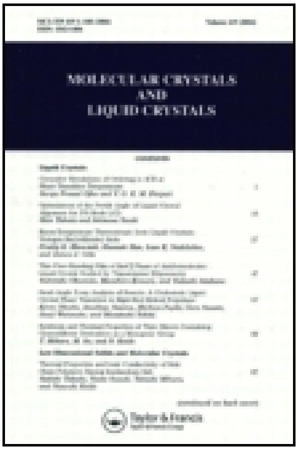

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The Internal Field Parameters for Liquid Crystals

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The Internal Field Parameters for Liquid Crystals†

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In this paper we calculate the internal field constants γ_e of four homologs in the nematic and crystalline phase, and found that in the nematic phase the $\gamma_e \sim S_2$ curve is nearly a straight line for each compound. When one extrapolates the straight line to $S_2 = 1$ the corresponding γ_e value is nearly equal to $\gamma_{\|}$, which is the crystalline internal field constant $\gamma_{\|}$. The birefringence data for the four compounds:

(1) *p*(*p*-ethoxyphenylazo) phenyl valerate,
(2) *p*(*p*-ethoxyphenylazo) phenyl hexanoate,
(3) *p*(*p*-ethoxyphenylazo) phenyl heptanoate,
(4) *p*(*p*-ethoxyphenylazo) phenyl undecylenate,

were taken from those reported by Somashekar *et al.*[1]

INTRODUCTION

In several recent papers[2-4] the authors have discussed the anisotropic nature of the polarization field in relation to the birefringence and the molecular order in nematic liquid crystals. They have also discussed the smectic A and smectic B mesophases. We feel that the investigation of the internal field constants γ_e and optical anisotropy factor α_e/α_o in the nematic and crystalline phases should be continued, especially the discussion of γ_e and α_e/α_0 as a function of the orientation parameters in a homologous series.

More recently Somashekar *et al.*[1] have reported birefringence data for eight liquid crystalline compounds. The first four compounds belong to a homologous series. These authors have given the birefringence data in the crystalline and nematic phases and the refrective indexes in the isotropic liquid phase, and also the densities at the different temperatures. We used their data to calculate the internal field constants γ_e of the first four compounds.

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RESULTS AND DISCUSSION

The calculation of the polarizabilities and internal field constants in the nematic, liquid and crystalline phases are made by using the following relations.

Neugebauer's relation for the crystalline phase:

$$\frac{1}{\alpha_{\parallel}} + \frac{2}{\alpha_{\perp}} = \frac{4\pi}{3} N_c \left[\frac{n_{\parallel}^2 + 2}{n_{\parallel}^2 - 1} + 2\,\frac{n_{\perp}^2 + 2}{n_{\perp}^2 - 1} \right] \tag{1}$$

$$n_{\parallel}^2 - 1 = 4\pi N_c \alpha_{\parallel} (1 - N_c \alpha_{\parallel} \gamma_{\parallel})^{-1} \tag{2}$$

$$n_{\perp}^2 - 1 = 4\pi N_c \alpha_{\perp} (1 - N_c \alpha_{\perp} \gamma_{\perp})^{-1} \tag{3}$$

$$\gamma_{\parallel} = \gamma_z = \frac{4\pi}{3} + [\sum_i (3z_i^2 - \gamma_i^2)\gamma_i^{-5}] / N_c \tag{4}$$

$$\gamma_{\perp} = \gamma_x = \frac{4\pi}{3} + [\sum_i (3x_i^2 - \gamma_i^2)\gamma_i^{-5}] / N_c \tag{5}$$

$$\gamma_{\parallel} + 2\gamma_{\perp} = 4\pi \tag{6}$$

We used Neugebauer's relation for the nematic phase:

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_0} = \frac{4\pi}{3} N_n \left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\,\frac{n_0^2 + 2}{n_0^2 - 1} \right] \tag{7}$$

$$n_e^2 - 1 = 4\pi N_n \alpha_e [1 - N_n \alpha_e \gamma_e]^{-1} \tag{8}$$

$$n_0^2 - 1 = 4\pi N_n \alpha_0 [1 - N_n \alpha_0 \gamma_0]^{-1} \tag{9}$$

We used Lorentz-Lorenz's relation for the liquid phase:

$$\bar{\alpha} = \frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3} = \frac{\alpha_e + 2\alpha_0}{3} = \frac{3}{4\pi N_l} \left(\frac{n^2 - 1}{n^2 + 2} \right) \tag{10}$$

where N_n, N_l, and N_c refer to the number of molecules per unit volume in the nematic, liquid and crystalline phases. α_e and α_0 are the effective average polarizabilities of the molecules for the electric vector parallel and perpendicular to the optic axis of the medium. $\alpha_{\parallel}$ and $\alpha_{\perp}$ refer to the principal polarizabilities of the molecule parallel and perpendicular to the long axis.

