

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### A simple molecular theory of double reentrance exhibited by highly polar compounds

N. V. Madhusudana<sup>a</sup>; Jyotsna Rajan<sup>a</sup>

<sup>a</sup> Raman Research Institute, Bangalore, India

**To cite this Article** Madhusudana, N. V. and Rajan, Jyotsna(1990) 'A simple molecular theory of double reentrance exhibited by highly polar compounds', *Liquid Crystals*, 7: 1, 31 – 40

**To link to this Article:** DOI: 10.1080/02678299008029191

**URL:** <http://dx.doi.org/10.1080/02678299008029191>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## A simple molecular theory of double reentrance exhibited by highly polar compounds

by N. V. MADHUSUDANA and JYOTSNA RAJAN  
Raman Research Institute, Bangalore 560080, India

(Received 15 December 1988; accepted 12 July 1989)

We show by simple model calculations that dipole-induced dipole and inter-chain interactions lead to a *parallel* alignment of molecules with strong longitudinal dipoles for intermolecular separations below a certain value. On the other hand an antiparallel alignment is favoured for larger separations because of dipole–dipole interactions. We incorporate this change in the intermolecular configuration, which naturally leads to two ‘lengths’ in the problem, in developing a simple McMillan type molecular theory of the double reentrance phenomenon in which the following phase sequence is observed on cooling the sample: isotropic–nematic–smectic  $A_d$ –reentrant nematic–smectic  $A_1$ . The calculated properties including the phase diagram are in broad agreement with experimental trends.

### 1. Introduction

Since the discovery of the phenomenon of reentrance in liquid crystals by Cladis [1] a large number of pure compounds have been found to exhibit one or more reentrant phases [2–5]. In particular, we consider homologous series in which the molecules are tri- (or in a few cases [6] tetra-) aromatic, having the highly polar nitrile group at one end, an alkyl chain at the other, and with the dipole moment of at least one of the bridging groups being parallel to that of the nitrile group (see fig. 1 for a typical structure). It is often found that one or two homologues (with 7 to 10 carbon atoms in the chain) exhibit the following sequence of phases as the temperature is lowered [3–5]

isotropic–nematic–smectic  $A_d$ –nematic–smectic  $A_1$ .

The higher temperature smectic phase indicated by the symbol  $A_d$  has a ‘partial bilayer’ structure with a layer spacing  $d$  which is incommensurate with the molecular length  $l$ . Usually  $d \simeq 1.4l$ . The reentrant smectic phase indicated by  $A_1$  has  $d \simeq l$  [7].

There have been a number of attempts to account for the reentrant phases in such compounds in terms of molecular theories [8–17]. However, none of them appears to have taken into account all the important contributions to the intermolecular potential in such compounds. In this paper, we demonstrate that such a calculation leads to a natural explanation of the sequence of phases mentioned above.

### 2. The theoretical model

The electrostatic interaction between the strongly dipolar nitrile groups of neighbouring molecules favours an antiparallel orientation between them [18]. The aromatic moieties of the molecules have large polarizabilities and the strong dispersion interaction between such moieties of neighbouring molecules leads to an antiparallel structure as shown in figure 2, i.e. the partial bilayer structure. In this configuration

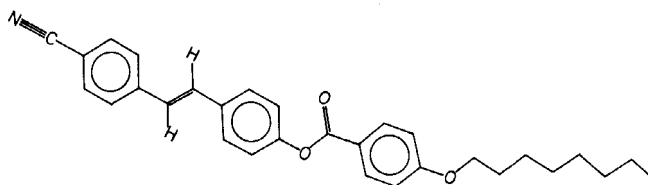


Figure 1. The molecular structure of octyloxybenzoyloxy cyano-stilbene (T8) the prototype compound exhibiting double reentrance.

the effective dipole moment of the molecule is enhanced, as the induced dipole moment due to the field created by the nitrile group of a neighbour is parallel to the permanent dipole moment of the nitrile group of the given molecule. On the other hand, the chains are so far apart that the dispersion interaction between the chains of the two neighbours is negligibly small.

