transformation from the crystal to the isotropic liquid via a variety of mesophases would be obtainable from the entropic viewpoint.

We report in this paper the results of heat capacity measurements of HBAC which is a true smectogenic liquid crystal. Contrary to the case for HBAB,[1] no solid–solid phase transition was observed in the present compound. However, a new intermediate phase, considered to be a kind of smectic was observed.[6] We predicted in the previous paper[1] that the solid–solid phase transition of HBAB might be due to the onset of melting process and thus the entropy of the transition should be included in the total entropy change from the crystal to the isotropic liquid states. The validity of our prediction will be evident below from the determination of the melting entropy of HBAC.

2 EXPERIMENTAL

HBAC was synthesized by the dehydration reaction of *p-n*-hexyloxybenzaldehyde and *p*-chlorobenzene. Both reagents were purchased from Tokyo Kasei Kogyo, Co. Ltd. The procedure of purification was the same as that reported previously.[1] The results of elemental analyses for carbon, hydrogen, nitrogen and chlorine agreed well within ±0.1% with the calculated values.

Differential thermal analysis (DTA) was carried out between 80 K and 400 K to determine the transition temperatures.[2,3] The heat capacity was measured between 15 K and 385 K by using an adiabatic calorimeter.[1] The amount of the sample employed was 12.2435 g.

3 RESULTS

The heat capacity of HBAC is shown in Figures 1 and 2. The numerical data are listed in Table I. HBAC has been known to yield a smectogenic liquid crystal and it was reported that the crystal transforms directly to the smectic B phase.[2,3] Although the existence of the known phase transitions of HBAC was confirmed from our DTA experiment, HBAC showed peculiar thermal behavior around its crystal–smectic B phase transition during the measurements of the heat capacity. This crystal–smectic B transition turned out to be composed of two successive phase transitions and the new phase was discovered[6] between 327.7 K and 333.90 K.

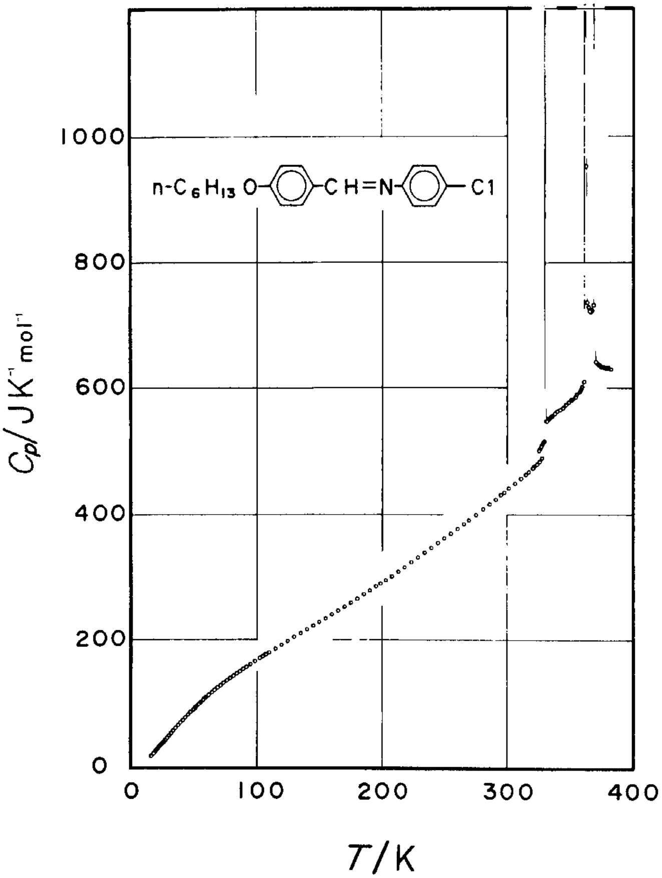

FIGURE 1 Heat capacity curve of HBAC.

