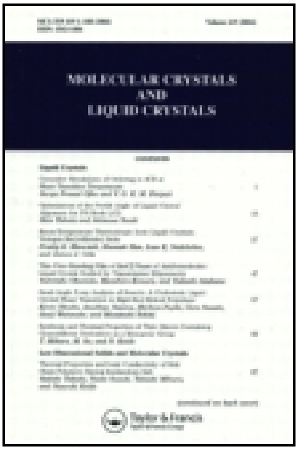

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Heat Capacity and Thermodynamic Properties of p'-Substituted p-n-Hexyloxybenzylideneaniline. IV. p-n-Hexyloxybenzylidene-p'-toluidine (HBT)

Kazuhiro Tsuji [a b] , Michio Sorai [a] , Hiroshi Suga [a] & Syŭzŏ Seki [a b]

[a] Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan
[b] Department of Chemistry, School of Science, Kwansei Gakuin University, Nishinomiya, 662, Japan

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Heat Capacity and Thermodynamic Properties of *p*′-Substituted *p*-*n*-Hexyloxybenzylideneaniline.

IV. *p*-*n*-Hexyloxybenzylidene-*p*′-toluidine (HBT)†

KAZUHIRO TSUJI,‡ MICHIO SORAI, HIROSHI SUGA and SYÛZÔ SEKI‡

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(*Received April 4, 1982*)

The heat capacity of HBT has been measured between 17 and 385 K with an adiabatic calorimeter. A new crystal phase, which exists stably between the known crystal and nematic phases, was discovered. The transition temperatures were determined to be 317.5 K (low temperature crystal $C_{II} \rightarrow$ high temperature crystal C_I), 334.26 K ($C_I \rightarrow$ nematic phase), and 346.90 K (nematic → isotropic liquid phase). The enthalpy and entropy of these transitions were 5.04 kJ mol^{-1}/15.89 J K^{-1} mol^{-1}, 25.04/74.90, and 1.37/3.9, respectively. The standard thermodynamic functions were calculated up to 385 K. The sum of the three transition entropies was compared with those previously reported for three homologous compounds which possessed essentially identical degrees of freedom of molecule with that of HBT. Hindered rotational motion of the methyl group attached to the aniline ring was observed in the crystal C_{II} phase and its hindering potential was evaluated to be about 3 kJ mol^{-1}.

1 INTRODUCTION

All the three compounds in the present homologous series we have studied hitherto own strong polar groups at their *p*-positions. Among

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† Preceding paper of this series is Ref. 3. Contribution No. 40 from Chemical Thermodynamics Laboratory.

‡ Present address: Department of Chemistry, School of Science, Kwansei Gakuin University, Nishinomiya 662, Japan.

them, *p-n*-hexyloxybenzylideneamino-*p*'-benzonitrile (HBAB) having nitrile-group was a pure nematogen[1] and *p-n*-hexyloxybenzylideneamino-*p*'-chlorobenzene (HBAC) was a pure smectogen,[2] whereas *p-n*-hexyloxybenzylideneamino-*p*'-fluorobenzene (HBAF) exhibited both a nematic and two smectic phases.[3] From a viewpoint of relationship between molecular structure and liquid crystalline behavior it is interesting to study a compound which has a weak polar group at the *p*-position of *p-n*-hexyloxybenzylideneaniline (HBA).

Methyl group can be regarded as being essentially nonpolar. The homologue of HBA having a methyl group at its *p*-position, *p-n*-hexyloxybenzylidene-*p*'-toluidine (HBT), has been known as a nematogen showing the mesophase between 333 and 346 K.[4] Since HBT has only one nematic phase as a liquid crystalline state, it may be reasonably compared to HBAB, which exhibits also only one nematic phase.[1] On the analogy of HBAB, a crystal-to-crystal phase transition may likewise be expected to exist in HBT. Otherwise the entropies of the crystal-nematic and/or nematic–isotropic liquid transitions might be larger than those of HBAB. Although direct evidence of the crystal–crystal phase transition has not yet been reported, Bhide *et al.*[5] have observed an interesting thermal behavior of HBT. In fact, they observed that the crystalline HBT took place a transition into the nematic phase at 331 K and the nematic state was transformed into the isotropic liquid at 347 K. In the cooling process three exothermic peaks were observed in addition to the isotropic liquid–nematic transition peak. However, for the rapidly cooled specimen another transition appeared at 336 K in the reheating run. Relative magnitude of the two peaks at 331 and 336 K was found to depend on the cooling rates notwithstanding the constancy of the total enthalpy of transitions. Although their explanation on this phenomenon is not straightforward, their results seem to suggest a crystal–crystal transition in HBT.

