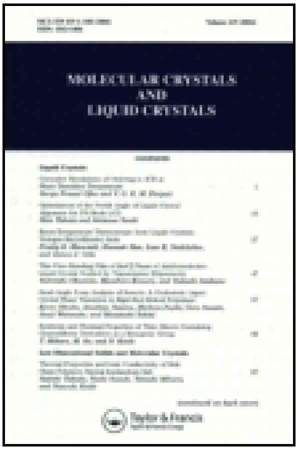

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BEND AND SPLAY ELASTIC CONSTANTS AND DIAMAGNETIC SUSCEPTIBILITY ANISOTROPIES OF FOUR MESOGENIC CYCLOHEXANE CARBOXYLATES

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Bend and Splay Elastic Constants and Diamagnetic Susceptibility Anisotropies of Four Mesogenic Cyclohexane Carboxylates

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Splay (K_{11}) and bend (K_{33}) elastic constants and magnetic susceptibility anisotropies have been determined for four mesogenic compounds with structural formulae R1-C6H10-COO-C6H4-R2. Two of the compounds, namely, CPPCC (R1=C3H7,R2=CN) and CPBCC (R1= C4H9, R2=CN) have terminal cyano groups, while the others are BPPCC (R1=C3H7,R2=OC4H9) and PPPCC (R1=C5H7, R2= OC5H11). As expected, the magnetic susceptibility anisotropies are larger for the cyano compounds than those of the others. K_{33}/K_{11} ratios are greater than one for the cyano compounds and are less than one for the others. With the exception of PPPCC, this ratio decreases with increasing temperature. X-ray diffraction studies on the nematic phase of PPPCC show the presence of cybotactic groups at lower temperature. The local smectic ordering of these groups increase the value of K_{11} and thus reduce the value of K_{33}/ K_{11} at lower temperatures.

Keywords: Magnetic susceptibility; splay and bend elastic constants; cybotactic group

INTRODUCTION

Liquid crystalline compounds, due to their anisotropic properties, show various electro-optical and magneto-optical phenomena, which are utilised in Liquid Crystal Displays (LCDs). To fabricate an efficient LCD, it is essential to know the birefringence and elastic properties of the liquid crystalline materials to be used. It is also necessary to know how these properties change with molecular structure of the compounds, so that better LCD chemical may be synthesised. With this motivation we present experimental splay and bend elastic constants and magnetic susceptibility anisotropy data on four liquid crystalline compounds having same core structure. The compounds studied with their chemical structures and transition temperatures are given below:-

I. p-cyanophenyl trans-4-propyl cyclohexane carboxylate (CPPCC)

C3H7-Cy-COO-Ph-CN

$$K \underset{47\,^{\circ}C}{\overset{54.5\,^{\circ}C}{\longleftrightarrow}} N \overset{70\,^{\circ}C}{\longleftrightarrow} I$$

II. p-cyanophenyl trans-4-butyl cyclohexane carboxylate(CPBCC)

C4H9-Cy-COO-Ph-CN

$$K \underset{<29.5\,^{\circ}C}{\overset{55\,^{\circ}C}{\longleftrightarrow}} N \overset{68.3\,^{\circ}C}{\longleftrightarrow} I$$

III. p-butoxyphenyl trans-4-propyl cyclohexane carboxylate (BPPCC)

C3H7-Cy-COO-Ph-O-C4H9

$$K \overset{43\,^{\circ}C}{\longleftrightarrow} N \overset{72.6\,^{\circ}C}{\longleftrightarrow} I$$

IV. p-pentoxyphenyl trans-4-pentyl cyclohexane carboxylate.(PPPCC)

C5H11-Cy- COO-Ph-O-C5H11

$$K \overset{33.5\,^{\circ}C}{\longleftrightarrow} S \overset{35.4\,^{\circ}C}{\longleftrightarrow} N \overset{75\,^{\circ}C}{\longleftrightarrow} I$$

(Ph= Phenyl ring, Cy = Cyclohexyl ring)

The transition temperatures were recorded by observing the textures under a polarising microscope using Mettler FP 80/ 82 hot stage. The compounds were procured from commercial source and used without further purification. We have also studied density, x-ray diffraction and refractive indices of these compounds. These results will be published in a separate paper[1]. These compounds have been studied previously by different workers. Takahasi et al[2] have measured density and refractive indices of CPPCC, CPBCC and PPPCC. Bend to splay elastic constant ratios of CPPCC and CPBCC have been measured by Scharkowski et al[3]. However, no elastic constants values have been reported for other two compounds. No magnetic susceptibility data of these compounds have been reported previously.

