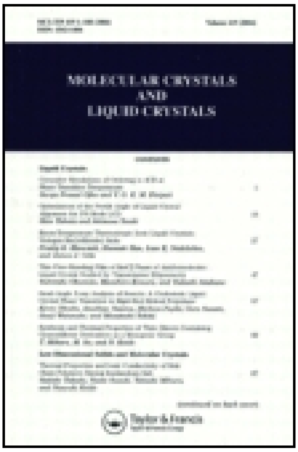

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Thermal Pressure Coefficients and Specific Volumes of Cyanobiphenyls and their Transition Entropies at Constant Volume

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Thermal Pressure Coefficients and Specific Volumes of Cyanobiphenyls and their Transition Entropies at Constant Volume

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Specific volumes and thermal pressure coefficients $(\partial p/\partial T)_V$ of 5CB, 7CB, 5OCB, and 8OCB were measured from temperatures near their crystalline melting points to above their nematic-isotropic transitions. At T_{NI}, volume changes ΔV of 0.52, 0.67, 0.25, and 0.48 cm^3 mol^{-1}, respectively, were found. A discontinuity of 0.02 cm^3 mol^{-1} in the volume of 8OCB was observed at its smectic A-nematic transition. The entropy change at constant volume ΔS_V was determined at T_{AN} and T_{NI} by subtracting the entropy of dilation $(\partial p/\partial T)_V \,\Delta V$ from the entropy change at constant pressure. The latter quantity was obtained from the slope of the phase boundary curve according to the Clapeyron equation. This was judged to be a more reliable procedure than using transition heats from DSC. Values of ΔS_V vary from $0.03R$ to $0.10R$ for the nematic-isotropic transition, where R is the gas constant.

INTRODUCTION

A measure of the ordering in the nematic phase is the difference between the transition entropy ΔS_p at constant pressure and the entropy of dilation at the transition.[1–4] For the small latent volumes ΔV encountered at the nematic-isotropic transition, this is

$$\Delta S_V = \Delta S_p - (\partial S/\partial V)_T \Delta V \tag{1}$$

We have determined the entropies of disordering ΔS_V of four nematogens by finding this difference for each. The systems studied are the 4′-pentyl, 4′-heptyl, 4′-pentyloxy, and 4′-octyloxy derivatives of 4-cyanobiphenyl, abbreviated hereafter as 5CB, 7CB, 5OCB, and 8OCB.

Most reported values of $\Delta S_p = \Delta H/T_{NI}$ for nematogens have been obtained from heats of transition ΔH measured using differential scanning calorimetry (DSC). A second source of values for ΔS_p is the product of ΔV and the slope of the boundary separating the nematic and isotropic regions on the p-T phase diagram as prescribed by the Clapeyron equation. Both methods are examined below.

The second term on the right-hand side of eq. 1, the entropy of dilation, can be evaluated from the latent volume and the thermal pressure coefficient $\gamma = (\partial p/\partial T)_V$, since $(\partial p/\partial T)_V = (\partial S/\partial V)_T$. In this article measurements of both ΔV and γ are reported for the four nematogens.

Additionally, we have measured the densities and thermal expansion coefficients of these compounds over extended ranges of temperature. The smectic A-nematic transition of 8OCB is included in this study.

EXPERIMENTAL

Chemicals. The cyanobiphenyls 5CB, 7CB, 5OCB, and 8OCB were gifts of Hoffmann-La Roche, Inc. and used without additional purification.

Dilatometry. Volumes were determined as a function of temperature as described previously.[5] Temperatures were measured with a Hewlett-Packard 2801A quartz-crystal thermometer.

For each nematogen a plot of ln V *vs.* temperature was divided into short (typically 6 or 8°C) overlapping segments. Each slightly curved line was fitted by the method of least squares to a polynomial, quadratic in temperature. The thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_p$ for a particular temperature was determined directly by differentiating the quadratic for the segment centered at that temperature.

The volumes of the dilatometers used for 5CB and 7CB were calibrated using the densities of the isotropic fluids at T_{NI} as found by Dunmur and Miller,[6] who reported an uncertainty of ± 0.0002 cm^3 g^{-1} in the specific volumes. The dilatometers used for 5OCB and 8OCB were calibrated with mercury; the uncertainty in their specific volumes is ±0.002 cm^3 g^{-1}. Since the method[5] permits high precision with typical reproducibilities of ±0.00002 cm^3 g^{-1}, thermal expansion coefficients and volume changes at phase transitions could be obtained with high accuracy.

Thermal Pressure Coefficients. The procedure employed for directly measuring $\gamma = (\partial p/\partial T)_V$ has already been described in detail.[5,7] Known quantities of mesogen (3–10g) and mercury were loaded into an evacuated glass cell so that the mercury blocked the liquid crystal sample from the outlet to the cell. Leading to the outlet is a vertical capillary along whose axis is fixed a fine wire from outside the cell. The wire is positioned in the capillary so that one end points down toward the mercury. When the contents of the cell expanded as a consequence of increasing temperature or decreasing pressure, the mercury rose, made contact with the wire, and closed an electrical circuit. This provided an electrical signal outside the visually inaccessible pressure bomb indicating that the mercury and mesogen just filled a known volume.