In this paper we present the results of heat capacity measurements of the stable states of HBT. The presence of a new crystalline form will be reported below.

2 EXPERIMENTAL

HBT was synthesized by the dehydration reaction of *p-n*-hexyloxybenzaldehyde and *p*-toluidine (Tokyo Kasei Kogyo Co., Ltd.). The procedures of synthesis and purification were the same as those reported previously.[1] The results of elemental analyses for C, H and N were

81.39% (theoretical: 81.31%), 8.51% (8.53%) and 4.77% (4.74%), respectively.

Differential thermal analysis (DTA) was carried out to study preliminarily the thermal behavior of HBT. The heat capacity was measured with an adiabatic calorimeter previously reported.[1] The amount of the sample used was 19.4236 g.

3 RESULTS

DTA

DTA was carried out for the sample purified with molecular distillation. The results are shown in Figure 1. In run 1, the specimen melted into the nematic phase at about 330 K and then was transformed into isotropic liquid at about 346 K. Run 2 recorded in the cooling direction showed four exothermic peaks. The highest temperature peak corresponds to the isotropic liquid–nematic transition. Other three are due to the transitions between metastable phases reported by Bahadur.[6] According to Bahadur, two of the three peaks are to be assigned to the nematic–smectic B and smectic B–solid II phase transitions. The lowest temperature peak is to be of the irreversible transition of the solid II into the crystal phase shown in run 1. In passing, run 3 was performed to confirm the reversibility of the nematic–smectic B transition. However, the reheating curve, run 4, was somewhat different from the curve of run 1. A small peak and a large one appeared at about 330 and 334 K, respectively. Interestingly, the sum of the areas of these two peaks was nearly identical with that of the peak of crystal–nematic transition in run 1. On the other hand, Coates and Gray[7] have reported that the crystal–nematic transition of HBT occurs at 334 K.

In general, if a melting point of a crystal obtained by cooling the isotropic liquid is lower than that of an as-grown crystal, the former crystal modification is metastable as exemplified by EBBA.[8] In the present case, however, the former crystal gave a higher transition temperature than that of the latter. This fact suggests that the larger peak at 334 K in run 4 may be due to the melting of a more stable crystal modification. The single peak at 330 K in run 1 may be the melting point of the superheated crystal. When the specimen was annealed at room temperature for several hours it gave the same DTA curve as run 1.

Although a clear evidence of crystal–crystal transition was not obtained by DTA, a possibility of the presence of two crystal modifications seemed to remain. We did not carry out further DTA experiments