EXPERIMENTAL RESULTS AND DISCUSSION

Magnetic susceptibility anisotropy, $\Delta\chi$, was measured by using a modified Curie balance, described in detail by Mitra and Paul[4]. The experimental values of $\Delta\chi$ against $T-T_{NI}$ are given in Figure 1. In all cases $\Delta\chi$ decreases monotonically as temperature approaches the nematic-isotropic transition temperature and show a discontinuity at the transition temperature. The $\Delta\chi$ values of two cyano compounds (CPPCC and CPBCC) are some what larger than those of other two compounds at the same reduced temperature $T-T_{NI}$. This is as expected from the theory. The bend and splay elastic constants of these compounds have been determined by observing Freedericksz transition in a magnetic field, using a set up described by Das and Paul[5]. The splay (K_{11}) and bend (K_{33}) elastic constant values are calculated from the threshold magnetic field, H_c, for Freedericksz transition, by using the well known relation

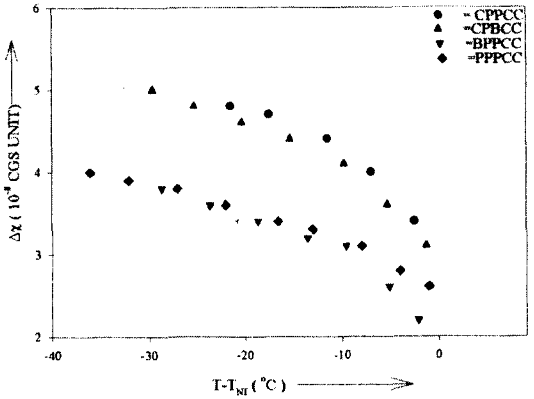

FIGURE 1. Variation of diamagnetic susceptibility anisotropy with reduced temperature.

$$(H_c)_i = (K_{ii}/\Delta\chi)^{1/2} (\pi/d),$$

where d is the thickness of the sample, $\Delta\chi$ is the magnetic anisotropy and $i = 1$ and 3 correspond to splay and bend deformation respectively.

The values of splay (K_{11}) and bend (K_{33}) elastic constants as function of reduced temperature ($T-T_{NI}$) are given in Figure 2 and Figure 3 respectively. For all compounds K_{11} and K_{33} values decrease with increasing temperature as is expected, since elastic constants are approximately proportional to the square of the orientational order parameter. Figure 4 shows the K_{11}/K_{33} ratios for the compounds as a function of reduced temperature.

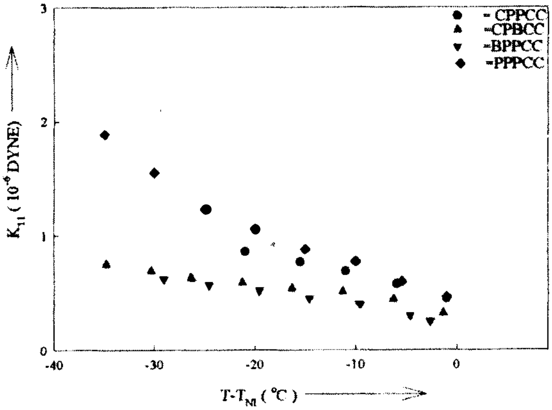

FIGURE 2. Variation of splay elastic constants with reduced temperature.