The pressure required to maintain the top of the column of mercury at the tip of the wire was measured as a function of the temperature of the sample. Over the accessible range of pressures (1–58 bar), the p *vs.* T isochore is linear. The slope $(\partial p/\partial T)_V$ was found with a least-squares fit of at least four points, but usually more, a majority of which fall within 0.4 bar of the least-squares line. Corrections (typically 10–20%) in the observed slopes for the compression and thermal expansion of the mercury and glass were made.[5]

Pressures were generated with a Ruska Instruments Model 2400 deadweight pressure gage. Temperatures were determined with the same quartz thermometer used in the dilatometry studies.

RESULTS

Dilatometry. The specific volumes v_{sp} and thermal expansion coefficients α obtained in these studies are plotted in Figures 1–4 and tabulated at 5° intervals in Table I. Each plot was prepared from a large number of observations as indicated in the first row of Table I. The qualitative dependence on temperature of the thermal expansion coefficients for these systems is typical for nematogens.[8] In the ordered phase, α increases rapidly in the pretransition region as the temperature approaches T_{NI}; then it decreases with increasing temperature over a *ca.* 5° range above T_{NI}.

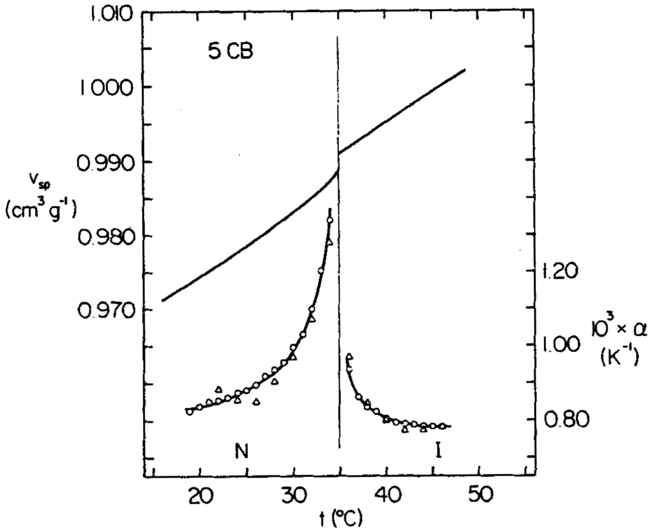

FIGURE 1. Specific volume (upper curves and left axis) and thermal expansion coefficient (lower curves and right axis) for 5CB in the nematic (N) and isotropic (I) phases. Circles represent results from this study; triangles represent the results of Labno and Jadzyn.[9]

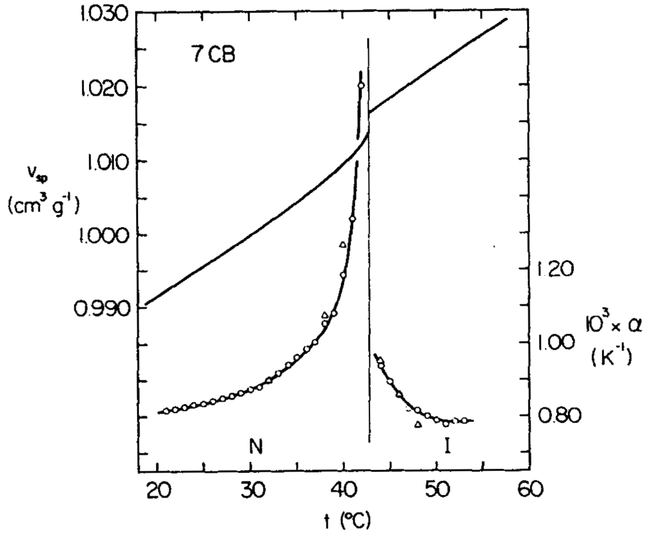

FIGURE 2. Specific volume (upper curves and left axis) and thermal expansion coefficient (lower curves and right axis) for 7CB in the nematic (N) and isotropic (I) phases. Circles represent the results of this study; triangles represent the results of Labno and Jadzyn.[9]

