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R. Kiefer [a] & G. Baur [a]

[a] Fraunhofer-Institut für Angewandte Festkörperphysik, Eckerstr. 4, D-7800, Freiburg, FRG

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The Dependence of Volumetric Properties on the Molecular Composition of Nematic Liquid Crystals

R. KIEFER and G. BAUR

Fraunhofer-Institut für Angewandte Festkörperphysik, Eckerstr. 4, D-7800 Freiburg, FRG

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Density studies on various terminally polar and non-polar nematic liquid crystals, measured as a function of temperature, are reported. The molar volumes were fitted to model equations by a non-linear numerical least squares fit. These equations contain non-linear terms of the form $c_I\ (T - T_c^I)^{\beta I}$ for $T > T_c^I$ and $-c_N\ (T_c^N - T)^{\beta N}$ for $T < T_c^N$. It is shown that the coefficients c_N and c_I are correlated with the extrapolated volume discontinuity $\Delta V_{c,99}$ at the nematic-isotropic phase transition temperature T_c. Furthermore, for all liquid crystals investigated there exists a correlation between $\Delta V_{c,99}$ and the order parameter S_{zz} ($t_r = 0.99$) as determined by infrared dichroism. Our density measurements suggest that c_N and c_I depend on the molecular structure of the liquid crystal and are not universal for the nematic-isotropic phase transition. Assuming universal exponents β_N and β_I we evaluate the average values $\beta_N = 0.388^{+0.096}_{-0.085}$ and $\beta_I = 0.135^{+0.065}_{-0.045}$.

INTRODUCTION

The liquid crystalline state is characterised by the long range orientational ordering of its constituent molecules. Different mesophases may exist and transitions between them are accompanied by changes in various tensor properties. Depending on the order of the transition they may also show changes in scalar quantities such as enthalpy content or density. The alterations in density and thermal expansivity which accompany the nematic to isotropic phase transition have been the subject of many investigations.[1–5] A discontinuous increase in the density at the isotropic–nematic phase transition appears which is related to an enhancement of molecular packing in the orientationally ordered mesophase. Further, a pretransitional anomaly of the thermal expansivity in both the nematic and the isotropic phase close to the transition temperature is experimentally well-established.[1] In a number of studies attempts have been made to determine the critical behaviour of this transition[3–7] for selected liquid crystals.

However, there exist no systematic studies on the influence of molecular composition on density. On the other hand, such investigations have been accomplished for physical properties such as elastic constants, dielectric constants, viscosities,[8,9]

and recently for order parameters S_{zz} and D.[10–12] In order to improve the physical understanding of molecular interaction, it is of general interest to search for relationships between molecular stucture and material parameters for as many physical properties as possible.

According to theory relating to elastic constants, there should exist a relationship between the ratio of elastic constants for bend and splay K_3/K_1 and the dimensions of the assumed short range lattice.[13] From this point of view, it would also be of interest to know the dependence of densities on molecular structure. Many data about material properties have been collected through the work of Schadt[8] and Scheuble.[9] In order to include classes of substance possessing just a monotropic phase or to broaden the nematic phase ranges, the cited authors have chosen mostly to study binary mixtures. To benefit from the cited papers we have also taken binary mixtures with the same mixture ratios as those in References 8–12. After presenting results of density measurements made as a function of temperature for various liquid crystal classes, we investigate the correlation between discontinuities in molar volume ΔV_c and long range orientational order parameter S_{zz} across the first order nematic–isotropic phase transition.

EXPERIMENTAL

Measurements were made with the familiar PARR digital precision density meter system (DMA 60 + 2 × DMA 602 HT) which counts the resonance frequency of a hollow glass tube filled with the liquid crystal material to be studied. A second measuring cell filled with nonane is used and operates as a reference cell. The temperatures of both measuring cells are controlled simultaneously by a water-filled circulation thermostat (Hake F3). The temperature in the cell is measured by a platinum resistance thermometer (Pt 100), placed as near as possible to the measuring cell, and a Fluke 2180A-RTD digital thermometer. The measured average temperature fluctuation amounts typically to 0.005° by using 10 average values. The measuring signal from the nonane-filled cell is used as a reference signal for the measurement of the cell filled with liquid crystal. Temperature fluctuations, due to the temperature regulation procedure occurring correlatively in both measuring cells, show a considerably reduced influence on the density values because nonane and the liquid crystal materials have very similar thermal expansion coefficients (except at the first order phase transition). By this method the relative precision of the evaluated density data is considerably increased and should be better than 5×10^{-6}. The absolute error in our density data amounts to 2×10^{-4} and is determined completely by the absolute precision of the densities of our calibration substances, air and nonane. The whole measuring system is fully computer controlled, enabling us to obtain automatically density-temperature curves. In Figure 1, the molar volume of PCH 7/5 as a function of reduced temperature is given as a typical experimental example.

