Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Theoretical Investigation of the Lattice of Symmetric and Asymmetric Rigid Rods with Anisotropic Dispersion Forces and Rigid Body Repulsions

N. C. Shivaprakash [a] & J. Shashidhara Prasad [a]
[a] Department of Physics, University of Mysore, Mysore, 570 006, India
Version of record first published: 14 Oct 2011.

To cite this article: N. C. Shivaprakash & J. Shashidhara Prasad (1981): A Theoretical Investigation of the Lattice of Symmetric and Asymmetric Rigid Rods with Anisotropic Dispersion Forces and Rigid Body Repulsions, Molecular Crystals and Liquid Crystals, 74:1, 215-226

To link to this article: http://dx.doi.org/10.1080/00268948108073707

Mol. Cryst. Liq. Cryst., 1981, Vol. 74, pp. 215–226
0026-8941/81/7404-0215 $06.50/0

Printed in the United States of America

A Theoretical Investigation of the Lattice of Symmetric and Asymmetric Rigid Rods with Anisotropic Dispersion Forces and Rigid Body Repulsions†

N. C. SHIVAPRAKASH and J. SHASHIDHARA PRASAD
Department of Physics, University of Mysore, Mysore 570 006, India

(*Received July 31, 1980; in final form February 9, 1981*)

The method of symmmetry breaking potential and first order cluster expansion technique for the partition functions adopted for the theory of ordering in liquid crystals has been extended to symmetric and asymmetric molecules. The order parameter is calculated as a function of temperature and packing coefficient as a function of chainlength for homologous series of liquid crystals having symmetric and asymmetric molecules. The theoretical calculations account fairly well for the gradient differences in the order parameters of symmetric and asymmetric molecules and packing coefficients.

INTRODUCTION

Two types of mechanisms have been described for orientational order of molecules in liquid crystals viz., ordering due to the anisotropic part of dispersion forces between rod-like molecules as described for the first time by Maier and Saupe[1] and rigid body repulsive interactions first described by Onsager.[2]

Maier and Saupe have found in a molecular field approximation, a first order phase transition between ordered (nematic) and isotropic phases at certain temperature T_c. This has been further confirmed by Lebwohl and Lasher[3] and by Kimura.[4] Onsager has used a second order virial expansion method and has shown a first order transition from an isotropic to a denser anisotropic (nematic) phase. The qualitative conclusions of Onsager have been arrived at by different approaches by various workers.[5-10] It is believed that these mechanisms play an important role in real liquid crystals.[11-13]

† Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

It is observed from several experimental studies on the orientational order parameter of mesogenic materials that there is a difference in the rate of variation of S factor with temperature for symmetric and asymmetric molecules. This factor has not been explained by the earlier theories on ordering of liquid crystals.

In view of this, we discuss the mesogenic ordered state of the system of rod-like molecules considering both the anisotropic dispersion and rigid body repulsion along with an additional force which destroys order when there is asymmetry for the rigid rod-like molecules under consideration. The method of symmetry breaking potential has been employed for the calculation.[14,15]

CALCULATION OF ORDER PARAMETER

Consider a system of N molecules of rigid spherocylinders having cylindrical length l radius r. For such molecules length $L = l + 2r$ and diameter $D = 2r$. The interaction potential φ_{ij} between molecules i and j is assumed as

$$\varphi_{ij} = \begin{cases} -\infty \text{ if molecules } i \text{ and } j \text{ intersect} \\ -a(r_{ij})P_2(\cos\theta_{ij}) + b(r')P_2(\cos\theta_i) \text{ otherwise} \end{cases} \tag{1}$$

where $a(r_{ij}) \alpha r_{ij}^{-6}$ is the coefficient indicating the strength of the anisotropic part of dispersion force and r_{ij} is the distance between the centers of molecules. $b(r')$ takes account of strength of the torque which depends on the distance (r') between the center of gravity of the rigid rod-like molecule and the geometric center of the molecule. The length and asymmetry of the alkyl chains determine the dispersive forces and the off set between the geometrical molecular center and the molecular center of gravity which significantly affect the translational displacement ability of the molecules.[16] Also it is known from X-ray diffraction analysis of mesogenic homologous series[17-19] that the anisotropic thermal vibration of the molecules increase with the increase in the length of the alkyl chains. This splay motion of the alkyl chain will contribute to the reduction of anisotropic part of the dispersion forces if the molecule is asymmetric and has no effect if the molecule is symmetric. As written, the term $b(r')$ represents an interaction of molecule i with the mean molecular field and determines the amount by which the aligning force is reduced by the asymmetry of molecules. However, for convenience it is still taken in the interaction between two molecules as an additional parameter along with the factor $a(r_{ij})$ and it would inhibit alignment of molecules and hence contributes to the repulsive part of the potential that tends to reduce the alignment. $P_2(\cos\theta_{ij})$ is the second order legendre polynomial and θ_{ij} is the angle between the axes of the molecules. If we neglect the size of the molecule, the potential is reduced to

that of Maier and Saupe, on the other hand, letting $a(r_{ij}) = b(r') = 0$ we obtain a rigid rod model similar to that employed by Onsager.

