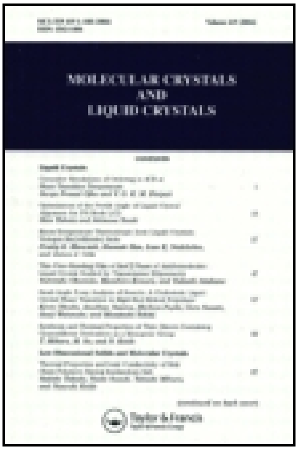

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High Pressure Studies of the Phase Transition Enthalpies of the Liquid Crystal EBBA up to 2.5 kbar

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High Pressure Studies of the Phase Transition Enthalpies of the Liquid Crystal EBBA up to 2.5 kbar

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The liquid crystal *p*-Ethoxy-benzylidene-*p*-*n*-butylaniline (EBBA) exhibits one nematic–liquid isotropic and two solid–nematic coexistence lines.

With a high pressure micro calorimeter based on differential scanning calorimetry (DSC) previously described the phase transition enthalpies of these three phase transitions have been measured in the pressure range 1 bar to 2.5 kbar. Numerical data are presented for the transition temperatures, the enthalpy changes, the entropy changes, and the volume changes for both solid–nematic transitions as well as for the nematic–liquid isotropic transition.

Additionally the effect of impurities on the nematic–liquid isotropic transition enthalpy at normal pressure is discussed.

EXPERIMENTAL

a Apparatus

Details of the high pressure DSC calorimeter, the calibration and the experimental procedure have been described recently.[1] See also[2,3].

b Thermal pretreatment of the liquid crystal EBBA

It has been recently shown by Spratte and Schneider[4] that EBBA exists in two different solid phases s_1 and s_2 yielding the same nematic phase n on melting. The difference between the melting temperatures of the two solid phases varies from about 2 K at 1 bar to 6 K at 3 kbar, see Figure 2.

The melting behaviour depends strongly on thermal pretreatment. Heating the solid immediately after freezing from the nematic phase yields melting along the melting-pressure curve of the higher melting solid phase s_2, see Figure 2. When the crystals are tempered at 20 K to 40 K below the melting temperature at a given pressure, however, both solid–nematic transitions occur on heating. The longer the time and the lower the temperature of annealing the larger is the amount of the lower melting phase s_1. Annealing more than 12 hours at 40 K below the melting temperature of solid s_1 yields pure phase s_1 which does not change into phase s_2 on heating. Annealing a mixture of s_1 and s_2 only a few degrees below the melting temperature, say 5 K to 10 K, gives the opposite effect: the longer the annealing time the larger is the amount of the higher melting phase s_2.

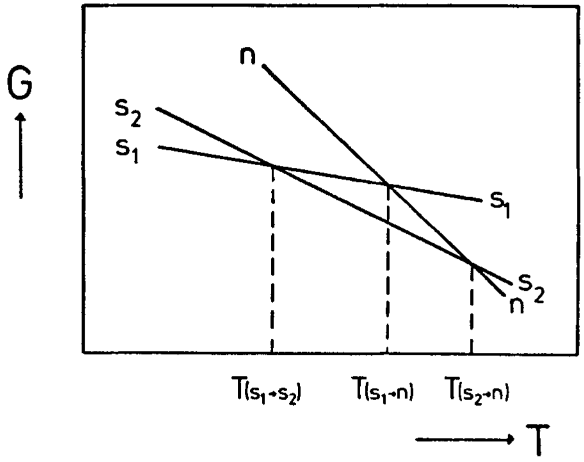

FIGURE 1 G–T diagram of EBBA at constant pressure (schematic).

This behaviour can be explained from the schematic G–T diagram for constant pressure in Figure 1; a similar diagram has been proposed for the nematic liquid crystal trans-4-Ethoxy-4'-n-heptanoyloxyazoxybenzene.[5] According to thermodynamics the phase with the lowest G value is the most stable in such a diagram. For annealing at $T < T(s_1 \to s_2)$ solid s_1 and at $T(s_1 \to s_2) < T < T(s_1 \to n)$ solid s_2 will be the most stable phase respectively. From this and with the additional assumption that the transition between the two solid phases s_1 and s_2 is hindered at $T(s_1 \to s_2)$ the complete melting behaviour described above can be understood.