Starting far away from the nematic-isotropic phase transition, in the isotropic region, the temperature interval between successive data points amounts to 1°. On approach to the isotropic-nematic phase transition temperature T_c, this interval is

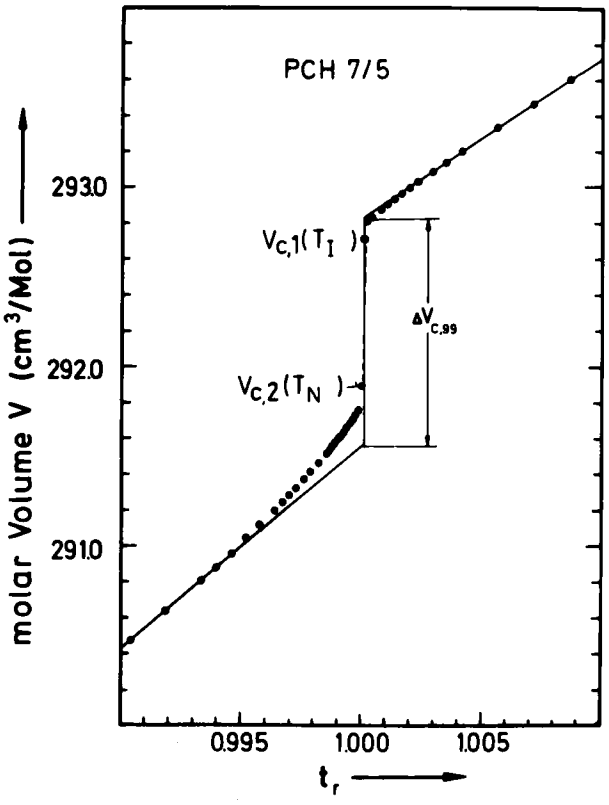

FIGURE 1 The molar volume of PCH 7/5 *versus* the reduced temperature $t_r = T/T_c$ is given as an experimental example. $\Delta V_{c,99}$ was determined by a straight line extrapolation procedure from the data points at $t_r = 0.99$ and $t_r = 1.01$ to $t_r = 1.00$. The nematic-isotropic transition temperature T_c was taken by microscopic texture observation. This value agrees very well with the maximum of the thermal expansion coefficient as determined by differentiation of the experimental volumetric data.

diminished discontinuously until a minimum value of about 0.04° is reached at T_c. After passing T_c, the temperature interval increases again in the nematic phase, until it saturates at the maximum value of 1°. In consideration of the abundance of data, we have preferred to present them in a compact, easily comparable form. We have fitted our molar volumes to the following model equations[3,5,7]:

$$V(T) = V_c - b_N (T_c^N - T) - c_N (T_c^N - T)^{\beta_N} \qquad T < T_c^N$$

$$V(T) = V_c + b_I (T - T_c^I) + c_I (T - T_c^I)^{\beta_I} \qquad T > T_c^I \qquad (1)$$

$$\text{with } T_c^I < T_c < T_c^N$$

Both equations contain together nine unknown parameters. The quantities b_N and b_I represent the linear expansion coefficients for $T < T_c^N$ and $T > T_c^I$. The terms $-c_N (T_c^N - T)^{\beta_N}$ and $c_I (T - T_c^I)^{\beta_I}$ describe the pretransitional behaviour near T_c with the "critical coefficients" c_N and c_I, the "critical exponents" β_N and β_I, and

the virtual transition temperatures T_c^N and T_c^I, whereas T_c is the equilibrium temperature at which both the nematic and the isotropic phase coexist.

