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Heat Capacity and Thermodynamic Properties of *p*′-Substituted *p*-*n*-Hexyloxybenzylideneaniline III.† *p*-*n*-Hexyloxybenzylideneamino-*p*′-fluorobenzene (HBAF)

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The heat capacity of HBAF has been measured between 15 K and 385 K. Four phase transitions were found at 328.07 K (crystal-smectic B); 330.33 K (smectic B-smectic A); 334.88 K (smectic A-nematic); and 336.33 K (nematic-isotropic liquid), respectively. The enthalpies and entropies of these transitions were determined to be 23.22 kJ mol^{-1}/70.7 JK^{-1} mol^{-1}; 3.05/9.2; 3.41/10.2; and 1.17/3.5, respectively. The total transition entropy of HBAF agreed well with those previously reported for the present homologues. The standard thermodynamic functions were estimated up to 385 K. The heat capacity curve of HBAF in the transition region had a close resemblance to that of *p*-*n*-hexyloxybenzylideneamino-*p*′-chlorobenzene. The entropies of the smectic A-nematic and nematic-isotropic liquid transitions were compared with those theoretically derived by McMillan. The smectic B-smectic A transition entropy was interpreted in terms of order-disorder phase transition associated with the orientation of molecule.

1 INTRODUCTION

An effect of terminal substituent groups on the appearance of a liquid crystal phase was studied by Gray,[1] who proposed a group efficiency or-

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der. The average group efficiency order proposed is $C_6H_5 > NHCOMe > CN > OMe > NO_2 > Cl > Br > NMe_2 > Me > F > H$ for the nematic liquid crystal and $NHCOMe > C_6H_5 > Br > Cl > F > NMe_2 > Me > H > NO_2 > OMe > CN$ for the smectic liquid crystal. In fact, the group efficiency order accounts reasonably for nonexistence of any liquid crystalline phases in *p*-*n*-hexyloxybenzylideneaniline (HBA)[2,3] because it possesses a hydrogen atom at the terminal position. Likewise accounted for are the pure nematogenic tendency for *p*-*n*-hexyloxybenzylideneamino-*p*'-benzonitrile (HBAB)[4] and the pure smectogenic tendency for *p*-*n*-hexyloxybenzylideneamino-*p*'-chlorobenzene (HBAC),[5] since they have cyano- and chloro-groups at the terminal position.

Introduction of fluorine atom at *p*'-position of HBA is expected to yield a true smectogenic compound. However, such is not the case.[6] It exhibits the phase sequence crystal-smectic B-smectic A-nematic-isotropic liquid. The temperature range of the nematic phase of HBAF is very narrow. In the McMillan theory for the smectic A,[7] HBAF seems to be located near the triple point where smectic A, nematic and isotropic liquid coexist. In the theory the triple point is realized when the theoretical model parameter, α, is 0.98. For $\alpha \leqq 0.98$, the smectic A is transformed into the isotropic liquid via a nematic phase, whereas for $\alpha > 0.98$ it undergoes a phase transition directly into the isotropic liquid.

We shall report in this paper the heat capacity of HBAF between 15 K and 385 K. The results will be compared with those of HBAC. Further the results for HBAF and HBAC will also be compared with McMillan's theory.

2 EXPERIMENTAL

HBAF was synthesized by the dehydration reaction of *p*-*n*-hexyloxybenzaldehyde and *p*-fluoroaniline. Both reagents were purchased from Tokyo Kasei Kogyo Co. Ltd. The procedure of purification was the same as that previously reported.[4] The elemental analyses for carbon and hydrogen agreed within ±0.04% with the calculated values.

The apparatus used for the heat capacity measurements was previously described.[4] The amount of the sample employed was 18.8360 g.

