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Heat Capacity of Nematogenic *N-p*-Ethoxybenzylidene-*p'*-butylaniline between 14 and 375 K

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The heat capacity of a low-temperature liquid crystal EBBA (*N-p*-ethoxybenzylidene-*p'*-butylaniline) of 99.75% (mol) purity was measured in the range 14—375 K with an adiabatic calorimeter. The melting point T_m was 305.62 K, and the enthalpy and entropy of fusion 27.09 kJ mol^{-1} and 88.71 J K^{-1} mol^{-1}, respectively. The temperature of mesomorphic transition T_C from nematic to isotropic liquid was 349.08 K, and the enthalpy and the entropy changes due to the mesomorphic transition were 1.553 kJ mol^{-1} and 4.524 J K^{-1} mol^{-1}, respectively. Excess heat capacity due to the mesophase transition, C(excess), is represented by $C(\text{excess}) \sim \varepsilon^{-0.7}$ in the range $10^{-4} < \varepsilon < 10^{-1.5}$, where $\varepsilon \equiv |T - T_C|/T_C$. This implies that the mesomorphic transition of EBBA can be regarded as of critical phenomena, characterized by a second-order rather than a first-order nature.

Liquid crystals are recently being reinvestigated both experimentally and theoretically. Studies on thermotropic liquid crystals are mainly devoted to elucidating the relationship between molecular geometry and liquid crystallinity and to clarifying the mechanism of mesomorphic transition based on the intermolecular forces and the order of molecular arrangements. The revival has been partially promoted by recent development in the industrial application of liquid crystals.

From a thermodynamic point of view the study of liquid crystals is interesting in the sense that a cooperative phase transition can be realized even in a liquid state. Thermodynamic quantities such as heat capacity, enthalpy, entropy, and free energy provide useful information on the energetic aspects inherent to a mesophase transition and are indispensable for understanding of the mesophase transition.

Compared with thermal analytic studies, precise calorimetric investigations are extremely scarce, which is partly due to the simplicity of thermal analyses. Mesophase transitions can be estimated qualitatively by simple thermal analyses, but quantitative information can be obtained only by significant calorimetric measurements.

As an extension of previous studies[1-4] we deal in this paper with the heat capacity of *N-p*-ethoxybenzylidene-*p'*-butylaniline (EBBA), which is known to exhibit a nematic mesophase in the range 36—80 °C.[5-7] The heat capacity of a more simple compound in this homologous series, MBBA (*N-p*-methoxybenzylidene-*p'*-butylaniline), has been measured by Mayer *et al.*[8] and Shinoda *et al.*[9] We have determined the heat capacity of OHMBBA, an *o*-hydroxy analog of MBBA, and found a glassy state of the nematic phase.[2,3] We attempted to establish a glassy liquid crystalline state for EBBA without success, though a glass transition phenomenon was found in many compounds of this homologous series.[4]

The order of mesomorphic transitions in liquid crystals is a current problem. We have attempted to analyze the mesophase transition from nematic to isotropic liquid in terms of critical phenomena.

Experimental

Material. The nematogenic substance EBBA was prepared by the usual condensation reaction of *p*-butylaniline (Wako Pure Chemical Industries, Ltd.) with *p*-ethoxybenzaldehyde (Tokyo Kasei Kogyo Co., Ltd.) in ethanol. The product was recrystallized twice from ethanol and then twice from *n*-hexane. Found: C, 81.14; H, 8.30; N, 4.98%. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98%.

Thermal Analysis. Differential thermal analysis (DTA)[10] was carried out between −170 and 100 °C for a preliminary study of the thermal behavior of EBBA, about 500 mg of specimen being used.

Heat Capacity Measurement. The heat capacity of EBBA was measured with an adiabatic calorimeter[11] in the range 14—275 K. The all-gold calorimeter cell of approximately 35 cm^3 internal volume contained 17.8685 g (0.0634983 mol) of EBBA. The empty space was filled with helium gas at 1 atm pressure and room temperature to aid the heat transfer. A platinum resistance thermometer has been calibrated based on IPTS-68 scale.