For the first order phase transition, $T_c^N \# T_c^I$ holds. T_c^N and T_c^I are respectively model transition temperatures which determine the metastable region of the nematic phase ($T_c < T < T_c^N$) and the isotropic phase ($T_c^I < T < T_c$). The quantities b_N, c_N, β_N, T_c^N, b_I, c_I, β_I and T_c^I were obtained by a non-linear numerical least squares fit. Taking T_c as a start value of T_c^N being intermediate between T_N and T_I, according to Figure 1, and a corresponding V_c value by linear connection of the data points $V_{c,1}$ and $V_{c,2}$, the first fit was performed. After this, further fits were carried out by varying T_c^N in the phase transition region until the minimum least mean squares error was obtained. Then the whole procedure was repeated for the isotropic part of the molar volume curve, with the same V_c value. The method described works very well as a variation of T_c^I or T_c^N of about 0.08° (within the phase transition region) produces an uncertainty of only about 5% for b_N, c_N and c_I, 2% for b_I, 15% for β_N and 30% for β_I, but leads on the other hand to a very sensitive change in the mean squares error by an order of magnitude. The same procedure has been employed successfully by Press *et al.*.[3] for fitting thermal coefficient data. It should be noted that our fits are not valid for the whole temperature range stated in equation (1). Our description is correct for the nematic phase temperatures $T \leq T_N$ with $T_N \leq T_c^N$ and for the isotropic phase for $T \geq T_I$ with $T_I \geq T_c^I$, as there are no data points available in the phase transition region between T_I and T_N. In any case $T_N < T_I$ holds and $T_I - T_N$ typically amounts to 0.05°. The mean relative deviation, over the whole temperature range, between measured and calculated values of molar volumes typically amounts to 3×10^{-3} %. A more precise evaluation of the fit parameters would clearly require an improved temperature resolution and a better temperature stability of the measurement apparatus.

The actual volume jump ΔV_c at T_c is extremely difficult to determine, as it is influenced by the strong pretransitional behaviour and depends on the temperature resolution and fluctuation in the measuring cell. So values of ΔV_c may be very inexact and, more important, not free of an element of arbitrariness. In view of the intended comparison with the order parameter jump ΔS_{zz} at T_c presented later, we have preferred to evaluate $\Delta V_{c,99}$ as depicted in Figure 1 by a straight line extrapolation from the data points at $t_r = 0.99$ and $t_r = 1.01$ to $t_r = 1.00$. $\Delta V_{c,99}$ includes, besides ΔV_c, the volume change caused by the increase of the order parameter S_{zz} on going from the reduced temperature $t_r = 1.00$ to $t_r = 0.99$. So it is natural to compare $\Delta V_{c,99}$ with S_{zz} ($t_r = 0.99$) and not with ΔS_{zz} at T_c which is again very inaccurately determined. By doing this, we introduce a small error caused by the extrapolation in the isotropic part of the molar volume from $t_r = 1.01$ to 1.00, where a weak pretransitional behaviour is observed, but actually a change in the order parameter S_{zz} no longer appears. We think that this small error can well be accepted.

We have investigated two different liquid crystal classes as shown in Figure 2a and 2b:

a) Terminally polar liquid crystals

b) Terminally non-polar liquid crystals

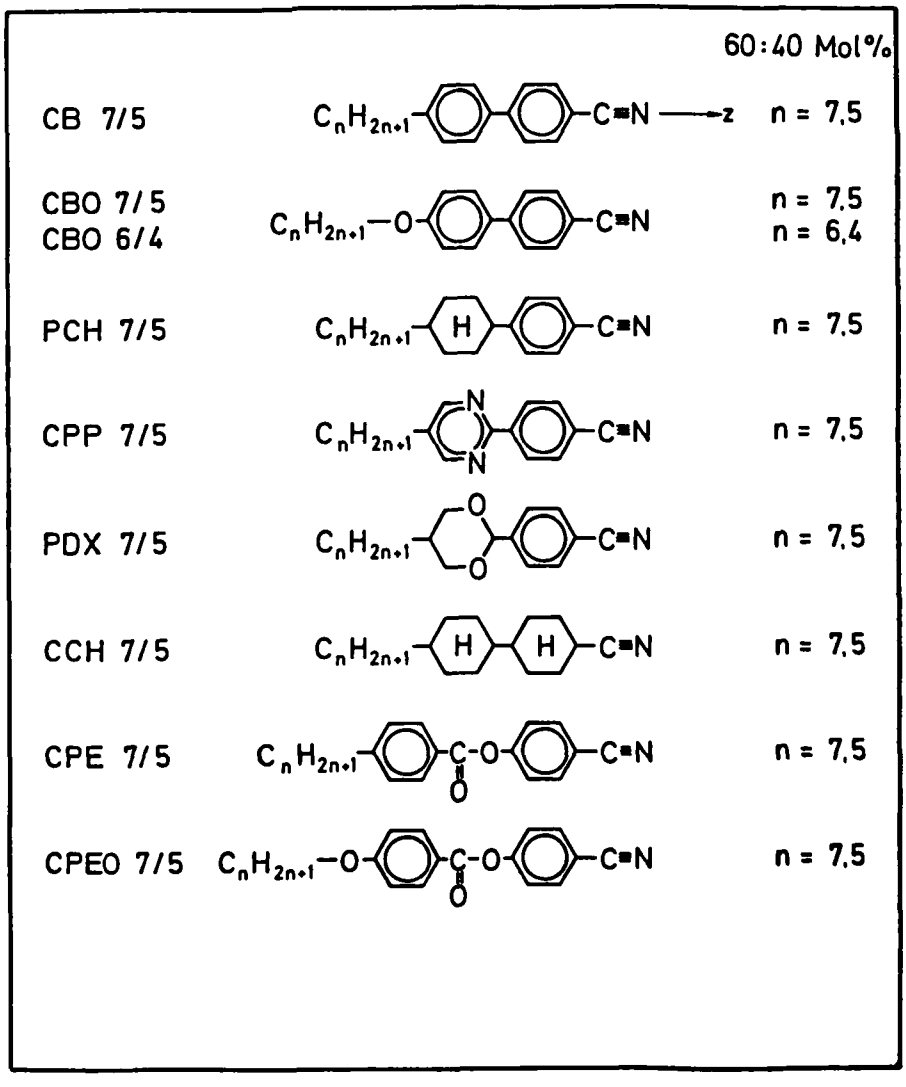

FIGURE 2a Schematic structures and molecular compositions of the terminally polar liquid crystal materials.

Table I contains the results of our fit calculations. In addition, the molar volumes at the reduced temperature $t_r = 0.95$, the volume discontinuity $\Delta V_{c,99}$ and the phase transition region ΔT_c, as determined by microscopic texture observation, are presented. T_s and T_F are the temperatures at which the density measurements were started and finished. The phase transition temperatures T_c^N and T_c^I, evaluated from minimizing the means squares error in the fit calculation, are interpreted as virtual phase transition temperatures according to the Landau theory.[14]