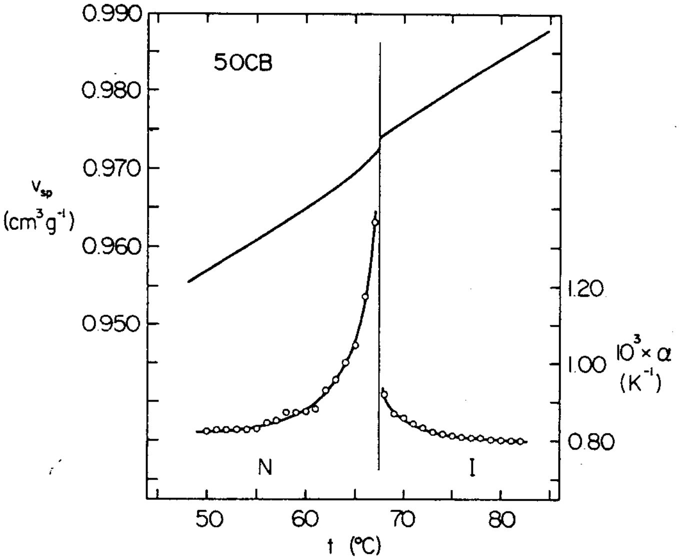

FIGURE 3. Specific volume (upper curves and left axis) and thermal expansion coefficient (lower curves and right axis) for 5OCB in the nematic (N) and isotropic (I) phases.

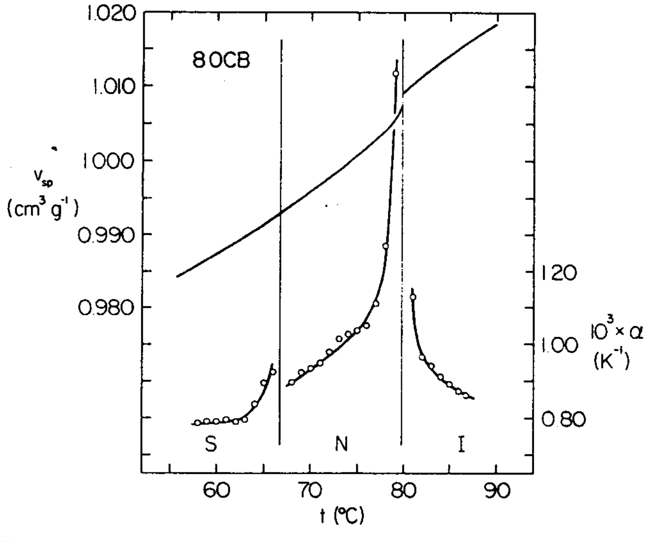

FIGURE 4. Specific volume (upper curves and left axis) and thermal expansion coefficient (lower curves and right axis) for 8OCB in the smectic (S), nematic (N), and isotropic (I) phases.

TABLE I

Specific volumes and thermal expansion coefficients

	v_{sp}(cm^{3}g^{-1})				$10^3 \times \alpha$(K^{-1})			
	5CB	7CB	5OCB	8OCB	5CB	7CB	5OCB	8OCB
(No. of observations)	(99)	(40)	(61)	(62)				
Temp (°C)								
20	0.9744	0.9915			0.84			
25	0.9787	0.9956			0.88	0.83		
30	0.9829	0.9998			0.99	0.88		
35	0.9909	1.0044			1.0–1.3	0.96		
40	0.9951	1.0095			0.81	1.18		
45	0.9991	1.0184			0.79	0.90		
50		1.0225	0.9572			0.79	0.82	
55			0.9611				0.83	
60			0.9653	0.9876			0.87	0.79
65			0.9698	0.9915			1.02–1.07	0.89
70			0.9760	0.9961			0.86	0.93
75			0.9801	1.0010			0.81	1.03–1.06
80			0.9840	1.0092			0.80	1.1–1.4
85				1.0141				0.89
90				1.0184				

Other investigators[3,6,9-16] have determined specific volumes for these materials. Our results for v_{sp} for 5CB exceed the values found by Labno and Jadzyn[9] by 0.0001 to 0.0005 cm^3 g^{-1} over the range 20–48°C, with these differences showing no trend with temperature. Thermal expansion coefficients, computed from Labno and Jadzyn's data, agree well with our determinations of α (see Figure 1). Karat and Madhusudana[10] report a density of 5CB at 25°C that agrees within their limits of accuracy ($\pm 0.1\%$). Values of v_{sp} found by Sen, *et al.*[11] exceed those found in this study by 0.0002 to 0.0026 cm^3g^{-1} between 24 and 43°C. Densities for 5CB given by Shirakawa, *et al.*[12] are very different from the others cited here and are judged to be in error.

The specific volumes of 7CB found by Labno and Jadzyn[9] are greater than ours by 0.0005 to 0.0010 cm^3g^{-1} over the range of temperature 29–50°C. As with the 5CB, thermal expansion coefficients determined from their data are in good agreement with ours (see Figure 2). Karat and Madhusudana[10] find v_{sp} for 7CB to be lower than our value at 25°C by 0.006 cm^3g^{-1} while Sen, *et al.*[11] report volumes that exceed ours by 0.014 to 0.016 cm^3g^{-1} from 29 to 55°C. Shirakawa, *et al.*[12] found values between 31 and 45°C that are less than ours by 0.010 to 0.011 cm^3g^{-1}. Ibrahim and Haase[13] measured specific volumes for 7CB over the range 29–53° that are 0.0034 to 0.0046 cm^3g^{-1} greater than those found for this study.

