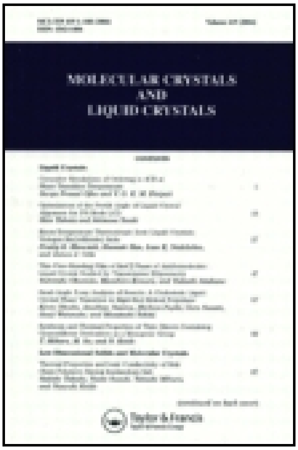

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# Physical Studies of Homologous 4-Cyanophenyl Esters of 4′- n-Alkylcinnamic Acids

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# Physical Studies of Homologous 4-Cyanophenyl Esters of 4′-*n*-Alkylcinnamic Acids

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The mean polarizabilities of homologous series of nematic liquid crystals of 4-cyanophenyl esters of 4′-*n*-alkylcinnamic acids are evaluated by using the ML$\delta$P method. From these polarizabilities the mean diamagnetic susceptibilities of the liquid crystals are also calculated. The orientational order parameters of these compounds are also estimated using the Vuks and Neugebauer methods. The variation of the order parameter with temperature is discussed.

## INTRODUCTION

The most important parameter of a liquid crystal which governs nearly all its physical properties is its order parameter. According to de Gennes,[1–3] any of the bulk tensorial properties like electric and magnetic susceptibilities, elastic constants, refractive indices etc can be used to determine the order parameter. Most of the practical applications of liquid crystals utilize the optical anisotropy of liquid crystals. The temperature dependence of the order parameter gives us an idea of the temperature dependence of the optical anisotropy of the nematic phase. It constitutes a measure of the degree of ordering of location of the elongated molecules in the liquid crystal.

In the present communication we report the mean polarizabilities for the homologous series of nematic 4-cyanophenyl esters of 4′-*n*-alkylcinnamic acids $C_kH_{2k+1}$—$C_6H_4$—CH—CH—COO—$C_6H_4$—CN for $k = 2$ to 8 by using the ML$\delta$P method.[4–8] The mean diamagnetic susceptibilities of these compounds are estimated from the polarizability data.[6-8] The orientational order parameters of this homologous series are also evaluated using the Vuks and Neugebauer methods.

## THE METHOD

### (I) Calculation of mean polarizability

The ML$\delta$P method has been used to calculate the mean polarizability in terms of the parallel bond component ($\Sigma\alpha_{\parallel p}$), the perpendicular bond component ($\Sigma\alpha_{\perp}$) and the non-bond region electron contribution ($\Sigma\alpha_{\parallel n}$). Applicable relations are given in Eqs. (1)–(5).

$$\alpha_l = \frac{1}{3}(\Sigma\alpha_{\parallel p} + \Sigma\alpha_{\parallel n} + \Sigma 2\alpha_{\perp}) \tag{1}$$

where

$$\alpha_{\parallel p} = \frac{4nA[\exp(T - T_c)/T_c]}{a_0}\left[\frac{R^2}{4} + \frac{1}{2C_R^2}\right]^2 \times \exp -\left[\frac{(X_A - X_B)^2}{4}\right] \tag{2}$$

Here $n$ is bond order, $A$ the $\delta$-function strength, $R$ the bond length; $X_A$, $X_B$ are Pauling's electronegativities for the atoms $A$ and $B$ in the bond $A$—$B$,

$$\Sigma\alpha_{\parallel n} = \Sigma f_j \alpha_j \tag{3}$$

where $f_j$ is the fraction of the non-bonded electrons of the $j$th atom and $\alpha_j$ is its atomic polarizability.

$$\Sigma 2\alpha_{\perp} = n_{df}\left[\frac{\Sigma x_j^2 \alpha_j}{\Sigma x_j}\right] \tag{4}$$

where $n_{df}$ is the number of degrees of freedom given by $n_{df} = (3N - 2n_b)$, $N$ is the number of atoms and $n_b$ is the number of bonds in the liquid crystal; $n_{df}$ for the phenyl ring is taken as 19.

$$\alpha = \alpha_l[1 - \frac{m}{\rho_l}(T - T_c)] \tag{5}$$

where $m$ is the slope of the $\rho$ versus $t$ curve, $T_c$ is the transition temperature, $\rho_l$ is the density in liquid phase and $\alpha$ is the mean polarizability in the liquid crystalline phase. Details of the derivation of Eq. (5) are discussed in our previous paper.[4]

The necessary data on bond lengths are taken from Ref. (9). The density data and transition temperatures for these systems are taken from Ref. (10).