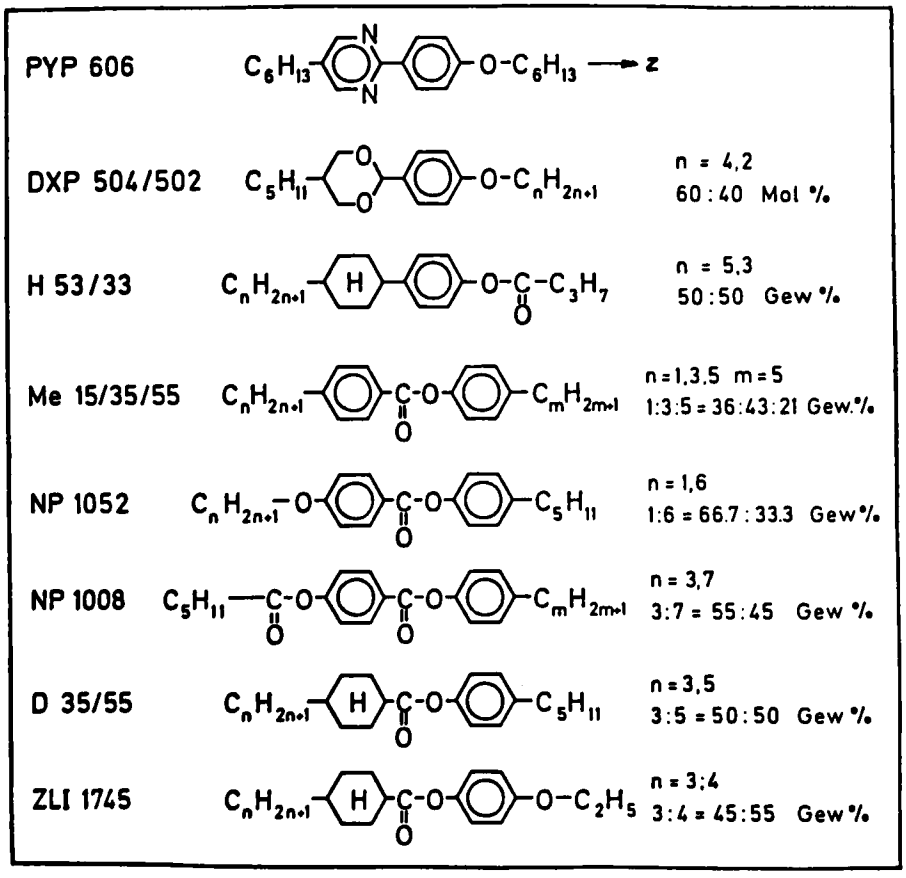

FIGURE 2b Schematic structures and molecular compositions of the terminally non-polar liquid crystal materials.

RESULTS AND DISCUSSION

Looking at Table I, and considering errors due to measuring uncertainty and fit calculation, we can conclude that b_N, c_N, b_I and c_I depend on the molecular composition of the nematics. As for the "critical exponents" β_N and β_I, the situation is more difficult to judge, as the corresponding errors may be distinctly larger and the impurity of the materials might play a more decisive role. The β_N-values are quite closely clustered with the exception of the two extreme values (0.246 and 0.549). Believing in the universal nature of β_N, we average over the remaining 15 β_N's and obtain an average β_N given by:

$$\beta_N = 0.388^{+0.096}_{-0.085}$$

All β_N's used are contained within the given limits. This value agrees very well with $\beta_N = 0.44 \pm \frac{0.11}{0.09}$ which was observed by Press and Arott with MBBA[3]. Lor-

TABLE I

Volumetric parameters as evaluated from a least squares fit to the model equations (1) for all liquid crystal materials given in Figure 2*a* and 2*b*. The fit parameters apply for temperatures $T \leq T_N$ in the nematic phase and $T \geq T_I$ in the isotropic phase, with $T_N \leq T_c^N$ and $T_I \geq T_c^I$. T_N, T_c^N, T_I and T_c^I are also given in the Table. T_c^N and T_c^I are interpreted as virtual transition temperatures. In addition, the molar volumine V_N at $t_r = 0.95$, as well as the volume discontinuity $\Delta V_{c,99}$ are presented. The phase transition region, ΔT_c, where nematic and isotropic phases coexist was determined by microscopic texture observation. T_s and T_F denote the temperatures at which the density measurements were started and finished.

Substanz	T_c^N [°C]	T_N	V_c	b_N	c_N	β_N	T_c^I	T_I	b_I	c_I	β_I	$\Delta V_{c,99}$ [cm³/Mol]	$T_S \leftrightarrow T_F$ [°C]	$V_N(t_r = 0.95)$ cm³/Mol	ΔT_c
CB 7/5	38.90	38.84	267.387	0.194	0.564	0.344	38.84	38.88	0.206	0.385	0.151	0.753	80 - 15	262.893	0.04
CBO 6/4	74.85	74.79	262.149	0.179	0.366	0.484	74.82	74.83	0.212	0.251	0.134	0.536	85 - 52	257.571	0.06
CBO 7/5	71.17	71.13	278.817	0.167	0.380	0.549	71.12	71.16	0.224	0.201	0.198	0.470	86 - 32	274.115	< 0.04
CPP 7/5	50.90	50.79	259.159	0.187	0.348	0.415	50.83	50.90	0.199	0.202	0.170	0.487	80 - 33	255.036	< 0.08
PDX 7/5	47.87	47.85	271.711	0.199	0.378	0.402	47.86	47.89	0.215	0.164	0.238	0.452	70 - 32	267.382	0.12
PCH 7/5	55.69	55.64	292.280	0.204	0.821	0.325	55.63	55.69	0.232	0.593	0.104	1.250	80 - 20	286.832	0.04
CCH 7/5	83.38	83.30	315.377	0.211	0.869	0.410	83.36	83.40	0.254	0.508	0.178	1.252	90 - 50	308.783	0.20
CPE 7/5	55.80	55.72	296.007	0.222	0.619	0.305	55.73	55.81	0.227	0.439	0.131	0.678	80 - 33	290.886	< 0.09
CPEO 7/5	78.05	77.98	306.291	0.213	0.392	0.450	78.016	78.03	0.242	0.255	0.134	0.574	90 - 55	301.120	< 0.04
PYP 606	60.53	60.47	349.545	0.252	0.728	0.376	60.516	60.52	0.292	0.481	0.102	1.035	78 - 34	343.201	0.05
DXP 504/502	51.59	51.52	296.797	0.219	0.517	0.399	51.52	51.59	0.247	0.349	0.115	0.765	80 - 26	291.643	< 0.07
H 53/33	38.33	38.28	311.261	0.235	0.426	0.344	38.31	38.32	0.248	0.274	0.116	0.609	65 - 20	306.503	0.06
Me 15/35/55	18.98	18.93	298.358	0.235	0.492	0.246	18.953	18.96	0.229	0.370	0.091	0.788	50 - 5	294.009	0.08
NP 1052	48.03	47.99	305.768	0.212	0.492	0.359	48.002	48.02	0.238	0.293	0.108	0.685	70 - 20	300.999	0.08
NP 1008	56.100	56.04	364.561	0.256	0.548	0.399	56.075	56.08	0.287	0.424	0.151	0.852	70 - 25	358.519	0.09
D 35/55	41.66	41.60	346.893	0.244	0.518	0.409	41.635	41.64	0.278	0.332	0.123	0.713	70 - 15	341.433	0.04
ZLI 1745	76.33	76.27	283.700	0.203	0.475	0.398	76.292	76.30	0.231	0.299	0.148	0.678	86 - 46	278.642	0.05