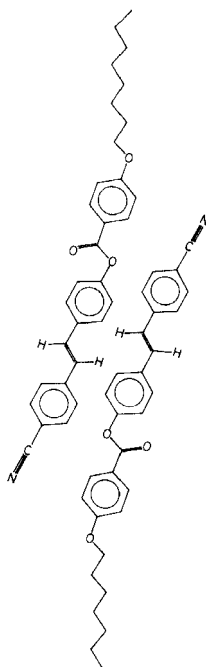


Figure 2. The antiparallel configuration of two T8 molecules favoured at intermediate inter-molecular separations.

Let us now consider a parallel configuration of the pair of molecules as shown in figure 3. The dispersion interaction energy between the aromatic moieties can be taken to be the same as before, but that between the chains adds to the total attractive potential. On the other hand, the dipolar interaction is repulsive, but the effective dipole moment itself is considerably reduced as the induced dipole due to a neighbouring nitrile group is antiparallel to the permanent dipole of the given molecule. As both the dipole-induced dipole and dispersion interactions vary at  $1/r^6$  where  $r$  is the intermolecular separation, while the permanent dipole-permanent dipole interaction is  $\propto 1/r^3$ , the 'parallel' configuration can in principle be favoured at smaller values of  $r$ . Indeed writing the 'configurational' parts of the interaction energy in the

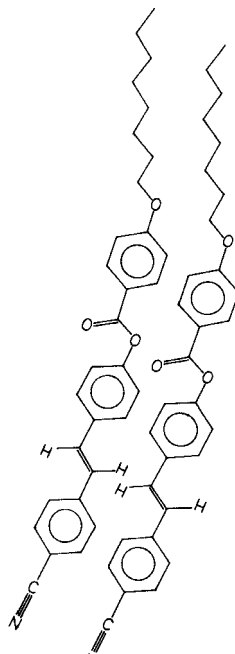


Figure 3. The parallel configuration of two T8 molecules favoured at relatively low values of intermolecular separation.

antiparallel ( $\uparrow\downarrow$ ) and parallel ( $\uparrow\uparrow$ ) orientations as

$$E_{\uparrow\downarrow} = -\mu_{\text{net}}^2/r^3$$

and

$$E_{\uparrow\uparrow} = \mu_{\text{net}}^2/r^3 - C/r^6 \quad (1)$$

where  $\mu_{\text{net}} = \mu_{\text{perm}} + \mu_{\text{induced}}$  and  $C$  is the coefficient of the dispersion interaction between the chains,  $\mu_{\text{net}} = \mu_{\text{perm}}/(1 \mp \chi/r^3)$  where  $\chi$  is the longitudinal component of the polarizability of the part of the core which is close to the dipole of the neighbour, the negative and positive signs corresponding to the antiparallel (A-type) and parallel (P-type) configurations respectively. If  $\mu_{\text{perm}} = 4$  Debyes,  $C = 6.6 \times 10^{-76}$  SI units and  $\chi = 20 \text{ \AA}^3$ , we find that while the A configuration is favoured for  $r > 5.05 \text{ \AA}$ , the P configuration has a lower energy for a range of values of  $r < 5.05 \text{ \AA}$ .

In the nematic liquid crystal it is more realistic to assume that each molecule interacts with many neighbours. If the molecules are assumed to form a 2 dimensional hexagonal lattice (figure 4), it is clear that not all the nearest neighbours can be antiparallel with one another. The arrangement shown in figure 4 maximises the number of such neighbours. The potential energy of the central molecule with all the neighbours lying within nine shortest lattice spacings can be written as

$$E_{\text{A}} = \frac{-\mu_{\text{perm}}^2(1.7806)}{(1 - 1.7806\chi/r^3)^2} \frac{1}{r^3} - \frac{2.1857}{r^6} C$$

and similarly

$$E_{\text{P}} = \frac{\mu_{\text{perm}}^2(9.1752)}{(1 + 9.1752\chi/r^3)^2} \frac{1}{r^3} - \frac{6.3684}{r^6} C. \quad (2)$$

