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Molecular Theory of Nematic Liquid Crystals†

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Abstract—The thermodynamic conditions of nematic stability are discussed on the basis of the molecular statistical theory of orientational order developed in previous papers. Theoretical calculations of the order parameter in the nematic phase and the volume change at the nematic–isotropic transition point are presented for 2-4-nonadienic acid, 2-4-undecadienic acid, *p*-azoxyanisole, *p*-azoxyphenetole and anisaldazine. The significance of the results are discussed briefly.

1. Introduction

Since the high geometrical anisotropy of the molecule appears to be a necessary condition for the occurrence of the nematic mesophase, it is to be expected that repulsion forces play a significant role in determining orientational order. Recent theoretical studies(1,2) have shown that when repulsion and dispersion interactions are taken into account the orientational potential energy of a molecule in a nematic assembly is expressible as a power series in $\cos^2\theta_i$, where θ_i is the angle which the long axis of the molecule makes with the uniaxial direction of the medium. In these calculations the repulsion energy was worked out by replacing the rod-like molecules by $(2n+1)$ centres of repulsion, and the dipole–dipole and dipole–quadrupole contributions to the dispersion energy were evaluated in terms of the anisotropic oscillator model of van der Merwe.(3,4) Assuming an average volume dependence of V^{-3} for the sum of the repulsion and dispersion energies,§ using a mean field approximation and imposing

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§ The theory of melting(5,6) which treats the crystal–nematic and nematic–isotropic transitions as order–disorder phenomena supports the assumption that the volume dependence of the orientational energy is V^{-3}.

the condition that the orientational energy vanishes in the isotropic phase, the potential function reduces to the form

$$U_i = -V^{-3}\left[Bs_1\left(\frac{3\cos^2\theta_i - 1}{2}\right) + D\left(s_1\frac{5\cos^4\theta_i - 1}{4} + s_2\frac{3\cos^2\theta_i - 1}{2}\right)\right], \tag{1}$$

where B and D are constants, V is the molar volume,

$$s_1 = \frac{3\overline{\cos^2\theta} - 1}{2} \quad \text{and} \quad s_2 = \frac{5\overline{\cos^4\theta} - 1}{4}.$$

Based on (1) a statistical theory of orientational order was developed which led to a quantitative explanation of many of the properties of *p*-azoxyanisole and *p*-azoxyphenetole.

When $D = 0$ and the volume dependence is taken to be V^{-2}, (1) reduces to the potential function of the form used by Maier and Saupe.(7) The theory then gives a universal curve for the order parameter as a function of the reduced temperature.

In the present communication, we shall discuss in detail an aspect of the theory which was touched upon only briefly in previous papers(1,2) viz., the stability of the nematic phase. We shall also apply the theory to evaluate the order parameter and the volume change at the nematic-isotropic transition point for a few compounds.

2. Stability of the Nematic Phase

The potential energy function (1) may be conveniently written as

$$U_i = -V^{-3}(a'x_i^4 + b'x_i^2 + c'), \tag{2}$$

where $x = \cos\theta$, $x_i = \cos\theta_i$,

$$a' = \tfrac{5}{4}Ds_1,$$

$$b' = \tfrac{3}{2}(Bs_1 + Ds_2)$$

and $$c' = -\tfrac{1}{4}[2Bs_1 + D(s_1 + 2s_2)].$$

The component of the Helmholtz free energy due to orientational order is

$$F_s = NkT\left[\tfrac{1}{2}(a\overline{x_i^4} + b\overline{x_i^2} - c) - \log\int_0^1 \exp(ax_i^4 + bx_i^2)\,\mathrm{d}x_i\right]. \tag{3}$$

For a stable equilibrium of the ordered system

$$\left(\frac{\partial F_s}{\partial s_1}\right)_{V,T} = \left(\frac{\partial F_s}{\partial s_2}\right)_{V,T} = 0 \tag{4}$$

and

$$\left(\frac{\partial^2 F_s}{\partial s_1{}^2}\right)_{V,T} > 0, \qquad \left(\frac{\partial^2 F_s}{\partial s_2{}^2}\right)_{V,T} > 0. \tag{5}$$

