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Volume Measurements and Transitions of MBBA at High Pressures*

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The volumes of MBBA in expansion at constant pressure and compression at constant temperature to about 180°C and 7 kbar were measured. Expansion and compression curves and the P-T phase diagram for the crystal-nematic and nematic-isotropic equilibria are presented. The first two sets of curves display the volume changes associated with phase transformations. Optical observations in a diamond cell to about 8 kbar and 200° failed to indicate any new liquid crystal phase. The enthalpies and entropies estimated for C-N, N-I transformations were respectively about 3500 and 12 cal/mol for C-N and about 100 and 0.3 cal/mol for N-I.

INTRODUCTION

A number of pressure-temperature phase diagrams for liquid crystals have now been published, for example in references 1–4, 16, 17. Optical,[5] NMR,[6] and compression[13] and expansion measurements have helped assess the degree of ordering at phase transitions, especially the nematic–isotropic transition, at various pressures. Relatively few high pressure measurements have been made on properties away from the transitions.

In this work a direct measurement of the volume change at the crystal–nematic transformation for 4′-methoxybenzylidene-4-*n*-butylaniline (MBBA) was obtained. From this measurement, a density value for the crystal phase was derived. Also the expansion curves for the temperature range 20–180°C at 1.8, 2.1, 3.9 and 6 kbars and compression curves from 1/2 to 7 kbars at 25, 56 and 85° were obtained. The volume changes associated with the

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crystal-nematic (C-N) and nematic-isotropic (N-I) transitions were observed and used to plot a P,T phase diagram for MBBA. The Clausius-Clapeyron equation was applied to the slopes of the phase boundaries and the measured volume changes at the transformations were used to derive the entropies and enthalpies for the C-N and N-I transformations. These results are compared to those of other workers[1-6,10,16] who used other methods of measurement.

EXPERIMENTAL

For volume measurements the sample was contained between two opposed tungsten-carbide pistons in a tungsten carbide cylinder of quarter-inch diameter. The force was provided by hydraulic rams; oil pressure in the hydraulic system was regulated by a hand pump, to within 0.02 lb/in^2 of the desired value (in constant pressure experiments), giving ± 3 bar regulation in the cylinder. The sample was contained in a Teflon capsule and was sealed in the cylinder by various gasket combinations including Bridgman's "unsupported area" method.[7]

Length (volume) changes in the contents of the cylinder were measured by a Teclock dial gauge mounted between the rams. Distance differences were read to 10^{-5} inch. Measurements of the lengths of a block of solid Teflon over the same temperature and pressure paths gave corrections for eliminating the effects of expansion or compression of the Teflon capsule.

Temperature was measured by a chromel-alumel thermocouple, whose hot junction was attached to the cylinder, and potentiometer. The sample temperature was known within ±1°C, as was shown by comparison of melting points measured inside and outside the cylinder, and by direct comparisons between thermocouples located inside and outside the cylinder.

There were two ways to measure pressure in the cylinder. First, it was calculated from the geometry of the situation, given the oil pressure. Pressure calculated this way did not include the effects of friction in the seals. Calibration with urethane and water, whose phase diagrams are known, does indicate that this calculation was within 200 bars of the actual pressure. Secondly, for each pressure experiment up to ~5 kbar our data showed a volume jump due to a phase transition in the Teflon sample holder and gaskets. Comparison of its temperature with the known Teflon phase diagram[8] gave the pressure. These two methods agree within about 200 bars. The results presented here assume that the Teflon indication of pressure was correct.

The volume of the MBBA sample used while in the nematic state at one atmosphere pressure and 25° was 188.5 mm.[3] The initial volume of the sample, V_0, applicable to the isobars and isotherms plotted in Figures 1-3 was adjusted in each case to initial P and T values, using published thermal expansion data together with compression data from this work. The corresponding molar volumes are listed in Table I.

For optical observations, a pressure cell with opposing diamond anvils was used.[9] The sample was held in a 0.010 inch hole in a 0.005 inch thick inconel disc between the anvils. Our experience showed that the various liquid crystal phases were clearly distinguished by their textures in microscopic observation.