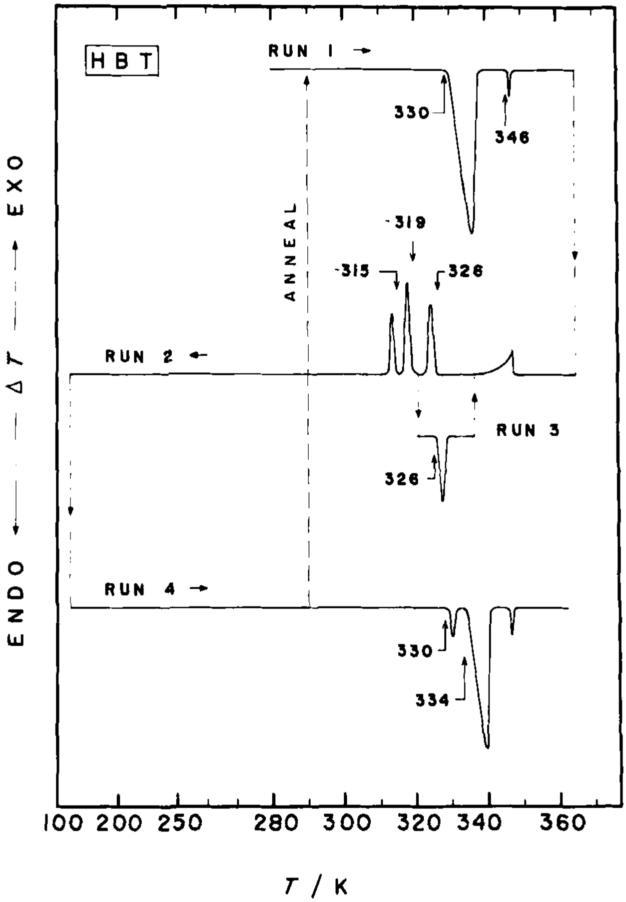

FIGURE 1 DTA curves of HBT.

about the metastable state. Recently Miyajima *et al.*[9] revealed a phase relation among various metastable phases and their stabilities with temperature by means of DTA and microscope.

Heat capacity

The results of heat capacity measurements are shown in Figure 2 and the numerical data are listed in Table I. A vertical line at 317.5 K in the figure shows a newly found crystal–crystal transition. The transition accompanies a tremendous superheating phenomenon (similar to that observed for HBAC[2]) appeared at about 324 K. This phenomenon clearly indicates a sign of the existence of a new phase.

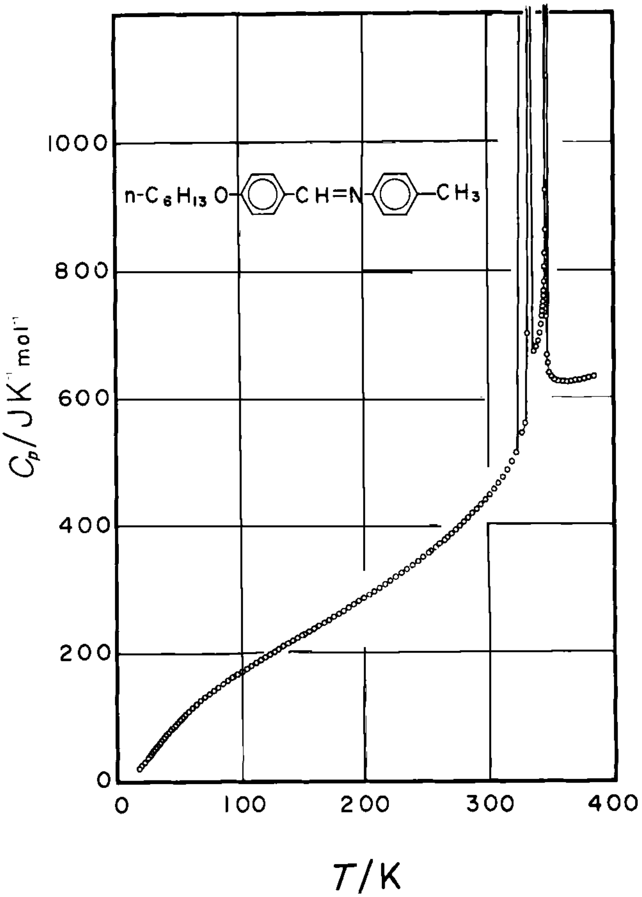

FIGURE 2 Molar heat capacity curve of HBT.

To clarify the superheating phenomenon and the existence of the new crystal phase, the enthalpy of HBT including the sample cell is shown in Figure 3. Curve (a) corresponding to the first series for the crystalline state of HBT clearly showed temperature decrease in spite of the energy supply. The difference of the enthalpy between the high and low temperature curves at 320 K amounted to about 350 J. We regarded this difference as the enthalpy change of the specimen due to the crystal–crystal phase transition. Supposing that the ideal first-order transition took place at 320 K, the entropy of the transition amounted to 16.3 J K^{-1} mol^{-1}, which is nearly identical with that of the crystal II–crystal I transition found for HBAB,[1] 16.7 J K^{-1} mol^{-1}. Curve (b) corresponds to the third series of the measurements. Prior to the measure-

TABLE I

Molar heat capacities of HBT.