It has been shown(1,2) that (4) is satisfied when

$$\left.\begin{aligned} \overline{x_i{}^2} &= \overline{x^2} \\ \text{and} \qquad \overline{x_i{}^4} &= \overline{x^4} \end{aligned}\right\} \tag{6}$$

Figures 1–3 illustrate that the free energy is also a minimum under these circumstances. The integrals involved in the theory were evaluated to an accuracy of 1 in 10^5 by the use of a computer for a range of values of a and b (see Refs. 1 and 2). From these data, the free energies for a representative set of values of a, b, B and D have been plotted in the figures. In each figure there is a family of curves connecting F_s/NkT versus s_1 for a given value of a/b and various values of $(B/kTV^3, D/kTV^3)$. The minimum of the free energy in every curve occurs at a particular value of s_1 (and therefore of s_2) satisfying the equilibrium conditions (6). The broken curve shows the variation of the free energy with the stable value of s_1. The point of intersection of this curve with the zero line, which represents the free energy of the completely disordered system or isotropic phase, fixes the order parameters s_1 and s_2 at the transition point. (Strictly speaking, it is the Gibbs free energy which is equalized at the transition (see Ref. 1 and 2), but the volume change is so small that the error in the order parameters so determined is only of the order of 1–2%). Figure 4 shows how the order parameters at the transition point should vary for a range of materials with different a/b. The Maier–Saupe case corresponds to $a/b = 0$.

Currently used experimental methods of determining the order parameter lead to a measure of s_1 only and not of s_2. An approximate estimate of s_2 has been made recently(8) in p-azoxyanisole from the polarized light scattering intensity data of Chatelain.(9,10)

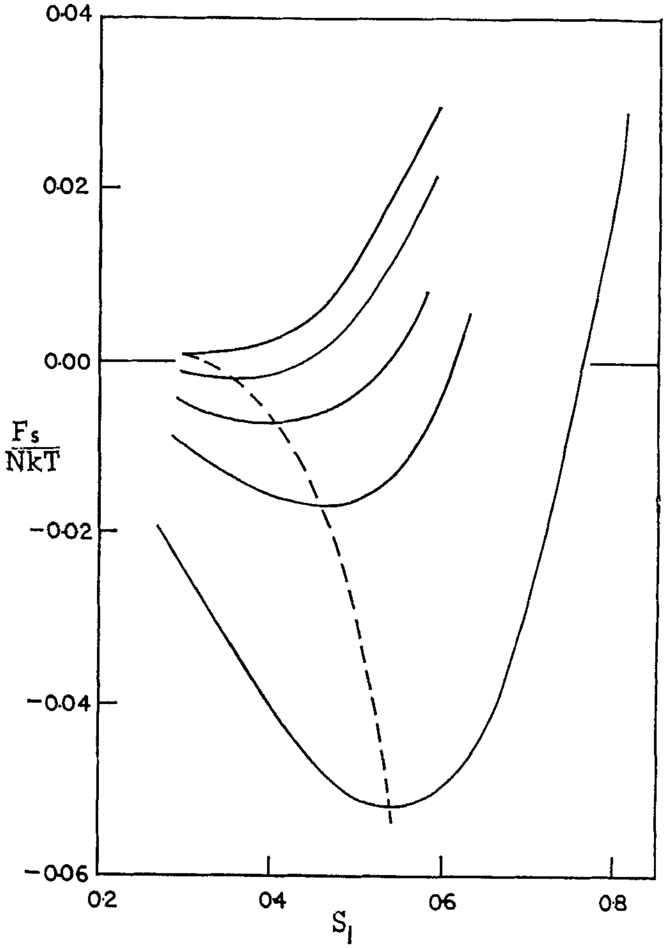

Figure 1. Variation of F_s/NkT with s_1 for $a/b = -\frac{1}{5}$. The values of (B/kTV^3, D/kTV^3) for the curves from top to bottom are (6.6132, −1.3435), (6.6745, −1.3530), (6.7794, −1.3714), (6.9244, −1.3979) and (7.3192, −1.4721) respectively.