Somashekar *et al.*[1] have reported the birefringence data for the following four compounds:

1. *p*(*p*-ethoxyphenylazo) phenyl valerate,
2. *p*(*p*-ethoxyphenylazo) phenyl hexanoate,
3. *p*(*p*-ethoxyphenylazo) phenyl heptanoate,
4. *p*(*p*-ethoxyphenylazo) phenyl undecylenate.

These compounds belong to a homologous series of liquid crystals. The structural formulae of the compounds are shown in Figure 1.

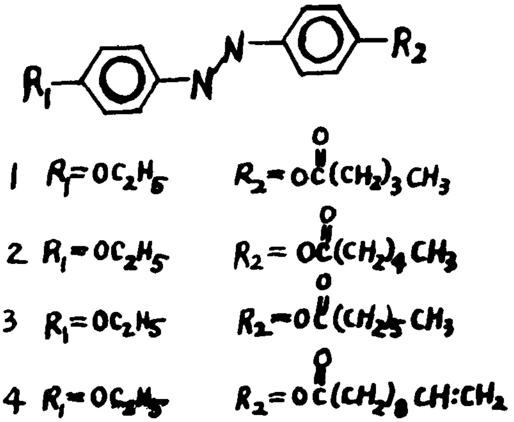

FIGURE 1 Structural formulae of the four compounds.

Using Neugebauer's formulae we calculated the internal field constants $\gamma_{\parallel}$ for the crystalline phase of the four compounds. The results are tabulated in Table I. Subramhanyam *et al.*[2] calculated the internal field constants $\gamma_{\parallel}$ in the crystalline phase for the PAA and PAP liquid crystals. We put Subramhanyam's data in the fifth and sixth columns Table I. They found that the $\gamma_{\parallel}$ of PAA and PAP were practically equal. From the first four columns in Table I we found that the differences between the four $\gamma_{\parallel}$ values are small, but we also found that from the first liquid crystal to the fourth liquid crystal the $\gamma_{\parallel}$ values decrease progressively. This progressive decrease of $\gamma_{\parallel}$ is equivalent to an increase of the anisotropy of the internal local field. This result can be explained as follows:

Compounds 1, 2, 3 and 4 have the same central rigid portion and differ from one another only in that the end chain is different in the four cases. From Compound 1 to Compound 4 the length of the end chain increases progressively. In the crystalline phase all the molecules are aligned parallel to one another. The longer the molecule is the more the internal field deviates from the isotropic field and so in this case $\gamma_{\parallel}$ is much less than $4\pi/3$.

Using Neugebauer's formula we calculate γ_e for the four compounds at different temperatures. The calculated data with regard to γ_e and α_e/α_0 as a function of the orientation parameter S_2 are represented graphically in Figures 2 and 3 respectively.

TABLE I

COMPOUND	1	2	3	4	PAA	PAP
$\gamma_{\parallel}$	3.26	3.20	3.12	2.98	3.17	3.20

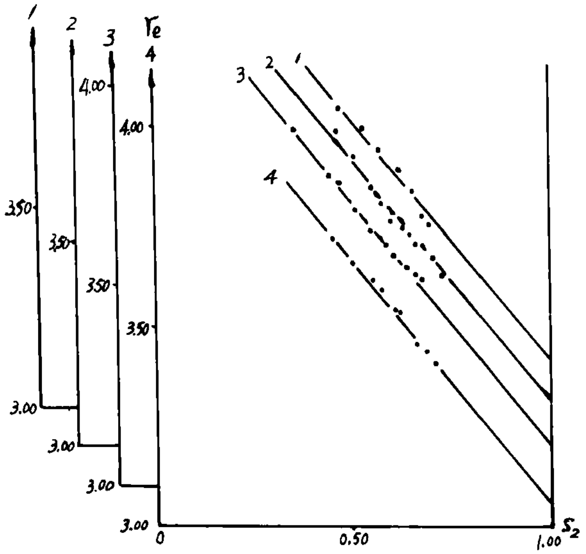

FIGURE 2 Variation of γ_e with the orientation parameter S_2.

