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Effect of Pressure on the Mesomorphic Transitions in Para-Azoxyanisole (PAA)†‡

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Abstract—We report the study of the effect of hydrostatic pressure on the phase transitions in PAA up to 3 kbar. The different phases (solid, nematic and isotropic) are characterized by their NMR spectra.

The observed temperature dependences of the two transitions are:

Solid to Nematic: $T(P) = 116\,^\circ\mathrm{C} + 24.5 \pm 1.0\,^\circ\mathrm{C/kbar}$

Nematic to Isotropic: $T(P) = 133\,^\circ\mathrm{C} + 27.0 \pm 1.0\,^\circ\mathrm{C/kbar}$

The ratio of the corresponding slopes is in qualitative agreement with the existing data on latent heats and volume changes at both transitions.

On the other hand, the study of NMR spectra in the nematic phase allows the determination of the order parameter S. Our observed value of S in the nematic phase at the nematic to isotropic transition is independent of pressure within experimental error

$S(T_c) = 0.40 \pm 0.015$ from 1 bar to 3 kbar.
$N \rightarrow I$

The same is true for the solid to nematic transition

$S(T_M) = 0.55 \pm 0.015$ from 1 bar to 3 kbar.
$S \rightarrow N$

1. Introduction

The order–disorder transitions in nematic systems are commonly studied as a function of temperature. However, temperature is not the only interesting parameter in this problem. Indeed, the anisotropic intermolecular potentials, which are frequently considered as essential for nematic order in thermotropic liquid crystals, depend strongly on density. Moreover, the excluded volume effects, which

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are dominant in other nematics (larger rod-like molecules) are essentially density dependent. This suggests that a study of order (or disorder) as a function of density, in a typical nematic, might cast some light on the nature of the various effects contributing to the nematic order. We present an NMR determination of the shift with pressure of the solid–nematic and nematic–isotropic phase transition temperatures(1) ($\mathrm{d}T_M/\mathrm{d}P$, $\mathrm{d}T_c/\mathrm{d}P$)(2), and also measurements of the corresponding values of the order parameter along these transition lines ($S(T_M) = S_M$, $S(T_c) = S_c$) in PAA; the pressure range is 0–3 kbar and the temperature range 120–220 °C.

2. Experimental Techniques

We used a hydrostatic high pressure equipment, allowing to work up to 7 kbar, with purified helium gas as a pressure medium. The main advantage of using helium is that it does not interact at all with the sample; on the other hand, it requires a rather careful job to avoid leaks. The high pressure vessel is made of nonmagnetic Cu–Be and Cu–Ni alloys; the useful volume of the cavity is 6.5 cm^3 ($h = 45$ mm, $\phi = 13.5$ mm). The pressure is measured through a manganine gauge located in a part of the apparatus which is at room temperature. More details about this equipment are given in Ref. 3.

The heating filament is located inside the cavity, thermally insulated from the walls by a single thickness of pyrophyllite (1.5 mm); its winding is noninductive. The NMR coil and the sample are then placed inside the heating tube; the sample temperature is measured by a copper–constantan thermocouple whose emf is practically independent of pressure.(4) Some care must be exercised about the compensation of temperature gradients, because helium, at 3 kbar, is an extremely good heat conductor. For that reason, the sample volume was reduced down to 0.15 cm^3. Various complicated convection regimes can also develop in the helium gas, especially at high temperatures(5); they can give rise to long term temperature instabilities. One way to cut them down is to reduce as much as possible the volume allowed to the fluid.

Finally, NMR CW measurements were made with a conventional Pound–Watkins marginal oscillator on the proton resonance at 18 MHz.

Our para-azoxyanisol sample was purchased from Eastman Kodak company; we did not make any purification before or during its handling, however the transition temperatures were checked after each measurement: in particular, their values were not changed after experiments up to 3 kbar; this indicates that there is no substantial degradation in the corresponding temperature range.

