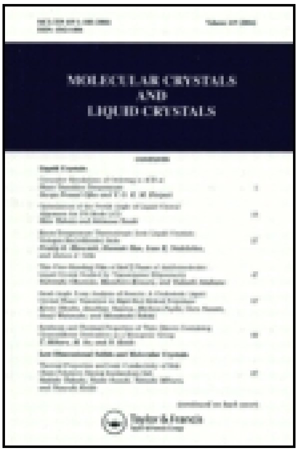

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The Structure Property Relationship of a Homologous Series of Mesogenic Compounds

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THE STRUCTURE PROPERTY RELATIONSHIP OF A HOMOLOGOUS SERIES OF MESOGENIC COMPOUNDS.

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Abstract In this paper efforts have been made to investigate a relation between the molecular structure, packing coefficient and phase transition behaviour for a homologous series of liquid crystals. We have undertaken the studies of the twelve members of the series (nOCB) The molecules belonging to this series are asymmetric. The orientational order parameters in the nematic phase have been calculated for the molecules (n=5 to 9) introducing asymmetry and the variation of order parameter with chain length near the transition temperature is discussed.

INTRODUCTION

The physical properties of liquid crystals such as thermal stability, orientational order parameter, optical properties etc. play an important role in the design of liquid crystal devices. These properties are strongly dependent on molecular structure and their packings coefficients. In these paper efforts have been made to investigate a relation between the molecular structure, packing coefficients and phase transition behaviour for a homologous series 4-alkoxy-4-cyanobiphenyl (nOCB, n=1 to 12). This series have been studied extensively by various experimental techniques[1-7]. The molecules belonging to this series are asymmetric. The orientational order parameters have been calculated introducing this asymmetry for the molecules (n=5 to 9) in the nematic phase near the transition temperature and the variation of order parameter with chain length is discussed.

CALCULATION

Packing coefficient

Molecular packing coefficient is defined as the ratio of the geometric volume of a molecule to that of the volume per molecule in the crystal. The volume increments for atomic combinations are calculated using the following formula given by Kitaigorodsky[8]

$$V= 4/3\pi R^3 - 1/3\pi h_i^2(3R-h_i)$$

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

$$h_i=R -(R^2+d_i^2-R_i^2)/2d_i$$

Relevant data for packing coefficient calculations are taken from the crystal structure analysis of first seven compounds[9-11]. For higher homologues (n=8 to 12) the cell

TABLE 1 Physical data for the series nOCB

n	Vol ($Å^3$)	Z	Cry. Class	Density (gm/cc)	T_m (^oC)	T_c (^oC)	Packing Coeff.
1	2237	8	Mono	1.24	85.5*	105.0	0.69
2	4856	16	Mono	1.22	90.5*	102.0	0.69
3	1317	4	Mono	1.19	64.0*	74.5	0.67
4	2904	8	Or tho	1.14	75.5*	78.0	0.64
5	1496	4	Mono	1.17	47.5	67.5	0.66
6	3263	8	Mono	1.14	57.0	75.5	0.64
7	1738	4	Ti	1.12	54.0	74.0	0.63
8	1804	4	Mono	1.13	54.5	79.5	0.64
9	1795	4	Mono	1.18	64.0	80.0	0.68
10	2028	4	Mono	1.09	59.5	84.0	0.63
11	2121	4	Mono	1.09	71.5	87.5	0.63
12	2214	4	Mono	1.09	70.0	90.0	0.63

* :mono tropic nematic.

parameters have been determined from the powder diffraction data indexed by the program PPLP of the package program NRCVAX used for crystal structure analysis[12,13]. Values of the packing fractions along with other crystallographic data are given in Table I.

Orientational order parameter

We determined orientational order parameter (S) in the nematic phase of the molecule (n = 5 to 9) 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[14] and calculated the order parameter from the following equation

$$S = \frac{\int P_2(\cos\theta)\ \exp(\Gamma S P_2(\cos\theta))\sin\theta\ d\theta}{\int \exp\ (\Gamma S P_2(\cos\theta))\ \sin\theta\ d\theta}$$

$$\text{where } \Gamma = \frac{(a - b)z}{KT} + \frac{5\pi}{32}\Delta vn$$

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 co-ordination number of the molecules, n the concentration of molecules, Δv change in volume. The geometrical data have been obtained from crystal structure analysis.

