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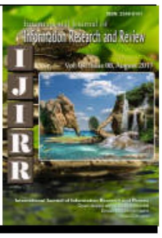

RESEARCH ARTICLE

THE STRUCTURE PROPERTY RELATIONSHIP OF A HOMOLOGOUS SERIES OF 4–ALKENYL BICYCLOHEXYLNITRILE COMPOUNDS

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ABSTRACT

The method of symmetry 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 position of double bond in alkenyl chain length for homologous series of 4–alkenyl bicyclohexylnitrile Compounds. 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 crystal: ordering due to the anisotropic part of dispersion forces between rod-like molecules as described by Maier and Saupe (Maier, 1959), and rigid body repulsive interactions described by Onsager (Onsager, 1949). According to Maier and Saupe a first order phase transition was formed between ordered (nematic) and isotropic phase at certain temperature T_c. Onsager has shown a first order transition from an isotropic to a denser anisotropic (nematic) phase on the basis of a second order virial expansion method. 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, Shivaprakash et al (Shivaprakash, 1981), calculated orientational order parameter of 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. We adopted the method of Shivaprakash et al, (Shivaprakash, 1981) and calculated orientational order parameter of the homologous Series of 4–alkenyl bicyclohexylnitrile compounds in the nematic phase. The structures have been solved (Sakuntala Gupta, 1999, 1994, 2001, 2002). Molecular packing coefficients play an important role in the design of liquid crystal devices. We adopted the formula given by Kitaigorodsky (Kitaigorodsky, 1973), to determine the packing coefficient for the homologous series of 4–alkenyl bicyclohexylnitrile.

Calculation

Packing coefficient

Molecular packing coefficient is determined as the ratio of the geometrical volume of a molecule to that of the volume per molecule in the crystal. The volume increments for atomic calculations are calculated using the following formula given by Kitaigorodsky (Kitaigorodsky, 1973).

$$V=4/3\pi R^3-1/3\pi h_i^2(3R-h_i) \qquad \text{…..…. (i)}$$

Where R is the intermolecular radius of the atom concerned and R_i's are the intermolecular radii of the atoms those are valance-bonded with this atom and are positioned at distance d_i from this atom. The height cut off segment is given by

$$h_i=R-(R^2+d_i^2-R_i^2)/2d_i \qquad \text{............. (ii)}$$

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Relevant data for packing coefficients calculation taken from the crystal structure analysis of 4 members of homologous series of 4–alkenyl bicyclohexylnitrile compounds as determined by S. Gupta et al (Sakuntala Gupta, 1999; Gupta, 1994; Sakuntala Gupta, 2002 and Sakuntala Gupta, 2001). Values of packing coefficients along with other crystallographic data are given in table 1. The compounds of this homologous series can be considered in three parts namely the alkenyl chain, the central core and the cyano group.

Orientational order parameter

We determined orientational order parameter(s) in the nematic phase of homologous series 4–alkenyl bicyclohexylnitrile Yd$_x$CC. The alkenyl double bond is denoted by as d$_x$, where x designates the position of the double bond from the nearest cyclohexyl ring. Y is the number of carbon atoms beyond the double bond. S has been calculated considering both the anisotropic dispersion and rigid body repulsion along with an additional force which destroys order when there is asymmetry in the molecules. We adopted the method of Shivaprakash et al (Shivaprakash, 1981), and calculated the order parameter from the following equations

$$S = \frac{\int P_2(\cos\theta)\,\exp.\,[\Gamma S\, P_2(\cos\theta)]\,\sin\theta d\theta}{\int \exp.\,[\Gamma S\, P_2(\cos\theta)]\,\sin\theta d\theta} \quad \ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