Sen, *et al.*[11] also reported measurements of the densities of 5OCB and 8OCB. In the former case they found v_{sp} that are greater than ours by 0.0001 to 0.0024 cm^3g^{-1} from 49 to 76°C. For 8OCB their values exceed those obtained in this study by 0.009 to 0.010 cm^3g^{-1} between 69 and 87°C. For both 5OCB and 8OCB as well as 5CB and 7CB, the disparity between the values of Sen, *et al.*[11] and ours increases with temperature.

Volume changes measured for the nematic-isotropic transitions and, in the case of 8OCB, the smectic-nematic transition are presented in Table II. The recorded uncertainties in Δv_{sp} at T_{NI} are principally a consequence of the rapid increase in the slope of v_{sp} *vs.* T as T_{NI} is approached from lower temperatures. Nevertheless, agreement with other studies[3,6,9,12-16] is good.

A discontinuity of 0.07 ± 0.03 mm^3g^{-1} in the volume of 8OCB was found at its smectic A-nematic transition. This provides additional evidence of first-order behavior in a phase change whose order has been questioned.[17,18] The results of these measurements obtained in several passes through T_{AN} are displayed in Fig. 5. Six determinations of v_{sp} for the smectic phase were made between 65°C and the tran-

TABLE II

Volume changes at T_{tr}

		This work		Other studies		
Compound	Transition	Temp (°C)	Δv (cm^{3}g^{-1})	Temp (°C)	Δv (cm^{3}g^{-1})	ref
5CB	N–I	34.9–35.0	0.0021 ± 0.0001	34.8	0.0025	3
				35.0	0.00202	6
				36.0	0.0018	9
				35.38	0.0020	12
				35.7, 36.7	0.0021 ± 0.0001	16
7CB	N–I	42.7–43.0	0.0024 ± 0.0002	42.7	0.0022	6
				42.1	0.0027	9
				42.46	0.0022	12
				42.2	0.002	13
				42.63	0.0021	14
5OCB	N–I	67.5–67.6	0.0009_5 ± 0.0001			
8OCB	S_A–N	66.6–66.7	0.00007 ± 0.00003		0.0000 ± 0.0002	15
	N–I	79.8–79.9	0.0015_5 ± 0.0001	90.0[a]	0.0018	15

[a] $p = 303$ bar

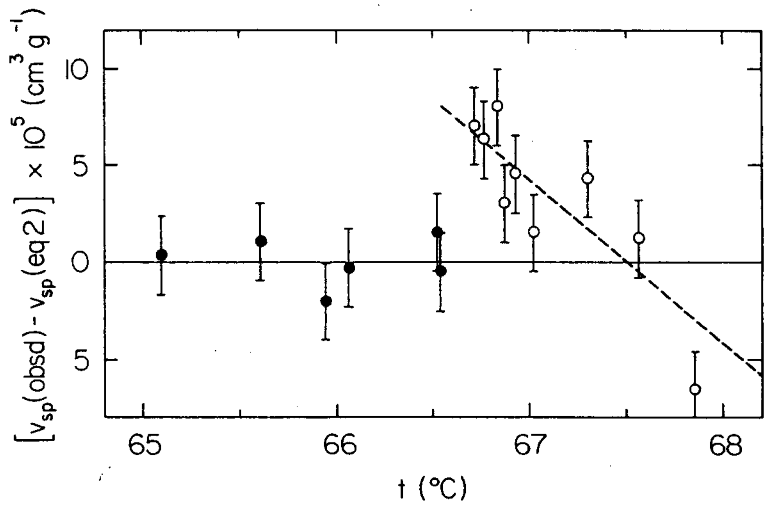

FIGURE 5. Observed specific volumes of 8OCB minus values given by eq. 2. (See text.) Filled circles: smectic A phase; open circles: nematic phase. The dashed line is a linear, least-squares representation of the nine points between the transition and 68°C.

sition at 66.6°C and fitted to a relationship linear in the Celsius temperature by the method of least squares. The result is

$$v_{sp}(\text{eq } 2) = 9.220 \times 10^{-4}t + 0.93465 \text{ cm}^3\text{g}^{-1} \qquad (2)$$

Differences between the observed volumes and values calculated with this equation were then plotted (Fig. 5) for all data, both smectic and nematic, collected over the range 65–68°C. The latent volume was determined accordingly. In a study of the same system, Johnson and Collings[15] were not able to measure Δv_{sp} directly but estimated a value of 0.16 ± 0.02 mm^{3}g^{-1}.

Thermal Pressure Coefficients. Table III presents the values of γ found in this study. Uncertainties are less than ±3%. Unlike non-mesogenic fluids for which γ generally decreases monotonically with temperature[5] these cyanobiphenyl systems exhibit positive temperature coefficients for γ below T_{NI} and large negative coefficients just above T_{NI}.