3. Phase Diagram

The effect of pressure on the transition temperatures is shown in Fig. 1; clearly, this is a very large effect: common slopes for the

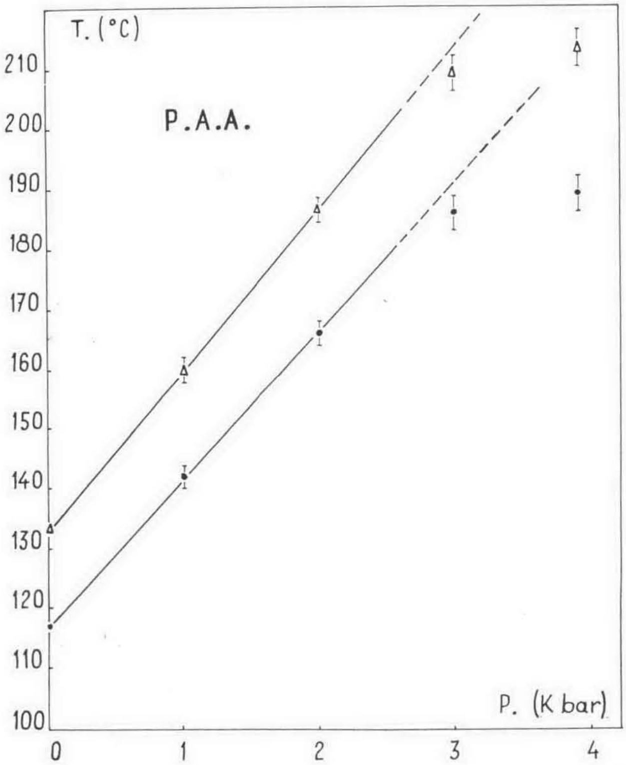

Figure 1. Variation with pressure of the temperatures of the solid–nematic (dots) and nematic–isotropic (triangles) transitions in T, P. The slopes are roughly coherent with other existing thermodynamic data, if one applies the Clausius–Clapeyron equation (see Table 2). The non linearity above 3 kb is due to thermal degradation of the sample: the points at 4 kb are not significant

TABLE 1

	Slope of solid–nematic transition line: $\frac{\mathrm{d}T_M}{\mathrm{d}P}$	Slope of nematic–isotropic transition line: $\frac{\mathrm{d}T_c}{\mathrm{d}P}$
G. A. Hulett(7)	32°/kbar up to 300 bars	48.6°/kbar up to 300 bars
G. Puschin and W. Grebenschtschikov(8)	25.6°/kbar up to 2 kbar	39.4°/kbar up to 1 kbar
J. Robberecht(9)	32°/kbar up to 850 bars	48°/kbar up to 935 bars
This work	a) 24.5°/kbar up to 3 kbar b) 23.7°/kbar up to 3 kbar(10)	27°/kbar up to 3 kbar 28.7°/kbar up to 3 kbar(10)

TABLE 2

	Relative jump in specific volume at melting point $\left(\frac{\Delta V}{V}\right)_M$	Relative jump in specific volume at clearing point $\left(\frac{\Delta V}{V}\right)_c$
W. Maier and A. Saupe(18)		0.30% 0.35% " extrapoled " value
E. McLaughlin, A. Shakespeare and R. Ubbelohde(11)	11.03%	0.36%
	Latent heat at melting point: $(\Delta H)_M$	Latent heat at clearing point: $(\Delta H)_c$
R. Schenck(12)		735 joules/mole
C. Kreutzer and W. Kast(13)		1730 joules/mole
H. Arnold(14)		600 joules/mole
I. G. Chistyakov(15)	29.570 joules/mole	574 joules/mole
E. M. Barral, R. S. Porter and J. F. Johnson(16)	30.200 joules/mole	735 joules/mole
L. C. Chow and D. E. Martire(29)		760 joules/mole
This work, from Clausius–Clapeyron equation	a) 35.000 joules/mole b) 36.000 joules/mole(10)	1.080 joules/mole 1.000 joules/mole(10)