The change of the slopes of the G–T isobars at the melting temperatures correspond to the transition entropies. It can be deduced from Figure 1 that $\Delta S(s_1 \to n)$ will be larger than $\Delta S(s_2 \to n)$. It will be shown below that this prediction is in accordance with the measured data.

c Substance

EBBA was obtained from Riedel de Haen AG, Seelze, Federal Republic of Germany. The purity was 99.7 % controlled by DSC according to a thermal analysis method proposed by Rossini.[6,7]

RESULTS

a Temperatures and enthalpies of transformation

The melting enthalpies $\Delta H(s_1 \rightarrow n)$ and $\Delta H(s_2 \rightarrow n)$ obtained experimentally at normal pressure are presented in Table I. Here the first row refers to solid EBBA crystallized from the nematic liquid whereas in the second row data for material being crystallized from ethanol are given, these latter results being larger by about 50%. All data given in the following correspond to EBBA crystallized from the nematic phase.

TABLE I

Melting enthalpies $\Delta H(s \rightarrow n)$ of EBBA at normal pressure

	$\Delta H(s_1 \rightarrow n)$ kJ · mol^{-1}	$\Delta H(s_2 \rightarrow n)$ kJ · mol^{-1}
EBBA crystallized from nematic phase	18.6 ± 0.8 19.6 ± 2.0 (Lit.[4])	15.1 ± 0.2
EBBA crystallized from ethanol	27.3 ± 0.8 27.1 (Lit.[6])	21.4 ± 0.6

The transition temperatures found are in good agreement with those measured by Spratte and Schneider[4] with a high pressure DTA apparatus. Because of the higher accuracy of DTA compared with DSC for the determination of transition temperatures, the DTA data have been used in the following calculations; they are plotted in Figure 2.

The transition enthalpies of EBBA obtained are represented in Figure 3. Here the melting enthalpies have been evaluated by comparing the DSC peak area of the EBBA transitions with the peak areas corresponding to the known melting enthalpies of gallium[9] and hexacosane $n\text{-}C_{26}H_{54}$[1] used as reference substances. The enthalpy change of the nematic(n)-liquid isotropic (l) transition, $\Delta H(n \rightarrow l)$, has been obtained by comparing the corresponding DSC peaks with the area of the melting peaks of EBBA itself. For details see Ref. 3. The experimental $T\text{-}p$ and $\Delta H\text{-}p$ curves were fitted to polynomials in p of the type

$$Z = a + b \cdot p + c \cdot p^2 \qquad (1)$$

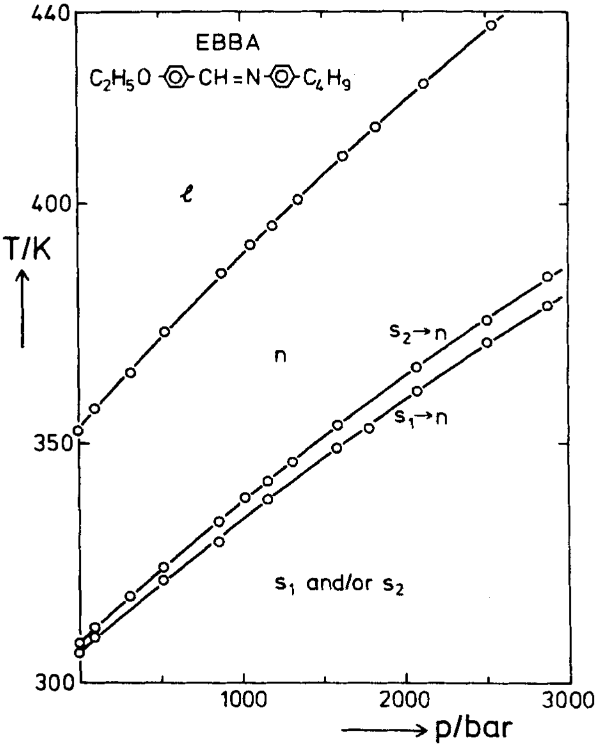

FIGURE 2 Transition temperatures of EBBA (according to Spratte and Schneider[4]).

by a least square procedure. The values of the coefficients *a*, *b*, and *c* thus obtained are given in Table II.

b ΔS and ΔV values

From the enthalpies of transformation and the transition temperatures the entropy changes ΔS_i along the coexistence curves were calculated from Eq. (2)

$$\Delta S_i = \Delta H_i / T_i \tag{2}$$

and the corresponding volume changes ΔV_i from Clapeyron's equation (3)

$$(dp/dT)_{\text{coex}} = \Delta H_i / (T_i \, \Delta V_i) \tag{3}$$

using the values of $(dp/dT)_{\text{coex}}$ in Figure 2. The ΔS-p and the ΔV-p curves thus obtained were also fitted to polynomials in p of the type of Eq. (1). The values of the coefficients *a*, *b*, and *c* are given in Table II. Table III gives a summary of the results; all values were calculated from the polynomials in Table II.