Horn and Faber[3] reported measurements of the refractive index of 5CB as a function of p and T from which they extracted a value for γ. Their finding, γ = 14 bar K^{-1} at 34.8°C and atmospheric pressure

TABLE III

Thermal pressure coefficients

	5CB		7CB		5OCB		8OCB	
phase	t(°C)	γ(bar K^{-1})	t(°C)	γ(bar K^{-1})	t(°C)	γ(bar K^{-1})	t(°C)	γ(bar K^{-1})
smectic							51.2	13.7
							55.2	13.4
							55.8	13.2
							57.7	13.6
							60.5	13.9
							61.9	13.6
nematic	25.3	15.3	27.9	15.5	53.9	14.5	69.1	14.1
	29.4	16.1	40.6	17.7	63.2	15.2	72.9	15.2
					65.2	15.1	76.5	15.4
					67.1	17.3	79.4	17.3
isotropic	37.0	14.6	44.0	14.6	68.0	13.9	89.2	11.6
			48.0	13.6	72.4	13.2	98.3	12.0
					76.8	13.0		

for the isotropic state, although slightly smaller, is in agreement with ours.

Phase Boundary Lines. One of the plots of *p vs.* T constructed for finding the thermal pressure coefficients of 5OCB has been reproduced as Fig. 6. The data are best represented by two straight lines intersecting near 68.9°C. The upper line has a slope of 23.2 bar K^{-1}; its intercept at zero pressure (67.4°C) corresponds to the nematic-isotropic transition (67.5–67.6°) observed at atmospheric pressure. Although the pressure bomb housing the sample prevented visual confirmation, we conclude that pressures along this line are the minimum pressures required to prevent the transformation from the nematic to isotropic phase and that this upper line represents the boundary between those phases while the lower corresponds to an isochore in the nematic phase. Tranfield and Collings[19] reported similar findings in their *p*-V-T measurements on azoxybenzenes.

8OCB gave a similar pair of intersecting lines with the phase boundary line intercepting the temperature axis at 79.7°C with a slope

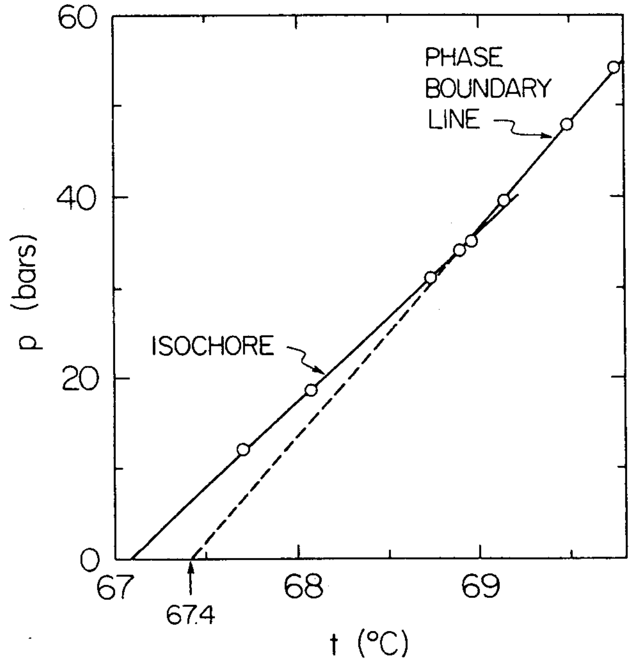

FIGURE 6. Pressure *vs.* temperature data for 5OCB showing the intersection of the line used to calculate $(\partial p/\partial T)_V$ (lower temperatures) and the phase boundary (higher temperatures).

dp/dt = 23.8 bar K^{-1}. One set of p *vs.* T measurements for 5CB yielded dp/dT = 24.2 bar K^{-1} with an intercept at 35.2°C. This was also designated a phase boundary line, even though no break appears in the line over the range of pressures studied.

These three values of dp/dT have been recorded in the fifth column of Table IV with other[3,15,20–26] determinations of slopes of coexistence curves. Although these other studies of phase behavior were at pressures up to at least 1 kbar, the slopes in Table IV are those of the tangents drawn near atmospheric pressure.

DISCUSSION

Transition Heats. Enthalpy changes ΔH for the nematic-isotropic and, in the case of 8OCB, the smectic A-nematic transitions of the four compounds studied here are collected in Table IV from a number of sources.[3,15,17,20–34] Some values[17b,25–34] are the direct results of differential scanning calorimetry (DSC) studies while others[3,15,20–26] were obtained with the aid of the Clapeyron equation from the slopes dp/dT of the phase boundary curves at atmospheric pressure and from the molar volume change ΔV_{tr} recorded in Table II:

$$\Delta H_{tr} = T_{tr}\Delta V_{tr} dp/dT$$

Here and below the subscript *tr* refers to the first-order nematic-isotropic (NI) or smectic A-nematic (AN) transition.

For 5CB and 8OCB measurements of dp/dT on the same compound by different workers show good agreement. The uncertainties given in Table IV for ΔH calculated from dp/dT are a consequence of uncertainties in ΔV_{tr}. On the other hand, values of ΔH from DSC vary considerably from one investigator to another.