melting points of usual compounds are on the order of a few °C/kbar only. The slopes of these transition lines differ slightly(6) from those found by other authors,(7–9) especially for the nematic–isotropic transition; all these slopes are summarized in Table 1. The temperature range, and consequently also the pressure range, are severely limited by thermal degradation of the sample; in fact, above 3 kbar, we observed a strong decrease of the transition temperature values: the azoxy groups probably react with the unevacuated air, and some molecules break; the nematic state then disappears. For that reason, the experimental points above 3 kbar do not represent states of thermodynamic equilibrium, and do not have any physical meaning.

The latent heats at both transitions, and the corresponding changes in specific volume are respectively in the same ratio, which is about 30: this explains why the two slopes are so similar. The weakness of the volume change and of the increase in entropy at the nematic–isotropic transition suggests that a substantial short range order is preserved in the isotropic phase: this is commonly mentioned as characterizing the weak first order character of this transition. There is some dispersion in the latent heat data found in the literature(12–16,29); we assume that volumetric data(11,18) are more reliable, and apply the Clausius–Clapeyron equation:

$$\Delta H = T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)\Delta V$$

to estimate the latent heats from our $\mathrm{d}P/\mathrm{d}T$ data. The resulting values of ΔH are listed in Table 2; they are in almost reasonable agreement with the most recent measurements of ΔH.

4. Order Parameter

The NMR CW spectrum of PAA in the nematic phase is characterized by a doublet which is produced by unaveraged dipolar interactions of the benzene ring protons. The separation between the peaks of that doublet is proportional to the order parameter

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle,^{(17)}$$

θ being the angle between the long axis of the molecule and the optical axis of the nematic. This allows a direct determination of the order parameter in the nematic phase at various temperatures and pressures.

For most thermotropic nematics, the order parameter S_c, at the nematic–isotropic transition, is about 0.42, although their transition temperatures show substantial variations.(18) On the other hand, S_c appears to be smaller than 0.4 in the *p*-methoxybenzylidene-*p*,*n*-butylaniline (MBBA),(19) anisaldazine(20) and in some Schiff bases,(21) but significantly higher in the 4,4′-azoxydiphenetole (PAP), the 4-(*n*-hexyloxy) benzoic acid (PHBA),(22) and a few more exotic nematic mixtures.(23) Of course, in some of these systems, the molecules may well be more or less flexible than the usual azoxy-molecules, and the respective importance of attractive potentials and excluded volume effects is probably not at all the same as in PAA.

It is tempting to speculate that attractive anisotropic potentials and hard core effects will perhaps not have the same dependence on intermolecular distances: going to higher pressures would enhance one of these effects with respect to the other, and might result in a change in the value of S close to the transition. We have been looking for such an effect, changing the absolute temperature of the transition by 17% and the specific volume by 15% (the isothermal compressibility is $\beta = 5 \times 10^{-11}$ cm²/dyne(24)). In fact, we find that the order parameter S_c at the nematic–isotropic transition is *constant* within experimental errors from 0 to 3 kbar (Fig. 2):

$$S_c = 0.40 \pm 0.015.$$

The same is true for the solid–nematic transition:

$$S_M = 0.55 \pm 0.015.$$

Maier–Saupe's theory of the nematic to isotropic phase transition(18) does indeed predict that the value of S should not change along the transition line. In this respect our result agrees with Maier–Saupe's theory, but it is not yet clear that it is a proof of it. We shall now try to find what is the minimum set of assumptions which can lead to our result.