3 RESULTS

Heat capacity measurements

Figure 1 shows the heat capacity curve of HBAF measured in the

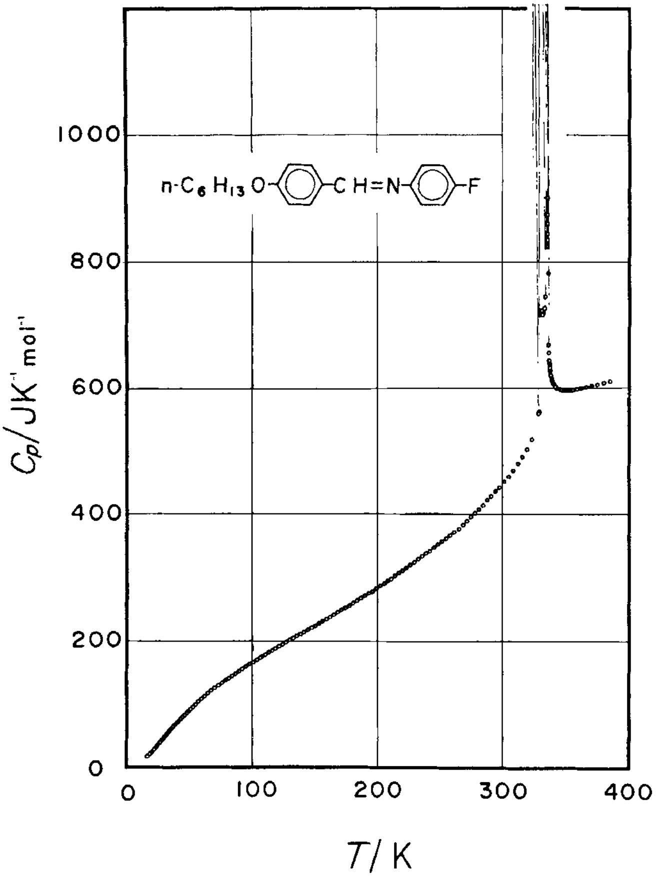

FIGURE 1 Heat capacity curve of HBAF.

whole temperature range. The heat capacity curve in the phase transition region is shown in Figure 2 in an enlarged scale. The numerical data are listed in Table I.

The heat capacity curve of the crystalline phase of HBAF showed a remarkable upward trend above 270 K in comparison with those of HBAB and HBAC. This type of pre-melting effect was not observed in the two homologous compounds previously reported.[4,5] In this temperature region the time required for thermal equilibration was longer than two hours. From about 324 K, the heat capacity of crystal rose steeply and finally went into the smectic B phase. Based on the analysis of the fractional melting curve data (Table II), purity of the sample was determined to be 99.96%. The peak value of the heat capacity