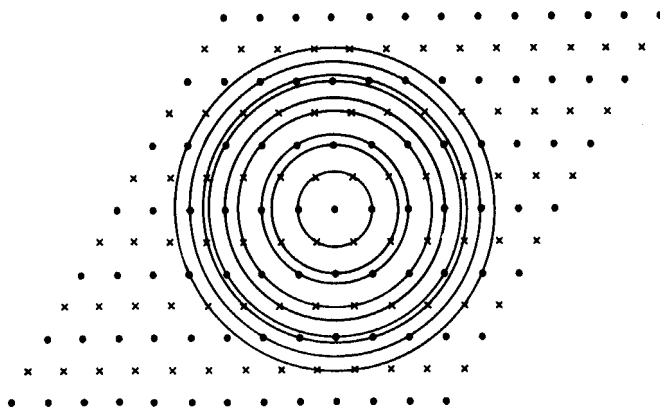


Figure 4. The two dimensional hexagonal lattice used to calculate the potential energy of the central molecule. The molecules in the two sublattices indicated by crosses and dots respectively are oriented in mutually anti-parallel orientation in the 'A' configuration while they are parallel at all lattice points in the 'P' configuration.

Using  $\mu_{\text{perm}} = 6$  Debyes,  $C = 7 \times 10^{-76}$  SI units,  $\chi = 20 \text{ \AA}^3$ , the energy difference  $\Delta E = E_A - E_P$  has been plotted as a function of  $r$  in figure 5. It is clear that once again the P configuration becomes more favourable than the A configuration below  $r \simeq 5.5 \text{ \AA}$ .

The A configuration leads to a partial bilayer arrangement (figure 2) and the P configuration to a monolayer arrangement of the molecules (figure 3). Our calculations thus lead to a molecular interpretation of the 'two lengths' concept introduced by Prost [19, 20] in developing rather successful Landau models for a variety of phase transitions exhibited by compounds with highly polar end groups [21].

In the present paper, we incorporate the dependence of the configurational energy difference  $\Delta E$  on  $r$  in developing a simple molecular statistical theory of the reentrant phases on the basis of the McMillan model. In order to simplify the theory, we make the following assumptions;

- (1) Following Kventzel *et al.* [22], we decouple the translational and orientational parts in McMillan's 'mixed' order parameter, i.e., we write it as  $\langle P_2(\cos \theta) \rangle \langle \cos(2\pi z/d) \rangle$  rather than as  $\langle P_2(\cos \theta) \cos(2\pi z/d) \rangle$  where  $P_2(\cos \theta)$  is the second Legendre polynomial,  $\theta$  the angle made by the molecular long axis with the director,  $z$  the coordinate of the molecular centre along the direction of the layer normal and  $d$  the layer thickness.
- (2) The density and hence the intermolecular separation can be expected to be monotonic functions of temperature. We can then write

$$\Delta E = R_1 k T_{\text{NI}} (R_2/T_r - 1), \quad (3)$$

where  $R_1 k T_{\text{NI}}$  is an interaction parameter expressed in terms of the nematic-isotropic transition temperature  $T_{\text{NI}}$  and  $k$  the Boltzmann constant.  $R_2$  is the reduced temperature  $T_r = T/T_{\text{NI}}$  at which the intermolecular separation  $r$  takes a value such that  $\Delta E = 0$  (see figure 5). In this paper we ignore the density dependence of the orientational and translational potentials.