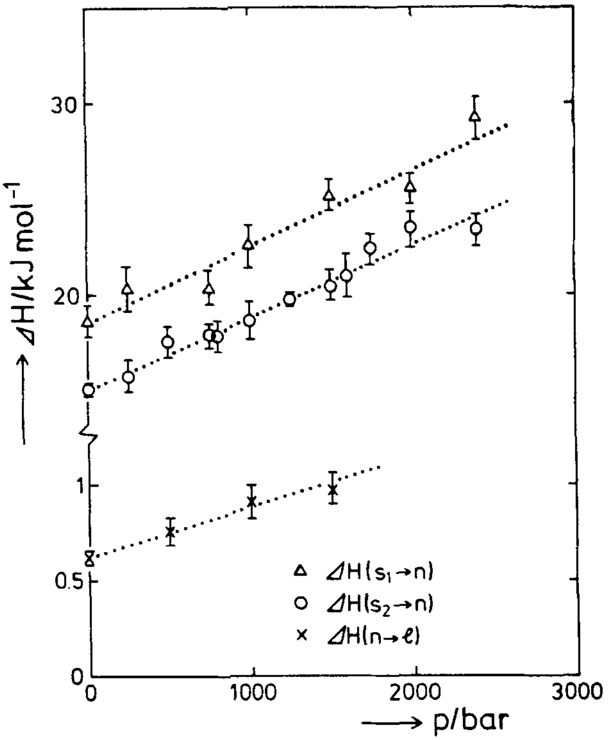

FIGURE 3 Transition enthalpies of EBBA along the coexistence curves. (Note that the enthalpy scale is interrupted and differs by a factor of 10).

c $\Delta C_p(\mathrm{n} \to \mathrm{l})$ at normal pressure

With Planck's equation for phase transitions (4) the change of heat capacity at constant pressure ΔC_p was calculated for the phase transition from the nematic phase n to the liquid isotropic phase l

$$(d\Delta H(\mathrm{n} \to \mathrm{l})/dp)_{\mathrm{coex}} = \Delta C_p(\mathrm{n} \to \mathrm{l})(dT/dp)_{\mathrm{coex}} + \Delta V(\mathrm{n} \to \mathrm{l}) - T(\partial \Delta V(\mathrm{n} \to \mathrm{l})/\partial T)_p \tag{4}$$

The last term of the Eq. (4) was not available from the experimental data given in this paper; therefore data of the specific volume of the nematic and the liquid isotropic phase of EBBA as a function of temperature given by Bahadur and Chandra[10] were used.

From this a value of $\Delta C_p(\mathrm{n} \to \mathrm{l}) = -(40 \pm 13)\ \mathrm{J\,K^{-1}\,mol^{-1}}$ was calculated. The error given is the maximum error; thus in spite of the poor accuracy obtained the sign of the value will be correct in each case. This result

TABLE II

T, ΔH, ΔS, and ΔV for the phase transitions of EBBA along the coexistence curves. Coefficients of $Z = a + b \cdot p + c \cdot p^2$ obtained by least square fitting, p in bar

	$s_1 \rightarrow n$			$s_2 \rightarrow n$			$n \rightarrow l$		
Z	a	$10^3 b$	$10^6 c$	a	$10^3 b$	$10^6 c$	a	$10^3 b$	$10^6 c$
T/K	307.1	28.1	−1.10	309.3	30.0	−1.37	353.3	39.7	−2.52
ΔH/kJ mol^{-1}	18.5	4.1	—	15.0	4.1	−0.14	0.62	0.25	—
ΔS/J K^{-1}mol^{-1}	61.6	6.0	—	48.6	8.1	−0.6	1.8	0.5	—
ΔV/cm^3 mol^{-1}	17.1	0.26	—	14.9	0.24	—	0.71	0.08	—
validity range	1–2500 bar			1–2500 bar			1–1500 bar		

TABLE III

Phase transition data of EBBA as a function of pressure along the T-p coexistence curves