Where

$$\Gamma = (a-b)\, z/kT + (5\pi/32)\, \Delta vn \quad \ldots\ldots\ldots\ldots \text{(iv)}$$

a is the coefficient indicating the strength of the anisotropic part of the dispersion, b indicates the strength of the force that contribute to the destruction of the order, z is the coordination number of the molecules, n the concentration of molecules, Δv change in volume. The geometrical data have been obtained from crystal structure analysis (Sakuntala Gupta, 1999; Gupta, 1994; Sakuntala Gupta, 2002 and Sakuntala Gupta, 2001). The transition temperatures of different phases of the homologous series 4–alkenyl bicyclohexylnitrile compounds as determined from texture studies are given below:

1d$_1$CC: $\quad C \xrightarrow{64.9^\circ c} N \xrightarrow{99.7^\circ c} I$

1d$_3$CC: $\quad C \xrightarrow{79.5^\circ c} N \xrightarrow{100^\circ c} I$

0d$_3$CC: $\quad C \xrightarrow{50.7^\circ c} N \xrightarrow{79.8^\circ c} I$

3d$_1$CC: $\quad C \xrightarrow{59.5^\circ c} N \xrightarrow{91.7^\circ c} I$

The data to calculate equation (iv) for the four compounds of bicyclohexylnitrile have been taken from the crystal structure analysis of this compounds (Sakuntala Gupta, 1999, 1994, 2001 and 2002) We obtained the expression for Γ of four compounds as given below:

1d$_1$CC: $\Gamma = 549.15\rho^2/T + 4.3542\rho$
1d$_3$CC: $\Gamma = 436.87\rho^2/T + 5.6167\rho$
0d$_3$CC: $\Gamma = 488.22\rho^2/T + 4.6519\rho$
3d$_1$CC: $\Gamma = 436.877\rho^2/T + 4.1749\rho$ ……...(v)

RESULTS AND DISCUSSIONS

The variation of thermal stability with the position of double bond in the alkenyl chain (Sakuntala Gupta, 1999; Gupta, 1994; Sakuntala Gupta, 2002 and Sakuntala Gupta, 2001) and are given in Table 1.

Table 1. Crystal data of four compounds of bicyclohexylnitrile

Compound	Volume V$_c$ (Å^3)	Z	Crystal Class	Density mg/m^3	T$_m$ (˚C)	T$_c$ (˚C)	Packing Coefficient	Molecular Length (Å)	Associated Length (Å)	Molecular long axis makes angle with a, b, c axis (˚)
1d$_1$cc	736.41	2	Tri Clinic	1.043	64.9	99.7	0.573	13.6938	16.6206	83.39, 67.92, 23.15
1d$_3$cc	1663.43	4	Mono clinic	1.084	79.5	100	0.612	16.0760	30.0300	54.18 , 37.67, 79.63
0d$_3$cc(A)	2990.56	8	Mono Clinic/ Centro symmetric	1.090	50.7	79.8	0.601	14.4444	23.8121	41.11, 89.56, 48.89
0d$_3$cc(B)	2990.56	8	Mono Clinic/ Centro symmetric	1.090	50.7	79.8	0.602	14.5797	22.4004	41.91, 70.98, 54.33
3d$_1$cc	1601.7	4	Ortho rhombic	1.076	59.3	91.7	0.588	16.0781		51.58, 86.58, 38.63

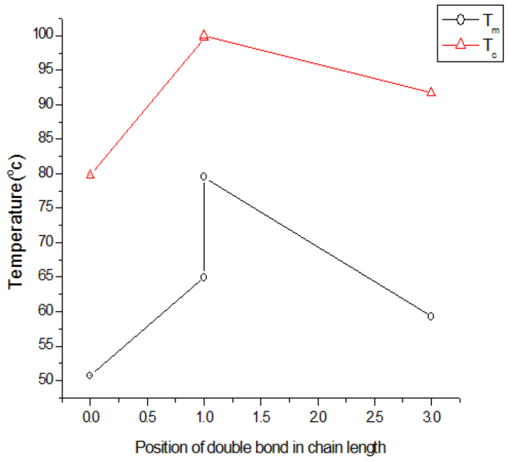

Fig. 1. Variation of thermal stability with the position of double bond in alkenyl chain length