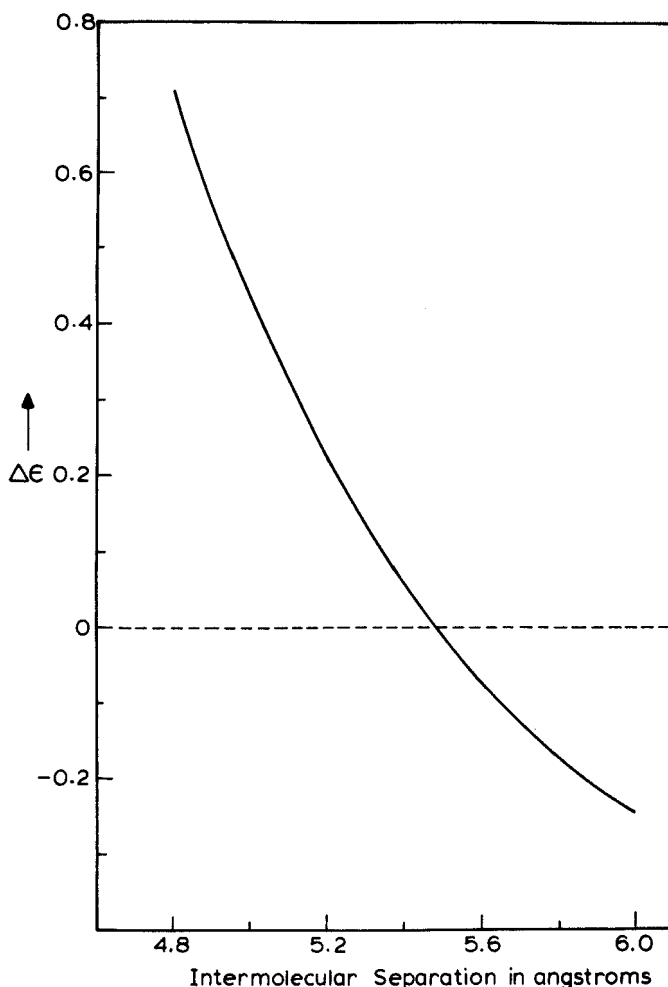


Figure 5. The difference  $\Delta E = E_A - E_P$  in the potential energy of a molecule in the antiparallel and parallel lattices (in  $10^{-19}$  J).

- (3) The Maier-Saupe potential  $u_0$  (see equation 4) is assumed to be the same for both A-type and P-type configurations.
- (4) We assume that the system is made up of *pairs* of molecules which have either a P type (figure 3) or A type (figure 2) of configuration. While 'frustration effects' can be expected to lead to the formation of antiparallel pairs, there is no such reason to limit the parallel configuration to just two molecules. However the assumption of pairs drastically simplifies the statistical treatment of the problem.  $\Delta E$  given by equation (3) would then represent the configurational energy difference between 'effective' pairs with the two possible mutual orientations.
- (5)  $R_2$  of equation (3) can be expected to depend weakly on the chain length in a homologous series. We ignore this dependence and use the same parameters for all the homologues in a series, i.e. for different values of the McMillan parameter  $\alpha$ .

We can now write in the mean field approximation the molar internal energy  $U$  of the system as

$$2U = \frac{-u_0 N}{2} [(x_a S_a + x_p S_p)^2 + \alpha_a x_a^2 S_a^2 \tau_a^2 + \alpha_p x_p^2 S_p^2 \tau_p^2 + 2\alpha_e x_a x_p S_a S_p \tau_a \tau_p] - x_p N \Delta E, \quad (4)$$

where  $x_a$  and  $x_p$  are the mole fractions of the A-type and P-type of pairs respectively,  $S_a$  and  $S_p$  the corresponding orientational order parameters and  $\tau_a$  and  $\tau_p$  the translational order parameters respectively and the factor 2 on the left hand side arises from the fact that the medium is assumed to consist of molecular pairs. The McMillan parameter for the antiparallel configuration is

$$\alpha_a = 2 \exp \{ -[\pi r_0 / (r_0 + 2c)]^2 \}, \quad (5)$$

where  $r_0$  and  $c$  are the lengths of the aromatic and chain moieties of the molecule respectively. For the parallel configuration we have

$$\alpha_p = 2 \exp \{ -[\pi r_0 / (r_0 + c)]^2 \}, \quad (6)$$

which is obviously related to  $\alpha_a$ , and  $\alpha_e$  is the parameter for the interaction of 'A' and 'P' types of pairs in the layers. We have assumed in the present paper that  $\alpha_e = (\alpha_a + \alpha_p)/2$ . The order parameters are given by

$$S_a = \int_0^1 P_2(\cos \theta) f_{a0} d(\cos \theta), \quad (7)$$

where  $f_{a0}$  the normalized orientational distribution function corresponding to the A type of configuration is given by