The equilibrium value of S, at given P and T, is the one which minimizes the free enthalpy (or Gibbs energy) of the nematic phase. We write it for one molecule (chemical potential), try to show up the

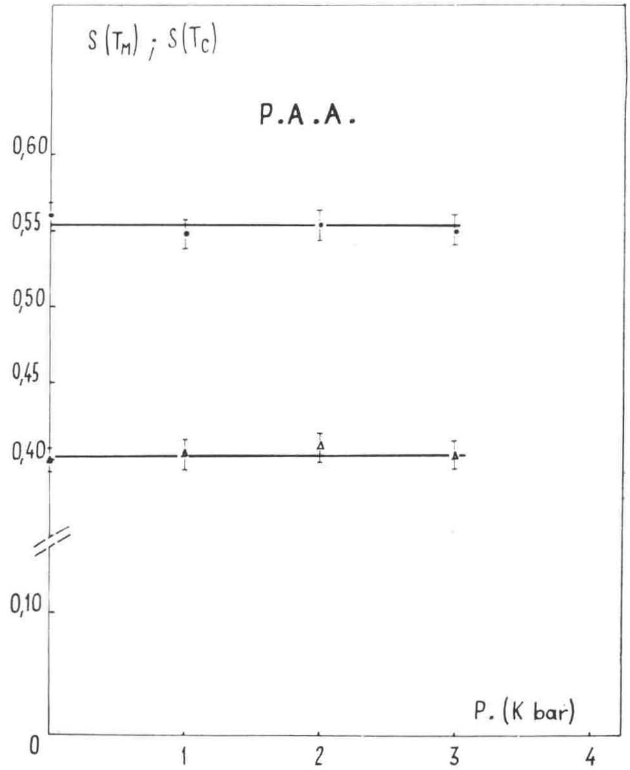

Figure 2. Nematic phase order parameter *versus* pressure, at the solid nematic (dots) and nematic–isotropic (triangles) transitions. The volume change associated with our maximal pressure (3 kbar) is about 15%, and the corresponding variation of the absolute temperature of the transition is 17%.

dependence on S of the various terms, and then make a list of the different assumptions implicated by this expression:

$$\mu_N(P, T, S) = \mu_I(P, T) - \tfrac{1}{2}g(P, T)S^2 - T\Sigma_0(S).$$

A qualitative picture of the variation of μ_N with S close to the transition is shown in Fig. 3.

4.1. $\mu_I(P, T)$ is the part of μ_N which is independent of the long range order S; it can be considered as the chemical potential of the isotropic phase at the same P and T.$^{(25)}$

4.2. Coupling free energy $\tfrac{1}{2}S^2g(P, T)$. This is the free energy corresponding to the interactions between molecules of different orientations. It will contain two contributions:

(α) Van der Waals attractions.

(β) Steric repulsions.

The contribution from (α) is expected to be roughly proportional to $1/V^2$(18) and independent of T (at constant volume). The contribution from (β) was disregarded by Maier and Saupe, but might well be important; it has been discussed by Onsager for the very special case of hard rods(26): in such a case it is linear in T. The volume dependence of (β) for a dense nematic is not known (the Onsager analysis applies only for dilute rods).(27)

Here our main assumption is that both contributions (α) and (β) can be approximated by a term $-\frac{1}{2}g(P, T)S^2$ quadratic in the order parameter. The limits of validity of this assumption are unclear (in the Onsager model this approximation would be in fact rather poor), but it leads to values of S_c which are quite reasonable ($S_c \sim 0.43$)(28).

4.3. Orientational entropy Σ_0. This is the orientational entropy *for one molecule*. It is defined by:

$$\Sigma_0 = -\int P \log P \, \mathrm{d}\Omega$$

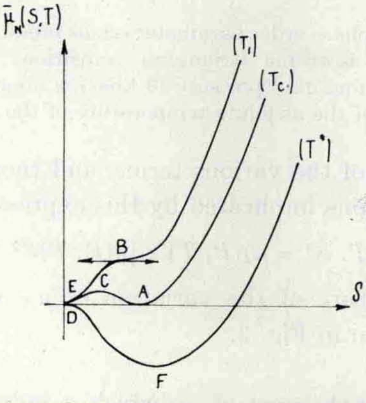

Figure 3. Chemical potential $\overline{\mu}_N(S, T/g)$ *versus* order parameter S at various temperatures close to the nematic–isotropic transition. Points E and A correspond to the actual transition, D is the supercooling limit of the isotropic phase, and B the (hypothetical) limit of superheating of the nematic phase: the system converts from A to E or *vice versa* before points B or D are actually reached.