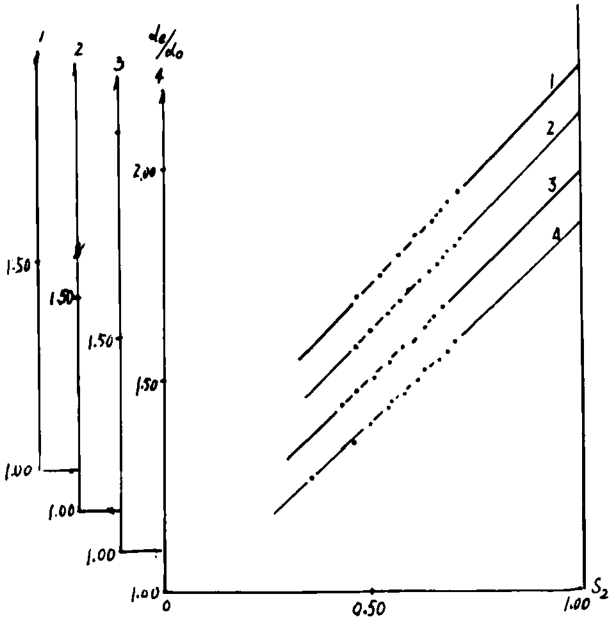

FIGURE 3 Variation of α_e/α_0 for 5893 Å with the orientation parameter S_2.

TABLE II

COMPOUND	1	2	3	4
Calculated	3.26	3.20	3.12	2.98
Extrapolation to $S_2 = 1$	3.12	3.10	3.14	3.04

From Figure 2 we found that for a liquid crystal the plot of $\gamma_e \sim S_2$ is nearly a straight line, and the slopes of the four $\gamma_e \sim S_2$ lines are nearly equal. From the four curves the values of γ_e^i corresponding to $S_2 = 0.5$ are $\gamma_e^1 = 3.71$, $\gamma_e^2 = 3.70$, $\gamma_e^3 = 3.70$ and $\gamma_e^4 = 3.67$. So corresponding to $S_2 = 0.5$ the γ_e values for the four compounds are nearly equal. We extrapolate the $\gamma_e \sim S_2$ straight line to $S_2 = 1$, which is assumed to correspond to $\gamma_{\parallel}$ in the crystalline phase. From the extrapolation we found four values of $\gamma_{\parallel}'$, these values can be compared with the $\gamma_{\parallel}$ value which were calculated from the birefringence data of the crystalline phase, and are tabulated in Table II. In Table II we found that the discrepancy between $\gamma_{\parallel}'$ and $\gamma_{\parallel}$ for a given compound is small.

In a recent paper[5] the authors found that graphical plots of the values of S_2 *versus* $(\gamma_o - \gamma_e)$ also exhibit approximately linear variations for the liquid crystals, PBPA and BBPA. Their results are consistent with ours.

From Figure 3 we found that the $\alpha_e/\alpha_o \sim S_2$ curve is a straight line for each compound. We also extrapolated the $\alpha_e/\alpha_o \sim S_2$ straight line to $S_2 = 1$, which is assumed to correspond to $\alpha_{\parallel}/\alpha_{\perp}$ in the crystalline phase. From the extrapolation procedure we found four $(\alpha_{\parallel}/\alpha_{\perp})'$ values. We have tabulated these values in Table III. We have also listed in Table III the $(\alpha_{\parallel}/\alpha_{\perp})$ values which are calculated from the birefringence of the crystalline phase for the four compounds. From Table III we found that the values of $(\alpha_{\parallel}/\alpha_{\perp})'$ are in agreement with the values of $(\alpha_{\parallel}/\alpha_{\perp})$ for each liquid crystal.

From Figure 3 we found that the $\alpha_e/\alpha_0 \sim S_2$ curve is a straight line for each compound. We also extrapolated the $\alpha_e/\alpha_0 \sim S_2$ straight line to $S_2 = 1$, liquid crystals. But the basic approximations involved in this point dipole model give a rather simplified model. Actually the molecules are of finite size and have irregular shapes and consist of groups which are polarizable to different extents.

TABLE III

COMPOUND	1	2	3	4
$(\alpha_{\parallel}/\alpha_{\perp})$ Calculated	2.01	1.98	1.94	1.95
$(\alpha_{\parallel}/\alpha_{\perp})'$ Extrapolation to $S_2 = 1$	1.97	1.94	1.90	1.89

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