Let η be the strength of the potential and θ_i be the angle between the long axis of molecule i and a certain fixed direction, namely the nematic axis, then the following "symmetry-breaking potential" can be introduced

$$kT\eta \sum_i P_2(\cos\theta_i). \tag{2}$$

The order parameter S characterizing the nematic phase is defined as

$$S = \frac{1}{N} \sum_i P_2(\cos\theta_i). \tag{3}$$

Our task now is to calculate the partition function

$$Z(\eta) = \int \cdots \int dr^N d\Omega^N \exp\left\{\eta \sum_i P_2(\cos\theta_i) - \frac{1}{kT} \sum_{i>j} \varphi_{ij}\right\}, \tag{4}$$

where the integral is made over both the configurations and orientations of molecules. The orientation of a molecule i, is indicated by Ω_i; this is a set of the Eulerian angles $(\theta_i, \varphi_i, \psi_i)$ referring to the coordinate system of which the polar axis is taken to be parallel to the nematic axis and $d\Omega_i = \sin\theta_i d\theta_i d\varphi_i d\psi_i$. The interaction potential φ_{ij} can be expressed in terms of Mayer f factors as

$$f_{ij} = \exp(-\varphi_{ij}/kT) - 1. \tag{5}$$

By expanding the exponential to the first order, one gets the values for f factors as

$$f_{ij} = \begin{cases} -1 \text{ if molecules } i \text{ and } j \text{ intersect} \\ [a(r_{ij})P_2(\cos\theta_{ij})/kT] - (b(r')P_2(\cos\theta_i)/kT) \end{cases} \tag{6}$$

Expanding (4) to the first order in the f factors, we obtain

$$Z(\eta) = \{(2\pi)^2 V I_0\} N \left[1 + \left\{\frac{1}{2N(2\pi)^4 I_0^2}\right\} \iint d\Omega_i d\Omega_j \times \left\{-v(\theta_{ij})n + \frac{az}{kT} P_2(\cos\theta_{ij}) - \frac{bz}{kT} P_2(\cos\theta_i)\right\} \exp\{\eta[P_2(\cos\theta_i) + P_2(\cos\theta_j)]\}\right]. \tag{7}$$

The following result of the irreducible integral is used in obtaining (7)

$$\int f_{ij} dr_j = -v(\theta_{ij}) + \frac{az}{nkT} P_2(\cos\theta_{ij}) - \frac{bz}{nkT} P_2(\cos\theta_i), \tag{8}$$

where $v(\theta_{ij})$ is an excluded volume of a pair of molecules i and j due to the rigid body repulsion, which is given by

$$v(\theta_{ij}) = \Delta v\{|\sin\theta_{ij}| + 2\pi r/l + 8\pi r^2/3l^2\}, \tag{9}$$

where

$$v = 4r^2 = 2DL^2(1 - D/L)^2. \tag{10}$$

The second term in (8) is the result of integral over the space out of the $v(\theta_{ij})$. We have assumed that the dispersion forces are effective between only the nearest neighbor molecules. The constant "a" indicates the strength of the nearest neighbor interaction, b indicates the strength of the force that contributes to the destruction of order, z is the coordination number of molecules, $n = N/V$ is the concentration of molecules. V is the volume of system. In the Eq. (7) I_0 corresponds to

$$I_0 = 2\int_0^{\pi/2} \exp\{\eta P_2(\cos\theta)\}\sin\theta d\theta. \tag{11}$$

The evaluation of the integrations is carried out using the approximation

$$v(\theta_{ij}) \simeq (\pi\frac{\Delta v}{4})(1 - 8r/l + 32\,r^2/3l^2) - (5\pi/32)\Delta v P_2(\cos\theta_{ij}). \tag{12}$$

This can be obtained by expanding the $v(\theta_{ij})$ of Eq. (9) in the even order Legendre polynomials and retaining only terms to the second order. This is fairly a good approximation as the difference between (9) and (12) is significantly small.