$\frac{p}{\text{bar}}$	$\frac{T}{K}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{\Delta S}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta V}{\text{cm}^3\text{ mol}^{-1}}$
		$s_1 \rightarrow n$		
1	307.1	18.5	62	17.1
500	320.9	20.6	65	17.2
1000	334.2	22.6	68	17.4
1500	346.8	24.7	71	17.5
2000	358.9	26.7	74	17.6
2500	370.5	28.8	77	17.8
mean error:				
±3	±0.4	±5%	±5%	±7%
		$s_2 \rightarrow n$		
1	309.3	15.0	49	14.9
500	324.0	17.0	53	15.0
1000	337.9	19.0	56	15.1
1500	351.2	20.8	59	15.3
2000	363.8	22.6	62	15.4
2500	375.7	24.4	65	15.5
mean error:				
±3	±0.4	±5%	±5%	±7%
		$n \rightarrow l$		
1	353.3	0.62	1.8	0.71
500	372.5	0.75	2.1	0.75
1000	390.5	0.87	2.3	0.79
1500	407.2	1.00	2.6	0.83
mean error:				
±3	±0.4	±10%	±10%	±12%

shows that near the nematic–liquid transition the heat capacity is considerably larger in the nematic phase than in the isotropic liquid.

d Effect of impurities on $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$ in EBBA

In order to investigate the effect of impurities on the value of $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$ EBBA was thermally cracked stepwise and both the purity and the $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$ value were determined after each step by DSC at normal pressure according to a thermal analysis method proposed by Rossini.[6,7] The results[3] are given in Figure 4.

According to Figure 4 $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$ at normal pressure decreases to about half of its value at 99.7% purity when the purity decreases to 97.5% only. Thus Figure 4 demonstrates the dramatic influence of impurities on $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$. Besides the solid phase s_1 was only found in EBBA with a purity better than about 99%.

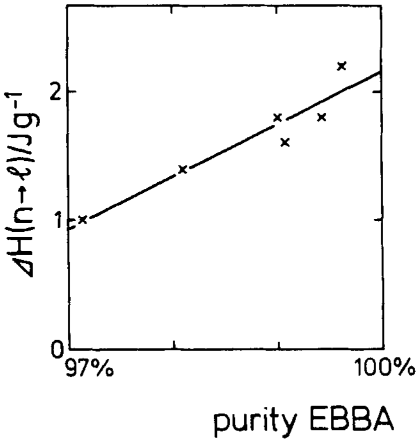

FIGURE 4 $\Delta H(\mathrm{n} \rightarrow \mathrm{l})$ of EBBA as a function of purity.

DISCUSSION

All transition enthalpies measured show a distinct increase with pressure such as given in Figure 3. Additionally the data demonstrate that $\Delta H(p)/\Delta H(p = 1 \text{ bar})$ is considerably more pressure dependent for the n → l than for the two s → n transitions. The same effect is found for the transition entropies ΔS.

a $s \rightarrow n$ transitions

From the difference between $\Delta V(s_1 \rightarrow n)$ and $\Delta V(s_2 \rightarrow n)$ it can be deduced that s_1 will be more dense than s_2 by about 0.8 %. This density difference is probably caused by a different steric arrangement of the *n*-butyl chain in s_1 and s_2.[11]

Since the solid and the nematic phase are both ordered the compressibilities and the thermal expansivities might be assumed to be rather similar; thus the $\Delta V(s \rightarrow n)$ values along the coexistence curves in Table III are essentially constant within the limits of experimental error.

It is difficult to explain the dramatic influence of crystallization on the melting enthalpies at normal pressure such as shown in Table I. Probably different solid modifications crystallize from the nematic melt or from alcoholic solution.

b $n \rightarrow l$ transition

The calculated $\Delta V(n \rightarrow l)$ values show a slight increase with pressure. Similar $\Delta V(n \rightarrow l)$ values such as given in Table III can be extrapolated from pVT data of EBBA[10] and MBBA[12] taken from the literature.

The nematic range increases with rising pressure. This behaviour can be qualitatively understood from the following arguments. In literature it is always found that both compressibility and thermal expansivity are larger for the nematic than for the liquid isotropic phase. These two opposite effects finally result in increasing $\Delta V(n \rightarrow l)$ values with increasing pressure along the coexistence line. Since consequently the density of the nematic phase increases more rapidly with rising pressure than that of the liquid isotropic phase, high pressure stabilizes the nematic phase. This effect even overcompensates the destruction of the nematic order at higher temperatures along the transition line and as a result the nematic range increases with rising pressure.

In 1968 Torgalkar *et al.*[13] have published $C_p(n)$ and $C_p(l)$ data for the nematic crystal 4,4′-Dimethoxyazoxybenzene (PAA) measured by Barrall *et al.*[14] and Arnold[15] that have been compared with calculations from a modified heterophase fluctuation theory according to Frenkel. From these data a value of $\Delta C_p(n \rightarrow l)$ can be obtained that is near the value given in this work as far as a transition range of about 1 K to 2 K is assumed.

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