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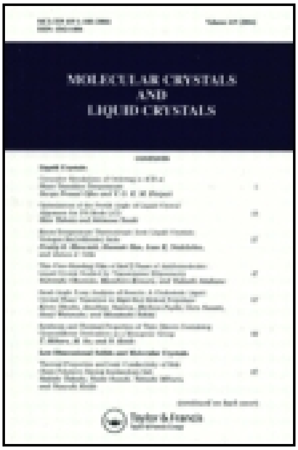

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Liquid Crystals in my Memories and Now—the Role of Anisotropic Viscosity in Liquid Crystals Research

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Liquid Crystals in my Memories and Now—the Role of Anisotropic Viscosity in Liquid Crystals Research

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The viscosity coefficients of nematic substances for corresponding orientation geometry introduced and measured for PAA and PAP by the author in the thirties are discussed from the actual point of view.

The great universality of these coefficients of viscosity and their utility for describing several dynamical phenomena has been shown. There is a quantitative agreement between the experimental data of those investigations and continuum hydrodynamical theory of nematics with the numerical values of viscosities measured by the author.

As a new field of application of flow in definite orientation geometry, the properties of smectics and closely connected problems of phase transitions, pretransition effects and reentrant phase has been discussed.

REMINDER OF A VERY OLD EXPERIMENT

I worked in the field of liquid crystals for a rather short time, starting in 1934 with professor M. Jeżewski, known from his investigations on dielectric constant of nematic fluids. I finished my investigations on the anisotropy of viscosity in 1938. Final results were sent as a letter to "Nature", but because of the war it appeared as late as 1946, under the title "The Three Coefficients of Viscosity of Anisotropic Liquids".[4]

The anisotropy of viscosity, although it is so large, as we well know now, was not known till 1935.

The only direct measurements of the influence of magnetic field on the viscosity of nematics, done by Neufeld[1] had given a negative result. But Neufeld's experiments had been done by the capillary flow method, with capillaries of ≈ 0.1 mm in diameter, with a rather high velocity of flow.

The magnetic field of ≈10 kOe, perpendicular to the capillary axis, did not change the time of flow. But I did not consider that result definitive as regards the problem of the influence of reorientation of molecules on viscosity.

I decided to measure the viscosity of PAA and PAP in a strong magnetic field giving a fixed orientation of molecules competing with flow alignment. The necessary condition for the method should be a very low velocity gradient in flow. I prepared an unconventional method of an oscillating thin plate immersed in the liquid investigated, performing small and very slow oscillations. The results of measurements for PAA and PAP were published long ago.[2–5]

But studying the literature, even quite recent papers, I have concluded that some details in the experiment should be explained even after more than 40 years. This concerns especially the measurements of the viscosity η_1 corresponding to the orientation of molecules parallel to the flow direction. Therefore, I give some details of the apparatus here, reproduced from one of my old papers,[3] which is not generally known. In Figure 1 we see the apparatus and on the right hand side the rectangular geometry of measurements corresponding to the three principal viscosity coefficients η_1, η_2, η_3, defined for proper geometry of orientation of molecules in relation to flow characteristics. The orientation is described by the director $\vec{n}$. We defined the following viscosities:

η_1 for $\vec{n} \parallel \vec{v}$, η_2 for $\vec{n} \parallel \text{grad } v$, η_3 for $\vec{n} \perp \vec{v}$, $\vec{n} \perp \text{grad } v$
(See Figure 1.)

A glass plate was suspended from one arm of an analytical balance, by a thin glass thread, specially loaded to minimize the irregular movements of the plate in consequence of thermal streams in the liquid. The plate could oscillate in its own plane in vertical direction. The amplitude was ≈3 mm and the period of oscillations was ≈5 sec. In this way I got an extremely low gradient of velocity, about three orders of magnitude smaller than in Neufeld's experiments. This problem was discussed in detail by Zwetkoff, *et al.*, in 1938.[6]

The magnetic field of up to 8 kOe was horizontal, i.e. perpendicular to the flow direction. The angle φ between magnetic field and normal to the plate, could be varied from 0° to 90°.

The numerical values of η_1, η_2, η_3 obtained in these measurements were published in 1946 and are often quoted in literature.[4] (See Table I.)