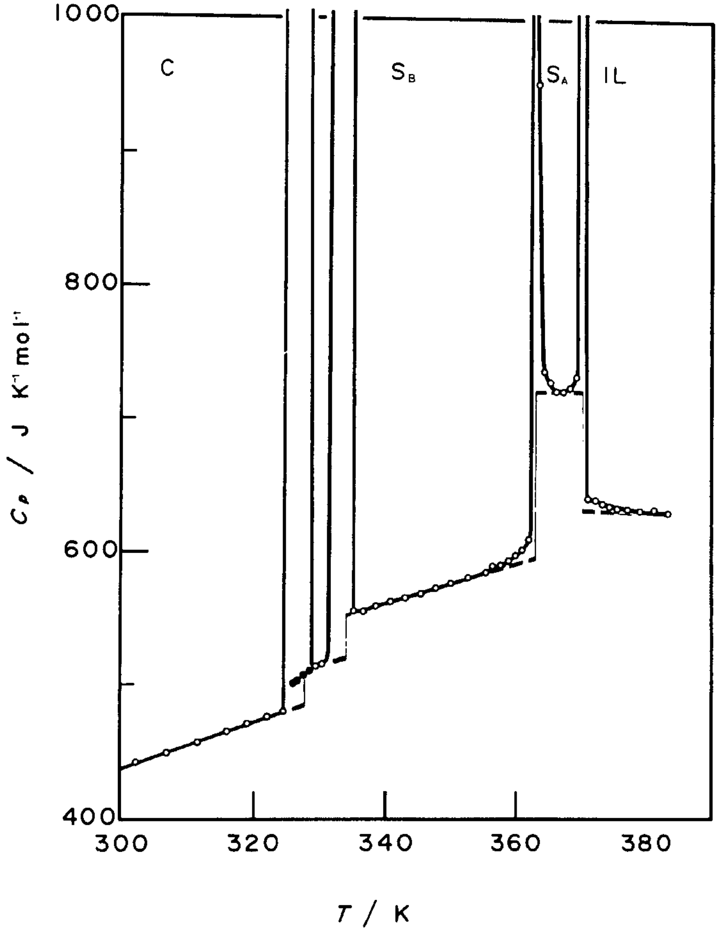

FIGURE 2 Heat capacity curve of HBAC around its phase transition region.

In order to make clear the existence of the new phase, the experimental data of the supplied electric energy are plotted in Figure 3 against the corresponding equilibrium temperatures. The ordinate corresponds to the enthalpy of the sample including the sample cell. The numerical data are also listed in Table II. Two series of the enthalpy diagrams are normalized so as to give the same value at 340 K. In this figure, the numbered solid circles mean the cumulative increment of the first series. Although no anomalous temperature drift was observed in the first series up to the point 3 in the figure, the sample temperature started to decrease below the initial temperature, as shown by the points 4 and 5,

TABLE I

Molar heat capacities of HBAC

T_{av}/K	C_p/JK^{-1}mol^{-1}	T_{av}/K	C_p/JK^{-1}mol^{-1}	T_{av}/K	C_p/JK^{-1}mol^{-1}
15.52	16.97	165.20	246.50	359.86	597.32
16.42	17.95	170.30	252.77	360.90	601.74
17.48	20.90	175.45	259.29	361.94	609.43
18.52	23.09	180.56	265.89	362.67	2379.8
19.57	25.59	185.65	272.47	362.92	18291
20.57	27.78	190.67	279.00	362.98	27653
21.54	30.08	195.63	285.72	363.41	952.57
22.61	32.48			364.29	735.75
23.89	35.44	199.19	290.02	365.23	727.92
25.21	38.31	203.11	295.49	366.21	721.03
26.52	41.27	207.82	301.61	367.21	720.82
28.03	44.81	213.14	309.07	369.21	731.47
29.56	48.39	218.54	316.31	370.01	1704.9
31.26	52.14	224.02	324.23	370.33	2254.2
32.96	55.98	229.43	331.94	370.38	31112
34.97	60.44	234.77	339.67	370.43	29563
37.08	65.06	240.05	347.21	370.50	12267
38.99	69.14	245.29	354.71	371.09	640.24
40.88	72.85	250.48	362.54	372.15	639.45
42.90	77.11	255.62	369.95	373.19	636.52
45.11	81.23	260.70	377.56	374.28	634.79
47.34	85.28	265.72	384.84	375.50	633.13
49.42	89.05	269.90	390.93	377.02	632.59
50.65	91.29	275.71	399.75	378.98	631.25
51.76	93.56	281.46	408.88	381.15	631.85
		286.33	416.31	383.33	629.48
51.00	92.00	291.15	423.92		
53.04	96.20	295.12	430.69	325.90	500.67
55.11	100.51	298.29	434.71	326.64	502.72
57.22	104.52	302.22	441.55	327.49	506.97
59.38	108.55	306.91	448.78	328.43	509.93
61.70	112.34	311.56	456.46	329.36	513.71
64.16	116.50			330.31	515.60
66.53	120.33	294.34	431.09	331.27	532.10
68.85	124.19	297.42	434.79		
71.24	127.93	300.48	439.67	332.38	547.38
73.76	131.75	303.57	445.32	333.44	550.22
76.30	135.32	306.69	449.55	334.49	551.87
78.86	139.05	309.79	454.75	335.54	554.31
81.44	142.70	312.88	460.29	336.77	554.99
83.95	146.26	315.95	464.33	338.17	557.73
86.49	149.77	318.99	470.40	339.57	559.43
89.15	153.43	322.00	475.38	341.17	562.41
91.66	156.54	324.46	479.29	342.98	563.90
94.79	160.67	326.32	483.46	344.82	567.03
98.41	165.61	335.16	555.12	346.68	570.31
102.52	170.50	336.65	555.15	348.60	573.47
104.90	173.70	338.52	559.14	350.62	577.07