Results and Discussion

Thermal Behavior. The thermal behavior of EBBA is illustrated in Fig. 1. A heating curve at the rate 2.5 K min^{-1} is shown by run 1. Melting point T_m of the stable crystal is 32.5 °C and the transition point T_C from nematic to isotropic liquid is 79.5

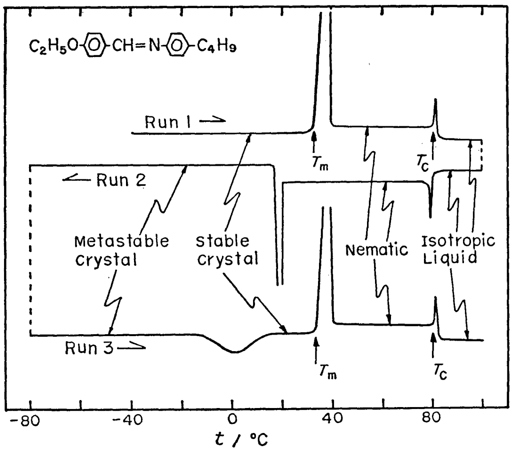

Fig. 1. DTA curves for EBBA.

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Table 1. Heat capacity of *N*-*p*-ethoxy-benzylidene-*p*′-butylaniline (Molecular Weight 281.4013.)

T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}
(Crystal)		86.111	142.79	226.323	312.93	334.975	580.97
14.519	10.332	88.570	146.22	229.678	317.94	336.285	583.96
15.417	12.133	91.353	149.92	233.991	323.40	338.469	590.88
16.297	13.473	94.199	153.66	238.581	329.47	339.491	595.68
17.184	15.302	96.983	157.36	243.116	335.84	340.629	601.27
18.085	16.984	99.711	160.84	247.594	342.01	342.240	609.25
19.033	18.865	101.900	163.56	252.019	348.89	343.315	613.46
20.044	20.991	104.855	167.31	256.388	355.19	343.909	619.94
21.126	23.199	107.758	170.88	261.008	362.60	344.382	623.43
22.298	25.542	110.613	174.31	265.868	370.04	345.269	629.94
23.505	28.239	113.423	177.77	269.472	376.37	345.970	638.01
24.739	30.838	116.191	181.22	275.260	384.84	346.661	657.66
26.050	33.634	118.918	184.67	279.849	392.21	347.346	673.87
27.439	36.709	121.676	187.63	284.673	399.73	348.013	701.15
28.896	39.910	124.603	191.10	289.419	408.56	348.632	825.96
30.629	43.736	128.095	195.00	294.101	417.27	349.041	2592.7
32.571	48.086	132.004	199.67	298.718	431.16	T_C=349.08 K	
34.509	52.388	135.853	204.31	302.568	548.86	(Isotropic Liquid)	
36.538	56.781	139.643	208.51	304.319	1586.0	349.493	931.81
38.998	61.882	143.378	212.79	305.240	10639	349.522	613.20
41.782	67.824	147.061	217.08	305.453	35171	350.976	598.21
44.448	73.539	151.051	221.79	T_m=305.62K		351.425	592.90
46.990	78.661	154.553	225.62	(Nematic Liquid Crystal)		351.892	591.21
49.449	83.530	158.327	230.35	306.455	781.74	352.992	589.31
51.842	87.946	162.413	235.27	308.325	537.58	353.670	585.60
54.189	92.449	166.807	240.09	310.425	539.22	355.073	588.31
54.914	93.594	171.252	244.74	312.594	541.86	355.919	586.06
57.430	98.213	175.748	249.68	314.837	544.24	358.464	586.48
59.829	100.42	180.185	255.40	317.071	548.23	361.576	585.12
62.127	106.39	184.561	260.33	318.381	550.93	364.965	585.58
64.451	110.26	188.881	265.74	319.295	552.38	368.344	589.53
66.805	114.15	193.149	270.35	322.061	554.74	371.719	588.27
69.082	117.67	197.351	276.24	322.214	554.49	(Supercooled Nematic Liquid Crystal)	
71.284	121.27	201.500	280.81	325.907	561.61		
73.425	124.46	205.615	286.05	326.423	561.96	298.910	526.70
75.522	127.52	209.680	291.55	329.634	568.68	300.138	528.96
77.704	130.95	213.693	296.03	330.399	570.02	301.977	530.60
79.215	132.93	218.314	302.51	331.864	572.82	304.415	533.38
81.567	136.43	223.209	308.97	334.077	579.26	306.844	535.42
83.862	139.73						

°C. The values of T_m and T_C are approximately the same as those previously given.[5–7] A cooling curve of the isotropic liquid at the rate $-2\sim-500$ K min^{-1} is shown by run 2. Within this range the isotropic liquid was transformed into the nematic phase at the same temperature T_C without indication of thermal hysteresis. The sample in nematic state was supercooled to 20 °C at which temperature it crystallized into a metastable crystalline form. The cooling rate -500 K min^{-1} was not great enough attaining a glassy state of liquid crystal.[1–4] A heating curve at the rate 2.5 K min^{-1} is shown by run 3. The metastable crystal was irreversibly transformed into a stable one with heat evolution between -15 and 15 °C. Once stabilized, the thermal behavior remained the same as that shown by run 1.

