Orientational order parameters of nematogenic trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates

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Abstract. The refractive indices and densities of three members of trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates are reported as functions of temperature in the nematic and isotropic phases. The principal molecular polarizabilities and order parameters (S) have been evaluated using the anisotropic internal field model (Neugebauer's approach). Also order parameters have been estimated by studying the dipole-dipole splittings in the wide line proton magnetic resonance (PMR) spectra. The results obtained are in close agreement with those obtained from refractive index measurements.

Keywords. Order parameter; refractive index; Nematic; proton magnetic resonance.

1. Introduction

It is very well established that the order parameter of liquid crystals governs most of its physical properties (de Gennes 1974; Chandrasekhar 1977). It is possible to describe the order parameter by any one of the tensorial properties. Presently, refractive index has been selected as a macroscopic property to represent the degree of ordering. Extensive studies have been made on refractive indices, birefringence and order parameters (de Jeu and Bordewijk 1978; Gasparoux et al 1979; Hanson and Shen 1976; Ibrahim and Haase 1979; Dabrowski et al 1980; Sarna et al 1979; Laurent and Journeaux 1976; Madhusudana et al 1971), but most of the compounds studied are those containing benzene groups in the central rigid core. In view of this we have carried out the refractive index and density measurements on the homologous series trans-4-propyl-cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates containing cyclohexane groups in the central core. When more polarizable benzene rings are replaced by much less polarizable cyclohexane rings most of the physical properties differ considerably (Gray 1981; de Jeu 1981). It is likely that the liquid crystalline behaviour of the compounds is directly related to the occurrence of associated entities. We have evaluated the order parameter as a function of temperature for the homologous series using Neugebauer's anisotropic internal field model (Neugebauer 1950, 1954; Subramhanyam et al 1974).

We have employed the PMR technique to evaluate the order parameter. The doublet splitting $\delta H$ arising from the dipole-dipole interaction of the adjacent ring protons was used to calculate the order parameter $S$ by the equation (Spence et al...
where \( a \) is an interaction parameter, \( \phi \) is the angle between the para axis of the benzene ring and the long axis of the molecule. For proton dipole-dipole interaction \( a = \frac{3}{2} \mu_H \gamma_{HH} \), where \( \mu_H \) is the proton nuclear moment and \( \gamma_{HH} \) is the distance between the two interacting protons. The experimentally observed dipolar spectra show good agreement with the results calculated for dipole interaction of orthoprotons of the phenyl ring. The values of \( \gamma_{HH} \) and \( \phi \) which have been estimated from molecular models (Maier and Saupe 1956) are taken to be 2.45 Å and 10° respectively. The order parameter as a function of the dipole-dipole splitting \( \delta H \) of the interacting protons turns out to be

\[
S = \frac{\delta H}{5.50}.
\]

The order parameters obtained by the wide line PMR studies are compared with those obtained by the optical studies.

2. Experimental

2.1 Optical studies

The samples of trans-4-propyl cyclohexyl-4 (trans-4-alkyl cyclohexyl) benzoates

\[
C_nH_{2n+1}H\text{H-CO-C}H_C_3H_7
\]

with \( n = 2, 3 \) and 5 used in our studies are manufactured by E Merck, Darmstadt and were recrystallized before use. The phase transitions are given below

(i) \( n = 2 \), trans-4-propyl cyclohexyl-4 (trans-4-ethyl cyclohexyl) benzoate (TPEB); Melting point 94°C; Clearing point 134°C
(ii) \( n = 3 \), trans-4-propyl cyclohexyl-4 (trans-4-propyl cyclohexyl) benzoate (TPPB); Melting point 92°C; Clearing point 158°C
(iii) \( n = 5 \), trans-4-propyl cyclohexyl-4 (trans-4-pentyl cyclohexyl) benzoate (TPEPB); Melting point 67°C; Clearing point 154°C.

2.1a. Refractive indices measurement. The refractive indices were measured by a prism technique by measuring the angles of minimum deviation and the angles of special hollow pyrex glass prisms with very small refracting angles (4–6°) with a precision coniometer spectrometer reading to 2” of arc. The specimens were aligned along the axis of the prism by rubbing the surface of the prism. The aperture of the optical system was chosen to be very small to guarantee uniform