The MBBA samples were from Eastman Organic Chemicals (Cat. No. 11246) loaded in a dry nitrogen atmosphere. While there was some scatter

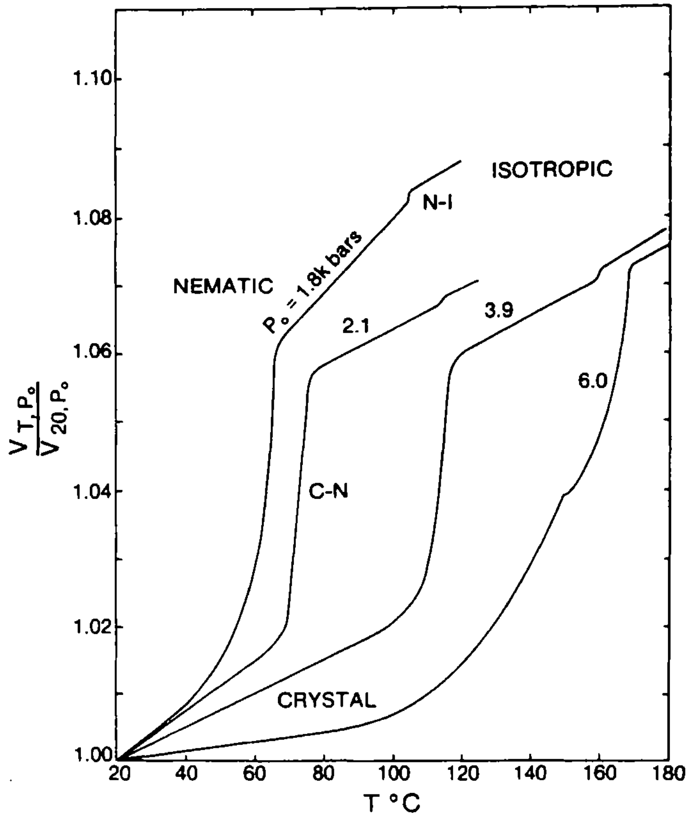

FIGURE 1 Volume changes with heating at various constant pressures. The steep nearly vertical rise in each curve was due to the crystal-nematic transformation (C-N). The small step at the high temperature end of three of the curves was due to the nematic-isotropic transformation (N-I). The cusp at 150° in the 6 kbar isobar may have been due to a 111-1 transformation in the Teflon capsule. Initial molar volumes, V_{20,P_0} are given in Table I for the origin of each curve.

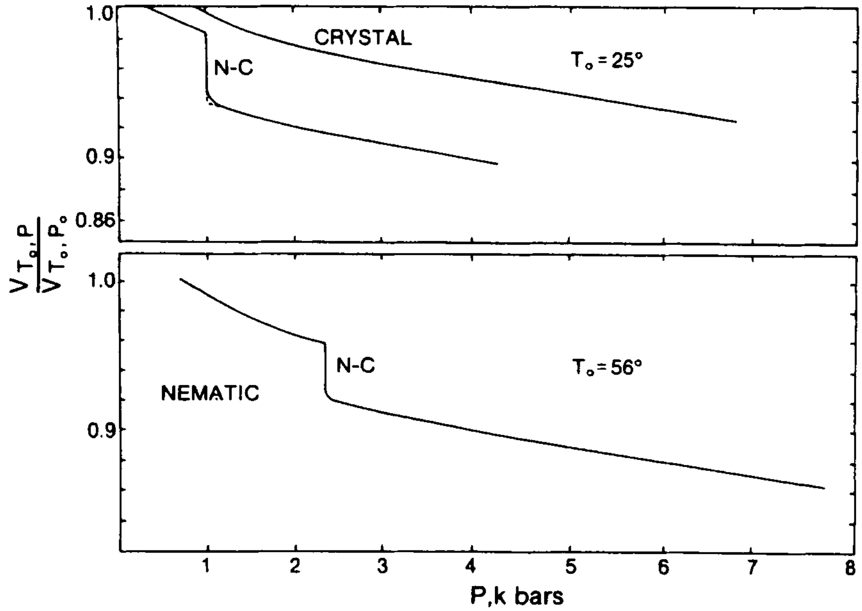

FIGURE 2 Compression at constant temperatures of 25 and 56°. The sharp discontinuities correspond to the "supercooled" N-I transition. Initial molar volumes V_{T_0,P_0} are given in Table I.