where P is the probability for one molecule to have its orientation in the solid angle $\mathrm{d}\Omega$.

To compute Σ_0 explicitly, we make a molecular field approximation on the distribution P. This amounts to taking:

$$P(\theta) = \text{const. } \exp \lambda \left(\frac{3 \cos^2 \theta - 1}{2}\right)$$

where the const. ensures $\int P \,\mathrm{d}\Omega = 1$, and λ is defined implicitly in terms of S by the condition:

$$\int P \,\mathrm{d}\Omega \,\frac{3 \cos^2 \theta - 1}{2} = S.$$

In such an approximation, the probabilities P (and therefore also Σ_0) depend explicitly only on S.

The detailed resulting form for $\Sigma_0(S)$ can be extracted numerically from the work of Maier and Saupe.

Equation of state

We get the equation of state for the nematic phase by minimizing $\mu_N(P, T, S)$ with respect to S:

$$\frac{\partial \mu_N}{\partial S} = 0 \quad \text{whence} \quad S = \frac{T}{g(P, T)} \left| \frac{\partial \Sigma_0}{\partial S} \right|. \tag{1}$$

This is an implicit equation for S as a function of the single parameter $T/[g(P, T)]$. It may also be written explicitly:

$$S = f\left(\frac{T}{g(P, T)}\right). \tag{2}$$

The general behaviour of S expected from such an equation of state is shown in Fig. 4.

Now it is clear that the equilibrium value of S in a certain state (P, T) of the nematic phase is fixed only by the value of the *reduced temperature* $T/g(P, T)$. In order words, if P and T vary along a line of constant T/g, the order parameter will be constant.

This is especially true at the nematic–isotropic transition; the chemical potentials of both phases are then equal:

$$\mu_N = \mu_I \quad \text{whence} \quad S_c^2 = \frac{T_c}{g(P_c, T_c)} \Sigma_0(S_c). \tag{3}$$

Equations (2) and (3) define completely the values of S and T/g at the transition: whatever the pressure, the transition always occurs

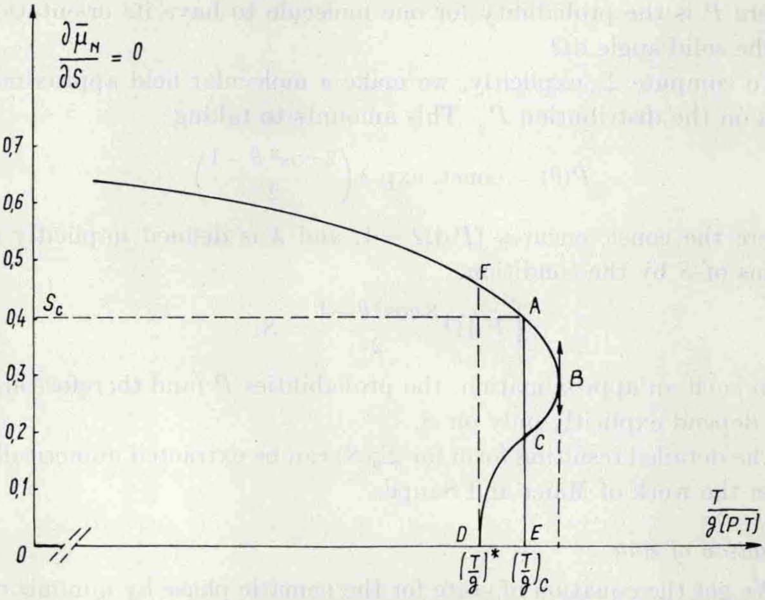

Figure 4. Qualitative behaviour of the equilibrium value of S (order parameter of the nematic phase) *versus* reduced temperature $T/g(P,T)$. Points A, B, C, D, E, F have the same meaning as in Fig. 3.