entz found, for homologues of the azoxybenzenes, a much stronger variation in the β_N-values between 0.189 and 0.48.[5] According to Landau theory one would expect $\beta_N = \beta_I = 0.50$.[14]

As far as the exponent β_I is concerned, the broader spread of the values is quite normal in consideration of the stronger influence of the measuring uncertainty. Neglecting the extreme value $\beta_I = 0.238$ (for PDX 7/5) and averaging again over the remaining 16 β_I's, we arrive at the average exponent

$$\beta_I = 0.135^{+0.065}_{-0.045}$$

This agrees quite well with $0.1 < \beta_I \leq 0.21$ found by Lorentz for homologues of the azoxybenzene.[5] Press and Arott determined for MBBA $\epsilon_I = 1 - \beta_I = 0.21$ which is equivalent to $\beta_I = 0.79$, deviating strongly from our result. But Press *et al.* probably used a sample of reduced purity, as they reported a broad two phase region ΔT_c of about 0.3° C. On the other hand, with the exception of PDX 7/5 and CCH 7/5, the width ΔT_c of the nematic-isotropic phase transition for all the nematics we have investigated did not exceed 0.1°C (see Table I). This indicates the high purity of our samples. We think that differences in the purity of the materials may strongly influence the results for β_N and β_I. Although we have checked a larger number of materials, and the spread of the β_N- and β_I-values is not too great, one must be careful about affirming the universal nature of β_N and