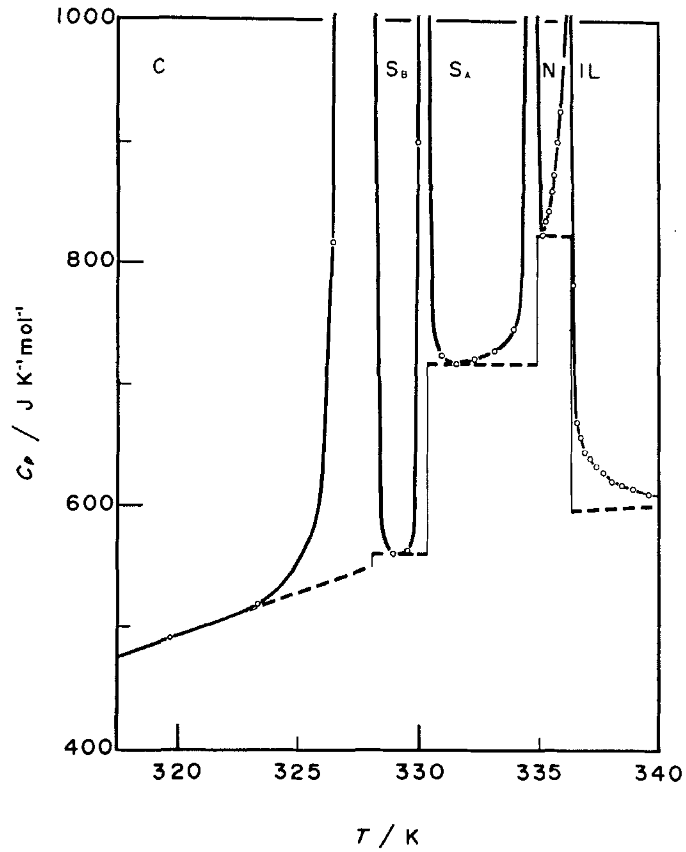

FIGURE 2 Heat capacity curve of HBAF around its phase transition region. Broken line denotes the so-called lattice heat capacity.

amounted to 474 kJK^{-1} mol^{-1} at 328.067 K. After the transition was over, the heat capacity measurements of the smectic B phase became to be possible over a temperature interval of 1 K. Extrapolation of the heat capacity curve of the crystalline phase coincided with that of the smectic B (Figure 2).

The smectic B-smectic A phase transition took place within very narrow temperature range between 330 K and 330.5 K. At 330.325 K, the heat capacity reached the maximum value, 50.5 kJK^{-1} mol^{-1}. The smectic A phase was stable between 330.33 K and 334.88 K. The smectic A-nematic transition took place at 334.88 K, where the heat capacity reached the maximum, 60.5 kJK^{-1} mol^{-1}.

As shown in Figure 2, the nematic phase immediately underwent a phase transition to the isotropic liquid. A marked pre-melting effect was observed in this transition. In the midst of the transition, however, a steep rise of the heat capacity, which means the phase transition bears a first-order character, was observed within narrow temperature range of 0.04 K. At the peak temperature, 336.332 K, the heat capacity amounted to 23 kJK^{-1} mol^{-1}. Above the transition temperature, a post-melting effect was also observed. The effect still persisted to 17 K higher than the transition temperature.

Enthalpies and entropies of transitions

The enthalpies and entropies of the four phase transitions were determined by the usual manner. In Figure 2, reasonable base lines, which correspond to the so-called lattice heat capacities, are drawn. Independent direct enthalpy measurements were also carried out to determine exact values of the enthalpies of the respective phase transitions. The obtained values are listed in Table III together with the transition temperatures. The standard thermodynamic functions are listed in Table IV.

4 DISCUSSION

Transition entropies

The entropy of the crystal-smectic B transition, 70.7 JK^{-1} mol^{-1}, agreed well with that of HBAC,[5] 70.2 JK^{-1} mol^{-1}. It was also comparable with the entropy of the crystal I-nematic transition of HBAB,[4] 71.2 JK^{-1} mol^{-1}. The entropy for the smectic B-smectic A transition of 9.2 JK^{-1} mol^{-1} was also in good agreement with that of HBAC,[5] 9.3 JK^{-1} mol^{-1}. The nematic-isotropic liquid transition entropy, 3.5 JK^{-1} mol^{-1}, was in the range of the values already reported.[4,8-13] Total sum of the transition entropies, 93.6 JK^{-1} mol^{-1}, is comparable with those of HBAB and HBAC, 91.2 JK^{-1} mol^{-1} and 95.1 JK^{-1} mol^{-1}, respectively.

There has been considerable discussion concerning the possible higher-order nature phase transition between various liquid crystal phases[14-18] as well as the liquid crystal-isotropic liquid transition.[18,19] For instance, the nematic-isotropic liquid transition is sometimes called as "almost second-order" or "weak first-order" transition, which means a small or essentially zero discontinuity in thermodynamic properties associated with the transition. In the present com-