The canonical average of S can be obtained as

$$S = N^{-1}\frac{\partial}{\partial\eta}[\ln z(\eta)], \tag{13}$$

and the free energy of the system as a function of the order parameter is expressed as

$$F(S) = F(0) + NkT\int_0^S \eta(S)dS \tag{14}$$

where η as a function of S is obtained by solving Eq. (13). The minimum condition for this free energy is expressed as[14]

$$\eta(S) = 0. \tag{15}$$

By putting Eq. (7) into (13), we get

$$S = \frac{I_1}{I_0} + \left(\frac{\Gamma}{2}\right) \frac{\partial}{\partial \eta} \left\{\frac{I_1}{I_0}\right\}^2, \tag{16}$$

where

$$I_1 = 2 \int_0^{\pi/2} P_2(\cos\theta) \exp\{\eta P_2(\cos\theta)\} \sin\theta d\theta \tag{17}$$

and

$$\Gamma = \frac{(a-b)z}{kT} + \left(\frac{5\pi}{32}\right) \Delta v n. \tag{18}$$

Solving (16) to the first order in Γ we obtain the expression for Eq. (15) as

$$\eta = \eta_0 - \Gamma \left(\frac{I_1}{I_0}\right)_{\eta=\eta_0} = 0, \tag{19}$$

where η_0 is a function of S defined by the relation

$$S = \left(\frac{I_1}{I_0}\right)_{\eta=\eta_0} \tag{20}$$

Equations (19) and (20) give the order parameter S as a function of Γ. By eliminating η_0 from these equations and writing explicitly the integrals in Eq. (20) we get

$$S = \frac{\int_0^{\pi/2} P_2(\cos\theta) \exp\{\Gamma S P_2(\cos\theta)\} \sin\theta d\theta}{\int_0^{\pi/2} \exp\{\Gamma S P_2(\cos\theta)\} \sin\theta d\theta}. \tag{21}$$

This equation has the identical form to the self consistent condition for the order parameter S derived by Maier and Saupe, although in their case the expression for Γ is not the same as the present. For this equation, the solutions S which minimize the free energy have been obtained. We can conclude that (a) for $\Gamma > \Gamma_c(4.38)$, the equilibrium state has the non vanishing values of S, that is an orientationally stable order whereas (b) for $\Gamma < \Gamma_c$ the order parameter S is identically vanished represents an isotropic state and (c) at $\Gamma = \Gamma_c$, value of S changes discontinuously from 0 to 0.225 and the first order phase transition occurs between the nematic and isotropic states.

The calculated values of S are indicated in Figure 1 as a function of Γ. Γ_c has the value 4.54 for PAA and this reduces to 4.38 when we introduce the asymmetry.

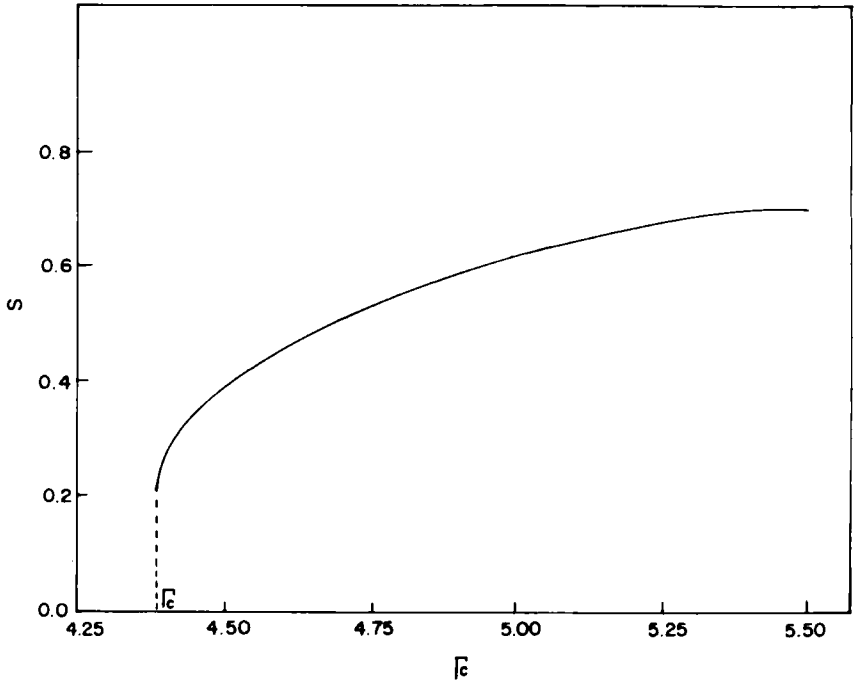

FIGURE 1 Order parameter S as a function of $\Gamma = (a - b)z/kT + (5\pi/32)\Delta vn$. Γ_0 is the critical value.