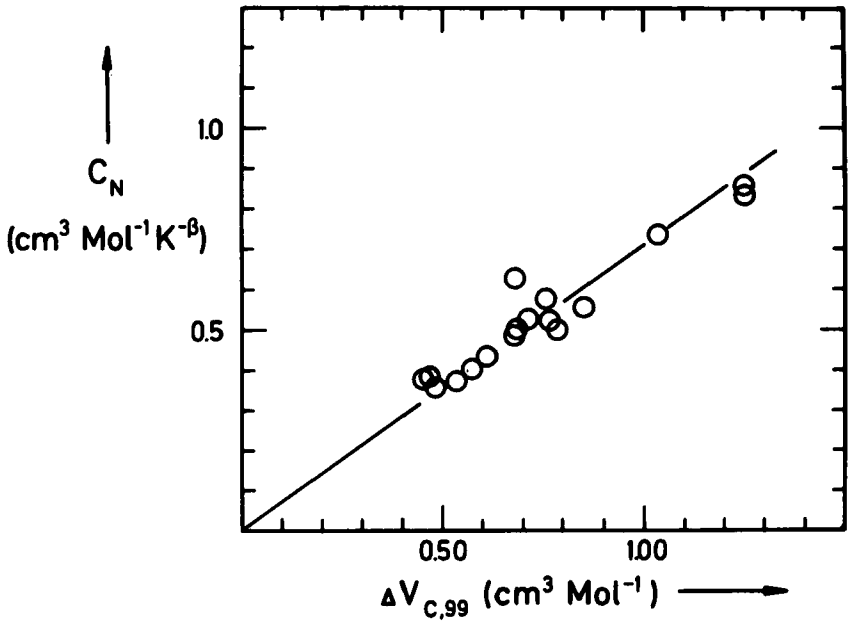

FIGURE 3 Coefficient c_N as a function of $\Delta V_{c,99}$ for the liquid crystal materials given in Figure 2*a* and 2*b*.

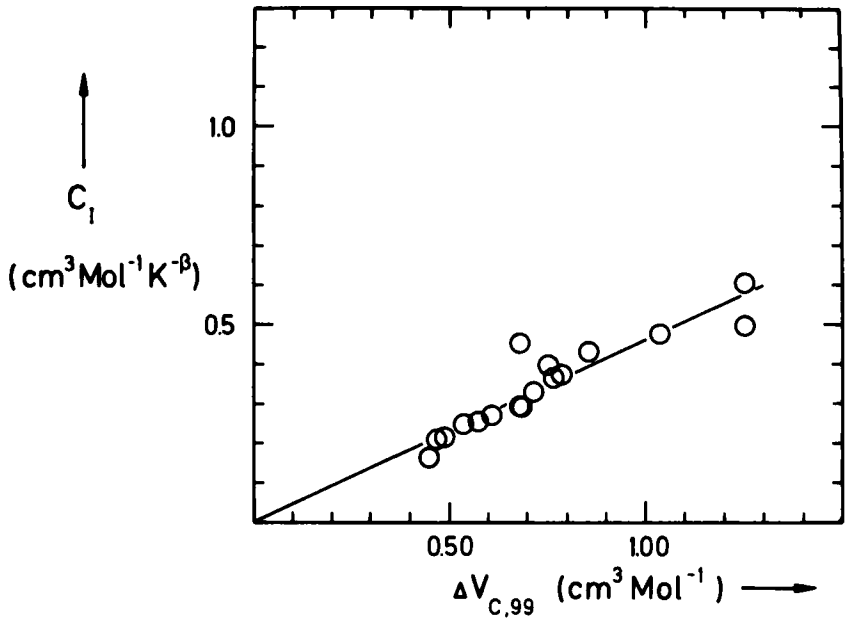

FIGURE 4 Coefficient c_I as a function of $\Delta V_{c,99}$ for the liquid crystal materials given in Figure 2*a* and 2*b*.

β_I. Measurements are clearly required using an apparatus with an improved temperature resolution and temperature stability.

As can be seen in Figure 3 and Figure 4, there exists a distinct correlation between c_N and $\Delta V_{c,99}$ as well as c_I and $\Delta V_{c,99}$. Therefore c_N or c_I can be utilized as a measure of the volume discontinuity. A correlation between c_N and ΔV_c has also been observed by Lorentz[5] for homologues of the azoxybenzenes. We have not found any correlation between b_N, β_N, b_I, β_I and $\Delta V_{c,99}$.

The first order isotropic-nematic phase transition is characterized by a discontinuity in the density and the order parameter S_{zz}. One can therefore suppose a relationship between these two quantities. As it is extremely difficult to evaluate the exact order parameter jump at T_c, we have preferred to determine the change in S_{zz} from $t_r = 1.00$ to $t_r = 0.99$ by analysing[10–12] the infrared dichroism of the cyano-vibration and the benzene ring skeletal vibrations at 1500 cm^{-1} and 1600 cm^{-1}. As Figure 5 shows, there exists a correlation between the molar volume jump $\Delta V_{c,99}$ and the order parameter S_{zz} ($t_r = 0.99$) for the various liquid crystals, with the exception of the result for CCH 7/5. The reason for the different behaviour of CCH 7/5 might be the non-planar geometry of the two cyclohexane rings. The direction of the C≡N-axis probably deviates from the long molecular principal axis, and the infrared measurement yields a smaller order parameter S_{zz}. Because of the correlation given in Figure 5, liquid crystals with a terminal alkyl chain show a larger volume jump $\Delta V_{c,99}$ than nematics with a corresponding alkoxy chain (for example compare CB 7/5 with CBO 6/4 or CBO 7/5, CPE 7/5 with CPEO 7/5 and