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}
51.288	96.54	16.950	19.184	334.038	14442
54.198	102.26	17.900	21.459	334.149	41878
57.253	108.21	18.943	23.561	334.193	82045
60.398	113.92	20.045	26.162	334.215	163350
63.665	119.38	21.138	28.954	334.229	196620
67.091	124.90	22.385	31.937	334.240	282750
70.573	130.37	23.853	35.602	334.249	287210
74.109	135.65	25.280	38.926	334.260	177530
77.593	140.71	26.755	42.573	334.281	91892
81.045	145.59	28.354	46.465	335.041	1327.3
		30.029	50.432	337.001	672.13
81.044	145.48	31.644	54.391	339.020	679.85
85.214	151.22	33.195	58.129	340.619	689.08
88.966	156.39	34.874	62.054	341.993	700.98
92.751	161.30	36.603	66.101	343.083	714.17
96.516	166.00	38.370	70.087	343.847	727.82
100.269	170.74	40.188	73.998	344.225	735.57
104.016	175.26	42.123	78.166	344.475	742.97
107.760	179.87	44.069	82.246	344.730	749.91
111.594	184.37	46.015	86.145	344.991	759.07
115.431	188.87	48.066	90.080	345.249	766.91
119.188	193.17	50.177	94.266	345.509	781.51
122.949	197.07	52.373	98.543	345.772	804.38
126.834	201.93			346.041	825.88
130.146	205.78	221.352	313.79	346.311	862.83
133.998	210.15	225.187	319.07	346.571	925.10
137.787	214.26	229.047	324.17	346.797	1270.3
141.597	218.60	232.935	329.23	346.903	29149
145.430	222.86	236.789	335.27	346.928	8225.8
149.096	226.98	240.622	340.58	347.097	726.60
150.885	228.79	244.449	346.17	347.574	666.27
154.813	233.43	248.318	352.14	348.413	651.81
158.753	237.71	252.217	358.13	349.659	639.20
162.711	242.16	256.085	364.00	351.348	632.51
166.691	246.78	259.977	370.44	353.659	628.04
170.693	251.36	263.928	376.69	356.573	625.59
174.745	256.10			359.820	624.61
178.776	260.78	263.030	374.89	363.187	624.43
182.784	265.57	266.349	380.47	366.614	625.39
186.842	270.29	269.760	386.23	370.098	626.63
190.969	275.39	273.161	392.23	373.576	627.10
195.093	280.35	276.548	398.13	377.182	628.82
199.182	285.39	279.924	404.42	381.080	630.96
		283.358	410.95	385.297	632.63
199.468	285.46	286.822	417.95		
203.605	290.80	290.261	424.19	309.329	469.08
207.787	296.09	293.744	431.88	310.585	472.89
211.993	301.45	297.269	439.36	311.834	476.25

TABLE I (*Continued*)

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}
216.303	307.09	300.829	447.52	313.076	480.01
220.642	312.17	304.411	456.12	314.313	483.40
224.946	318.50	307.969	465.35	315.547	487.68
229.285	324.50	311.564	475.27	316.781	488.95
233.648	330.57	315.256	486.00		
238.034	336.78	318.995	498.66	289.324	452.95
242.441	342.84	322.704	513.06	293.016	461.59
246.797	349.74			297.007	469.08
251.116	356.12	324.886	548.67	301.583	478.60
252.809	358.36	327.184	544.02	306.521	488.01
256.858	365.08	329.642	559.40	311.395	497.62
		331.952	700.45	316.223	507.51
		333.490	2256.6	320.963	536.89

ments, the sample was once cooled to 250 K and then raised up to 330 K. A small jump was observed at about 319 K. Curve (c) was the enthalpy increment for the specimen which was annealed at 300 K after once cooled at 78 K. This curve also showed the superheating phenomenon at a rather lower temperature than that of the curve (a). However, a small real existence of a vertical part was evidently detected in the measurement of this enthalpy curve. Although the accurate equilibrium transition temperature was unable to be determined because the phase transition being sluggish, a plausible transition temperature was estimated to be 317.5 K by fitting the temperature drift curve at an exponential function. Curve (d) drawn based on the curves (a) and (c) shows the estimated hypothetical enthalpy curve in which the ideal first-order transition takes place at 317.5 K.