Scharkowski et al[3] have given a figure showing the variation of K_{33}/K_{11} with reduced temperature for the two cyano compounds (CPPCC and CPBCC) studied by us. However, they have not given the values of K_{11} and K_{33} separately, so we cannot compare our splay and bend elastic constant values with their values directly. Our bend to

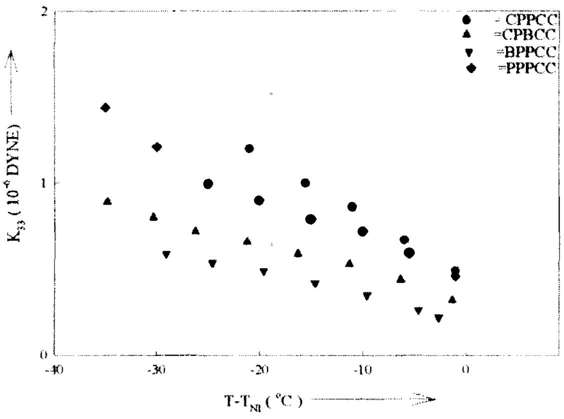

FIGURE 3. Variation of bend elastic constants with reduced temperature.

splay ratios show similar temperature variations as observed by Scharkowski et al[3]. In both CPPCC and CPBCC the ratios are always greater than 1 and increases with decreasing temperatures. The ratios are somewhat larger for CPPCC than for CPBCC. However, our bend to splay elastic constant ratios are almost 15% smaller than those given by Scharkowski et al[3]. We are unable to explain this discrepancy, since individual K_{11} and K_{33} values are not given by them. The other two mesogens (BPPCC and PPPCC) have the bend to splay ratios less than 1 at all temperatures. Schadt et al[6] have also reported that K_{33}/K_{11} is less than 1 for a related compound 5CEPO3 in which the pentyloxy group in PPPCC has been replaced by propyloxy group. According to Schadt et al[6], the K_{33}/K_{11} ratio in polar compounds are larger than non-polar compounds having related structure. Thus we find that polar CPPCC and CPBCC have K_{33}/K_{11} greater than 1, whereas in their related non-polar compounds BPPCC and PPPCC the same ratio is less than 1. In BPPCC the K_{33}/K_{11} ratio increases slowly as the temperature decreases as in CPPCC and CPBCC. However, in PPPCC the bend to splay ratio decreases quite rapidly with decreasing

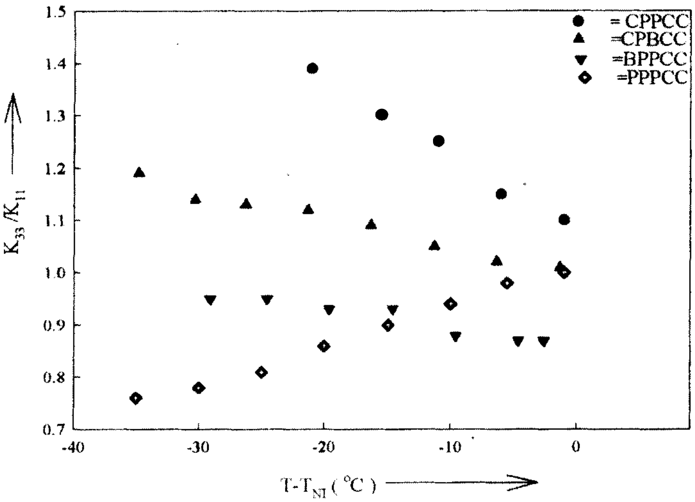

FIGURE 4. Variation of bend to splay elastic constants ratio with reduced temperature.

temperatures. It may be mentioned that from the x-ray diffraction studies PPPCC show formation of cybotactic nematic phase at lower temperatures[1]. In the cybotactic nematic phase small groups of molecules show smectic like order. It has been pointed out by Bradshaw et al [7] that smectic like local ordering in nematogens increases K_{11} and thus lowers the value of K_{33}/K_{11}. The temperature variation of K_{11} in PPPCC indeed shows rapid change (Figure-2). Hence the decrease in the K_{33}/K_{11} ratio in PPPCC with decreasing temperature can safely be attributed to the presence of smectic like cybotactic groups. Very near the smectic-nematic phase transition K_{33}/K_{11} ratio is expected to increase very rapidly[8]. Unfortunately, since we could not increase the magnetic field any more, we were unable to observe this effect.

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