Heat Capacity. The results of calorimetric measurements have not been converted into molar heat capacity under the saturation vapor pressure C_{sat}, due to the lack of data on density, vapor pressure, and heat of vaporization. The present results (Table 1, Fig. 2) correspond approximately to the molar heat capacity at constant pressure C_p, although a minor effect of vaporization of the specimen into the narrow empty space of the calorimeter cell might be included in the liquid state.

The temperature of the triple point and a concentration of impurity involved in the sample were evaluated from a series of temperature measurements with various fractions of the sample in the liquid state (Table 2). The values obtained closely follow the Mastrangelo-Dornte equation,[12] derived by assuming the formation of solid solution, rather than the ideal solution equation based on Raoult's law. The variation of temperature with the fraction melted could be represented by

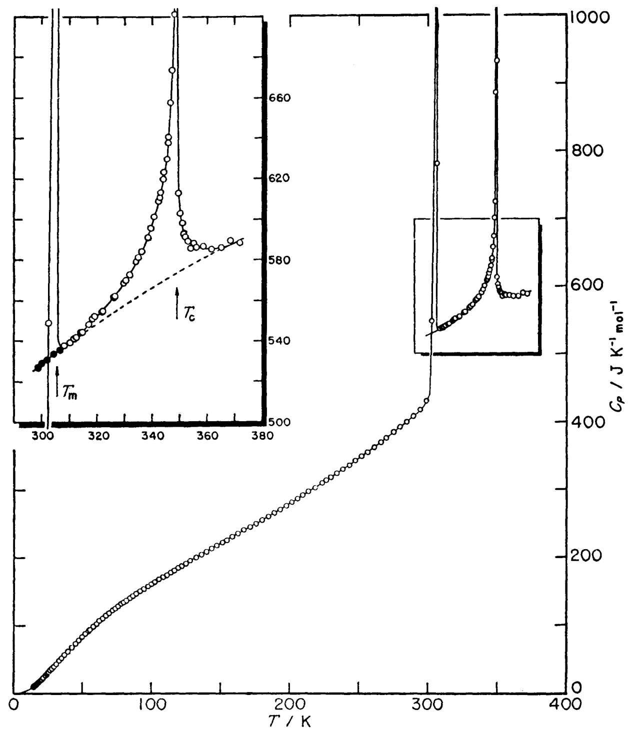

Fig. 2. Molar heat capacity of EBBA. Solid circles correspond to the heat capacity of supercooled nematic phase. Broken line indicates a normal heat capacity which separates the excess heat capacity due to phase transition from the total C_p.

TABLE 2. MELTING TEMPERATURE OF EBBA

Fraction melted (F)	Osberved T/K	Calculated T/K
0.1999	305.403	305.403
0.3287	305.503	305.502
0.4592	305.552	305.550
0.5245	305.566	305.566
0.5903	305.577	305.578
0.6562	305.583	305.589
0.7219	305.595	305.597
0.7878	305.602	305.604
0.8536	305.611	305.610
0.9194	305.622	305.616
Triple point of sample		305.621
Triple point of pure EBBA		305.688

$$T = 305.6876 - 0.06928/(0.04388+F),$$

where F is the fraction melted. The most probable numerical values were determined by computer-iteration. The melting point of EBBA could be derived from the value of triple point by means of Clausius-Clapeyron's equation if the data of molar volume were available for both solid and liquid states. Lack of such data prevented us from making the evaluation and the triple point is approximately regarded as equal to melting point. The concentration of impurity was determined to be 0.25 mol percent.