The main result in Table I is the existence of very high anisotropy of viscosity of PAP and PAA. That was later confirmed for other nematic

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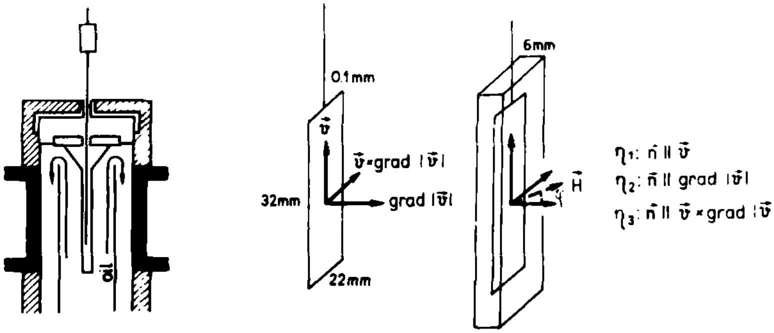

FIGURE 1 Apparatus used for measurement of viscosity of nematic liquids from damping of oscillations of a thin glass plate submerged in the liquid. Apparatus was calibrated by liquids of known viscosities. The liquid is contained in a rectangular vessel, heated by an oil-thermostat up to 200°C. The oscillating system is placed between the poles of electromagnet. The angle φ between the normal to plate and magnetic field could be changed. On the right hand side we see a rectangular system of vectors defining the geometry of orientation of molecules in relation to flow parameters.

substances. Taking additionally data of Gähwiller[27] we have the following viscosities η_1 and anisotropies η_2/η_1:

	PAP-144°,	PAA-125°,	HBAB-60°,	MBBA-25°C
η_1cP:	1.3	2.4	18.6	23.2
η_2/η_1:	6	4	5	4.5

In spite of large differences in viscosities the anisotropy η_2/η_1 has a rather similar value ~5.

For all substances mentioned above we observe as characteristics for nematics an inequality $\eta_1 < \eta_3 < \eta_2$.

TABLE 1

(Reprinted from Nature — 1946)[4]
Three Coefficients of Viscosity of Anisotropic Liquids

Substance and temperature	Molecules parallel to the direction of the flow, η_1	Molecules parallel to the gradient of velocity, η_2	Molecules perpendicular to the direction of flow and to the velocity gradient, η_3
p-Azoxyanisole 122°C	0,024 ± 0,0005	0,092 ± 0,004	0,034 ± 0,003
p-Azoxyphenetole 144,4°C	0,013 ± 0,0005	0,083 ± 0,004	0,025 ± 0,003

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But let us now discuss a very important problem of η_1 measured without magnetic field and considered as corresponding to orientation of molecules parallel to flow. (See discussion of Tseng *et al.*,[8] and de Feu.[9]

It is clear from Figure 1 that I could not have magnetic field in vertical direction, i.e. in flow direction. But I had arguments that it was not necessary, because I obtained for η_1 precisely the same value that has been obtained in all earlier measurements done by means of capillary methods. Figure 2 shows the results of measurements by capillary methods in dependence of temperature, collected much later by Porter *et al.*[7] All these measurements have been done for orientation parallel to flow. In the curve the values η_1 from my measurements are also indicated. The agreement of η_1 with the curve is a check for calibration as well as for orientation parallel to flow.

But there was an important reason for the vertical orientation. This was the existence of convection flow in the vertical vessel containing the liquid, induced by a temperature gradient in the vessel. I think that this effect is the main reason for the vertical orientation.

In conclusion we can say that in my measurements the molecules were oriented by either the strong magnetic field or by a temperature gradient. (See G. W. Gray,[10] and R. S. Porter *et al.*)[11]

But what concerns η_1-value, in the present time we know much more about the orientation by flow. As noted by Tseng *et al.*,[8] the value η_1 measured without magnetic field corresponds not exactly to the orientation