for the same values $S = S_c$ and $T/g = (T/g)_c$. From Maier–Saupe's analysis (i.e. from their computation of Σ_0) we know that: $S_c = 0.43$ and $(T/g)_c = 4.54$ *independently of the detailed form of* $g(P,T)$.

The knowledge of $g(P,T)$ would give (from Eqs. (2) and (3)) the dependence of the transition temperature versus pressure. Alternatively, we could use the measured $\mathrm{d}T_c/\mathrm{d}P$ to check a theoretical guess of $g(P,T)$. In particular, it would be interesting to know whether g is dominated by Van der Waals attractions or by steric repulsions. This can be attempted by the following arguments:

The total entropy Σ of the nematic phase can be divided into 2 parts:

- the " one molecule orientational entropy " Σ_0
- the entropy Σ_1 associated with the interactions of molecules of different orientations (excluded volume effects): this is the entropic part of the coupling free energy $\frac{1}{2}S^2g(P,T)$.

For example, in the hard rod gas, g is purely entropic:

$$\tfrac{1}{2}S^2g(P,T) = T\Sigma_1.$$

On the opposite, in Maier–Saupe's analysis, steric effects are neglected:

$$\Sigma_1 = 0.$$

The relative weight x of Σ_1 in $g(P, T)$ for the case of PAA can be estimated from the latent heat at the transition:

$$\Delta H = T\Delta\Sigma = T\frac{\partial(\mu_N - \mu_I)}{\partial T} = \tfrac{1}{2}S_c^2 g_c\Big(1 - \underbrace{\frac{T_c}{g_c}\Big(\frac{\partial g}{\partial T}\Big)_c}_{x}\Big).$$

Clearly, x is a measure of the entropic contribution to the couplings:

for hard rods, $g = T\Sigma_1(S)$ whence $\partial g/\partial T = g/T$ and $x = 1$; for Maier and Saupe, g is independent of T (at constant volume) and $x = 0$.

The actual value of x is:

$$x = 1 - \frac{2\Delta H}{S_c^2 g_c} = 1 - \frac{2\Delta H}{4.54\, S_c^2 T_c}.$$

Unfortunately, the dispersion of the existing data on ΔH (or alternatively $\mathrm{d}T_c/\mathrm{d}P$) does not permit a precise determination of x. Taking the data on ΔH(14), and a value of S coherent with the theoretical calculation of $(T/g)_c \cdot ((T/g)_c = 4.54,\ S_c = 0.43)$, we get:

$$x \simeq 0.5.$$

This suggests that the contributions of Van der Vaals attractions and entropic repulsions (excluded volume effects) to the intermolecular orientational couplings $\frac{1}{2}g(P, T)S^2$ are on the same order of magnitude.

5. Conclusions

(*a*) Experimentally S_c is independent of P on a rather broad range of pressure.

(*b*) This is compatible with all mean field models where the molecular interaction energy is proportional to S^2; thus our experiment does not give a very detailed check on the nature of the couplings. They might be temperature independent, as in Maier–Saupe's theory (Van der Waals attractions), or temperature dependent, as in the Onsager's calculation (excluded volume effects). In fact, we probably have a superposition of both effects; the relative weights of the two contributions can be estimated by certain other measurements, such as the latent heat of the transition. A rough estimate along these lines shows that the two effects are on the same order of magnitude.

(*c*) We are unable to devise a similar theory for the solid–nematic transition, because the order parameter for this transition is more complex: it depends on S, but also on the translational order of the molecules.

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