RESULTS AND DISCUSSIONS

The thermal stability data have been obtained from literature[14] and are given in Table 1. The variation of thermal stability with chain length is shown in figure 1. It is observed that the average thermal stability (clearing point) decreases with chain length, a common phenomenon for a homologous series of asymmetric molecules. There is a sudden change in slope at some member of this homologous series, indicating the onset of different mesomorphic state. This is in agreement with the experimental studies, which showed that this series have a systematic change of

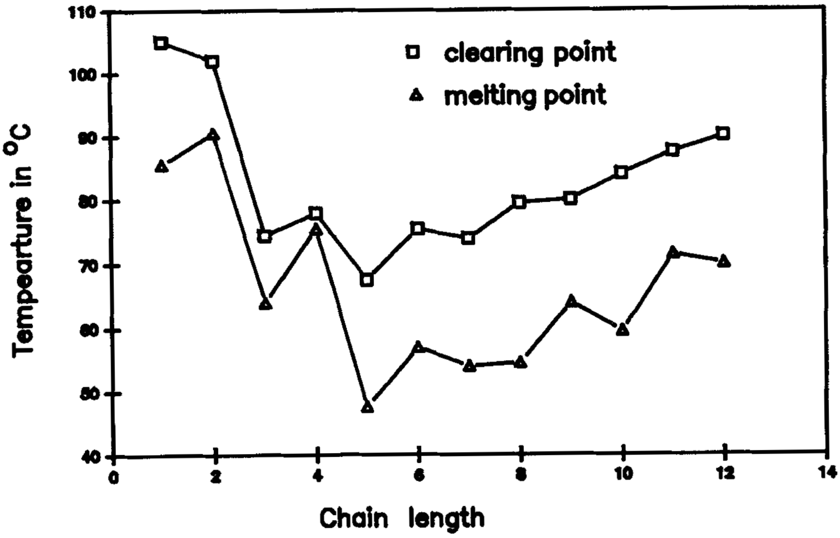

FIGURE 1

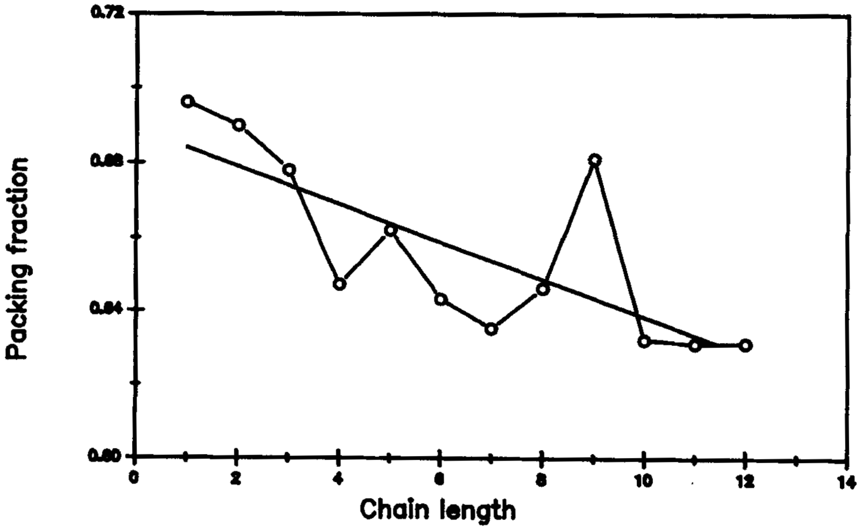

FIGURE 2 Packing coefficient against chain length.