TABLE I

Molar heat capacities of HBAF

$\frac{T_{av}}{K}$	$\frac{C_p}{JK^{-1}\ mol^{-1}}$	$\frac{T_{av}}{K}$	$\frac{C_p}{JK^{-1}\ mol^{-1}}$	$\frac{T_{av}}{K}$	$\frac{C_p}{JK^{-1}\ mol^{-1}}$	$\frac{T_{av}}{K}$	$\frac{C_p}{JK^{-1}\ mol^{-1}}$
51.789	93.459	104.583	170.75	268.193	382.46	336.242	1600.7
54.160	98.218	107.281	174.17	271.391	388.56	336.291	9848.4
56.578	103.04	110.019	177.38	274.554	395.26	336.314	10795
59.028	107.41	112.795	180.70	277.703	400.77	336.332	23018
61.651	111.74	115.608	183.95	280.828	406.94	336.405	782.54
64.379	115.99	118.379	187.12	284.092	413.15	336.552	669.51
67.057	120.20	121.186	190.31	287.495	421.12	336.715	657.17
69.802	124.39	124.040	193.15	290.862	427.57	336.909	644.76
72.607	128.63	126.858	196.82	294.307	435.65	337.144	639.48
75.369	132.59	129.713	200.34	297.805	441.47	337.401	633.03
78.144	136.50	132.422	203.21	301.350	450.67	337.688	628.06
80.922	140.35	135.361	206.58	304.977	459.08	338.053	621.13
83.546	143.82	138.335	209.96	308.571	468.56	338.471	617.64
86.276	147.62	141.279	213.29	312.241	479.28	338.967	614.57
89.059	151.39	144.243	216.97	315.983	490.21	339.617	610.34
91.772	154.80	147.223	220.17	319.669	502.32	340.397	607.28
94.585	158.48	150.176	223.53	323.297	518.02	341.573	603.63
97.499	162.08	153.174	226.94	326.447	817.25		
100.350	165.62	156.211	230.45	327.891	16195	337.751	622.89
103.142	169.02	159.217	233.89	328.005	84164	338.124	621.47
105.960	172.52	162.190	237.17	328.036	186763	338.585	615.28
108.806	175.86	165.205	240.90	328.051	375599	339.137	613.32
111.603	179.15	168.259	244.58	328.060	427642	339.846	608.86
		171.292	248.14	328.067	474109	340.774	605.53

16.493	15.324	174.373	251.60	328.334	4822.9	341.947	603.03
17.398	19.161	177.478	254.92	328.932	559.91	343.344	600.46
18.274	20.976	180.562	259.36	329.521	562.30	344.891	598.77
19.133	22.878	183.623	262.86	329.970	901.30	346.591	598.39
20.004	24.832	186.721	266.54	330.205	5898.0	348.563	597.34
21.051	27.197	189.859	270.46	330.265	14644	350.817	597.77
22.211	29.999	192.980	274.49	330.293	25155	353.332	597.26
23.336	32.526	196.074	277.90	330.311	34779	356.222	597.76
24.468	35.114	199.199	282.04	330.325	50496	359.439	599.04
25.617	37.716	202.359	286.34	330.475	1825.9	362.958	600.41
26.906	40.783	205.495	290.11	330.920	723.99	366.914	602.08
28.254	43.945	208.610	294.19	331.534	717.06	371.225	604.10
29.554	47.022	211.351	297.31	332.274	721.09	375.888	606.05
30.820	49.859	214.421	302.29	333.126	727.97	380.785	608.74
32.050	52.688	217.525	306.40	333.921	745.93	385.672	611.48
32.371	55.766	220.668	309.89	334.547	1258.4		
34.775	59.033	223.783	314.25	334.828	16146		
36.304	62.335	226.878	319.19	334.862	36288		
37.888	65.820	230.010	323.31	334.875	60507		
39.367	69.103	233.174	328.22	334.896	20646		
40.799	71.879	236.312	332.54	334.983	4412.3		
42.342	75.173	239.426	337.13	335.121	824.11		
43.933	78.423	242.512	340.99	335.255	835.38		
45.558	81.581	245.634	346.20	335.388	844.12		
47.219	84.679	248.790	351.61	335.519	860.92		
48.905	87.879	251.924	356.25	335.649	874.50		
		255.034	361.03	335.777	901.92		
48.595	87.221	258.173	366.04	335.903	927.38		
50.445	90.873	261.345	371.34	336.025	968.87		
52.203	94.317	265.020	375.78	336.143	1027.3		