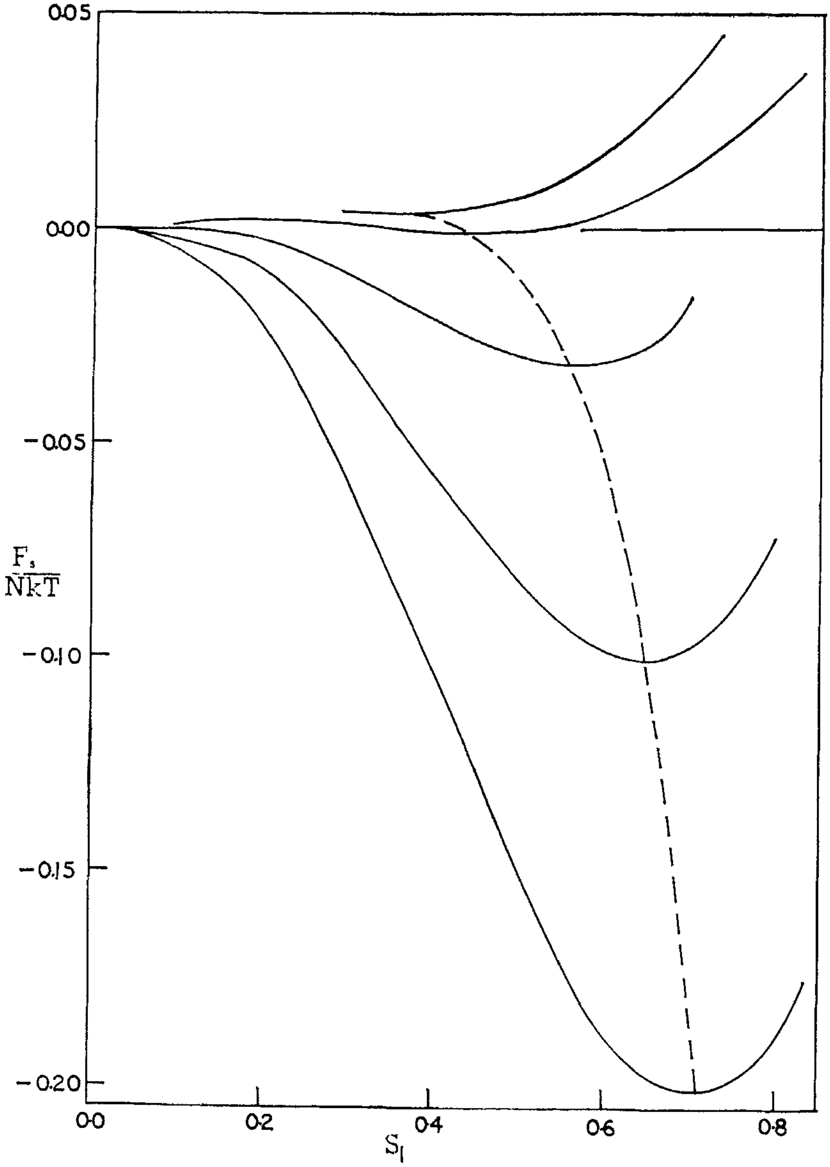

Figure 2. Variation of F_s/NkT with s_1 for $a/b = 0$. The values of B/kTV^3 for the curves from top to bottom are 4.4932, 4.5517, 4.7880, 5.1643 and 5.5982 respectively.