$$f_{a0} = \frac{\exp[(u_0/kT)\{x_a S_a(1 + \alpha_a \tau_a^2) + x_p S_p(1 + \alpha_e \tau_a \tau_p)\}P_2(\cos \theta)]}{\int_0^1 \exp[(u_0/kT)\{x_a S_a(1 + \alpha_a \tau_a^2) + x_p S_p(1 + \alpha_e \tau_a \tau_p)\}P_2(\cos \theta)]}, \quad (8)$$

$$\tau_a = \int_{-1/2}^{1/2} \cos(2\pi z') f_{at} dz', \quad (9)$$

where the reduced coordinate  $z' = z/d_a$  and the translational distribution function

$$f_{at} = \frac{\exp[(u_0/kT)\{x_a \alpha_a S_a^2 \tau_a + x_p \alpha_e S_a S_p \tau_p\} \cos(2\pi z')]}{\int_{-1/2}^{1/2} \exp[(u_0/kT)\{x_a \alpha_a S_a^2 \tau_a + x_p \alpha_e S_a S_p \tau_p\} \cos(2\pi z')] dz'}. \quad (10)$$

The order parameters  $S_p$  and  $\tau_p$  are obtained by interchanging the suffixes 'a' and 'p' in equations (7) to (10). The molar entropy  $S$  is given by

$$2S = -Nk \left[ x_a \int f_a \ln f_a + x_p \int f_p \ln f_p \right] - Nk(x_a \ln x_a + x_p \ln x_p), \quad (11)$$

where  $f_a = f_{a0} f_{at}$ , etc.

The molar free energy

$$F = U - TS. \quad (12)$$

The equilibrium value of  $x_a$  is obtained by imposing the condition  $\partial F / \partial x_a = 0$ . In the Maier-Saupe model  $u_0/kT_{N1} \approx 4.541$ . We use this relationship to eliminate  $u_0$  and

make all calculations as functions of the reduced temperature  $T_r = T/T_{NI}$ . We are then left with three parameters, viz.,  $R_1$ ,  $R_2$  and  $\alpha_a$ , the latter varying along a homologous series. At any given  $T_r$  we look for solutions with

- (i)  $S_a \neq S_p \neq 0$ ;  $\tau_a \neq \tau_p \neq 0$  (smectic phase)  
 (ii)  $S_a = S_p \neq 0$ ;  $\tau_a = \tau_p = 0$  (nematic phase)

In the computations we initially assume some values of  $S_a$ ,  $S_p$ ,  $\tau_a$ ,  $\tau_p$  and  $x_a$ , and check equations (7), (9), etc. for self-consistency. The integrals are evaluated by 32-point gaussian quadrature in double precision. The order parameters are adjusted by an iterative process to get self-consistent solutions for all of them, while scanning  $x_a$  in small steps between 0 and 1. We usually find more than one set in which  $x_a$  also has a self-consistent value. The stable solution corresponds to the one with the lowest value of the free energy given by equation (12). A phase transition occurs at some value of  $T_r$  when the free energies of two stable phases become equal.

### 3. Results and discussion

We illustrate the results for  $R_1 = 10$  and  $R_2 = 0.8$  which are consistent with the parameters used in calculations shown in figure 5. The main points are listed below:

- (1) The phase diagram is shown in figure 6. for  $\alpha_a < 0.902$  there is a direct transition from a smectic phase rich in the P type of pairs, i.e., the  $A_1$  phase, to the nematic phase.
- (2) For  $0.902 < \alpha_a < 1.088$ , we get the double reentrant behaviour. As the temperature is raised, the A type of configuration builds up and the corresponding layering interaction parameter  $\alpha_a$  is higher than  $\alpha_p$  since the A type of configuration (see figure 2) can separate the aromatic cores more efficiently into layers than the 'P' type of configuration (figure 3). However, the thermal energy is too large for the smectic A phase to appear again for  $\alpha_a < 0.902$ . For higher values of  $\alpha_a$ , the layering interactions can overcome the thermal energy if the mole fraction  $x_a$  of the A type of pairs is sufficiently large. For  $0.902 < \alpha_a < 1.088$  the reentrant nematic phase intervenes between the  $A_d$  and  $A_1$  phases since the layering interaction is not strong enough to form a smectic phase till the relative temperature is sufficiently high. On the other hand, when  $\alpha_a > 1.088$ , the  $A_1$  phase gradually goes over to the  $A_d$  phase without the intervention of the reentrant nematic phase. The double reentrant behaviour is seen only in a relatively narrow range of  $\alpha_a$  values, i.e. in a few homologues, as is found in experiments [4–6].
- (3) The temperature variations of all the four order parameters are shown in figure 7 for  $\alpha_a = 1.0$ . All the three AN transitions in this case are first order in nature. The theory predicts a decrease in the orientational order as the temperature is lowered across the  $A_d$ -reentrant nematic (RN) transition point. There is an experimental evidence for this trend [23].
- (4) The layer spacing in the smectic phase can be defined as the following average of the lengths of the two types of configurations

$$d = x_a(r_0 + 2c) + x_p(r_0 + c). \quad (14)$$

The calculated temperature variations of both  $x_a$  and  $d$  are shown in figure 8. We have assumed that  $r_0 = 14 \text{ \AA}$ , the value of  $c$  being then determined by the value of  $\alpha_a$  (see equation 5). The variations of the layer spacing in both the  $A_d$



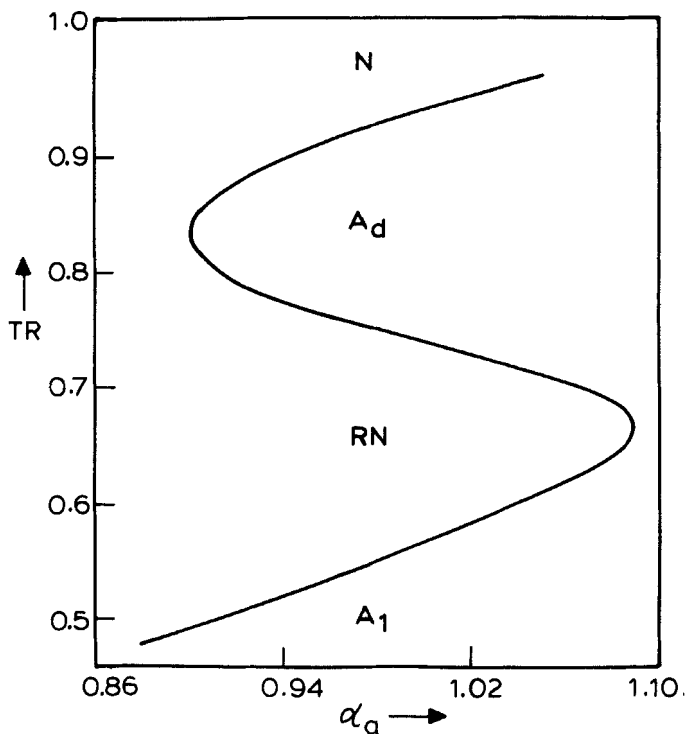


Figure 6. Calculated phase diagram for  $R_1 = 10$ ,  $R_2 = 0.8$ .