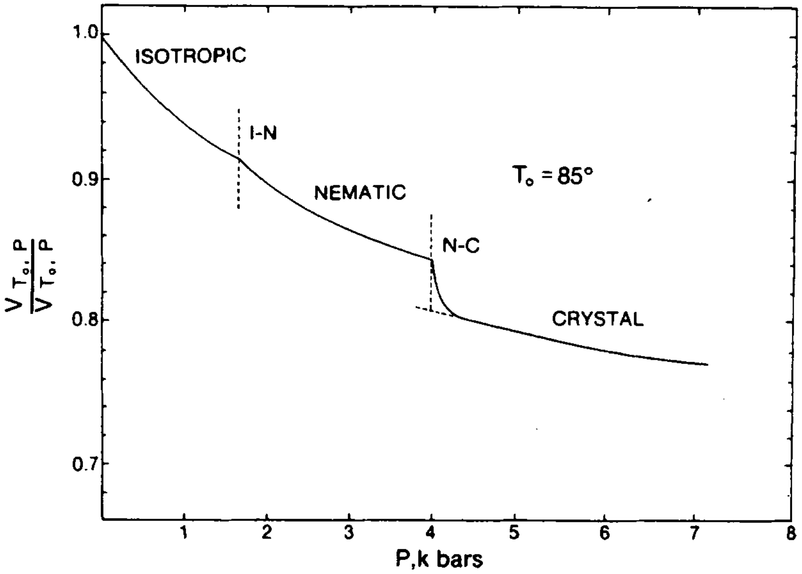

FIGURE 3 Compression at 85° through the I-N and N-C transitions. The I-N transition may be "supercooled" a few degrees. The N-C transition was supercooled about 10°.

TABLE I

Initial molar volumes for Figures 1–3

Pressure (P_0)	Temperature (T_0)	Molar volumes, cm^3		
		C	N	I
1 atm.	22°	243[b]	255[a]	
1 atm.	25°	244[b]	256	
1 atm.	56°			263[c]
1 atm.	85°			269[c]
1 kb	25°	243[d]		
1.8	20°	239		
2.1	20°	237		
3.9	20°	233		
6.0	20°	228		

Data rounded to three significant figures.

[a] Based on density of 1.049 gms/cm^3 (Ref. 14).

[b] Volume change of 12.3 cm^3/mol at 1 atm.

[c] Extrapolation of densities for I phase from Ref. 14.

[d] From compression at 25°, Figure 2.

Initial sample volume at 25°, 1 atm. in nematic state, 188.5 mm^3.

in our transition temperatures at a given pressure, there was no consistent variation between different bottles of MBBA, nor was there a consistent trend in transition temperatures with time. Thus, the samples were stable for our purposes.

TRANSITION TEMPERATURES AND VOLUME CHANGES

Three kinds of experiments were done. The sample was heated slowly at constant pressure (Figure 1), or was compressed slowly at constant temperature (Figures 2 and 3), in the piston-cylinder apparatus. In the diamond cell, the temperature was raised and lowered gradually with constant force on the anvils.

Transition temperatures were obtained from plots of expansion at constant pressure. The phase diagram obtained in this way is shown in Figure 4. Results from nine samples are plotted along with results by other workers. The error bars result from the uncertainty in the temperatures of the Teflon transitions which were used to find the pressure. Above 5 kbars, Teflon was not useful for internal pressure sensing, and the pressure uncertainty increased somewhat. For each type of transition, a nearly linear relationship between temperature and pressure was found. For the melting transition, $dT/dP = 25 \pm 2.0°/\text{kb}$. This agrees well with measurements of Sasabe and

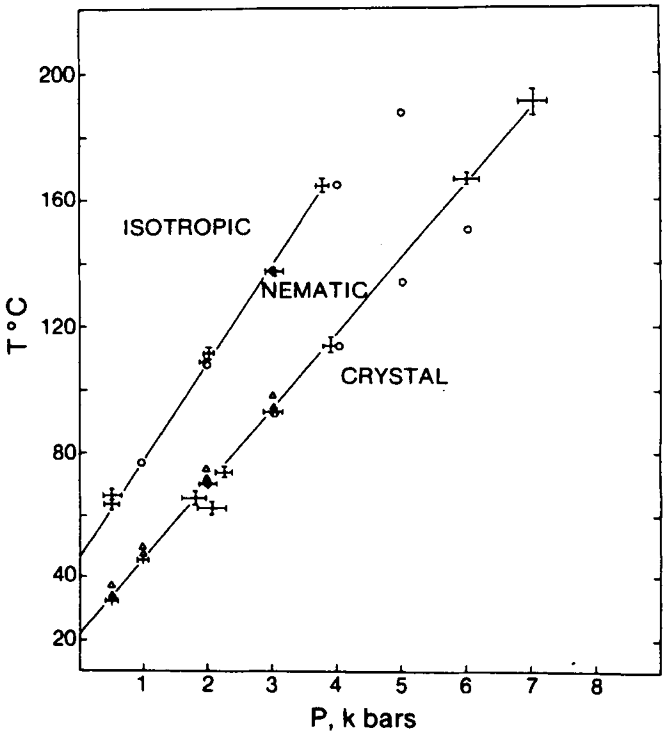

FIGURE 4 A pressure-temperature phase diagram for C-N and N-I transformations. Uncertainties in pressure and temperature measurements are indicated by bars for this work. The data of Keyes, *et al.* (0)[4] and Spratte and Schneider (Δ)[16] are plotted for comparison. The data of Spratte and Schneider for the stable crystal phase melting lie above both our data and that of Keyes, *et al.*

Ooizumi.[10] For the clearing transition, $dT/dP = 31.5 \pm 2.0^0/\text{kb}$. The results of Keyes, Weston, Lin, and Daniels[4] are also plotted. At higher pressures our lines run straighter than theirs.