The thermodynamic functions of EBBA were calculated from heat capacity data and the calorimetric enthalpies of fusion and mesomorphic transition (Table 3). Values are given for heat capacity $C_p°$, entropy $S°$, enthalpy function $(H°-H_0°)/T$, and the Gibbs energy function $-(G°-H_0°)/T$, at selected temperatures. The values at 5 and 10 K were estimated by means of an effective frequency-distribution method.[13)]

TABLE 3. THERMODYNAMIC FUNCTIONS OF *N*-*p*-ETHOXYBENZYLIDENE-*p*′-BUTYLANILINE IN THE STANDARD STATE

T / K	$C_p°$ / J K^{-1}mol^{-1}	$S°$ / J K^{-1}mol^{-1}	$(H°-H_0°)/T$ / J K^{-1}mol^{-1}	$-(G°-H_0°)/T$ / J K^{-1}mol^{-1}
		Crystal		
5	(0.5354)	(0.179)	(0.134)	(0.045)
10	(4.0435)	(1.398)	(1.044)	(0.354)
15	11.282	4.302	3.164	1.137
20	20.806	8.815	6.352	2.463
25	31.396	14.583	10.291	4.292
30	42.392	21.276	14.722	6.554
35	53.406	28.640	19.463	9.176
40	64.182	36.478	24.383	12.095
45	74.563	44.642	29.387	15.255
50	84.467	53.015	34.404	18.611
60	102.75	70.062	44.299	25.763
70	119.19	87.156	53.843	33.313
80	134.18	104.064	62.961	41.103
90	148.10	120.681	71.656	49.025
100	161.22	136.971	79.963	57.008
110	173.57	152.920	87.916	65.004
120	185.83	168.549	95.566	72.983
130	197.28	183.875	102.949	80.926
140	208.92	198.928	110.109	88.819
150	220.55	213.737	117.082	96.655
160	232.36	228.339	123.910	104.429
170	243.43	242.764	130.621	112.143
180	255.17	256.998	137.202	119.796
190	266.95	271.105	143.716	127.389
200	279.16	285.106	150.180	134.926
210	291.91	299.028	156.619	142.409
220	304.63	312.891	163.048	149.843
230	318.35	326.726	169.494	157.232
240	331.46	340.548	175.966	164.582
250	345.76	354.365	182.468	171.897
260	360.98	368.219	189.038	179.181
270	377.14	382.139	195.699	186.440
273.15	381.75	386.540	198.965	187.575
280	392.44	396.125	202.446	193.679
290	409.64	410.184	209.282	200.902
298.15	429.09	421.788	216.148	205.640
300	466.02	424.455	216.339	208.116
		Nematic Liquid Crystal		
310	538.89	528.586	311.940	216.646
320	552.52	545.887	319.222	226.665
330	569.36	563.124	326.524	236.600
340	598.24	580.644	334.053	246.591
		Isotropic Liquid		
350	606.54	598.596	342.239	256.357
360	585.81	615.197	349.101	266.096
370	589.05	631.267	355.517	275.750

Enthalpy and entropy of fusion are listed in Table 4 together with changes due to mesomorphic transition.

Mesomorphic Transition. As in the case of OHMBBA,[3)] the present mesomorphic transition is characterized by a remarkable effect of pretransition. The effect, which results from easy fluctuation of the orientational order parameter in the vicinity of T_C, is obviously reflected in a large tail of the heat capacity curve below the transition point T_C. Recently, Goren *et al.*[14] measured the proton spin-lattice relaxation time of this compound in a wide temperature range and found that fluctuation of the order parameter is predominant around the mesomorphic transition point. The present result obtained from the heat capacity measurements is quite compatible with that of their nuclear magnetic resonance experiment.

The excess heat capacity, C(excess), due to the mesophase transition was determined by subtracting a normal heat capacity, C_p(normal), from the experimental one, C_p. The following quadratic equation was assumed for C_p(normal):

$$C_p(\text{normal}) = -2.6387\times 10^{-3}T^2+2.6284T-22.214,$$

which corresponds to a curve passing through the three experimental C_p points at 300.138, 304.415, and 364.965 K. The enthalpy and entropy of transition were determined by integrating the C(excess) with respect to T and ln T, respectively (Table 4).

TABLE 4. ENTHALPY AND ENTROPY OF TRANSITION FOR EBBA

Transition	T / K	ΔH / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
Crystal→Nematic (T_m)	305.62[a]	27.09	88.71
Nematic→Isotropic Liquid (T_C)	349.08	1.553	4.524

a) Melting point for the pure material $T_m^\circ=305.69$ K.