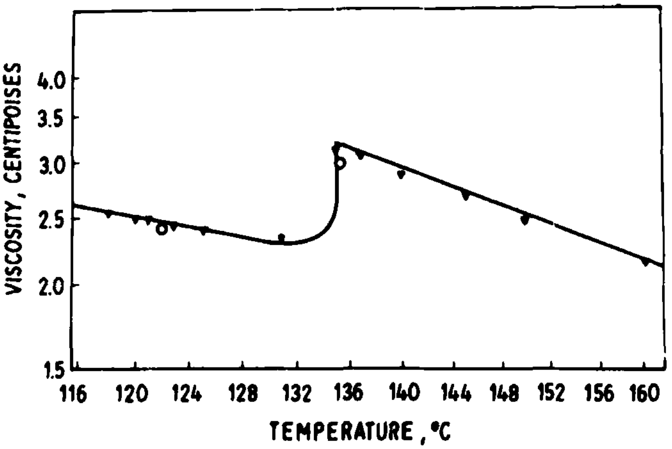

FIGURE 2 The temperature dependence of viscosity of PAA measured by capillary flow method (full triangles). Open circles correspond to viscosity measured by oscillating plate method. (Data taken from Porter *et al.*).[7]

parallel to flow. This orientation is characterized by an angle θ_0, called alignment angle, for which in my old measurements was assumed $\theta_0 = 0$. Really it could be a few degrees, what introduces some error in understanding my η_1 as corresponding to parallel orientation by flow (see de Jeu).[9] In this paper I will use η_1 as corresponding to $\theta_0 = 0$ as an approximation.[†]

All measurements in magnetic field were done in so strong magnetic fields that the saturation of measured viscosity was observed (Figure 3). In these conditions the alignment is not influenced by the flow.

Figure 4 shows the dependence of the viscosity for horizontal magnetic field on the azimuthal angle φ (Figure 1). It could be described in the form

$$\eta(\varphi) = \eta_2 \cos^2\varphi + \eta_3 \sin^2\varphi$$

[†] I am very grateful to Prof. A. F. Martins for discussion of this problem during the Conference.

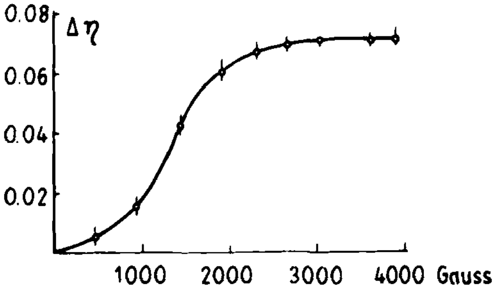

FIGURE 3 The influence of the magnetic field on viscosity of PAP. Saturation of the change of viscosity $\Delta\eta = \eta_2 - \eta_1$ in strong magnetic field.

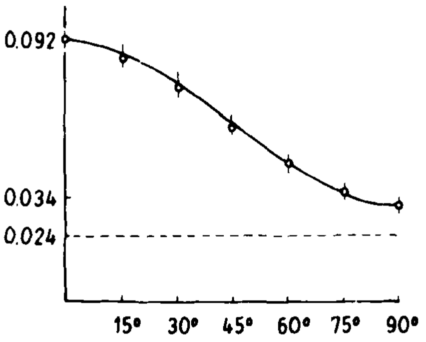

FIGURE 4 The dependence of viscosity on the azimuthal angle (see Figure 1 and text) — the curve represents the dependence $\eta(\varphi) = \eta_2 \cos^2\varphi + \eta_3 \sin^2\varphi$.

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On some dynamical problems solved using continuum theory of nematics with principal viscosities η_1, η_2, η_3

All that we have said so far concerned the first observation of the anisotropy of viscosity of nematic liquid crystals.

Since 1945 general interest in liquid crystals has increased enormously in many directions. But in this report we remain in the field of hydrodynamics. The most important progress here is the rise in the sixties and the later development of the continuum hydrodynamics of nematic liquid crystals. This theory has been developed mainly by Ericksen,[12] Leslie[13] and Harvard Group (Forster, *et al.*)[14] The viscosity coefficients η_1, η_2, η_3 can be calculated from the well known Leslie viscosity coefficients and also from constants of Harvard Theory.

It turned out that several phenomena earlier observed in our experiments, can be now deduced from the continuum hydrodynamical theory. As examples of such phenomena we can mention such well known facts as orientation by flow, the important inequality $\eta_1 < \eta_3 < \eta_2$, and the dependence of viscosity on azimuthal angle φ.

A very great achievement of continuum theory is the quantitative explanation of many dynamical phenomena. As examples we can mention:

Scattering of light in bulk nematic sample[14–17]
Scattering of light on superficial/capillary/waves[18]
Combined orientation analysed by Couette flow[21]
Attenuation of ultrasonic longitudinal waves[19]
Conduction-induced orientation by flow.[20]

I have summarized the comparison between the experimental data and theoretical expectation in the Table II. All the investigations included in the Table have been described in quoted literature and in known books and survey articles. (See Refs. 9, 17, 22 and 23.)