The Clausius–Clapeyron relation was applied to the phase line slopes and volume changes associated with C–N and N–I transformations to estimate their entropies and enthalpies. These results are summarized in Tables II and III. The ranges of values of the same quantities obtained by other workers, using different methods from ours, are also listed in Table III. Our experiments did not provide data at atmospheric pressure for the phase transitions. Volume changes for the C–N transformation under both compression and expansion tended to decrease with increasing pressure. Extrapolation of the more sharply defined compressional volume changes under compression back to atmospheric pressure indicated a ΔV for C–N of 12.0 to 12.5 cm^3/mol. From the slope of the C–N phase line, a value of 3470

TABLE II

T °C	P kb	V_i	$\frac{\Delta V}{V_i}$	ΔV (cm^3/mol)	
(1) Values of ΔV at C-N, from Figures 2-3, by compressions.					
25	1	256(N)	0.046	11.78	
56	2.4	263(I)	0.041	10.78	V_i = initial volume
85	4	270(I)	0.039	10.53	
(2) Values of V at C-N, N-I from Figure 1: by Expansion under pressure.					
			C-N		
65°	1.8	239	0.042	10.04	
72	2.1	237	0.041	9.71	
114	3.9	233	0.040	9.32	
167	6.0	228	0.036	8.21	
22°	1 atm.	243	0.051	12.5	Ref. 11
	1 atm.	243	0.068	16.5	Ref. 16
	1 atm.	243	0.051	12-12.5	By extrapolation to 1 atm. of our data.
			N-I		
104	1.8	239	0.0015 ± 0.0002	0.36 ± 0.02	
113	2.1	237	0.0015 ± 0.0002	0.35 ± 0.02	
159	3.9	233	0.0015 ± 0.0002	0.35 ± 0.02	
46°	1 atm.	243	0.0016	0.40	Ref. 15 and by extrapolation of our data.

cal/mol was obtained for the enthalpy of this transition at 1 atm. In a similar manner, but using expansion data, the volume change and enthalpy for the N-I transformation was estimated to be 0.40 cm^3/mol and 103 cal/mol at 1 atm. Literature values range above and below these values except for the 0.40 cm^3/mol ΔV for N-I which is in agreement with Ref. 15.

Two crystal phases were observed by both Mayer *et al.*[11] and Spratte and Schneider.[16] The stable phase had a melting point about 1.3° higher than the metastable phase, with a melting line running nearly parallel with that of the metastable phase (see Figure 4). We did not clearly detect the two phases as separate entities in this work. The melting line and enthalpy data seem to conform more to those values characteristic of the metastable phase than to the stable phase.

The expansion curve at 6 kbars, Figure 1, has a small cusp at 150° which may be associated with the 111-1 phase transformation in the Teflon capsule. This cusp conflicted with measurement of the volume change associated with the C-N transition in MBBA at this pressure. From cusp to the final isotropic state corresponds to $\Delta V/V_0$ of 0.036, which may be too low by 8 or 10%.

TABLE III

Entropy and enthalpy of C-N and N-I transformations

Transformations	P (kb)	T (K)	$\frac{dT}{dP}$ (deg kb^{-1})	ΔV $cm^3\ mol^{-1}$	ΔS cal $deg^{-1}\ mol^{-1}$	ΔH cal mol^{-1}
(1) By ΔV in Expansion (Figure 1).						
C-N	1.8	338	25	10.04	9.6	3245
C-N	2.1	346		9.71	9.3	3218
C-N	3.9	387		9.32	8.9	3244
C-N	6	439		8.21	7.85	3444
	1 atm.	295		12.3[a]	11.8	3469
N-I	1.8	377	31.5	0.36 ± 0.02	0.27	102
	2.1	386		0.35 ± 0.02	0.26	100
	3.9	432		0.35 ± 0.02	0.26	112
	1 atm.	339		0.40[a]	0.30	103
(2) By ΔV in Compression (Figures 2 and 3)						
C-N	1	298	(25)	11.78	11.3	3367
C-N	2.4	329		10.78	10.30	3389
C-N	4	358		10.53	10.1	3616

[a] Extrapolated values of ΔV.