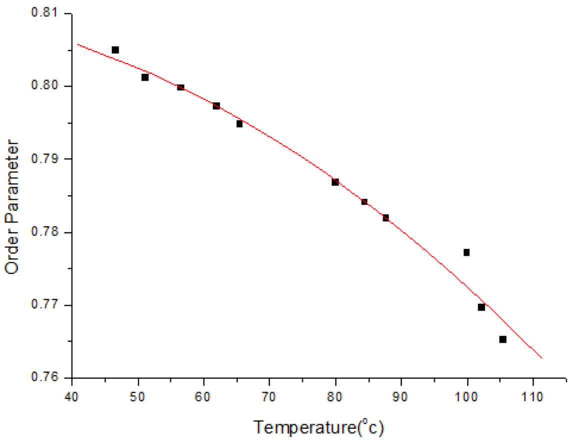

Fig. 2. Variation of order parameter with temperature for 1d$_1$CC

The variation of thermal stability with the position of double bond in alkenyl chain length is shown in Fig. (1). Variation of order parameter with temperature and Γ are shown in Fig. (2-9).

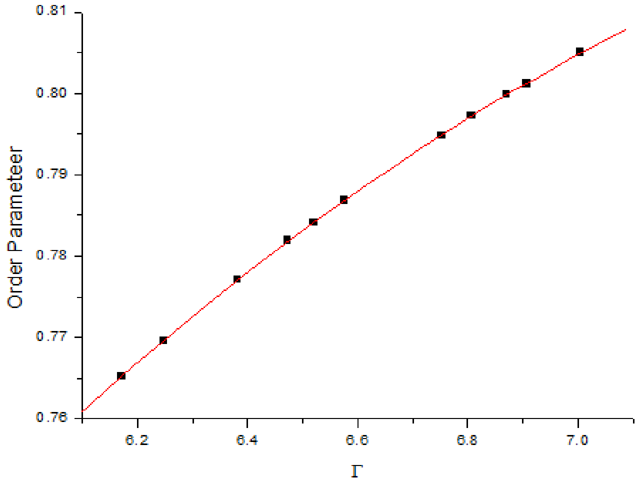

Fig. 3. Variation of order parameter with Γ for $1d_1CC$

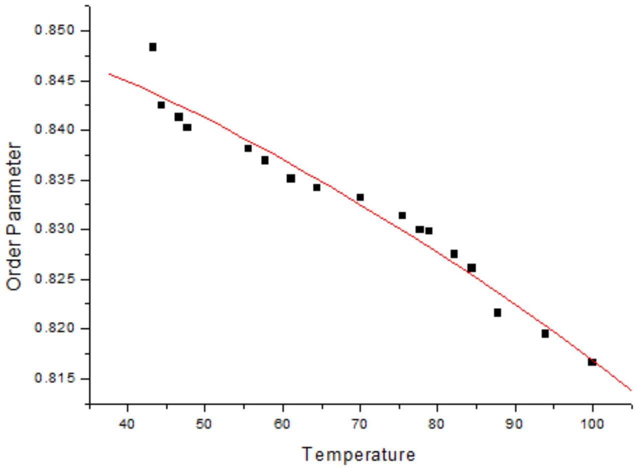

Fig. 4. Variation of order parameter with temperature for $1d_3CC$

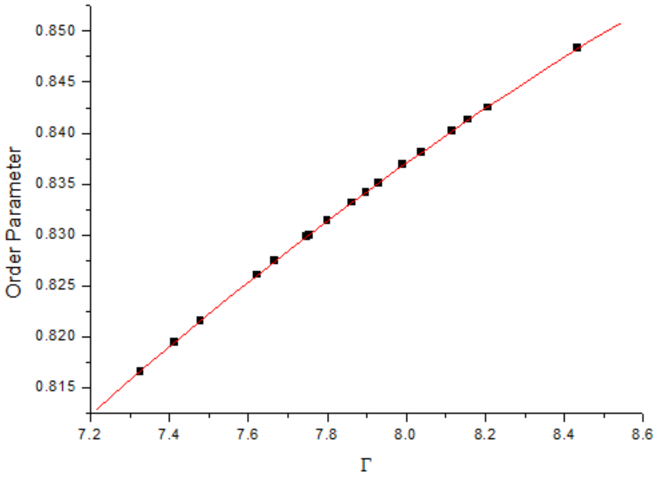

Fig. 5. Variation of order parameter with Γ for $1d_3CC$

It is of interest to compare the molecular packing of the homologous series of 4–alkenyl bicyclohexylnitrile compounds. It is evident from the Fig. (10) that compound $1d_1CC$ & $3d_1CC$ possess double bond after the first carbon chain from cyclohexyl ring and exhibit nearly same packing coefficient.