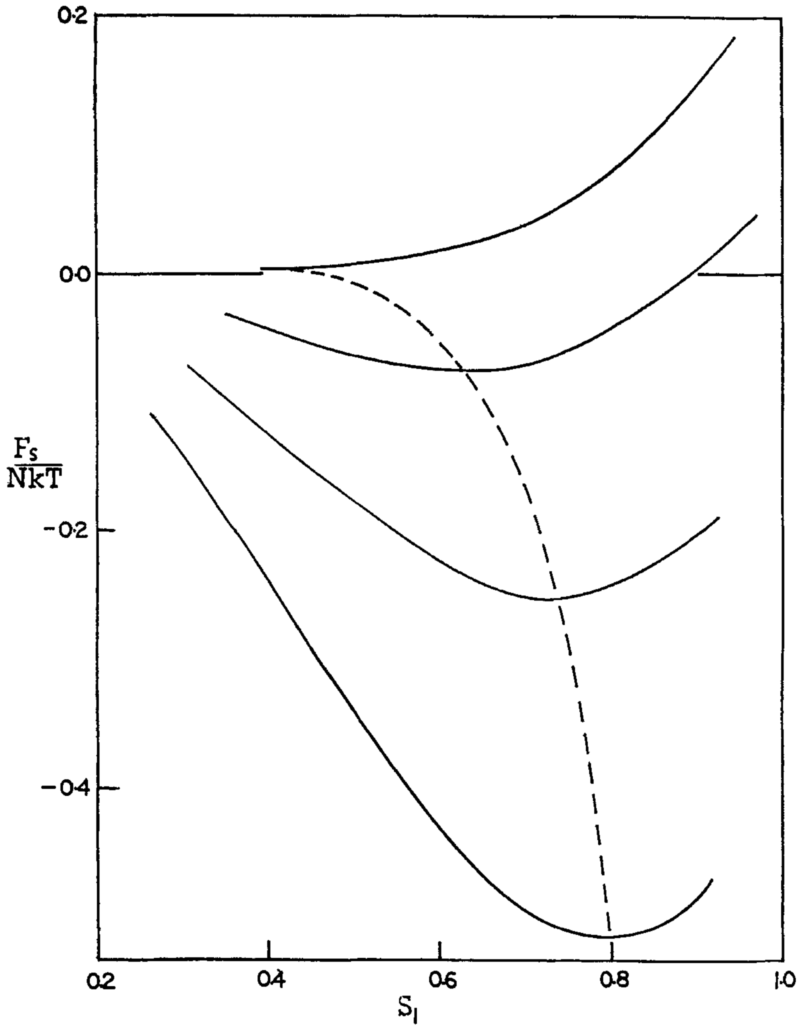

Figure 3. Variation of F_s/NkT with s_1 for $a/b = \frac{1}{15}$. The values of $(B/kTV^3, D/kTV^3)$ for the curves from top to bottom are (3.9539, 0.3377), (4.4044, 0.3778), (5.0406, 0.4334) and (5.8080, 0.5003) respectively.