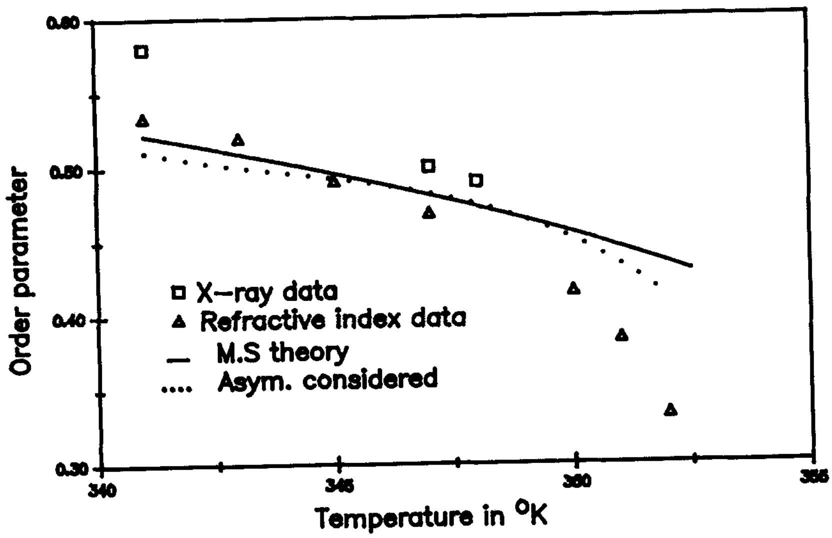

FIGURE 3 Dependence of order parameter on T°K

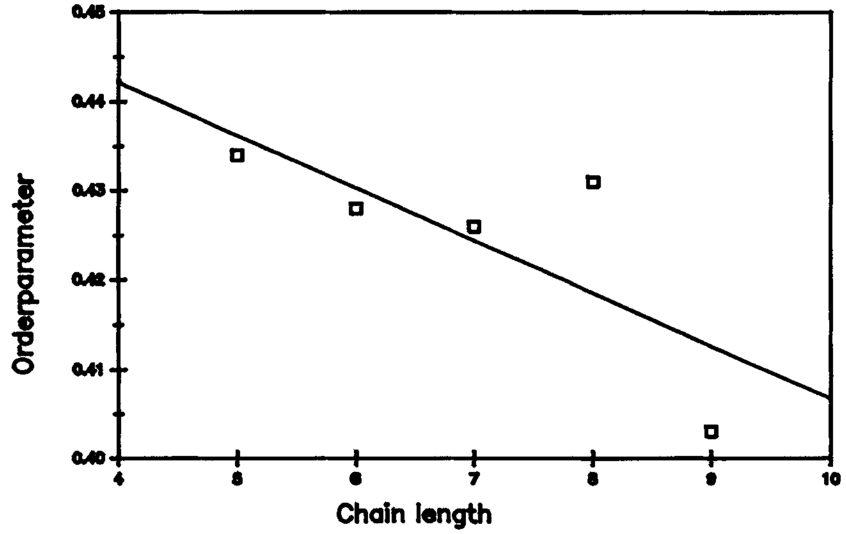

FIGURE 4 Order parameter versus chain length

phase sequences depending on chain length. The variation of melting point with chain length is also plotted in fig.1. Pronounced odd even effect is observed in the variation of melting point with the no of carbon atoms in the chain. The variation of packing confident with n is shown in fig.2. Packing confident decreases as n increases, which implies that an increase in packing confident increases the thermal stability. At n = 9 the packing confident is abnormally high.This is similar to the behaviour of thermal stability. The variation of order parameter S with temperature for the compound 8OCB is shown in the fig.3. At higher temperature S drops off more rapidly when asymmetry is considered. This is in conformity with the experimental values of S determined from optical studies. Calcite values of S at $T_c - T = 2^oC$ in the nematic phase, considering asymmetry, are plotted in fig.4 for the compounds (n = 5 to 9).

Order parameter decreases with chain length as is apparent from the figure. This is akin to the packing coefficient behaviour. We therefore find that order parameter depends on packing coefficient. Densely packed molecules have higher values of order parameter.

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