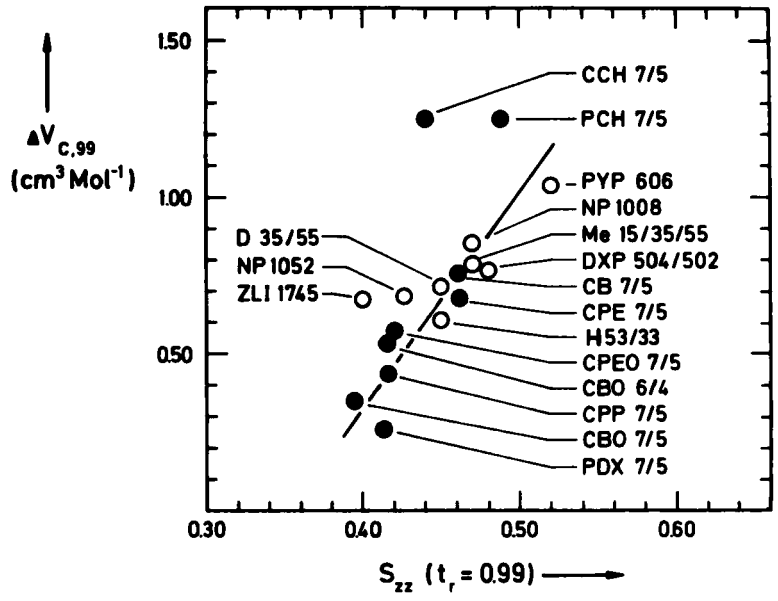

FIGURE 5 Molar volume jump $\Delta V_{c,99}$ as a function of the order parameter S_{zz} (t_r = 0.99). The S_{zz} values are derived from infrared dichroism measurements.[10-12]

Me 15/35/55 with NP 1052). Moreover the volume jump for the terminally polar mixtures CPP 7/5 and PDX 7/5 is considerably smaller than that for the terminally non-polar nematics PYP 606 and DXP 504/502.

There exists no correlation between the absolute values of the density (molar volume) and the order parameter S_{zz} for the various liquid crystals. One could argue that for a more correct comparison, one should use the molecular packing densities. But this would require an estimation of the molecular volumes in the nematic phase which can differ considerably from well known values relating to the crystalline phase.

Terminally cyano-substituted liquid crystals show smaller molar volumes, V_N (t_r = 0.95), V_{iso} and linear expansion coefficients b_N and b_I than nematics which possess a terminally non-polar alkyl-, alkoxy- or alkanoyloxy-chain (see for comparison Table II). One could argue that terminally polar molecules form dimers[15] and therefore achieve a higher packing density. On the other hand, the investigated non-polar nematics PYP 606, DXP 504/502, H53/33 and Me 15/35/55 possess—instead of the stiff and short cyano-group—the longer, more extended and more flexible alkyl chain which requires accordingly a larger volume. Therefore it is in our opinion not possible to correlate the lower values of b_N, b_I, V_N and V_{iso} with the dipole association of the terminally polar molecules.

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TABLE II

Comparison of volumetric properties for terminally polar compounds (CPP 7/5, PDX 7/5, PCH 7/5, CPE 7/5) and corresponding terminally non-polar nematics (PYP 606, DXP 504/502, H 53/33, Me 15/35/55).

	CPP 7/5 ⟷ PYP 606		PDX 7/5 ⟷ DXP 504/502	
b_N	0.187	0.252	0.199	0.219
V_N (t_r = 0.95)	255.04	343.20	267.38	291.64
V_{iso} (80°, 65°)	265.31 (80°)	355.85	275.73 (65°)	300.60
(ρ_{iso})	(1.010757)	(0.95620)	(1.00097)	(0.98145)
	PCH 7/5 ⟷ H 53/33		CPE 7/5 ⟷ Me 15/35/55	
b_N	0.204	0.235	0.222	0.235
V_N (t_r = 0.95)	286.83	306.50	290.89	294.01
V_{iso} (65°)	295.22 (65°)	318.28	298.711 (65°)	309.453*
(ρ_{iso})	(0.92215)	(0.94756)	(1.03771)	(0.98424)*

* extrapolated value

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