VARIATION OF ORDER PARAMETER WITH TEMPERATURE

The value of order parameter S depends on temperature only through Γ. We can obtain the variation of order parameter versus temperature using

$$\Gamma = \frac{(a - b)z}{kT} + \left(\frac{5\pi}{32}\right)\Delta vn. \tag{22}$$

We shall assume $(a - b)z = Bn^2$, where B is a constant independent of temperature and concentration. Eq. (22) becomes

$$\Gamma = \frac{Bn^2}{kT} + \left(\frac{5\pi}{32}\right)\Delta vn. \tag{23}$$

For example, let us take PAA, for which asymmetry has been introduced. Let the molecular length be 20 Å and $D = 5$ Å, using the values $T_c = 408$ K at pressure 1 bar, density $= 1.149$ gm/cm^3 at 408 K at pressure 1 bar, and molecular weight 258, we get from (22)

$$\Gamma = \frac{440.4}{T}\rho^2 + 2.5698\rho. \tag{24}$$

Assuming a linear relation between the density and temperature in the nematic phase, we can calculate Γ as a function of temperature at constant pressure 1 bar, and can find the values of S corresponding to each value of Γ from Figure 1. The calculated values of S for asymmetric and symmetric molecules ($b = 0$) are shown in Figure 2.

RESULTS AND DISCUSSION

The theoretical calculations show that the S factor drops off more rapidly in the case of asymmetric molecules than in symmetric molecules. Also when the asymmetry of the molecule increases as in the homologous series where alkyl chain is extended on only one side of the phenyl groups, the b value contribution increases, thereby making the S factor versus temperature curve steeper.

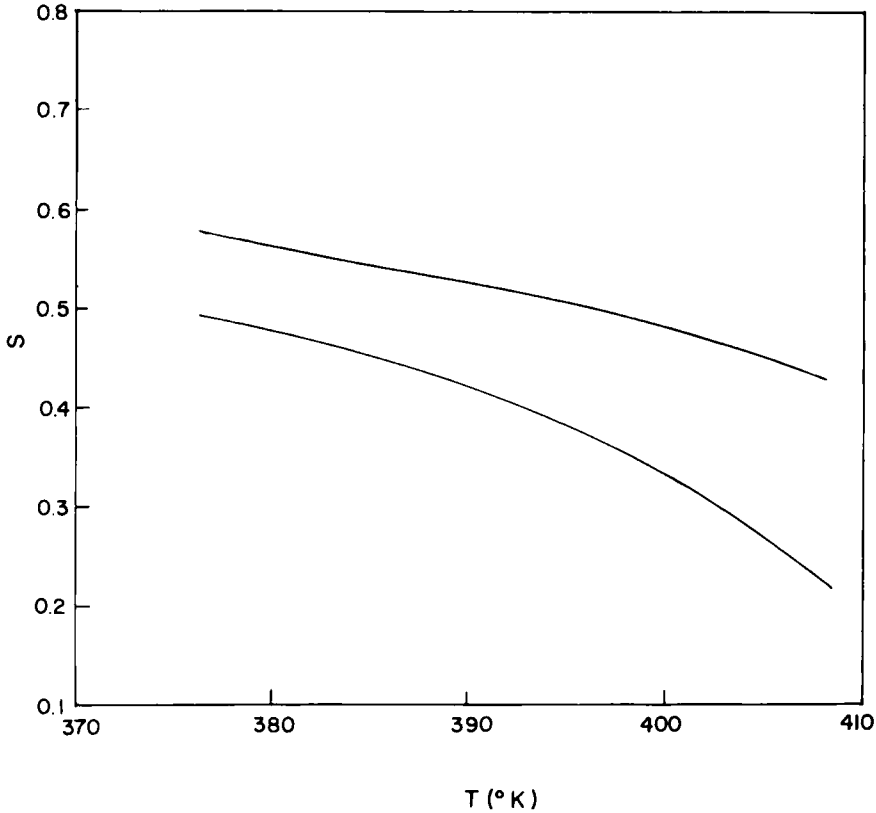

FIGURE 2 Order parameter versus temperature for *p*-azoxyanisole (PAA). For upper curve $b = 0$, and for lower curve $b \neq 0$.