### (II) Calculation of diamagnetic susceptibility

The semi-empirical relation between the diamagnetic susceptibility and the mean polarizability of liquid crystals is given as[6-8]

$$-\chi = (\gamma m \sigma')\cdot\alpha \tag{6}$$

where $\gamma = (0.9)^n$ gives the saturation state of the molecule with $n$ denoting the number of unsaturated bonds and rings in the molecule; $\sigma'$ is the degree of covalency of the characteristic group and is given as

$$\sigma' = (\sigma_1^{1/n_1}\cdot\ \sigma_2^{1/n_2}\ldots\sigma_p^{1/n_p})^{1/2} \tag{7}$$

where $\sigma_1, \sigma_2 \ldots \sigma_p$ are Pauling's percentage of covalence characters of the bonds present in the characteristic group, $n_1, n_2 \ldots n_p$ are the bond orders of the various bonds in the characteristic group, $m$ is a constant which is equal to $0.72 \times 10^{19}$. The values of $\sigma_i$ are taken from Ref. (11).

### (III) Calculation of order parameter

The orientation order parameter $S$ is defined as

$$S = \frac{3}{2}\langle\cos^2\theta\rangle - \frac{1}{2} \tag{8}$$

where $\theta$ is the angle made by the long molecular axis with the preferred direction and the brackets denote an average over the molecules in a macroscopic volume.

The principal polarizabilities of the molecules, the anisotropic nature of the polarization field in the medium and the orientational order parameter $S$, determine the birefringence of nematic liquid crystals. For calculations of the polarizabilities of the molecules and of the order parameter $S$ from birefringence data the Lorenz–Lorentz formula cannot be employed because its validity is restricted to cases where there is spherical (or cubic) symmetry associated with the molecular arrangement. According to Vuks formula[12] the ratio of the average local electric field to the applied field is the same for the two cases when the applied field is (i) parallel and (ii) perpendicular to the optic axis of the medium. Such a situation need not necessarily prevail when the molecular distribution is anisotropic. Neugebauer[13,14] has considered in detail the form of the polarization field in anisotropic media. In a nematic medium, as a result of the anisotropic distribution of the molecules, the average local electric field is of the form $E + \gamma P$, where $E$ is the applied field, $P$ the polarization, and $\gamma$ is a factor which is different for directions parallel and perpendicular to the optic axis

In the present study the order parameters of the homologous series of 4-cyanophenyl esters of 4'-*n*-alkylcinnamic acids have been evaluated using both the isotropic internal field model of Vuks[15] and the anisotropic internal field model of Neugebauer[13] are compared. In the Vuks method the order parameter is given by[16]

$$S = \left[\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right] \frac{n_e^2 - n_o^2}{n^2 - 1} \tag{9}$$

where $n^2 = 1/3(n_e^2 + 2n_o^2)$. $\alpha$ is the mean polarizability, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal polarizabilities in directions parallel and perpendicular to the optic axis. The scaling factor $(\alpha/\alpha_{\parallel} - \alpha_{\perp})$ can be determined from a plot of log $[(n_e^2 - n_o^2)/(n^2 - 1)]$ versus log $[1 - T/T_c]$.

In the Neugebauer method, the order parameter is given by[16]

$$S = \left[\frac{\alpha}{\alpha_{\parallel} - \alpha_{\perp}}\right] \cdot f(B) \tag{10}$$

where

$$f(B) = \frac{9}{4B}\left[\left(B^2 - \frac{10B}{3} + 1\right)^{1/2} + \frac{B}{3} - 1\right]$$

and

$$B = \frac{n^2 - 1}{n^2 + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_o^2 + 2}{n_o^2 - 1}\right]$$

The scaling factor in this method can be determined by plotting log $f(B)$ as a function of log $(1 - T/T_c)$.