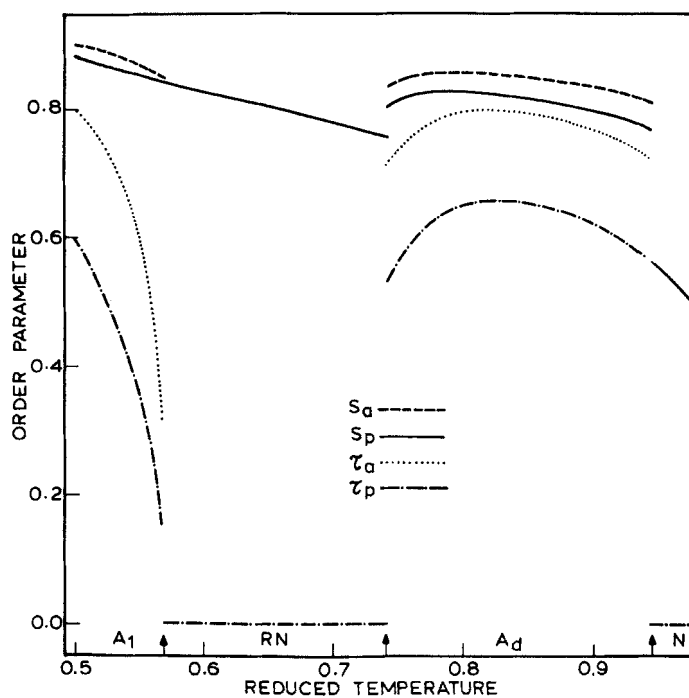


Figure 7. Temperature dependences of the order parameters for  $\alpha_a = 1.0$  in the different smectic A and nematic phases.

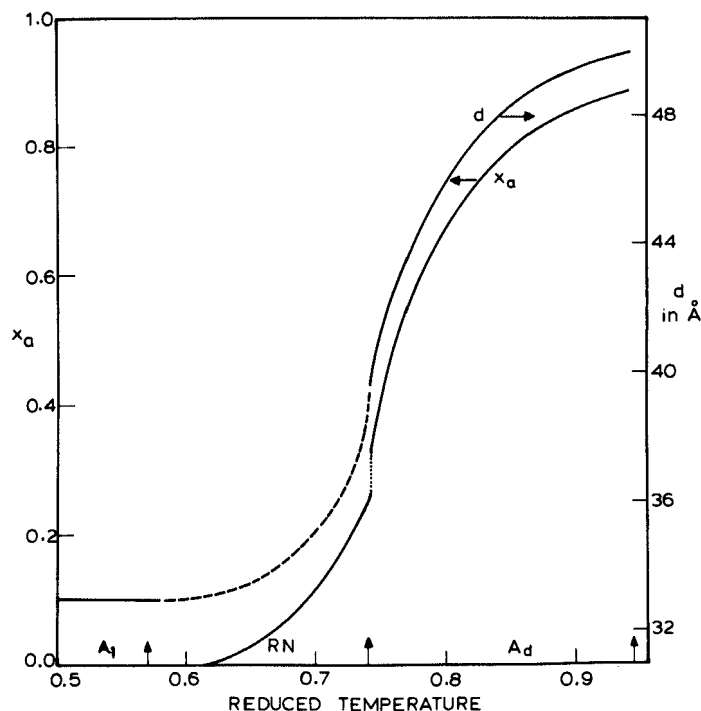


Figure 8. Temperature variations of the mole fraction  $x_a$  of the molecules in the antiparallel configuration and the layer spacing  $d$  calculated using equation (14). The dashed line in the reentrant nematic phase can be taken to represent the  $d$  values of the smectic like short range order.

and  $A_1$  phases as well as that of the short range smectic order in the reentrant nematic phase are in broad agreement with experimental trends [7].

- (5) The  $A_d$ -N boundary for  $\alpha_a$  values just above 0.902 has a 'parabolic' shape (see figure 6) as seen in experiments [24]. Further, the axis of this 'parabola' is horizontal, i.e. parallel to the nematic-isotropic phase boundary which is also in accord with experimental results [25, 26].
- (6) The reentrant nematic (RN)-A boundary for values of  $\alpha_a$  just lower than 1.088 also has a 'parabolic' shape with its axis horizontal. Though this trend is seen in some experimental phase diagrams of mixtures [27] there is no clear experimental evidence for this trend in a homologous series [4-6].

There is some experimental evidence that the  $A_1$  phase has parallel molecules rather than for example a random distribution of the head to tail molecular orientations in a monolayer. In the very first X-ray study of  $T_8$  the prototype compound exhibiting double reentrance, diffuse spots indicating a lateral spacing  $\approx 70$  Å were found in the  $A_1$  phase. The cross sections of the aromatic and aliphatic parts are known to be different and hence the layers in the  $A_1$  phase would get curved if all the molecules orient in the same direction. The layering arrangement can be preserved if neighbouring groups of an appropriate number of molecules orient in opposite directions.