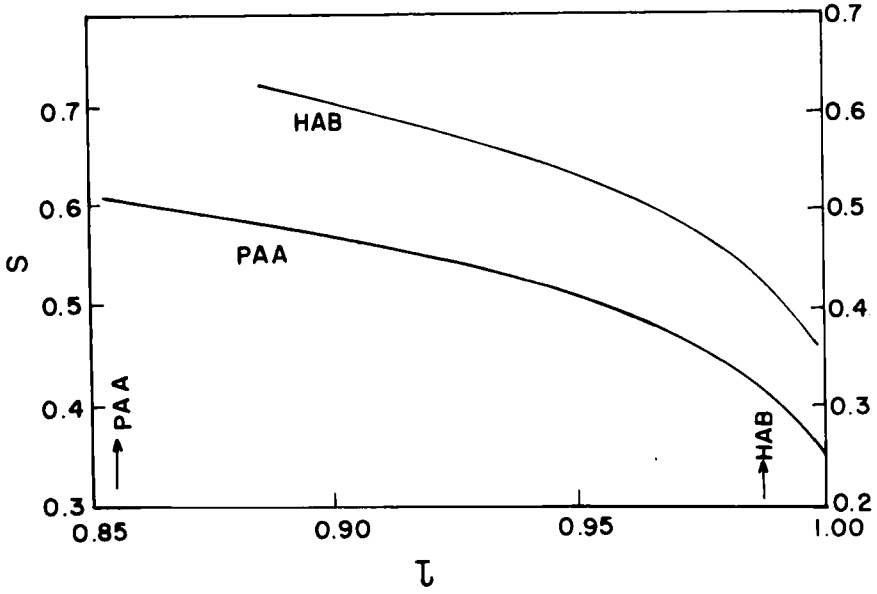

FIGURE 3 Order parameter versus reduced temperature for PAA and 4,4'-di-*n*-heptyloxyazoxy benzene.

It is found from the theory that the *S* factors at the transition temperature for asymmetric molecule should be lower than that of the symmetric molecules, when both of them have the same molecular size. Figure 3 and 4 give the plot of *S* factors, versus temperature for symmetric[20] (4,4'-di-*n*-alkyloxyazoxy benzene) and asymmetric[21] (*p*-(*p*-ethoxyphenylazo) phenyl alkanoates) molecules respectively. The experimental curves are in good qualitative agreement with the theoretical results.

The molecular packing coefficient is defined as the ratio of the geometric (van der Waals) volume of the molecule to the volume of the phase per molecule. The molecular packing coefficient has been shown to be a useful parameter when discussing the relationship between the structures and the thermal stabilities of molecular crystals. The packing coefficient has been shown to indicate the onset of new phase in mesogenic materials quite successfully. The packing coefficient increases as alkyl chain increases for symmetric homologous series[22] and decreases as alkyl chain increases for asymmetric homologous series[23,24] as shown in Figures 5 and 6. Also it shows an odd even effect. The *S* factors obtained for symmetric[20,25-27] and asymmetric[21,28] homologous series at a given temperature are plotted in Figures 7 and 8. Clearly they show exactly similar trend as observed for packing coefficients and also exhibit a strong odd-even effect. This suggests that the packing coefficient should have a meaningful relationship with the *S* factors. The increasing nature of the molecular packing coefficient for the symmetric homologous series suggests

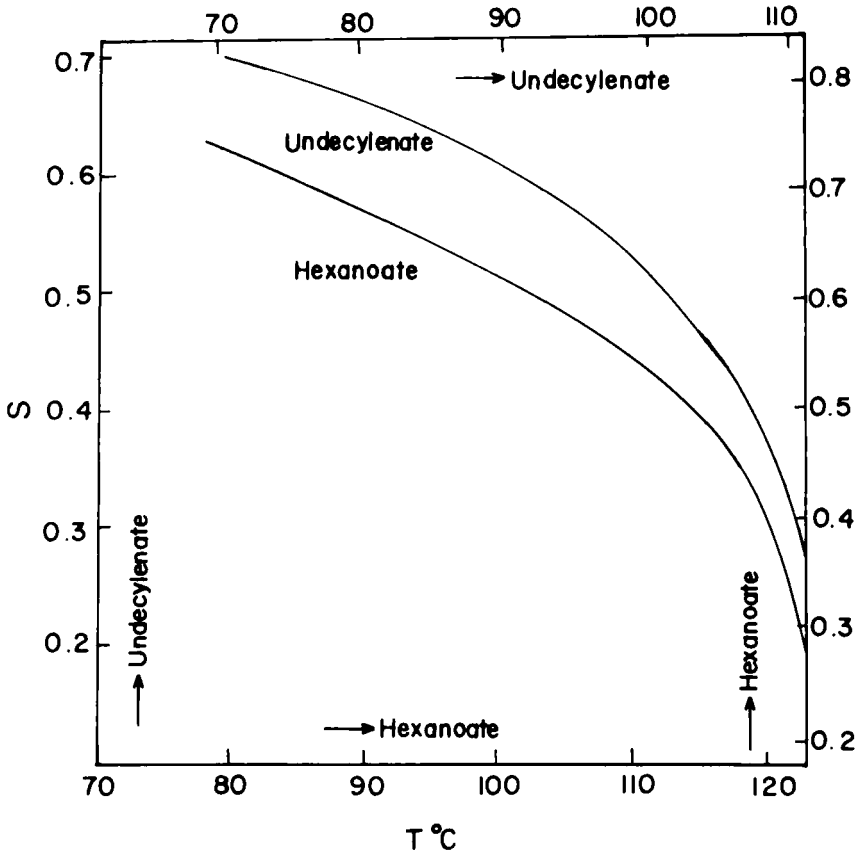

FIGURE 4 Order parameter versus temperature for *p*-(*p*-ethoxyphenylazo)phenyl hexanoate and undecylenate.