TABLE I

Polarizabilities ($\times 10^{24}$ cm$^3$) of $C_KH_{2k+1}$—$C_6H_4$—CH—CH—COO—$C_6H_4$—CN

| $k$ | $\Sigma\alpha_{\parallel p}$ | $\Sigma\alpha_{\parallel n}$ | $\Sigma 2\alpha_{\perp}$ | $m \times 10^4$ | $\alpha$ | |
|---|---|---|---|---|---|---|
| | | | | | Calculated | Experimental |
| 2 | 66.84 | 1.08 | 34.31 | 1.32 | 33.7 | 34.3 |
| 3 | 71.19 | 1.08 | 36.55 | 1.24 | 35.9 | 36.8 |
| 4 | 75.54 | 1.08 | 38.81 | 1.16 | 38.1 | 38.2 |
| 5 | 79.89 | 1.08 | 41.06 | 1.21 | 40.2 | 40.4 |
| 6 | 84.24 | 1.08 | 43.31 | 1.95 | 42.2 | 41.7 |
| 7 | 88.59 | 1.08 | 45.56 | 2.21 | 44.2 | 43.9 |
| 8 | 92.94 | 1.08 | 47.81 | 2.10 | 46.4 | 45.8 |

TABLE II

Diamagnetic Susceptibilities (×$10^5$ CGS units) of $C_kH_{2k+1}$—$C_6H_4$—CH—CH—COO—$C_6H_4$—CN

| $k$ | $-\chi$ |  |
|---|---|---|
|  | Calculated | Pascal's method |
| 2 | 14.66 | 14.28 |
| 3 | 15.60 | 15.46 |
| 4 | 16.58 | 16.65 |
| 5 | 17.50 | 17.83 |
| 6 | 18.36 | 19.01 |
| 7 | 19.25 | 20.20 |
| 8 | 20.29 | 21.39 |

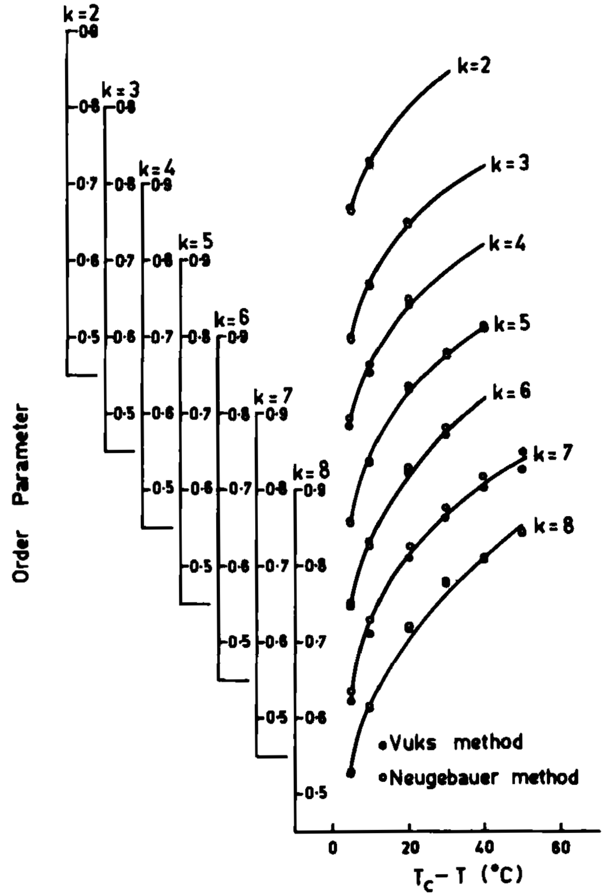

FIGURE 1 Order parameter versus temperature for the homologous 4-cyanophenyl esters of 4′-$n$-alkylcinnamic acids.

## RESULTS AND DISCUSSION

Mean polarizabilities calculated using Eq. (5) are presented in Table I along with the experimental values of Grozhik *et al.*[10] The diamagnetic susceptibilities of these liquid crystals are presented in Table II, along with the values calculated using Pascal's method.[6,17,18] The variation of order parameter with temperature is shown in Figure 1. The $n_e$ and $n_o$ values used in the calculations are taken from Ref. (10). The temperature dependence of the order parameter is the same in all cases. It may be pointed out that the trend of the variation of the order parameter with temperature, is in agreement with the studies of Hanson *et al.*[19]

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