TABLE I (*Continued*)

T_{av} / K	C_p / $JK^{-1}mol^{-1}$	T_{av} / K	C_p / $JK^{-1}mol^{-1}$	T_{av} / K	C_p / $JK^{-1}mol^{-1}$
106.95	176.12	340.76	562.53	352.73	581.28
109.68	179.75	342.99	565.20	354.83	584.85
114.72	185.73	345.21	568.01	356.93	589.82
119.81	191.81	347.48	572.66	359.02	595.63
124.92	197.71	349.80	576.22	361.09	603.43
130.05	204.15	351.72	580.32		
135.24	210.24				
140.33	216.32	353.09	576.70		
145.31	222.26	354.23	579.27		
150.25	228.18	355.29	584.43		
155.23	234.12	356.35	589.45		
160.21	240.32	357.58	590.40		
		358.81	593.55		

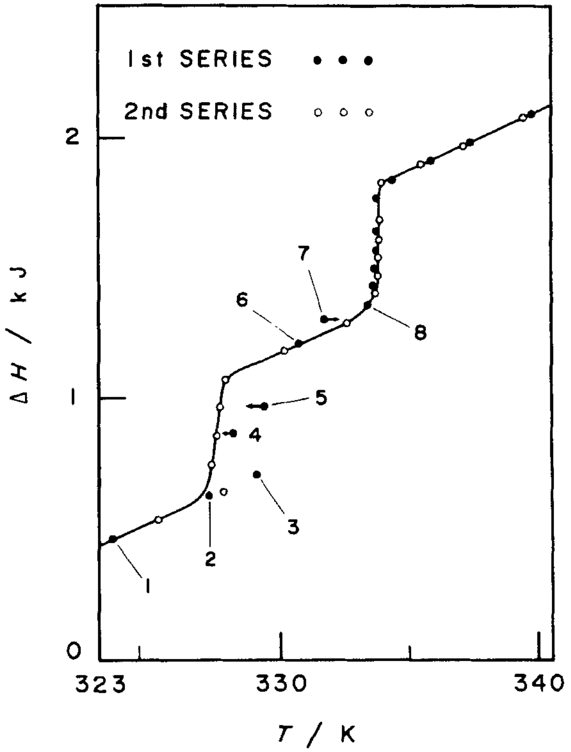

FIGURE 3 Accumulated supplied energy vs. temperature curve of HBAC. The arrows indicate the direction of the spontaneous change in the sample temperature.

TABLE II

Equilibrium temperatures and supplied electric energies

First series			Second series		
T_i/K	T_f/K	ΔQ/J	T_i/K	T_f/K	ΔQ/J
320.50	323.54	129.11	322.75	325.30	109.25
323.54	325.79	79.313	325.30	327.71	109.24
325.79	327.26	81.506	327.71	327.35	98.252
327.26	329.13	81.463	327.35	327.66	108.94
329.13	330.02	81.409	327.66	327.67	108.73
330.02	328.19	81.045	327.67	327.95	108.55
328.19	329.43	101.15	327.95	330.19	108.39
329.43	330.78	243.18	330.19	332.59	108.26
330.78	332.13	81.016	332.59	333.73	108.24
332.13	333.49	68.912	333.73	333.84	72.050
333.49	333.72	68.897	333.84	333.87	72.214
333.72	333.78	69.030	333.87	333.90	72.122
333.78	333.82	68.977	333.90	333.92	72.054
333.82	333.84	68.933	333.92	333.93	72.021
333.84	333.86	69.090	333.93	334.05	70.361
333.86	333.86	68.965	334.05	335.56	70.356
333.86	334.41	68.920	335.56	337.16	74.121
334.41	335.90	68.826	337.16	339.56	111.16
335.90	337.40	69.335			
337.40	339.64	103.96			
339.64	341.88	103.90			
341.88	344.10	103.85			
344.10	346.32	103.78			