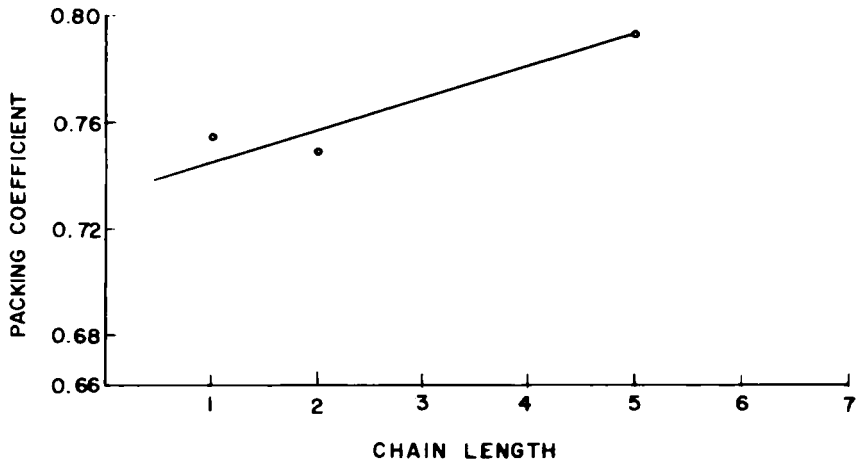

FIGURE 5 Packing coefficient versus number of carbon atoms in the alkyl chain for the homologous series 4,4′-di-*n*-alkyloxyazoxy benzene.

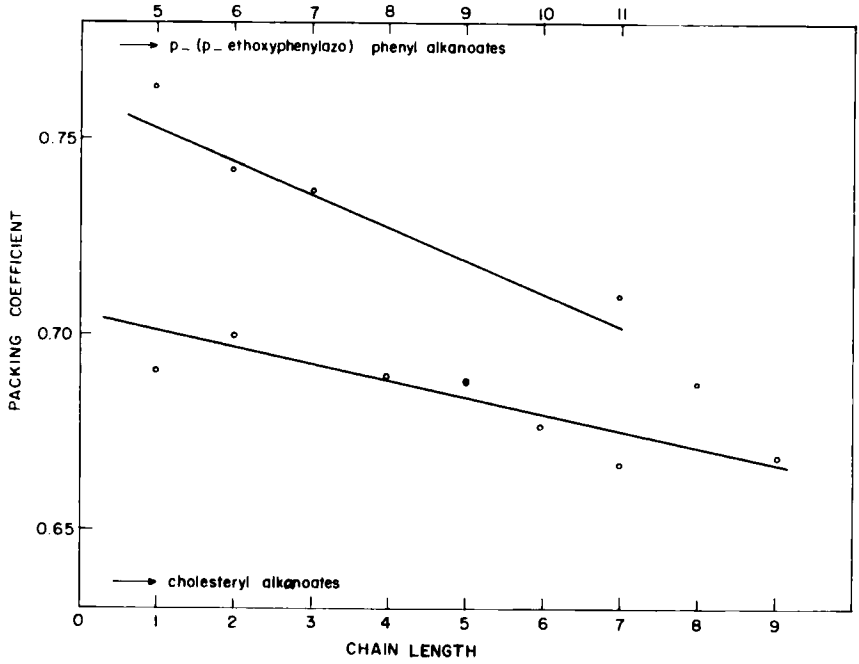

FIGURE 6 Packing coefficient versus number of carbon atoms in the alkyl chain for homologous series *p*-(*p*-ethoxyphenylazo)phenyl alkanoates (upper curve) and for the homologous series cholesteryl alkanoates (lower curve).