Summarizing the results presented in Table II we can say that there is a quantitative agreement concerning such quite different phenomena between the experimental data and theoretical description by means of continuum theory, with numerical values of principal viscosity η_1, η_2, η_3 defined for proper geometry of orientation of nematic molecules in relation to flow characteristics.

The viscosity of smectic liquids in defined geometry of orientation in research of phase transitions, pretransition effects, etc.

The results obtained in recent years have shown, however, that the approach presented above to dynamical problems in nematics, may have a more wider meaning.

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As a new field of application of flow in definite orientation geometry, which has been developed in recent years, we shall discuss the problem of flow of smectics and closely connected problems of phase transitions, pretransition effects and reentrant phase phenomena. We shall speak here about the phases: Isotropic (I), nematic (N), smectic A (S_A), smectic B (S_B) and nematic reentrant ($\tilde{N}$).

But it is necessary to mention that we have quite different physical conditions here. The numerical values of viscosities of the same compound in different phases differ by several orders of magnitude. The smectics are layered materials, each layer being a two dimensional fluid. They have a very strong anisotropy of mechanical properties, in particular of viscosities. The layers can usually slide on each other with viscosities comparable to that of ordinary fluids. On the other hand if the layers are fixed in space and a pressure gradient is normal to the layers, we observe a very weak flow, corresponding only to permeation of molecules of one layer through the other.

The pioneering work on applying oriented flow geometry in the sens discussed above for nematics, to characterizing flow phenomena in smectics, has been done in recent years by the group of Rhode Island University and MIT (S. V. Letcher *et al.*)[24–26] The materials studied were liquid crystals having N and S_A phases (CBOOA) or having N, S_A and S_B phases (BBOA). For nematic reentrant phase investigations a mixture of (7CB), (80CB) and (5CT) was used.

This idea is explained in Figure 5, for measurements with capillaries of rectangular cross section. The uniform alignment of molecules is maintained by a strong magnetic field, much stronger than the one used for nematics. Molecules are oriented along magnetic field and smectic layers are consequently normal to the field.

In Figure 5 we present both situations of geometry: for nematics (oscillating plate) and for smectics (rectangular capillary).

In geometry η_1 ($\vec{n} \parallel \vec{v}$) the smectic layers are normal to flow and, as was already mentioned, only a weak permeation flow occurs. Approaching from nematic phase to transition temperatures T_{N-S_A}, we observe a strong pretransition increase of viscosity η_1, and in the phase S_A a very high viscosity.

When we compare viscosities in all three geometries in nematic phase, far from transition $N - S_A$, we have $\eta_1 < \eta_3 < \eta_2$, but because of the pretransition effect for η_1, we have near transition temperature $\eta_3 < \eta_2 < \eta_1$.[24,26] We can speak about a divergence of anisotropy.

In geometry η_3 ($\vec{n} \perp \vec{v}$, $\vec{n} \perp \nabla v$), a very strong pretransition divergence of viscosity near $S_A - S_B$ transition was for the first time observed.[25] For

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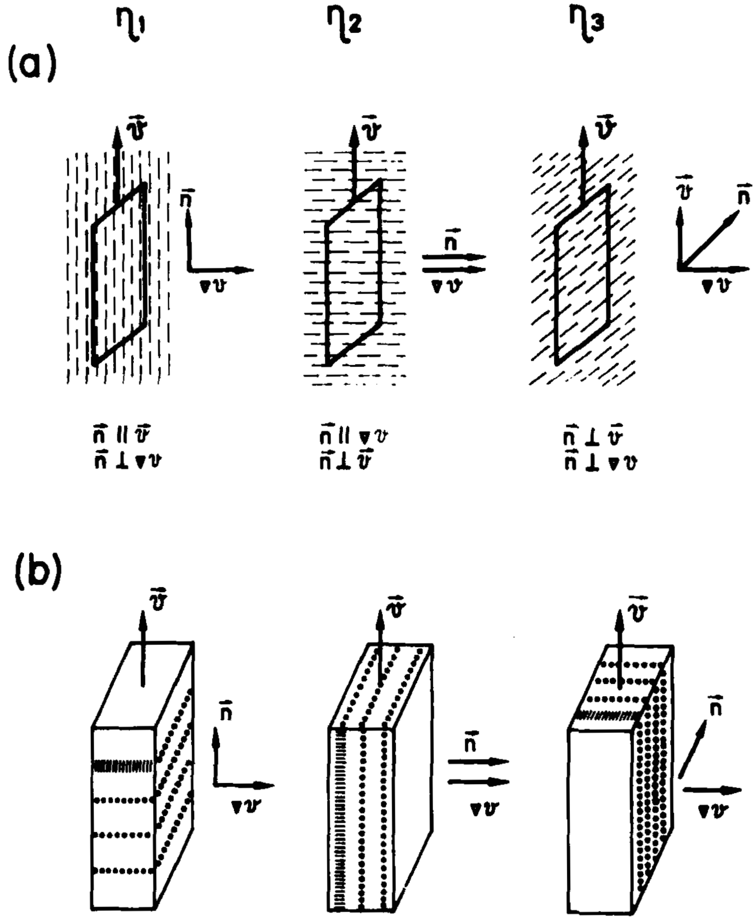