in spite of the energy supply. This temperature drift continued so long that achievement of thermal equilibrium was practically impossible. To save the experimental time, the drift period was truncated at the time when the rate of the temperature drift reached the magnitude of about 5×10^{-4} K min^{-1}. Up to the point 6, all the drifts were endothermic. At the point 7, however, it turned to be exothermic. From the 8th point, the drift became the normal endothermic one usually observed in a melting process.

In the second series a special attention was paid to obtain true thermal equilibrium of the sample. The results are shown by the open circles in Figure 3. The solid line represents the equilibrium enthalpy curve drawn on the basis of the results of the second series and obviously shows the existence of the new phase between 327 K and 334 K. Thus it can be concluded that the peculiar thermal behavior resulted from superheating of the crystalline phase of HBAC because the phase transition proceeds so sluggishly. For convenience, we designate the new phase as S_3. The S_3 phase was transformed into the hitherto known smectic B phase. The temperatures of the crystal–S_3 and of the S_3–smectic B transitions were determined to be 327.7 K and 330.90 K, where the slopes of the enthalpy curve were maximum.

The smectic B phase was transformed into the smectic A phase at 362.98 K. Finally the smectic A phase melted into the isotropic liquid at 370.38 K. All the four phase transitions were characteristic of first-order transition, although the smectic A-isotropic liquid transition bore a higher-order character even more than 15 K higher than the transition temperature.

Determination of the enthalpies and entropies of transitions

Because of the superheating phenomenon and the sluggish phase transition, the enthalpy of the crystal–S_3 transition was indirectly determined by the following procedure. At first the total change of the enthalpy, $\Delta H(\mathrm{C{-}S_B})$, from the crystal to the smectic B phase was determined. Then, the smectic B phase was cooled to be transformed into the S_3 phase and after that the enthalpy of the S_3–smectic B transition, $\Delta H(\mathrm{S_3{-}S_B})$, was measured. Finally the enthalpy of the crystal–S_3 transition, $\Delta H(\mathrm{C{-}S_3})$, was determined by the following equation: $\Delta H(\mathrm{C{-}S_3}) = \Delta H(\mathrm{C{-}S_B}) - \Delta H(\mathrm{S_3{-}S_B})$. Since the temperature of the crystal-S_3 transition was already determined as 327.7 K, the entropy of the transition was calculated from the following relation: $\Delta S(\mathrm{C{-}S_3}) = \Delta H(\mathrm{C{-}S_3})/327.7\ \mathrm{JK^{-1}mol^{-1}}$. These procedures are shown in Table III.

The enthalpies and entropies of the remaining three transitions were determined by an usual manner.[7] They are listed in Table IV together with the values concerning the crystal–S_3 transition. The standard thermodynamic functions are summarized in Table V at the selected temperatures.

4 DISCUSSION

Crystal–S_3–S_A phase transition

The process of the phase transition from the crystal to the smectic B phase is very peculiar. Originally the two transitions were unable to be separated by DTA and thereby the crystal was transformed directly into the smectic B phase. Even with an adiabatic calorimetric method, the crystal was found to be superheated about 2.3 K above its crystal–S_3 transition temperature, 327.7 K. Arora *et al.*[2] and Billard *et al.*[5] re-

TABLE III

Determination of the enthalpies and entropies of C–S_3 and S_3–S_B phase transitions of HBAC

T_i/K	T_f/K		ΔQ/J
Crystal to smectic B			
322.308	341.184		1748.946
Lattice contribution			
322.308	327.7		233.280
327.7	333.90		277.326
333.90	341.184		337.844
		$\Delta H(\mathrm{C}\text{–}S_B) =$	900.496
S_3 to smectic B			
330.791	337.237		769.530
Lattice contribution			
330.791	333.90		138.601
333.90	341.237		152.279
		$\Delta H(S_3\text{–}S_B) =$	478.650
Crystal to S_3			
$\Delta H(\mathrm{C}\text{–}S_3) = \Delta H(\mathrm{C}\text{–}S_B) - \Delta H(S_3\text{–}S_B)$		$=$	421.846
$\Delta H(\mathrm{C}\text{–}S_3) = 10.882$ kJmol^{-1}			
$\Delta H(S_3\text{–}S_B) = 12.348$ kJmol^{-1}			
$\Delta S(\mathrm{C}\text{–}S_3) = 33.2$ JK^{-1}mol^{-1}			
$\Delta S(S_3\text{–}S_B) = 37.0$ JK^{-1}mol^{-1}			