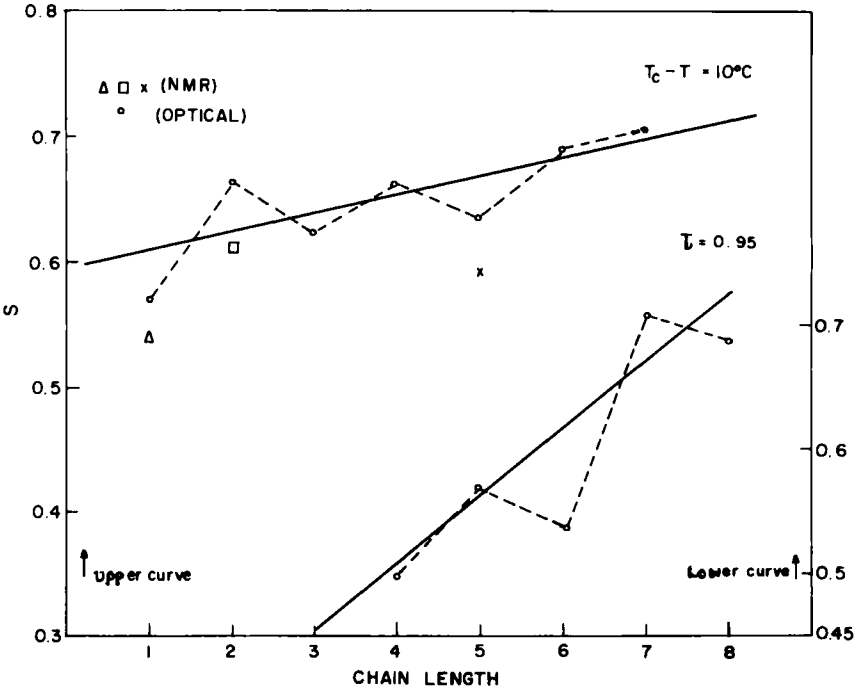

FIGURE 7 Order parameter versus number of carbon atoms in the alkyl chain for 4,4'-di-*n*-alkyloxyazoxy benzene (upper curve at $T_c - T = 10°C$) and for 4,4'-di-*n*-alkylazoxy benzene (lower curve, at τ_c (reduced temperature) = 0.95 $\tau_c = (T/T_{NI})/(v/v_{NI})^2$.

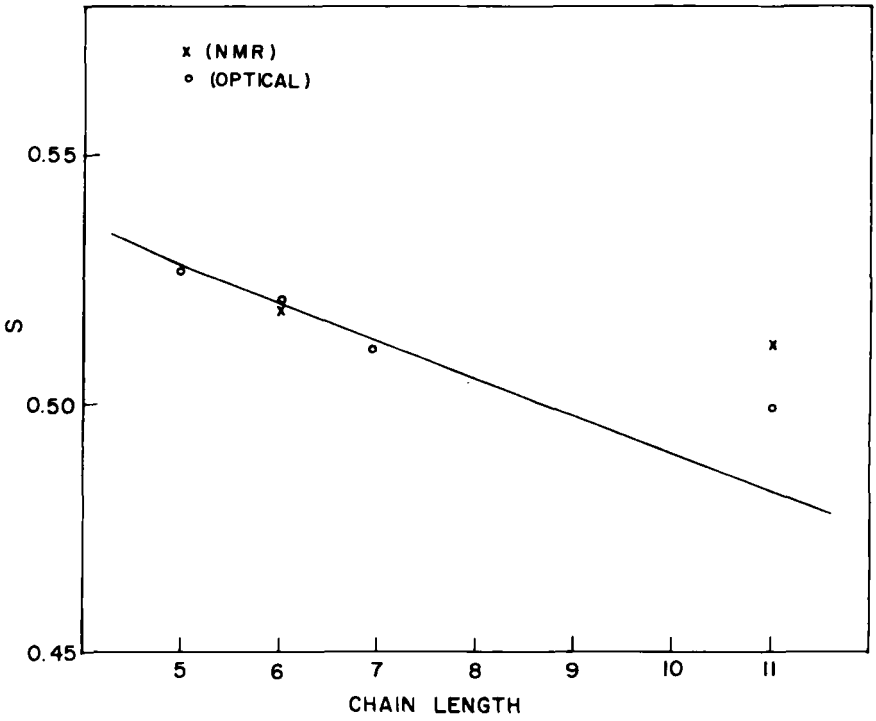

FIGURE 8 Order parameter versus number of carbon atoms in the alkyl chain for *p*-(*p*-ethoxyphenylazo) phenyl alkanoates.

stronger attractive forces i.e., increase in "*a*", which means the *S* factor should also increase. On the other hand, decrease in the packing coefficient in the asymmetric homologous series as carbon number increases suggests a decrease in the attractive forces, i.e., increase in *b*, which means a decrease in the *S* factor. This supports our assumption of an additional term *b* to account for the experimental results. In the case of a symmetric homologous series alkyl chain is extended on only one side of the central moiety, the molecule as a whole is asymmetric with respect to the central moiety whereas in the case of symmetric homologous series the side chain is extended symmetrically on both sides of the phenyl groups. A symmetric molecule will have greater tendency to be held in a particular orientation in spite of the fact that the molecular length is increased as compared to the addition of greater asymmetry into the system. Thus packing coefficient of symmetric molecules tend to increase in the beginning unlike in the case of asymmetric molecules. The tendency for a molecule to get flipped off from the mean orientation will be higher for asymmetric molecules than for symmetric molecules. Thus an *S* factor of asymmetric homologous series drops off more rapidly than that of symmetric molecules. This can be explained as the greater tendency of the symmetric

molecules to retain their orientational order as compared to asymmetric molecules when the temperature is raised.