The enthalpy of the newly found phase transition, ΔH_t, was determined as the jump at 317.5 K in the enthalpy curve (d). The entropy of this transition, ΔS_t, was obtained from the relation, $\Delta S_t = \Delta H_t/317.5$. They amounted to 5.04 kJ mol^{-1} and 15.89 J K^{-1} mol^{-1}, respectively. The order of magnitude of the transition entropy was comparable to that of crystal II–crystal I transition of HBAB. Therefore, the transition at 317.5 K and the nature of the high-temperature crystal phase seem to bear a close resemblance to those observed for HBAB. We shall designate hereafter the high-temperature crystalline phase as C_{I} and the low-temperature one as C_{II}, which is identical with Bahadur's solid I.[6]

Figure 4 shows the heat capacity curve of the phase transition region. The heat capacity measurements were possible for the under-

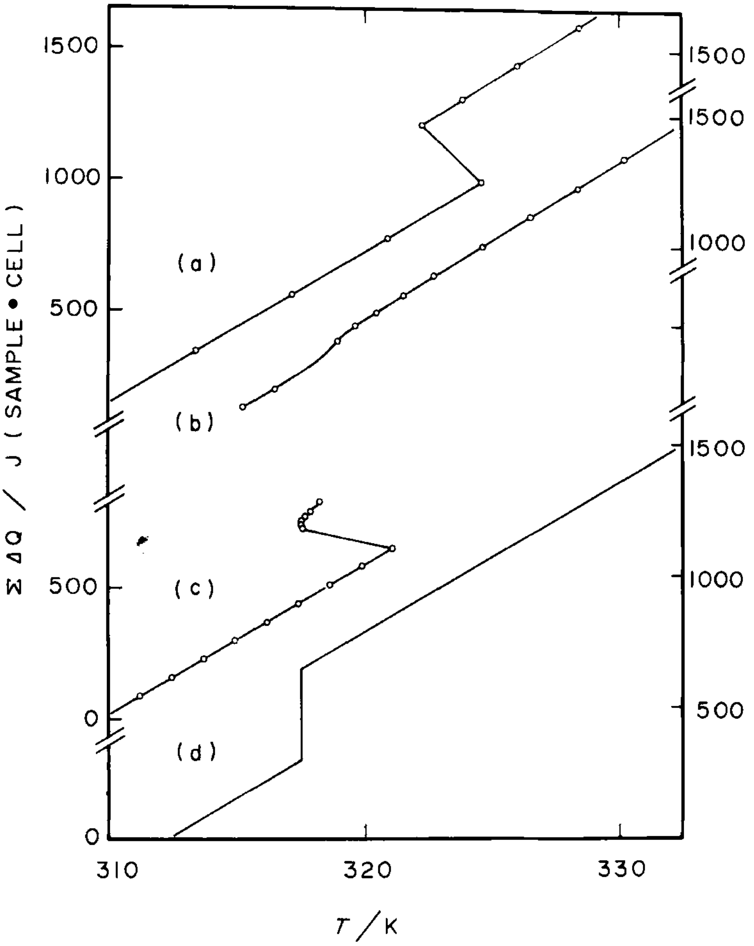

FIGURE 3 Enthalpy curves of HBT around the crystal–crystal phase transition region.

cooled C_I phase (the solid circles in Figure 4). The high-temperature crystal phase, C_I, melted into the nematic phase at 334 K, which was the same temperature as that observed by DTA (run 4 in Figure 1). Based on a fractional fusion method, purity of the specimen was determined to be 99.84 mole per cent (Table II). The heat capacity curve around the nematic–isotropic liquid transition showed remarkable pre- and post-transitional effects. However, a first-order character was observed in the close vicinity of the transition temperature just like as HBAF.[3] The enthalpy and entropy of the remaining two transitions were determined in usual manner. The thermodynamic quantities associated with all the transitions are listed in Table III. The standard