The heat determined with the Clapeyron equation is the discontinuity ΔH_{tr} in the enthalpy for a first-order transition at a single temperature T_{tr}. Heats from calorimetric measurements are understood to include both this first order enthalpy ΔH_{tr} and at least part of the integral ΔH_{pretr} of that portion of the heat capacity near the transition which is in excess of a baseline heat capacity determined at temperatures far removed from the transition.

$$\Delta H_{tot} = \Delta H_{tr} + \Delta H_{pretr} \qquad (3)$$

$$\Delta H_{pretr} = \int [C_p(\text{total}) - C_p(\text{baseline})]dt \qquad (4)$$

TABLE IV

Values of ΔH at T_{AN} and T_{NI}

Compound	Transition	Temp. (°C)	ΔH (J mol⁻¹)	Method[a]	Reference
5CB	N–I	34.8	430 ± 20	$dp/dT = 27$	3
		35.0	400 ± 20	$dp/dT = 25$	22
		35.0	410 ± 20	$dp/dT = 25$	23
		34.8	430 ± 20	$dp/dT = 27$	24
		35.2	390 ± 20	$dp/dT = 24$	this work
		34.73	417 ± 6	DSC	27
		35.5	650 ± 25	DSC	28
		34.5	350 ± 30	DSC	29
		34.9–35.1	340[b]	DSC	30
		34.3	330	DSC	32
7CB	N–I	41.5	440 ± 40	$dp/dT = 21$	22
		42.0	620 ± 50	$dp/dT = 30$	23
		42.05	920 ± 14	DSC	27
		42	560 ± 30	DSC	29
		42.6	630	DSC	32
5OCB	N–I	67.4	200 ± 20	$dp/dT = 23$	this work
		66.61	300 ± 5	DSC	31
8OCB	S_A–I	67	50 ± 20	$dp/dT = 71$	20
		68	50 ± 20	$dp/dT = 66$	21
		66	50 ± 20	$dp/dT = 70$	25
		67.12	40 ± 20	$dp/dT = 60$	26
		67.12	100	A.C. calorimetry	17[a]
		67.1	60	DSC	17[b]
		67	130	DSC	25
		67.1–67.2	0.4[b]	DSC	30
		65.58	78 ± 1	DSC	31
		66.8	~30	DSC	33
		68.4	32	DSC	34
	N–I	79.9	500 ± 30	$dp/dT = 30$	15
		80.1	500 ± 30	$dp/dT = 30$	20
		78.4	430 ± 30	$dp/dT = 25$	21
		80	580 ± 40	$dp/dT = 34$	25
		79.7	400 ± 30	$dp/dT = 24$	this work
		80	670	DSC	25
		80.6–80.8	370[b]	DSC	30
		79.03	980 ± 15	DSC	31

[a] Heats obtained from the slopes of the phase boundaries are indicated by values of dp/dT (bar K⁻¹) at atmospheric pressure.
[b] Heat determined "exclusive of pretransition effect."[30]

The latter enthalpy is a consequence of pretransition phenomena occurring on both sides of the transition and is a positive quantity.[17a] With the exception of one study[30] in which ΔH_{pretr} was reportedly eliminated from ΔH_{tot}, the calorimetrically determined heats listed in Table IV should equal or exceed the heats obtained from dp/dT and the Clapeyron equation. That this is not always the case points out the difficulty encountered in the DSC experiment of selecting a baseline.

Below, the entropy change at constant volume for each mesogen is treated in two different ways. In the first, only the entropy that occurs at the transition temperature is calculated; in the second, pretransitional effects are added.

Transition Entropies at Constant Volume. The increase in the molar entropy associated with the first-order transition at constant pressure is calculated directly from dp/dT and the volume change reported in Table II. Calorimetrically obtained values are not used because of their scatter. The contribution arising from the expansion ΔV_{tr} at the transition is deducted from the constant-pressure entropy. Thus

$$\Delta S_{tr,V} = \Delta H_{tr}/T_{tr} - (\partial S/\partial V)_T \Delta V_{tr} \tag{5}$$

$$\Delta S_{tr,V} = [dp/dT - (\partial p/\partial T)_V]\Delta V_{tr} \tag{6}$$

The results are tabulated in the third column of Table V. Used in each calculation are the thermal pressure coefficient (Table III) measured just above the transition and the mean of the slopes dp/dT (Table IV) from different investigations, excepting dp/dT for 7CB. In the latter instance, separate calculations were made for the two discordant values. The largest contribution to the uncertainty in most values for $\Delta S_{tr,V}$ is the uncertainty in the difference between the two derivatives in eq. 6.