TABLE II

Determination of the purity of HBAF

$\frac{T}{K}$	$\frac{1}{f}$		
327.983	6.37	Enthalpy of melting	23.21 kJ mol^{-1}
328.926	3.19	Triple point of sample	328.067 K
328.046	2.13		
328.056	1.59	Triple point of pure material	328.083 K
328.064	1.27		
328.070	1.10	Purity of sample	99.96%

pound we found a distinct first-order nature for the nematic-isotropic liquid transition as is shown below. Figure 3 represents the entropy increment associated with the nematic-isotropic liquid transition. This figure indicates obviously a discontinuity in the entropy curve; indicating that the transition is of a first-order in the Ehrenfest sense. The discontinuity amounts to 1.8 JK^{-1} mol^{-1}. Since the total entropy change of the nematic-isotropic liquid transition is 3.5 JK^{-1} mol^{-1}, the first-order component corresponds to almost one half of the total.

S_B-S_A-(N)-IL transition of HBAF and HBAC

Two heat capacity curves of HBAF and HBAC around their smectic B to the isotropic liquid transition region are shown in Figure 4 as a function of reduced temperature T/T_c, where T_c is taken as the nematic-isotropic liquid transition temperature for HBAF and the smectic A-isotropic liquid transition temperature for HBAC, respectively.

There are three heat capacity anomalies in HBAF because it possesses a nematic phase. The smectic B-smectic A transition temperatures of HBAF and HBAC are 0.982 and 0.980 in reduced scale, re-

TABLE III

Transition temperatures, the enthalpies and entropies of the phase transitions of HBAF

	$C-S_B$	S_B-S_A	S_A-N	$N-I$
T_t/K	328.07	330.33	334.88	336.33
ΔH_t/kJ mol^{-1}	23.22	3.05	3.41	1.17
$\Delta S_t/JK^{-1}$ mol^{-1}	70.7	9.2	10.2	3.5

TABLE IV

Standard thermodynamic functions of HBAF

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{JK^{-1}\,mol^{-1}}}$	$\frac{S^\circ}{\mathrm{JK^{-1}\,mol^{-1}}}$	$\frac{(H^\circ - H_0^\circ)/T}{\mathrm{JK^{-1}\,mol^{-1}}}$	$\frac{-(G^\circ - H_0^\circ)/T}{\mathrm{JK^{-1}\,mol^{-1}}}$
10	(5.56)	(2.49)	(1.67)	(0.82)
20	24.80	11.75	8.07	3.68
30	47.97	26.19	17.51	8.68
40	70.43	43.12	27.98	15.14
50	89.90	60.97	38.45	22.52
60	108.99	79.09	48.66	30.43
70	124.63	97.09	58.42	38.67
80	139.04	114.69	67.61	47.08
90	152.51	131.85	76.30	55.55
100	165.13	148.57	84.56	64.01
110	177.29	164.89	92.44	72.45
120	188.98	180.82	100.00	80.82
130	200.40	196.40	107.28	89.12
140	211.87	211.67	114.34	97.33
150	223.33	226.68	121.23	105.45
160	234.73	241.45	127.97	113.48
170	246.57	256.04	134.59	121.45
180	258.60	270.47	141.15	129.32
190	270.62	284.77	147.65	137.12
200	282.97	298.97	154.10	144.87
210	295.99	313.09	160.55	152.54
220	309.54	327.17	167.01	160.16
230	323.66	341.24	173.51	167.73
240	337.90	355.31	180.04	175.27
250	353.38	369.41	186.67	182.74
260	368.93	383.57	193.38	190.19
270	385.87	397.80	200.19	197.61
280	405.29	412.18	207.16	205.02
290	425.08	426.74	214.34	212.40
300	446.84	441.51	221.71	219.80
310	472.27	456.58	229.38	227.20
320	504.97	472.06	237.45	234.61
330	564.27	560.08	317.43	242.65
340	608.45	602.67	350.03	252.64
350	597.28	620.17	357.29	262.88
360	599.24	637.01	363.97	273.04
370	603.53	653.48	370.38	283.10
380	608.20	669.64	375.58	294.06
385	611.40	677.61	379.61	298.00
273.15	391.83	402.09	202.37	199.72
298.15	442.55	438.76	220.33	218.43
373.15	604.88	658.61	372.36	286.25