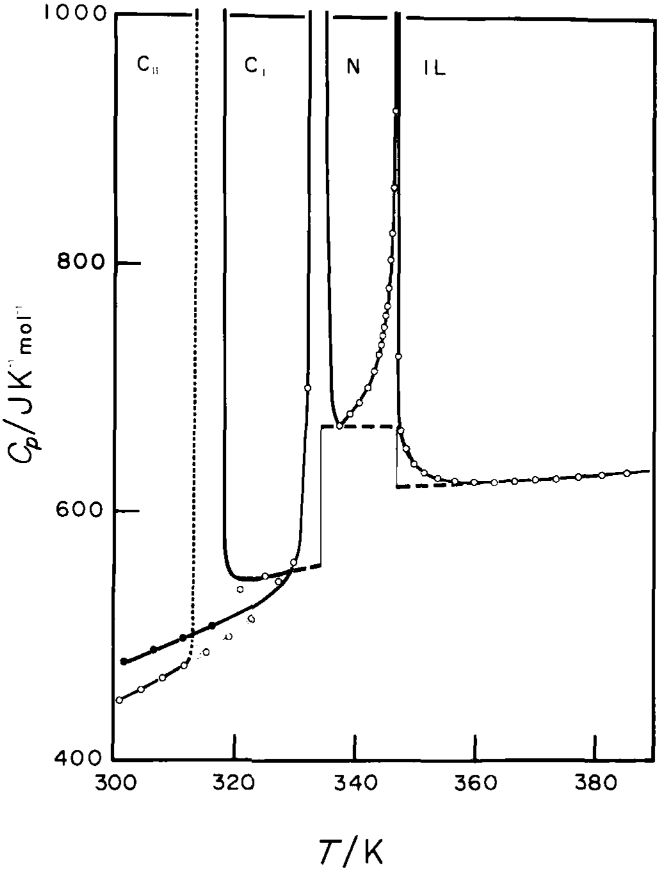

FIGURE 4 Heat capacity curve around the phase transition region. Dotted curve represents the heat capacity rise due to the first-order crystal–crystal transition. the symbol, O=O, shows the heat capacity of superheated crytal II. Solid circles represent the heat capacity of undercooled crystal I phase.

TABLE II

Determination of the purity of HBT.

$\frac{T}{K}$	$\frac{1}{f}$		
334.120	5.88	Enthalpy of melting	25.04 kJ mol^{-1}
334.178	3.76		
334.208	2.76	Melting point of sample	334.257 K
334.223	2.18		
334.235	1.79	Triple point of pure material	334.318 K
334.244	1.52		
334.253	1.32	Purity of sample	99.84%

TABLE III

Transition temperatures, enthalpies and entropies of transitions of HBT.

	C_{II}–C_I	C_I–N	N–IL
T/K	317.5	334.26	346.90
ΔH_t/kJ mol^{-1}	5.04	25.04	1.37
ΔS_t/J K^{-1} mol^{-1}	15.89	74.90	3.0

thermodynamic functions at selected temperatures are also listed in Table IV.

4 DISCUSSION

Internal rotation of methyl group

Among the series of compounds we have so far studied[1-3] the present one is unique in the sense that the substituent methyl group has a degree of freedom of its internal rotation. As the rotational barrier height of the methyl group attached to a benzene ring is generally low,[10] the rotational motion of methyl group of HBT may be expected to contribute to the heat capacity even at low temperatures. In fact, the heat capacity of HBT was the largest among the four compounds so far studied between 15 and 85 K.

The excess heat capacity arising from the rotational motion of the methyl group was estimated as follows. Since HBAF and HBT have similar magnitude of molecular weight, the heat capacity of HBAF may be regarded as the basal component of HBT. Figure 5 shows the heat capacity difference between HBT and HBAF, ΔC_p (HBT–HBAF), as a function of temperature. This curve resembles to the heat capacity behavior originated from hindered rotation of a methyl group.[11] Although the theoretical heat capacities converge to 4.2 J K^{-1} mol^{-1} in the high-temperature limit,[12] the actual heat capacity falls to zero around 270 K; probably owing to roughness of the employed estimation. From the same reason, the maximum value of the rotational heat capacity is smaller for the present estimation than for the theoretical model. However, these discrepancies do not necessarily lead to a serious error for an order-estimation of the hindering potential barrier. We estimated the barrier height to be 3 kJ mol^{-1} by comparing the experimental peak temperature with the theoretical one.[12] This value belongs to a low barrier category for the hindering potential of a methyl group.[10]

TABLE IV

Standard thermodynamic functions of HBT.