FIGURE 5 Schematic draft to definition of three principal viscosity coefficients η_1, η_2, η_3 for three geometries of orientation in relation to flow. (a) for nematics, (Mięsowicz)[4], (b) for smectics, (Letcher *et al.*).[24,25,26]

this geometry it means that in phase S_B the molecular motion within the layers becomes "frozen".

The advantages of knowing the definite geometry of orientation in meaning of Figure 5 have been demonstrated by Bhattacharya and Letcher in their investigations of the flow behavior of an oriented reentrant nematic liquid.[26] For the above mentioned mixture they observe a stable reentrant nematic phase in reversible transition $N - S_A - \tilde{N}$. The authors investigated capillary shear flow with rectangular capillaries in nematic,

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smectic A, and for the first time in reentrant nematic phase. The viscosity-temperature curves for all three geometries of Figure 5 are very different.

The viscosity in geometry η_1 ($\vec{n} \parallel \vec{v}$) shows striking divergence when the smectic A phase is approached from the nematic phase, but also from the reentrant $\tilde{N}$ phase. The viscosity in the S_A phase is so high that we can say that the flow is blocked.

For viscosities in geometry η_2 ($\vec{n} \parallel \nabla v$) and in geometry η_3 ($\vec{n} \perp \vec{v}$ and $\vec{n} \perp \nabla v$) the increase of viscosity in S_A phase is much smaller and the viscosities at the transitions $N - S_A$ and $S_A - \tilde{N}$ are not divergent.

Far from the transition temperatures the same universal inequality $\eta_1 < \eta_3 < \eta_2$ holds, both for normal nematic N and for reentrant nematic $\tilde{N}$ phases.

The main result of the discussed paper of Bhattacharya and Letcher is that from the dynamical point of view the reentrant nematic and normal nematic phases are identical. The values of viscosity η_1 for both nematic phases, far from transition temperature, are described by the same temperature dependence of Arrhenius type, with the same activation energy, although the transition from phase N to phase $\tilde{N}$ comes to existence through creation of smectic A phase, where the flow is blocked. It seems that the continuous dynamical theory is valid for the reentrant phase.

SUMMARY

Experimental details concerning measurements of the anisotropy of viscosity for nematic liquid crystals done in 1934–1936 are discussed from the point of view of the present. The investigated liquids were orientated by magnetic fields in saturation region or by the temperature gradient. Arguments are given supporting the understanding of η_1, measured without field, as corresponding to orientation of molecules parallel to flow-in approximation of flow alignment angle $\simeq 0$. The main results are now confirmed by different investigators:

1. Large anisotropy of viscosity. Near the melting point we have $\eta_2 : \eta_1 \simeq 5$.
2. The general inequality for nematics: $\eta_1 < \eta_3 < \eta_2$.
3. The azimuthal dependence: $\eta(\varphi) = \eta_2 \cos^2 \varphi + \eta_3 \sin^2 \varphi$.

The great universality of principal viscosities for the quantitative description of many dynamical phenomena, on the basis of continuum hydrodynamic theory is shown. (See Table II.)