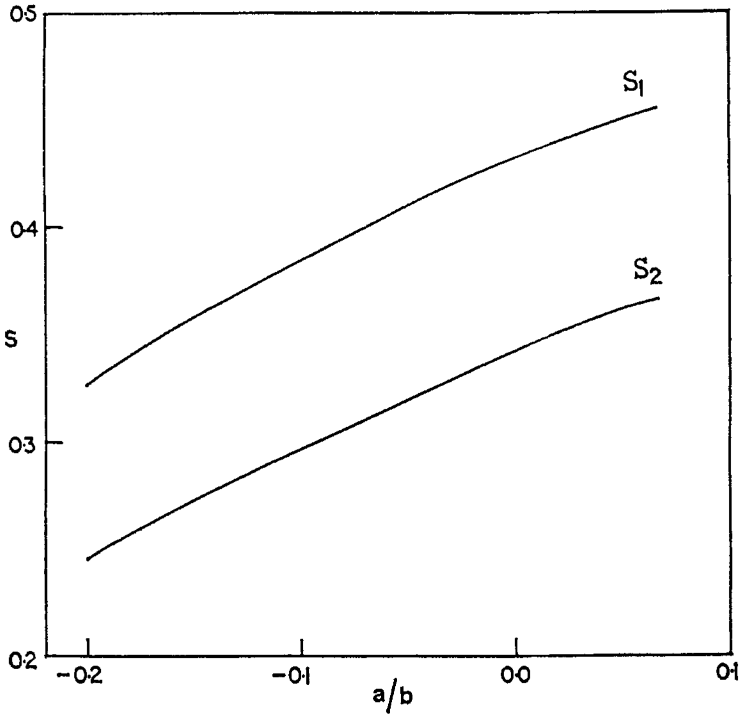

Figure 4. Order parameters at the nematic-isotropic transition point versus *a/b*.

3. Application of the theory to a few compounds

A theoretical calculation of the order parameter s_1 and its variation with temperature requires a knowledge of the thermal expansion of the liquid crystal. As far as we are aware, data on s_1 and V in the nematic range and on $\Delta V/V$ at T_c are available for only five compounds: *p*-azoxyphenetole (PAP),(11–13) 2-4-nonadienic acid,(14) 2-4-undecadienic acid,(14) anisaldazine(15–17) and *p*-azoxyanisole (PAA).(7,12,13,18) We have applied the theory to all these compounds. Figure 5 presents the theoretical curves for s_1 versus $T_c - T$ along with the available experimental data. (The magnetic resonance measurements of Rowell *et al.*(19) on deuterated PAA and PAP have not been included in the diagram as the values seem to be slightly higher than those reported by other authors; however, these