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}	$-(G^\circ - H_0^\circ)/T$ / J K^{-1} mol^{-1}
10	(6.32)	(2.73)	(1.86)	(0.87)
20	26.05	12.78	8.74	4.04
30	50.42	27.96	18.58	9.38
40	73.56	45.70	29.49	16.21
50	93.85	64.34	40.37	23.97
60	113.18	83.20	50.93	32.27
70	129.42	101.89	61.01	40.88
80	144.15	120.15	70.49	49.66
90	157.85	137.74	79.27	58.47
100	170.34	155.01	87.75	67.26
110	182.45	171.82	95.82	76.00
120	194.06	188.20	103.52	84.68
130	205.63	204.19	110.93	93.26
140	216.82	219.84	118.10	101.74
150	228.02	235.18	125.05	110.13
160	239.06	250.25	131.83	118.42
170	250.52	265.08	138.48	126.60
180	262.23	279.73	145.03	134.70
190	274.18	294.23	151.51	142.72
200	286.31	308.60	157.94	150.66
210	298.92	322.87	164.35	158.52
220	312.10	337.08	170.77	166.31
230	325.50	351.25	177.20	174.05
240	339.59	365.39	183.67	181.72
250	354.66	379.56	190.21	189.35
260	370.20	393.77	196.83	196.94
270	386.89	408.05	203.56	204.49
280	404.51	422.43	210.41	212.02
290	424.00	436.97	217.44	219.53
300	445.63	451.70	224.68	227.02
310	470.41	466.71	232.19	234.52
320	556.97	498.47	257.98	240.49
330	569.94	515.54	267.04	248.50
340	685.42	608.87	350.97	257.90
350	637.31	631.63	363.38	268.25
360	624.60	649.31	370.73	278.58
370	625.60	666.44	377.61	288.83
380	630.37	683.19	384.20	298.99
385	632.53	691.44	387.41	304.03
273.15	392.26	412.57	205.70	206.87
298.15	441.40	448.95	223.32	225.63
373.15	627.57	671.75	379.71	292.04

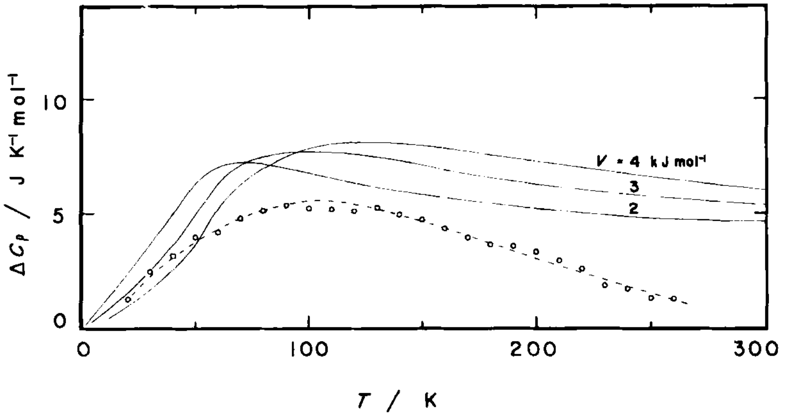

FIGURE 5 Difference of heat capacities, ΔC_p (HBT—HBAF), vs. temperature diagram. Solid lines are the contributions from the hindered rotation of methyl group derived by the method of Pitzer and Gwinn.[12]

Entropies of transitions

The degree of freedom which a molecule acquires through the phase transition from crystalline solid to isotropic liquid depends mainly on the molecular structure and the intermolecular forces. When two molecules have the same structure except for a minor substituent group having no effective internal degree of freedom, their melting entropies, even though the melting proceeds via various mesomorphic phases, seem to be identical. This account was really valid for the three homologues we have so far studied,[1-3] in which the substituent groups were CN, Cl and F, respectively. Although the substituent group of the present compound HBT has the internal degree of freedom, the melting entropy of 94.7 J K^{-1} mol^{-1} is nearly identical with 91.1 J K^{-1} mol^{-1} for HBAB, 95.1 (HBAC) and 93.6 (HBAF). This situation is caused by the fact that, because the hindering potential barrier of the present methyl group is so low that the rotational motion is well excited even in the solid state, the entropy change due to the methyl rotator is negligibly small at the melting point.