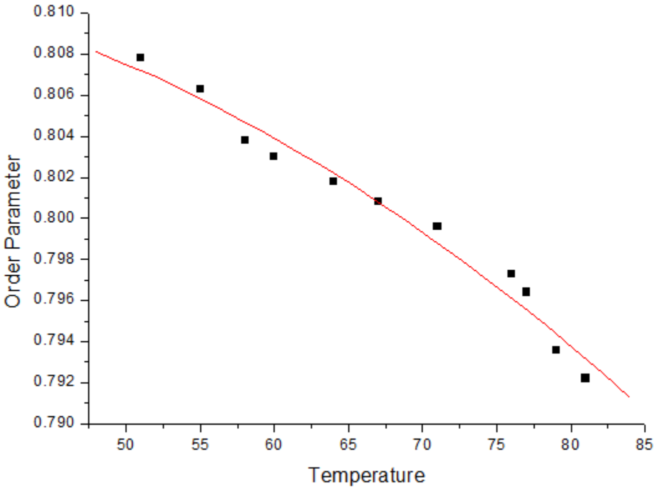

Fig. 6. Variation of order parameter with temperature for $0d_3CC$

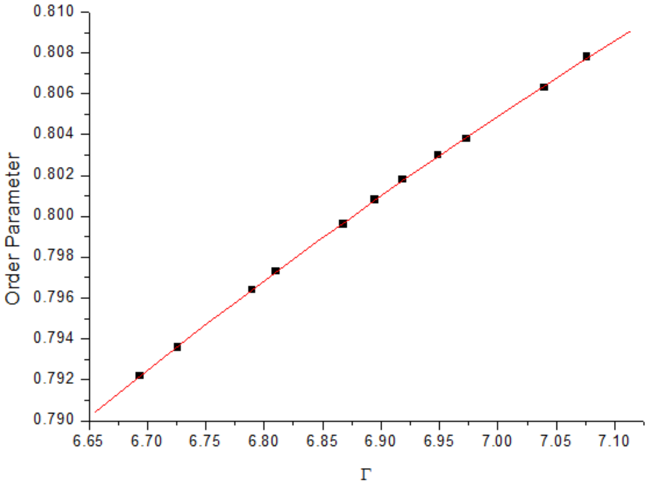

Fig. 7. Variation of order parameter with Γ for $0d_3CC$

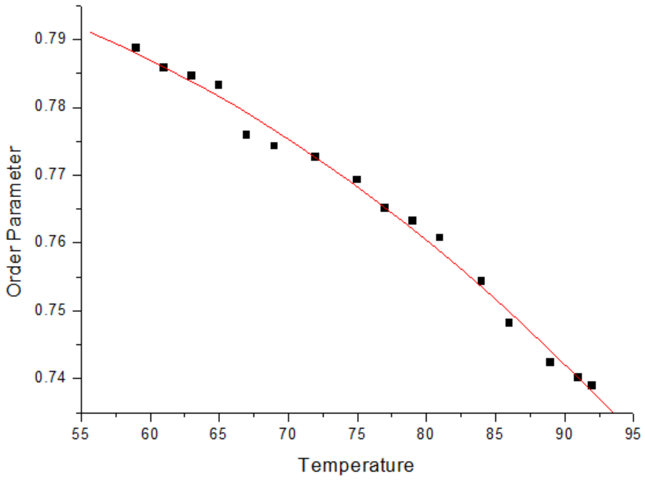

Fig. 8. Variation of order parameter with temperature for $3d_1CC$

It has been found that the bend elastic constants of $1d_1CC$ and$3d_1CC$ decreases strongly with increasing chain length as described by M. Schadt et al (Schadt, 1987). On the other hand, compounds $1d_3CC$ & $0d_3CC$ possess double bond after the third carbon chain from cyclohexyl ring and exhibit nearly same packing coefficient.

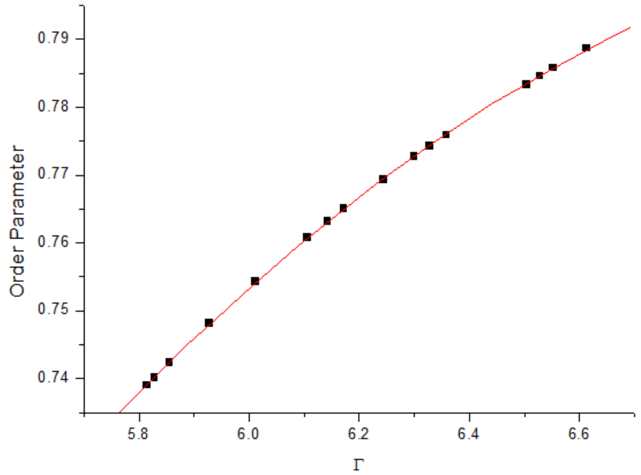

Fig. 9. Variation of order parameter with Γ for $3d_1CC$

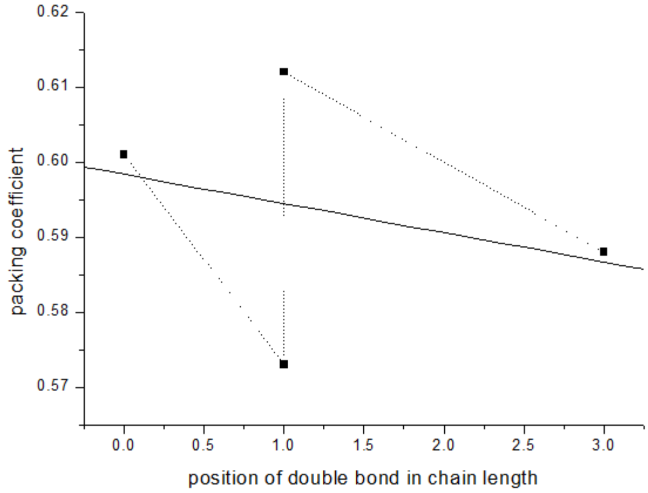

Fig. 10. Variation of packing coefficient with position of double bond in alkenyl chain length

The thermal stability data have been obtained from crystal structure analysis data (Sakuntala Gupta, 1999; Gupta, 1994; Sakuntala Gupta, 2002; Sakuntala Gupta, 2001). Some important crystal data of four compounds of bicyclohexylnitrile are summarized in table 1.Measured molecular length is almost equal to the length of single molecule for the compound $1d_1CC$ as observed by S. Gupta et al (Sakuntala Gupta, 1999). There is a presence of dimerization of $1d_3CC$ molecules as observed from X-ray diffraction studies in nematic phase as studied by S. Gupta et al (Gupta, 1994), $0d_3CC$, with respect to packing no contacts between polar cyano groups can be observed (from crystal data) (Sakuntala Gupta, 1999). There is no bimolecular association is found as studied by S. Gupta et al (Sakuntala Gupta, 2001).

Conclusion

The above study shows that the molecular packing studies of mesogenic materials in their solid state predetermine 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 (Boden, 1979).

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