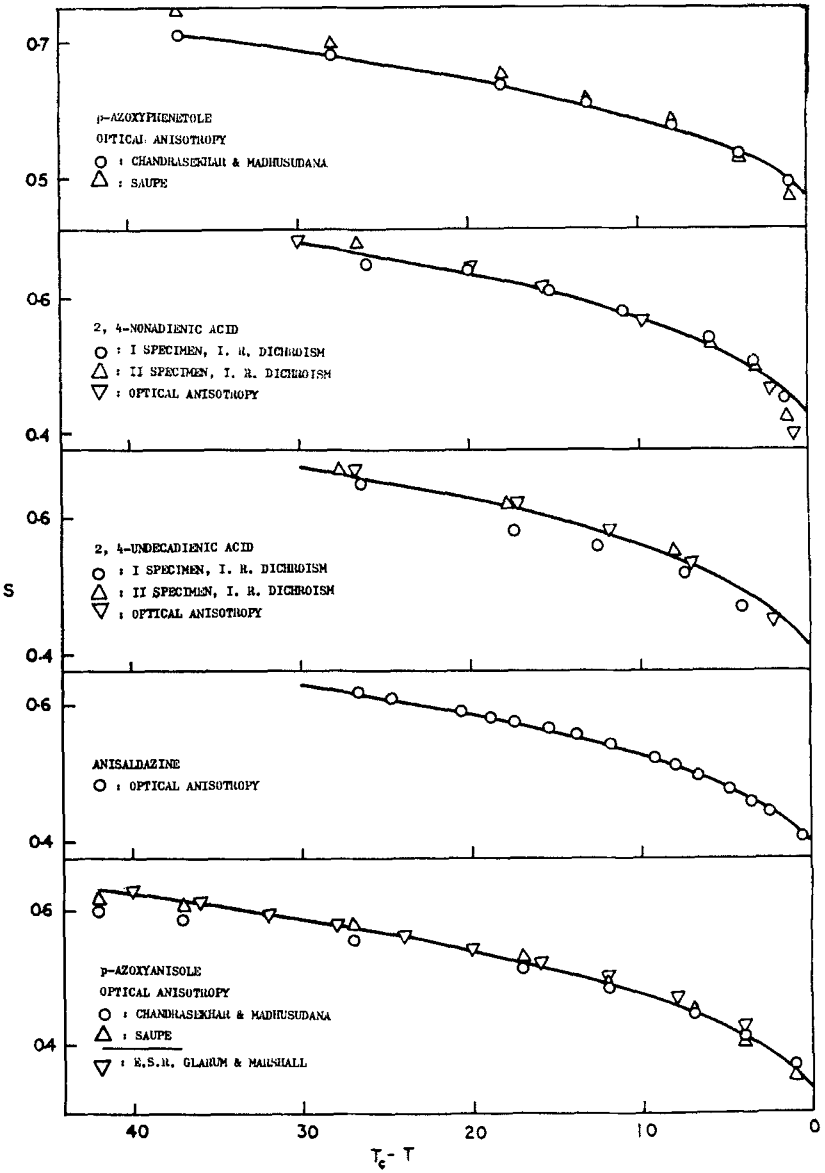

Figure 5. Orientational order parameter s_1 in some compounds. Curves represent the variations derived from theory.

measurements do confirm that s_1 of PAA is relatively much lower than that of PAP.) The constants B and D of the potential function, the calculated and observed $\Delta V/V$ are given in Table 1. From a preliminary study of these results, the following conclusions may be drawn:

TABLE 1

	T_c in °K	$B \cdot 10^6$ erg·cm^9	$D \cdot 10^6$ erg·cm^9	$(\Delta V/V)$ (theor)	$(\Delta V/V)$ (expt)
2–4-nonadienic acid	326.5	1.0285	− 0.0882	0.0047	0.0047
2–4-undecadienic acid	335.5	1.9840	− 0.2079	0.0039	0.0039
p-azoxyanisole	407	4.5448	− 1.0460	0.0035	0.0035
p-azoxyphenetole	438	5.2502	0.0675	0.0061	0.0060
anisaldazine	454	6.4578	− 0.9738	0.0054	0.0054

(i) B, which makes the predominant contribution to the potential energy, increases with increasing nematic-isotropic transition temperature T_c. The nematic-isotropic transition temperature is generally regarded as a measure of the " thermal stability " of the nematic phase, as evidenced by studies on a large number of homologous series of compounds (see, e.g., Ref. 20). The relation between B and T_c shows that the strength of the orientational barrier is directly related to the thermal stability. An important point to be noted is that the degree of orientational order does not follow this relationship.

(ii) B and D are of opposite signs for all the compounds except for PAP. The significance of this result is explained by the fact that PAP is the only compound in which the anisotropy of the end group coincides with that of the molecule as a whole. The end group is known to play a significant role in the stability of the nematic phase, as evidenced, for example, by the " odd–even " effect. The asymmetry of the end group may be expected to influence D to a greater extent than B, since D depends on the dipole–quadrupole part of the dispersion forces(4) and on the repulsion forces. Thus in PAP, D adds to the total anisotropy. In the other compounds, D has the effect of reducing the anisotropy of the potential energy. We are investigating these points in greater detail with a view of finding a relation between B and D and the molecular structure.

Of the five compounds, relevant data are available for only two, PAA and PAP, for calculating the heat of transition H, specific heat and compressibility. These two cases have been discussed in detail in previous papers.(1,2) The theory also leads to a relation between the elastic coefficients and the order parameters, and yields values in very good quantitative agreement with the experimental data for these two compounds.(21)

Alben(22) has expressed the view that the excellent agreement obtained by us for the pre-transition effects in specific heat is not a proof of the validity of the theory. According to him, we have ignored an additional condition, viz.

$$\frac{\Delta V}{V} = \beta_l \left(\frac{\partial F_s}{\partial V}\right)_{Tc} \tag{7}$$

where β_l is the isothermal compressibility of the disordered system (liquid phase), thus enabling the volume change to be fitted without the use of a cluster parameter (to allow for short range order). This condition has in fact been used by us in deriving the expression for $\Delta V/V$ (see Eqs. (17) and (18) of Ref. 1). It is true that (7) can be utilized to provide an independent estimate of the cluster parameter, but we find that such an estimate only confirms the validity of our calculations. To illustrate this point we give below the theoretical heats of transition of PAA and PAP obtained by substituting the cluster parameter derived from (7).