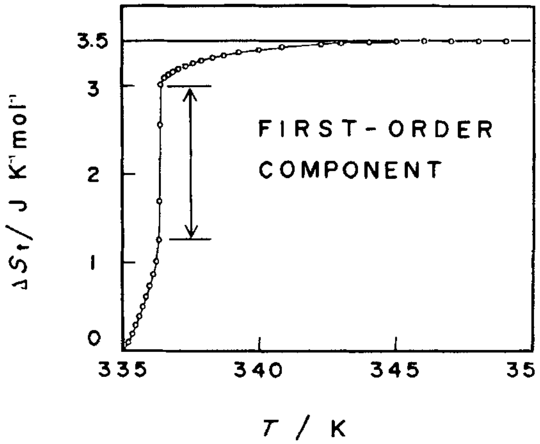

FIGURE 3 Temperature dependence of the entropy increase due to the nematic-isotropic liquid transition of HBAF. Vertical portion corresponds to a first-order component of the transition entropy.

spectively, and they coincide well with each other. These transitions do not show any sizable pre-transitional effects as observed in the nematic-isotropic liquid transition of HBAF. The absolute values of the heat capacity of the smectic A phase have almost the same magnitude between the two compounds. As described above, the entropies of the smectic B-smectic A transitions for the two compounds were also nearly identical. These facts suggest that the intermolecular correlation strength and the smectic order for the two compounds may be described by almost the same temperature dependence in their reduced temperature scale.

Comparison with McMillan's theory

In the case of HBAC, the smectic A phase transforms directly into the isotropic phase,[5] while for HBAF the smectic A phase transforms into the isotropic liquid via the nematic phase. The transition schemes of HBAF and HBAC seem to be well described by the theory of smectic A proposed by McMillan.[7] One of the results of the McMillan theory is that the transition sequence can be connected uniquely with the magnitude of the theoretical model parameter α. α is related to the length of molecule and varies from 0 to 2. When α is larger than 0.98 in the model system, the smectic A undergoes a phase transition to the isotropic liquid directly. When α is less than 0.98, the model system shows a transition sequence such as smectic A-nematic-isotropic liquid. At