With a differential scanning calorimeter (DSC) Smith and Gardlund[7] determined the enthalpy of mesophase transition to be 523 J mol^{-1}, which amounts to only one third of the present calorimetric value. A shortcoming inherent to thermal analysis with DSC is inability to detect a mild thermal change occurring gradually. In a mesomorphic transition, the contribution from the pretransitional region to ΔH is considerably large. In the DSC method, however, only a truncated part of a heat-capacity peak is detected. The large discrepancy between the DSC method and the present calorimetric measurement is therfore attributable to the underestimation of ΔH in the former method.

The order of phase transition provides useful information on the nature of transition. Except for the smectic-A to nematic (S_AN) transition[15,16] all other mesomorphic transitions are believed to be of first-order. No paper seems to have appeared dealing with the examination of the order of the nematic to isotropic liquid (NI) transition. It was difficult to decide whether the NI transition of EBBA is first-order or not, since, we have not measured the heat capacity in a cooling direction to examine the existence of thermal hysteresis, and the enthalpy of transition was too small to detect a latent heat.

We attempted to analyze the NI mesomorphic transition according to the treatment of critical phenomena.[17-19] If C(excess) is varied with the critical-point exponents α' and α for $\varepsilon(\equiv|T-T_C|/T_C)$, when $T\rightarrow T_C\pm 0$, by

$$C(\text{excess}) \sim \varepsilon^{-\alpha'} \qquad \text{for } T< T_C$$

and

$$C(\text{excess}) \sim \varepsilon^{-\alpha} \qquad \text{for } T> T_C,$$

linearity is expected in the vicinity of the critical point T_C in a log C(excess) *versus* log ε plot (Fig. 3). We see that there is a linear region $(10^{-1.5}>\varepsilon>10^{-4})$ for both $T<T_C$ and $T>T_C$. The critical-point exponents were determined to be $\alpha'=\alpha=0.7$ as the slopes of these straight lines. This implies that the present NI transition can be treated as a critical phenomenon fulfilling apparently a scaling relation $\alpha'=\alpha$. The NI transition in EBBA can be characterized by a second-order phase transition rather than a first-order one, though the numerical value of 0.7 seems to be rather large as compared with the values obtained for typical critical phenomena such as the gas-liquid or the ferromagnetic critical phenomena.

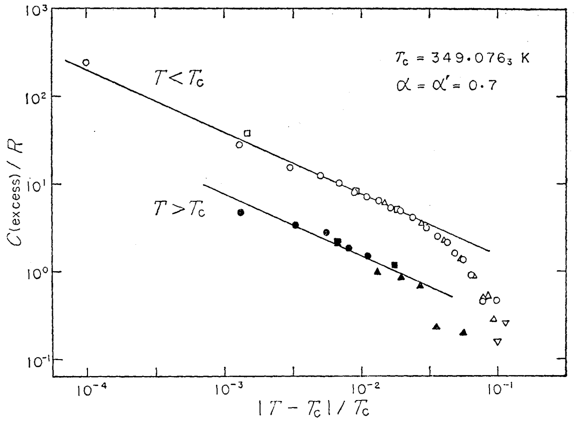

Fig. 3. Variation of excess heat capacity, C(excess), due to mesomorphic transition with the reduced temperature. Different symbols indicate different series of measurements.

McMillan[20] proposed a theory for the S_AN phase transition based on a simple microscopic model for the intermolecular interaction potential. One of the most interesting features of his theory is its prediction that the S_AN transition can be of first or second order, depending on the magnitude of the molecular interaction constants. Although this theoretical argument cannot be directly applied to the NI transition, it is very likely that the order of the NI transition depends on the nature of molecular interaction.

Existing chemical or physical impurity is also a dominant factor to control the transition behavior. High concentration of these impurities generally brings about (i) appreciable reduction of "a first-order character" in an intrinsic first-order phase transition[21] and (ii) incompleteness of the critical-exponent description for ideal critical phenomena.[22,23] We cannot determine whether a 0.25 mol percent concentration of chemical impurity is high enough to violate the intrinsic nature of the present NI transition or not, or what the physical impurity in a mesomorphic transition occurring in a liquid state is. Although a liquid crystalline state is characterized by an ordered trend of molecular orientation, no regularity such as a lattice structure in crystal exists. Lattice defects or vacancies therefore do not belong to physical impurity in a liquid crystalline state. Only the physical impurity to bring about a significant effect in the vicinity of T_C may be the heterophase fluctuation. The mechanism of a mesomorphic transition, occurring cooperatively in a liquid state, should be understood in terms of the fluctuation of order parameter as well as the intermolecular interaction.

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