Thus, dipole-induced dipole and interchain interactions appear to play an important role in the occurrence of the double reentrance phenomenon. We may note here that such a phase sequence has not been observed when the molecular core is non-aromatic.

We are now extending the calculations to include the dependence of the interaction energy on the intermolecular separation.

We are indebted to Professor S. Chandrasekhar for many valuable suggestions. Our thanks are due to Dr. G. S. Ranganath for some comments.

### References

- [1] CLADIS, P. E., 1975, *Phys. Rev. Lett.*, **35**, 48.
- [2] MADHUSUDANA, N. V., SADASHIVA, B. K., and MOODITHAYA, K. P. L., 1979, *Curr. Sci.*, **48**, 613.
- [3] HARDOUIN, F., SIGAUD, G., ACHARD, M. F., and GASPAROUX, H., 1979, *Solid State Commun.*, **30**, 265.
- [4] HEPPKE, G., HOPF, R., KOHNE, B., and PRAEFCKE, K., 1981, *Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon), p. 141.
- [5] TINH, N. H., GASPAROUX, H., MALTHETE, J., and DESTRADE, C., 1984, *Molec. Crystals liq. Crystals*, **114**, 19.
- [6] DABROWSKI, R., PYC, K., PRZEDMOJSKI, J., and PURA, B., 1985, *Molec. Crystals liq. Crystals*, **129**, 169.
- [7] HARDOUIN, F., and LEVELUT, A. M., 1981, *J. Phys., Paris*, **41**, 41.
- [8] LUCKHURST, G. R., and TIMIMI, B. A., 1981, *Molec. Crystals liq. Crystals*, **44**, 253.
- [9] LONGA, L., and DE JEU, W. H., 1981, *Phys. Rev. A*, **26**, 1632.
- [10] BERKER, A. N., and WALKER, J. S., 1981, *Phys. Rev. Lett.*, **47**, 1469.
- [11] INDEKU, J. O., and BERKER, A. N., 1988, *J. Phys., Paris*, **49**, 353.
- [12] KATRIEL, J., and KVENTSEL, G. F., 1985, *Molec. Crystals liq. Crystals*, **124**, 179.
- [13] DOWELL, F., 1985, *Phys. Rev. A*, **31**, 3214.
- [14] DOWELL, F., 1987, *Phys. Rev. A*, **36**, 5046.
- [15] HIDA, K., 1981, *J. phys. Soc. Jap.*, **50**, 3869.
- [16] MIRANTSEV, L. V., 1986, *Molec. Crystals liq. Crystals*, **133**, 151.
- [17] BOSE, T. R., MUKHERJEE, C. D., ROY, M. K., and SAHA, M., 1985, *Molec. Crystals liq. Crystals*, **126**, 197.
- [18] MADHUSUDANA, N. V., and CHANDRASEKHAR, S., 1973, *Pramana Supplement*, **1**, 57.
- [19] PROST, J., 1979, *J. Phys., Paris*, **40**, 581.
- [20] PROST, J., 1980, *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag), p. 125.
- [21] BAROIS, P., PROST, J., and LUBENSKY, T. C., 1985, *J. Phys., Paris*, **46**, 391.
- [22] KVENTSEL, G. F., LUCKHURST, G. R., and ZWENDIE, H. B., 1985, *Molec. Phys.*, **56**, 589.
- [23] CHEN, N. R., HARK, S. K., and HO, J. T., 1981, *Phys. Rev. A*, **24**, 2843.
- [24] HEPPKE, G., 1980, *Liquid Crystals*, edited by S. Chandrasekhar (Heyden), p. 147.
- [25] RAGHUNATHAN, V. A., SUBRAHMANYA RAJ Urs, M., and MADHUSUDANA, N. V., 1985, *Molec. Crystals liq. Crystals*, **131**, 9.
- [26] SHASHIDHAR, R., SOMASEKHARA, S., and RATNA, B. R., 1986, *Molec. Crystals liq. Crystals*, **133**, 19.
- [27] TINH, N. H., SIGAUD, G., ACHARD, M. F., GASPAROUX, H., and HARDOUIN, F., 1981, *Advances in Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon), p. 147.