Values of $\Delta S_{tr,V}$ are small compared to the gas constant R. For the transition from the nematic to isotropic phase, they vary between $0.03R$ and $0.10R$. At the smectic A-nematic transition of 8OCB, $\Delta S_{tr,V}/R$ is only 0.01–0.02. These values may be compared with $\Delta S_p = 4R$ and $6.6R$ found for 5CB and 7CB respectively, at their crystalline melting points.[27,35]

Entropies at Constant Volume including Pretransitional Effects. The fluctuations that lead to pretransitional anomalies on both sides of T_{tr} are usually not included in models of the nematic state. The ΔS_V computed using these theories is more appropriately compared to the total entropy change $\Delta S_{tot,V}$ which includes both the transitional en-

TABLE V

Entropy and enthalpy changes

Compound	Transition	$\Delta S_{tr,V}$ (J K^{-1} mol^{-1})	ΔV_{tot} (cm^3 mol^{-1})	Pretransition temperature range (°C)	$\gamma\Delta V_{tot}$ (J K^{-1} mol^{-1})	$T_{NI}(\Delta S_{tr,V} + \gamma\Delta V_{tot})$ (J mol^{-1})
5CB	N–I	$0.5_6 \pm 0.1_2$	1.0_6	26–38	1.5 ± 0.1	650 ± 50
7CB	N–I	0.4_2[a], 1.0[b]	1.6_2	31–46	2.4 ± 0.2	880, 1100
5OCB	N–I	0.23 ± 0.07	0.7_8	61–73	1.1 ± 0.1	450 ± 40
8OCB	S_A–N	0.12 ± 0.05				
	N–I	0.8 ± 0.2	1.3_3	73–83	1.5 ± 0.2	800 ± 100

[a] dp/dT reported in ref. 22

[b] dp/dT reported in ref.23

tropy $\Delta S_{tr,V}$, the subject of the preceding section, and the pretransitional entropy. The result is a latent entropy that would be observed at constant volume if the pretransitional enthalpy change and corresponding pretransitional volume increment became part of the first-order discontinuities at T_{tr}:

$$\Delta S_{tot,V} = \frac{\Delta H_{tot}}{T_{tr}} - \gamma \Delta V_{tot} \qquad (7)$$

The total latent volume ΔV_{tot} is found by extrapolating to T_{tr} the volumes for the two phases measured at temperatures beyond the pretransition region. Two different procedures were employed; they yielded similar results. One was a linear extrapolation of densities, since outside the pretransition regions the density seems to be well represented by a linear function of temperature. The second used the equation-of-state theory of liquids of Flory [36,37] in which the V *vs.* T isobar is represented in reduced form. The reduction parameters (T^* and V^*, see ref. 36 and 37) have been evaluated for the nematic phase from the densities and thermal expansion coefficients at least 15°C below T_{NI} for 5CB, 7CB, and 5OCB and 10°C below for 8OCB; for the isotropic phase, they were determined from values at least 6°C above T_{NI}. The isobars so obtained were assumed to represent the behavior that these fluids would exhibit in the absence of pretransitional phenomena. Ignoring a small dependence on temperature[36,37] of the characteristic parameters seems to be justified by the results illustrated in Fig. 7 for 7CB. Here differences between specific volumes measured in the nematic phase and the corresponding values computed from the isobar are plotted in the lower, left portion of the figure. The analogous differences for the isotropic phase are shown in the upper, right portion. The two baselines are separated in the figure by 0.0058 cm^3g^{-1}, the difference between the volumes calculated from the isobars for the two phases at the transition (42.8°C). The differences found for the same compound by extrapolating its densities in each phase linearly with temperature yielded a plot that almost coincides with the one in Fig. 7 and a value of 0.0060 cm^3g^{-1} for the difference in v_{sp} for the two phases at T_{tr}.

For each of the four nematogens differences in specific volumes computed by the two procedures agree to within ± 0.0002 cm^3g^{-1}. In each case the smaller value is tabulated in the fourth column of Table V. The considerable effect that pretransition phenomena can have on the volume is evident in Fig. 7. For the four compounds studied we find $2 < \Delta V_{tot}/\Delta V_{tr} < 3$. The ranges of temperatures over