T_i and T_f represent the initial and final temperatures, respectively. ΔQ is supplied electric energy.

ported the crystal–S_B transition temperature as about 332 K, which was 4.5 K higher than that of the crystal–S_3 transition temperature and 1.8 K lower than that of the S_3–smectic B transition temperature.

The situation can be explained as follows. When the heating rate is rather high, the crystal is superheated easily above the crystal–S_3 transition temperature because of the slowness of the transition rate. The transition is therefore liable to proceed along a single step path, where the crystal–S_B transition takes place at about 332 K. Around 332 K, the Gibbs energy difference between the crystal and S_3 phases becomes large enough to induce an irreversible change of the superheated crys-

TABLE IV

Transition temperatures, enthalpies and entropies of transitions of HBAC

	C–S_3	S_3–S_B	S_B–S_A	S_A–IL
T_t/K	327.7	333.90	362.98	370.38
ΔH_t/kJ mol^{-1}	10.88	12.35	3.39	5.79
ΔS_t/JK^{-1}mol^{-1}	33.2	37.0	9.3	15.6

TABLE V

Standard thermodynamic functions of HBAC

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{JK^{-1}mol^{-1}}}$	$\frac{S^\circ}{\mathrm{JK^{-1}mol^{-1}}}$	$\frac{(H^\circ - H_0^\circ)/T}{\mathrm{JK^{-1}mol^{-1}}}$	$\frac{-(G^\circ - H_0^\circ)/T}{\mathrm{JK^{-1}mol^{-1}}}$
10	(6.24)	(2.94)	(1.95)	(0.99)
20	26.65	13.13	8.91	4.22
30	49.25	28.18	18.57	9.61
40	71.07	45.39	29.01	16.38
50	90.37	63.34	39.37	23.97
60	109.38	81.52	49.47	32.05
70	126.02	99.65	59.24	40.41
80	140.80	117.46	68.53	48.93
90	154.55	134.83	77.32	57.51
100	167.50	151.79	85.69	66.10
110	180.01	168.35	93.70	74.65
120	192.08	184.53	101.40	83.13
130	204.23	200.37	108.83	91.54
140	215.89	215.92	116.04	99.88
150	227.84	231.22	123.10	108.12
160	239.99	246.31	130.03	116.28
170	252.40	261.24	136.86	124.38
180	265.09	276.02	143.63	132.39
190	278.06	290.70	150.37	140.33
200	291.12	305.30	157.08	148.22
210	304.63	319.82	163.78	156.04
220	318.54	334.32	170.50	163.82
230	332.73	348.79	177.24	171.55
240	347.15	363.25	184.02	179.23
250	361.70	377.72	190.83	186.89
260	376.40	392.19	197.69	194.50
270	391.10	406.67	204.58	202.09
280	406.53	421.17	211.51	209.66
290	422.11	435.71	218.51	217.20
300	437.87	450.28	225.56	224.72
310	453.84	464.90	232.66	232.24
320	470.92	479.58	239.84	239.74
330	515.93	528.85	281.45	247.40
340	559.17	583.04	325.47	257.57
350	575.81	598.49	332.38	266.11
360	593.56	614.96	339.39	275.57
370	720.76	643.22	358.15	285.07
380	630.73	675.81	380.69	295.12
385	629.43	684.06	383.94	300.12
273.15	395.92	411.24	206.76	204.48
298.15	434.94	447.58	224.25	223.33
373.15	636.08	663.59	375.38	288.21

tal into the S_3 phase which is the most stable state at this temperature. Such an irreversible change corresponds to the temperature decrease in the enthalpy curve in Figure 3. When further heating is carried out before the crystal–S_3 transition is completed, HBAC is heated again along the single step path and it might cross over the enthalpy curve of the S_3 phase. Thereafter the specimen would be stabilized. This stabilization was actually observed as the exothermic phenomenon as shown in Figure 3.