The definite geometry of orientation in relation to flow parameters, as was formerly used for definition of principal viscosities η_1, η_2, η_3 for

TABLE 2

Explanation in text—Viscosities in cP

PAA	η_1 $\vec{n} \parallel \vec{v}$	η_2 $\vec{n} \parallel \nabla v$	η_3 $\vec{n} \perp \vec{v}$ $\vec{n} \perp \nabla v$
(1) Oscill. plate (1946)	2.4	9.2	3.4
(2) Light scatt. Orsay, Theor. E. L. (1970)	1.5	8.6	3.3
(3) Capill. waves Langevin (1972)	2.4	9.6	3.6
(4) Combined orientation Couette flow Narasimhan, Eringen (1974)	2.6	9.3	—
(5) Light scatt, Orsay, Harvard Theory (1971)	Orsay parameter	calculated	measured
	f_1 (η_1)	0.059	0.051
	f_2 (η_2)	23	21
	f_3 (η_2,η_3)	8.5	10
(6) Ultrasonic absorption Kemp, Letcher Harvard Theory (1971)	$\alpha/f^2 = A \sin^2 \theta + B \cos^2 \theta + C \cos^2 2\theta$ Best fit for A, B, C in agreement with η_1, η_2, η_3		
(7) Anomalous alignment by flow in E, H fields. Helfrich (1969)	Critical ratios of E/H for flow stability Calculated with		
	η_1, η_2, η_3		measured
	$\vec{E} \perp \vec{H}$: 0.42		0.35
	$\vec{E} \parallel \vec{H}$: 0.57		0.45

nematics, was recently applied by Letcher et al. for studying flow behaviors in smectic phase. Especially interesting are results concerning phase transitions, pretransitional effects and properties of nematic reentrant phase.

References

1. M. W. Neufeld, *Phys. Z.*, **14**, 645 (1913).
2. M. Mięsowicz, *Nature*, **136**, 261 (1935).
3. Bull, *Intern. Acad. Pol., Ser. A.*, 228 (1936).
4. Nature, **158**, 27 (1946).
5. Proc. of the XIV Winter School, "Collected Effects in Condensed Matter," University Wrocław (1978).
6. W. N. Zwetkoff and G. M. Michailoff, *Acta Physicochimica U.R.S.S.*, **8**, 77 (1938).
7. R. S. Porter and J. F. Johnson, *Journ. Appl. Phys.*, **34**, 51 (1963).
8. H. C. Tseng, D. L. Silver and B. A. Finlayson, *Phys. of Fluids*, **15**, 1213 (1972).

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9. W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach Publ. (1980).
10. G. W. Gray, "Molecular Structure and Properties of Liquid Crystals," Academic Press (1962).
11. R. S. Porter and J. F. Johnson, *Rheology*, **4**, 317 (1967).
12. J. L. Ericksen, *Archs. Ration. Mech. Analysis*, **10**, 189 (1962).
13. F. M. Leslie, *Quart. J. Mech. Appl. Math.*, **19**, 357 (1966), *Archs. Ration. Mech. Analysis*, **28**, 265 (1968).
14. D. Forster, T. C. Lubensky, P. C. Martin, J. Swift and P. S. Pershan, *Phys. Rev. Lett.*, **26**, 1016 (1971).
15. Orsay Liquid Crystal Group, *Phys. Rev. Lett.*, **22**, 161 (1969).
16. L. Leger-Quercy, "These Université de Paris," December 1970.
17. P. G. de Gennes, "The Physics of Liquid Crystals," Clarendon Press (1974).
18. D. Langevin, *Journ. de Physique*, **33**, 249 (1972).
19. K. A. Kemp and S. V. Letcher, *Phys. Rev. Lett.*, **27**, 1634 (1971).
20. W. Helfrich, *Journ. Chem. Phys.*, **51**, 4092 (1969).
21. M. N. L. Narasimhan and A. C. Eringen, *Mol. Cryst. and Liq. Cryst.*, **29**, 57 (1974).
22. M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, **46**, 618 (1974).
23. S. Chandrasekhar, *Liquid Crystals*, Cambridge Mon. on Physics (1977).
24. M. G. Kim, S. Park Sr., M. Cooper and S. V. Letcher, *Mol. Cryst. Liq. Cryst.*, **36**, 123 (1975).
25. S. Bhattacharya and S. V. Letcher, *Phys. Rev. Lett.*, **42**, 458 (1979).
26. *Phys. Rev. Lett.*, **44**, 414 (1980).
27. Ch. Gähwiller, *Mol. Cryst. Liq. Cryst.*, **20**, 301 (1973).

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