CONCLUSION

The above study shows that the molecular packing studies of mesogenic materials in their solid state pre-determine the physical properties and molecular ordering in the mesogenic state. The orientational order parameter and the packing coefficient depend entirely upon the symmetry and asymmetry of the end chains and are not influenced by the detailed structure of the central rigid core. This is in conformity with the study of Boden *et al.*[29]

(JSP) and (NCS) thank UGC (India) for a Career Award and Senior Research Fellowship respectively.

References

1. W. Maier and A. Saupe, *Z. Naturforsch*, **14a**, 882 (1959); **15a**, 287 (1960); **16a**, 816 (1961).
2. L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).
3. P. A. Lebwohl and G. Lasher, *Phys. Rev.*, **A6**, 426 (1972).
4. H. Kimura, *J. Phys. Soc. Japan*, **35**, 1204 (1974).
5. A. Isihara, *J. Chem. Phys.*, **19**, 1142 (1951).
6. P. J. Flory, *Proc. Roy. Soc.*, **A234**, 73 (1956).
7. E. A. DiMarzio, *J. Chem. Phys.*, **35**, 658 (1961).
8. R. Zwanzig, *J. Chem. Phys.*, **39**, 1714 (1963).
9. M. A. Cotter and D. E. Martire, *J. Chem. Phys.*, **53**, 4500 (1970).
10. G. Lasher, *J. Chem. Phys.*, **53**, 4141 (1970).
11. B. Deloche, B. Cabana and D. Jerome, *Mol. Cryst. Liq. Cryst.*, **15**, 197 (1971).
12. J. R. McColl and C. S. Shih, *Phys. Rev. Lett.*, **29**, 85 (1952).
13. W. H. de Jeu, J. Van der Veen and W. J. A. Goossens, *Solid State Commun.*, **12**, 405 (1973).
14. H. Nakano and M. Hattori, *Prog. Theor. Phys.*, **49**, 1752 (1973).
15. H. Kimura, *J. Phys. Soc. Japan*, **36**, 1280 (1974).
16. R. Dabrowski, K. Kenig, Z. Raj Zewski, J. Kedzierski and K. Sadowska, *Mol. Cryst. Liq. Cryst.*, **61**, 61 (1980).
17. J. Shashidhara Prasad, *Acta Cryst.*, **B35**, 1404 (1979).
18. J. Shashidhara Prasad, *Acta Cryst.*, **B35**, 1407 (1979).
19. J. Shashidhara Prasad and N. C. Shivaprakash, *Acta Physica Polonica*, **A58**, 101 (1980).
20. W. H. de Jeu and W. A. P. Claassen, *J. Chem. Phys.*, **68**(1), 102 (1978).
21. C. L. Watkins and C. S. Johnson Jr., *J. Phys. Chem.*, **75**(16), 2452 (1971).
22. N. C. Shivaprakash, P. K. Rajalakshmi and J. Shashidhara Prasad, W. Helfrich, G. Heppke (eds): *Liquid Crystals of one and two dimensional order*. Springer Series in Chemical Physics (Springer, Berlin, Heidelberg, New York, 1980) **11**, 72 (1980).
23. J. Shashidhara Prasad and P. K. Rajalakshmi, *J. de Physique*, **40**, 309 (1979).
24. N. C. Shivaprakash, P. K. Rajalakshmi and J. Shashidhara Prasad, *Mol. Cryst. Liq. Cryst.*, **51**(3/4), 317 (1979).
25. E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **36**, 193 (1976).
26. J. Shashidhara Prasad, *Mol. Cryst. Liq. Cryst.*, **35**, 345 (1976).
27. J. C. Rowell, W. D. Phillips, L. R. Melby and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).
28. R. Somasekhar, D. Revannasiddaiah, M. S. Madhava, H. S. Subramhanyam and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **45**(3/4), 243 (1978).
29. N. Boden, R. J. Bushby and L. D. Clark, *Chem. Phys. Lett.*, **64**(3), 519 (1979).