The entropies of the two successive transitions are 33.2 and 37.0 JK^{-1} mol^{-1}, respectively. The lower temperature one, which is almost twice as large as the entropy of the crystal II-crystal I transition of HBAB,[1] seems to be too large for an entropy change of a solid-to-solid phase transition of organic crystals like the present compound. Therefore, we are inclined to conclude that the S_3 phase is a kind of smectic phase; a highly ordered mesomorphic state in comparison with the usual smectic B.

However, we cannot completely deny the possibility that the S_3 phase might be a highly disordered crystalline phase. According to the recent structural study by Seurin, Guillon and Skoulios,[8] from one to three crystal phases exist in the crystalline systems of *p*′-halogenated *p*-*n*-alkyloxybenzylideneanilines dependent on the number of carbon atoms in the alkyl group. In the case of $C_nH_{2n+1}O—C_6H_4—CH{=}N—C_6H_4—Cl$ ($6 \leqq n$ (even) $\leqq 18$), two types of crystalline forms are reported; the first type found for $n = 6$, 8 and 10 is characterized by a thickness of the aromatic sublayer, d_a, of ca. 11.5 Å and the second one for $10 \leqq n$ (even) $\leqq 18$ has a longer thickness of d_a = ca. 13.2 Å. In view of the facts that the compound with $n = 10$ exhibit two crystalline polymorphism and that these authors[8] have not been acquainted with existence of the new S_3 phase discovered in the present study, there remains a possibility that the S_3 phase might belong to the crystalline phase characterized by the second type of d_a. If this is the case, the compound with $n = 8$ would also be expected to exhibit one more crystalline phase.

Entropies of transitions

The total entropy change from the crystal to the smectic B of HBAC, 70.2 $JK^{-1}mol^{-1}$, agreed well with the entropy of the crystal I-nematic transition of HBAB,[1] 71.2 $JK^{-1}mol^{-1}$. This fact seems to suggest that the phase transition from the crystal to the mesogenic state (nematic phase for HBAB and smectic B for HBAC) induced by the same origin irrespective of the specimen or the kind of mesogenic state.

The entropy of the smectic B–smectic A transition amounts to 9.3 $JK^{-1}mol^{-1}$. Meyer and McMillan[9] extended the McMillan theory of the smectic A[10] to the smectic B, C and H phase transitions. They derived the entropy of the smectic B–smectic A transition as being constant (0.56 R or 4.65 $JK^{-1}mol^{-1}$). The experimental value obtained here is twice as large as that derived from the theory. The experimental entropy is rather comparable to $R \ln 3$(9.13 $JK^{-1}mol^{-1}$), which implies an increase of the molecular freedom by three degrees.

There are possible two transformation paths from the smectic A phase to the isotropic liquid: one is the direct transformation into the isotropic liquid and the other via the nematic phase (including the cholesteric phase). The former path has been followed in the present case and its entropy of the transition amounts to 15.6 $JK^{-1}mol^{-1}$.

The total entropy of transition from the crystal to the isotropic liquid is 95.1 $JK^{-1}mol^{-1}$, which is comparable with the entropy change from the crystal II to the isotropic liquid of HBAB,[1] 91.1 $JK^{-1}mol^{-1}$. This fact seems to lead to the conclusion that, irrespective of the mesophases involved in the transition, the entropy acquired for the transformation from the crystal to the isotropic liquid is substantially the same between HBAC and HBAB. In other words, the crystal II to I transition found for HBAB should be regarded as being due to the onset of a partial melting of the molecular conformation.

References

1. K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, **55**, 71 (1979).
2. S. L. Arora and J. L. Fergason, *Symposia of the Faraday Society*, No. **5**, 97 (1971).
3. J. Malthete, J. Billard, J. Canceill, J. Gabard and J. Jacques, *J. Phys.* (*Paris*), **37**, C3-1 (1976).
4. R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **44**, 83 (1978).
5. J. Billard, J. C. Dubois and A. Zann, *J. Phys.* (*Paris*), **36**, C1-335 (1975).
6. Brief description of the new phase has been reported: K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst. Letters*, **41**, 81 (1977).
7. E. F. Westrum, Jr., G. T. Furukawa and J. P. McCullough, *Experimental Thermodynamics*, (Butterworths, London, 1968), Vol. 1, pp. 133–214.
8. P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **71**, 51 (1981).
9. R. J. Meyer and W. L. McMillan, *Phys. Rev.*, **9A**, 899 (1974).
10. M. L. McMillan, *Phys. Rev.*, **4A**, 1238 (1971).