Table 2

	H in joules/mole theoretical	 experimental
PAA	760	690(23)
		740(24)
		780(25)
		760(26)
PAP	1500	1500(23)

These values of H differ slightly from our previous values, for, as explained clearly in our papers, we chose the cluster parameter to give the best over-all fit for H, C_p and β. This was necessary because of the wide scatter in the experimental values reported by the different authors, particularly for H and β. It is easily verified that the agreement for the pre-transition effect in the specific heat remains just as satisfactory.

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REFERENCES

1. Chandrasekhar, S. and Madhusudana, N. V., *Mol. Cryst. and Liq. Cryst.* **10,** 151 (1970).
2. Chandrasekhar, S. and Madhusudana, N. V. *Acta Cryst.* **27**A, 303 (1971).
3. van der Merwe, A. J., *Z. Physik.* **196,** 212 (1966).
4. van der Merwe, A. J., *Z. Physik.* **196,** 332 (1966).
5. Chandrasekhar, S., Shashidhar, R. and Tara, N., *Mol. Cryst. and Liq. Cryst.* **10,** 337 (1970).
6. Chandrasekhar, S. and Shashidhar, R., *Mol. Cryst. and Liq. Cryst.* (in press).
7. Maier, W. and Saupe, A., *Z. Naturforsch.* **15a,** 287 (1960).
8. Krishnamurti, D. and Subramhanyam, H. S., presented at the 3rd International Liquid Crystal Conference, West Berlin (1970) (to be published in *Mol. Cryst. and Liq. Cryst.*).
9. Chatelain, P., *Acta Cryst.* **1,** 315 (1948).
10. Chatelain, P., *Bull. Soc. franc. Miner. et Crist.* **77,** 353 (1954).
11. Bauer, E. and Bernamont, J., *J. Phys. Radium.* **7,** 19 (1936).
12. Saupe, A., *Angew. Chem. Internat. Edit.* **7,** 97 (1968).
13. Chandrasekhar, S. and Madhusudana, N. V., *J. Phys. Radium.* **30,** c4–24 (1969).
14. Maier, W. and Markau, K., *Zeit. fur Physik. Chem.* **28,** 190 (1961).
15. Conrat, F., *Physik Z.* **10,** 202 (1909).
16. Porter, R. S. and Johnson, J. F., *J. Appl. Phys.* **34,** 51 (1963).
17. Madhusudana, N. V., Shashidhar, R. and Chandrasekhar, S., *Mol. Cryst. and Liq. Cryst.* **13,** 61 (1971).
18. Glarum, S. H. and Marshall, J. H., *J. Chem. Phys.* **44,** 2884 (1966).
19. Rowell, J. C., Phillips, W. D., Melby, L. R. and Panar, M., *J. Chem. Phys.* **43,** 3442 (1965).
20. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals,* Academic Press, London and New York (1962).
21. Chandrasekhar, S., Madhusudana, N. V. and Shubha, K., *Acta Cryst.* (in press).
22. Alben, R., *Mol. Cryst. and Liq. Cryst.* **13,** 193 (1971).
23. Arnold, H., *Z. Phys. Chem.* **226,** 146 (1964).
24. Barrall, E. M., Porter, R. S. and Johnson, J. F., *J. Phys. Chem.* **71,** 895 (1967).
25. Sakevich, N. M., *Izz. Vyssh. Ucheb. Zavedi Fiz.* **10,** 52 (1967).
26. Chow, L. C. and Martire, D. E., *J. Phys. Chem.* **73,** 1127 (1969).