Literature values:

C-N (metastable crystal) Refs. 11, 15, 16, 17.

$\frac{dT}{dP}$ = 23.2 to 28 K/kbar

ΔS = 12 to 14.1 cal/K mol.

ΔH = 3100 to 6000 cal/mol.

C-N (stable crystal) Ref. 16.

ΔS = 18.6 cal/K mol.

ΔH = 5557 cal/mol.

N-I Refs. 4, 10, 13, 16, 17.

$\frac{dT}{dP}$ = 31.5–39.5 K/kbar.

ΔS = 0.31–1.65 cal/K mol.

ΔH = 67–560 cal/mol.

COMPRESSIBILITY AND THERMAL EXPANSION

The isotropic phase had a compressibility, $(1/V)(\Delta P/\Delta V)$, of 5×10^{-2}/kbar at 1 kbar pressure 85°C. Compressibility measurements by Zawisza and Stecki[13] on the isotropic phase up to 70 atm pressure near 47° gave values close to 6×10^{-2}/kbar. The two results are in reasonable agreement. Compressibility measurements obtained in this work under several other conditions on crystal, nematic and isotropic phases are listed in Table IV.

TABLE IV

Compressibilities of C, N, I phases from Figures 2–3

P kb	T °C	State	$\frac{1}{V}\frac{\Delta V}{\Delta P}$ k bar^{-1}	
			This work	Literature
1.5	25	crystal	2×10^{-2}	
0.67	25	nematic	2.7×10^{-2}	
2.5	25	crystal	1.0×10^{-2}	
2	56	nematic	1.8×10^{-2}	
2.6	56	crystal	1.5×10^{-2}	
1.0	85	isotropic	5	
3.5	85	nematic	2.4	
4.5	85	crystal	1.9	
1 atm.	47	isotropic		5.0 to 6.2×10^{-2} Ref. 13

Published measurements[12,14,15] on the expansion at atmospheric pressure of nematic and isotropic phases very close to the N–I transition gave values in the range of about 0.8 to 1.1×10^{-3} per degree. The expansions in the isotropic phase were slightly lower than in the nematic phase. R. Chang[12] gave 0.673×10^{-3}/deg. in the nematic phase at room temperature. In this work, approximate values for the expansion coefficients in crystal, nematic and isotropic phases were obtained at pressures of 1.8, 2.1, 3.9 and 6 kbars. These are listed in Table V. The values were approximate because they had to be separated from the expansion of the Teflon capsule that combined to

TABLE V

Approximate volume expansion coefficients (from Figure 1).

P kb	T range °C	$\alpha \times 10^3$/deg crystal	Nematic	Isotropic	
1.8	70–100		0.56		
1.8	103–120			0.3	
2.1	20–62	0.35		0.2	
2.1	80–110		0.25		
2.1	115–183			0.2	
3.9	20–90	0.25			
3.9	120–155		0.25		
3.9	160–180			0.25	
			Literature values		
1 atm.	~22		0.673		Ref. 12
1 atm.	~38	near trans.	~0.83–1.1		Ref. 14, 15
1 atm.	~52	near trans.		~0.76–0.83	Ref. 14, 15

give the overall expansion. They are generally considerably lower than the literature values at 1 atm. and show a tendency to decrease with increasing pressure. The range of data available for the nematic phase at 6 kbars was very short giving at best only a rough value.

Press and Arrot[14] gave a density value for the nematic phase at 22°, 1 atm. of 1.049 gm/cm^3. The extrapolated value of Gulari and Chu[15] from 30° to 22° at 1 atm. gave a density of 1.044 gms/cm^3. The molecular volume of the nematic phase near room temperature is thus close to 255 cm^3/mol (m.w. = 267.37 gms/mol). The density of the solid has not been published. Our value for the molar volume change at the C–N transition at 1 atm. pressure gives 243 ± 0.3 cm^3/mol for the molar volume of the solid at 1 atm., corresponding to a density of 1.100 ± 0.002 gms/cm^3.

OBSERVATIONS IN DIAMOND ANVIL CELL

Visual observations in the diamond anvil cell over a wide range of pressures and temperatures, 20° at 1 atm. to 220° at 8 kbars, gave phase transition points that were consistent with those observed in the piston and cylinder cell. No new liquid crystal phases of MBBA were observed. Decomposition of MBBA under pressure occurred above 200°.

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