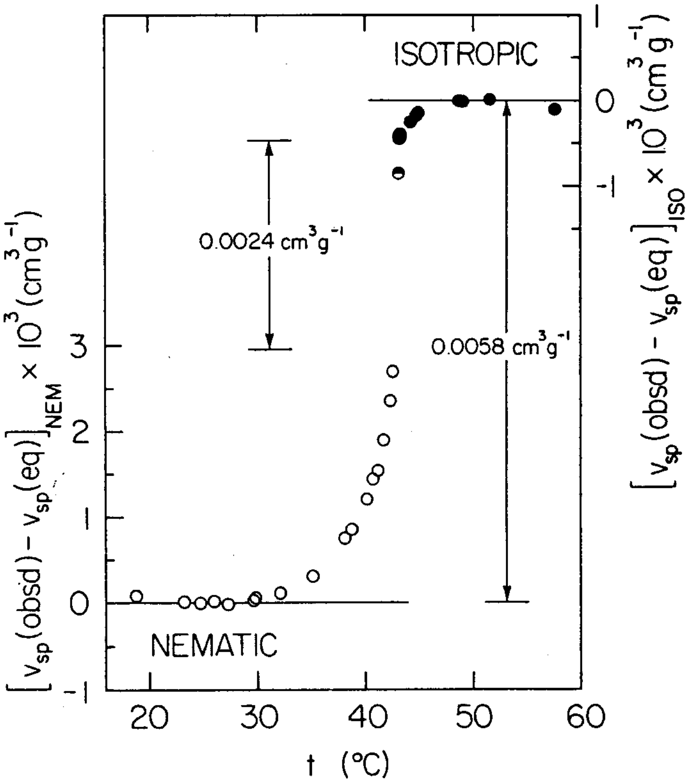

FIGURE 7. The effect of pretransitional phenomena on the volume of 7CB. Open circles represent differences (left-hand ordinate) between the observed specific volumes for the nematic phase and those calculated from Flory theory.[36,37] Filled circles are the corresponding differences for the isotropic phase (right-hand ordinate). The half-filled circle is a datum obtained when both phases were present. The vertical separations indicated with arrows show the volume change of 0.0024 cm^3 g^{-1} for the first-order phase transition and the sum (0.0058 cm^3 g^{-1}) of that value and the pretransitional volume change.

which anomalies in the volume are evident are listed in the fifth column of Table V.

The product of ΔV_{tot}, determined as just described, and the value of γ (Table III), measured for the isotropic phase close to T_{NI}, yields the entropy change for a dilation of ΔV_{tot}. The results are given in the sixth column of Table V.

According to this scheme, the total entropy that should be determined at constant pressure is the sum of the pretransitional entropy at constant volume, the first-order transition entropy at constant volume, and the total entropy of expansion which includes pretransitional dilations on both sides of T_{NI}:

$$\Delta S_{tot,p} = \Delta S_{pretr,V} + \Delta S_{tr,V} + \gamma \Delta V_{tot} \qquad (8)$$

Within the limits of the experimental uncertainties in the observed values, the total heat measured $\Delta H_{tot} = \Delta H_{tr} + \Delta H_{pretr}$ should be $T_{NI} \Delta S_{tot,p}$. Comparison of the contribution to $\Delta S_{tot,p}$ from only the second and third terms in eq. 8 (final column of Table V) with the reported values ΔH_{tot} from DSC measurements (fourth column of Table IV) reveals that in most instances ΔH_{tot} obtained by DSC is the smaller quantity, indicating that those DSC measurements have not included all the pretransitional heats.

To estimate total entropy changes at constant volume $\Delta S_{tot,V}$ from eq. 7 for the nematic-isotropic transition, we consider the four DSC measurements cited in Table IV that find $\Delta H \geqslant T_{NI}(\Delta S_{tr,V} + \gamma \Delta V_{tot})$. We believe that these are the only ones that may have most completely incorporated the pretransitional entropy changes $\Delta S_{pretr,V}$. Nevertheless, these values for $\Delta S_{tot,V}$ may still be low. The heat for 5CB measured by Oweimreen, Lin, and Martire[28] gives $\Delta S_{tot,V} = 0.5_6$ J K^{-1} mol^{-1} with $\Delta S_{pretr,V} \sim 0$. For 7CB the well documented DSC measurements by Barrall, Cox, *et al.*[27] yield $\Delta S_{tot,V} = 0.5_5$ J K^{-1} mol^{-1}, a credible value if the slope of the nematic-isotropic coexistence curve reported in ref. 22 is correct but questionable if *dp*/*dT* from ref. 23 is the more accurate. Cox, Barrall, *et al.*[31] also reported careful measurements on 5OCB and 8OCB which lead to 0.6_6 and 1.2_5 J K^{-1} mol^{-1}, respectively, for $\Delta S_{tot,V}$. These values for the four cyanobiphenyls exceed those which do not include the pretransitional contributions (column 3 of Table V) by amounts that vary between 0 (5CB) and 0.06*R* (8OCB).

SUMMARY AND CONCLUSIONS

The entropy of disordering $\Delta S_{tr,V}$ at the nematic-isotropic transition is small for the systems studied. Values range between 0.03*R* and 0.10*R*. These represent only 30–60% of the entropy changes $\Delta S_{tr,p}$ at T_{NI} and atmospheric pressure.

Anomalous increments in volume caused by pretransitional phenomena are as much as twice as great as the actual latent volumes ΔV_{tr} for the systems studied here. Owing to large uncertainties in calorimetrically determined heats of transition, it is not possible however, to estimate accurately the corresponding anomalous increments in entropy. The available evidence indicates that they may be considerably smaller than the latent entropies of disordering $\Delta S_{tr,V}$.

Reported heats of transition determined calorimetrically can vary substantially from one investigator to another; whereas, heats found from the slopes of coexistence curves are more consistent. Consequently we have used the latter as the more reliable source of the transition entropy at constant pressure.

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