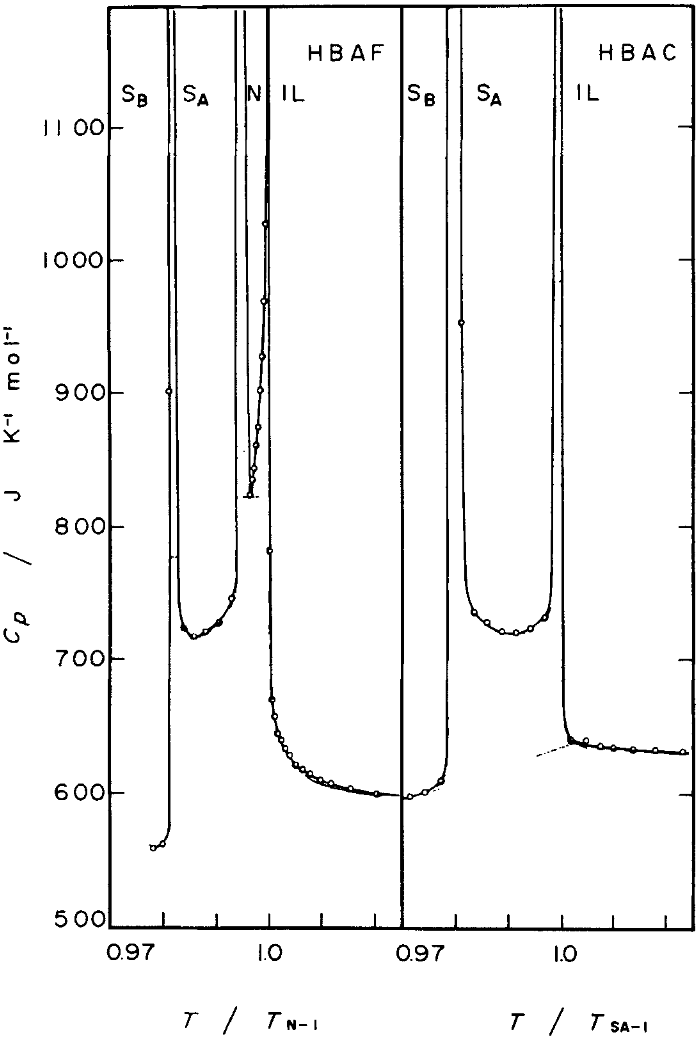

FIGURE 4 Heat capacity curves of HBAF and HBAC around their S_B-S_A-(N)-IL transition region. The temperatures are reduced by the N-IL transition temperature for HBAF and S_A-IL transition temperature for HBAC.

$\alpha = 0.98$, the entropies of the smectic A-nematic and the nematic-isotropic liquid transition of the model system are given as 10.17 JK^{-1} mol^{-1} and 3.56 JK^{-1} mol^{-1}, respectively.

Experimental values of HBAF are 10.2 JK^{-1} mol^{-1} for the smectic A-nematic transition and 3.5 JK^{-1} mol^{-1} for the nematic-isotropic liquid transition in excellent agreement with theory. The entropy of the smectic A-isotropic liquid transition of HBAC,[5] 15.6 JK^{-1} mol^{-1}, may be compared with the theoretical one at $\alpha = 1.05$, where the theory gives the transition entropy of 15.46 JK^{-1} mol^{-1}.

Entropy of smectic B-smectic A transition

The entropy of the smectic B-smectic A transition of HBAF, 9.2 JK^{-1} mol^{-1}, shows close agreement with that of HBAC, 9.3 JK^{-1} mol^{-1}. Coincidence of the transition entropy of both compounds suggests that the magnitude of the entropy in the homologous series of *p*′-substituted HBA remain nearly constant. However, Meyer and McMillan[20] predicted theoretically a constant smectic B-smectic A entropy value of 4.65 JK^{-1} mol^{-1} independent of the model parameters. Our experimental value amounts to twice that derived from their theory. Therefore, some molecular motions or additional smectic order may be overlooked in the theory. The experimental entropy is comparable to $R \ln 3$ ($= 9.13$ JK^{-1} mol^{-1}), which implies an increase in three degrees of freedom per molecule. From inelastic neutron scattering experiments on the smectic B phase of *p*-phenylbenzylidene-*p*′-butylaniline (PBBA),[21] a rotational motion of molecule about its long axis has been observed. However, its rotational motion is not of a free rotator but a jumpwise motion of the angle of $\pi/3$ with correlation between neighboring molecules. Since the molecule is regarded as having a lath like shape, the different number of orientations of the molecular plane seems to be three in the smectic B phase. A molecule in the smectic B phase may occupy one of the three orientations and it may sometimes jump into the other orientations in PBBA. If the rotational motion in the smectic B phase of HBAF and HBAC is similar to that in PBBA, one molecule would acquire three degrees of freedom with respect to the molecular orientation at the transition to the smectic A phase and would give rise to the observed entropies of transitions which are nearly equal to $R \ln 3$.

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