We found in the previous paper[3] that there exists a relationship between the magnitude of transition entropy and the kind of transition such as the crystal–smectic B and the smectic B–smectic A transitions. Similar relations were found for other types of transitions by comparing HBT and HBAB. They can be more clearly presented by the standard entropy curves shown in Figure 6. Two curves show nearly similar temperature dependence as a whole. The entropy of 15.9 J K^{-1} mol^{-1}

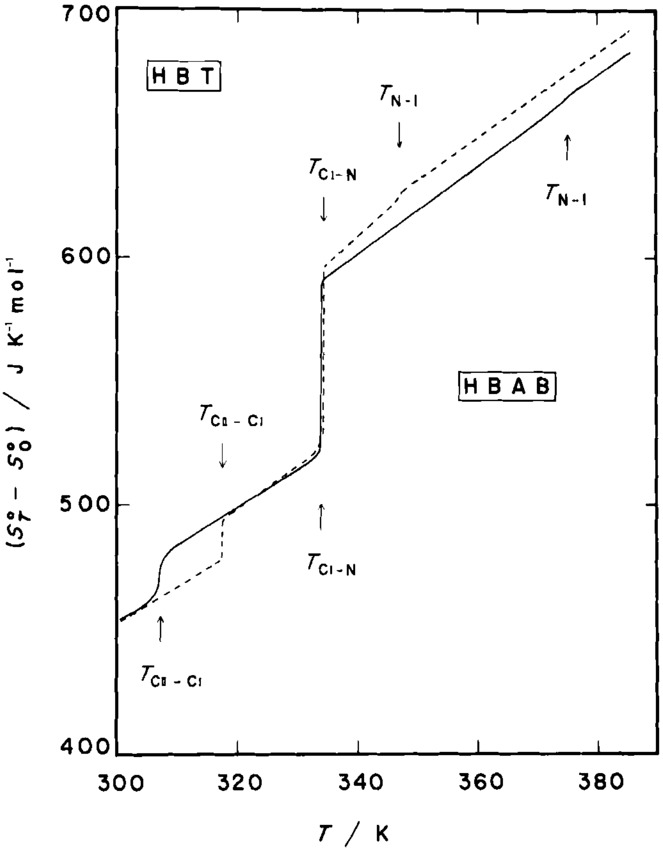

FIGURE 6 Standard entropy curves of HBAB and HBT. Solid and broken lines represent the entropy curves for HBAB and HBT, respectively.

for the crystal II–crystal I transition of HBT is comparable with 16.7 J K^{-1} mol^{-1} for HBAB. The entropies of the nematic–isotropic liquid transition for HBT and HBAB are 3.9 J K^{-1} mol^{-1} and 3.2 J K^{-1} mol^{-1}, respectively.

On the other hand, the entropy of the crystal I–nematic transition of HBT (74.9 J K^{-1} mol^{-1}) is somewhat larger than that of HBAB (71.2 J K^{-1} mol^{-1}). It is also larger than the entropies of the crystal–smectic B transition of HBAC (70.2 J K^{-1} mol^{-1}) and HBAF (70.7 J K^{-1} mol^{-1}). Even if the hindered rotation of the methyl group of HBT becomes a free rotator at the transition temperature, the entropy gain included in the melting of HBT is only 0.5 J K^{-1} mol^{-1}, provided that the hindering potential is 3 kJ mol^{-1}. Hence some freedoms other than the movement of hexyloxy chain[1] and the methyl group may be excited at the crystal I-nematic transition of HBT. Interestingly, however, the crystal I-nematic transition takes place at almost the same temperature for the two compounds.

We have studied the melting behavior of HBT and compared it with that of HBAB. They exhibited nearly the identical magnitude of the transition entropies. HBT showed also the same magnitude of melting entropy with those of HBAC and HBAF when the entropy of the crystal II–crystal I transition was included into the melting entropy. Based on these facts we can imagine that all these compounds may have similar crystal structures in their lowest temperature phases, and that other compounds having the same molecular structure as $C_6H_{13}O—C_6H_4—CH{=}N—C_6H_4—X$ will also exhibit the same magnitude of melting entropy independent of the phase sequence.

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