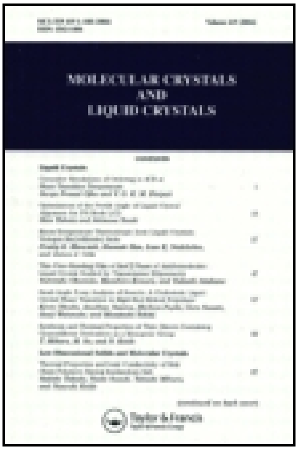

Molecular Crystals and Liquid Crystals

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He Xue-hua [a] & Zhang He-yi [a]

[a] Department of Physics, Beijing University, China

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The Internal Field Parameters for Liquid Crystals†

HE XUE-HUA and ZHANG HE-YI
Department of Physics, Beijing University, China

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This paper presents calculations of the internal field constants γ_e for four homologous liquid crystal materials in their nematic and crystalline phases. We find that for 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 $\gamma_{\|}$, the crystalline internal field constant. The birefringence data used are those reported by Somashekar *et al.*[4] The four compounds studied are:

(1) *p*(*p*′-ethoxyphenylazo)phenyl valerate;

(2) *p*(*p*′-ethoxyphenylazo)phenyl hexanoate;

(3) *p*(*p*′-ethoxyphenylazo)phenyl heptanoate;

(4) *p*(*p*′-ethoxyphenylazo)phenyl undecylenate.

INTRODUCTION

In several recent papers,[1-3] the authors have discussed the anisotropic nature of the polarization field in relation to the birefringence and the molecular order in nematic liquid crystals and also in smactic A and smactic B mesophases. We feel that investigations of the internal field constants γ_e and the optical anisotropy factors α_e/α_o for both nematic and crystalline phases should be continued, and especially that the question of γ_e and α_e/α_o as a function of the order parameters of liquid crystalline homologues should be discussed.

More recently Somashekar *et al.*[4] have reported birefringence data for eight liquid crystalline compounds of which four belong to a homologous series of liquid crystal materials. They have given birefringence data for the crystalline phase and the nematic phase and refractive indices for the isotropic liquid

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phase; also the densities at different temperatures have been given. They have not however calculated the internal field constants γ_e. We have used their data to calculate the internal field constants γ_e for the four homologous compounds.

RESULTS AND DISCUSSION

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

Neugebauer relation for the crystalline phase:

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

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

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

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

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

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

Neugebauer relation for the nematic phase:

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

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

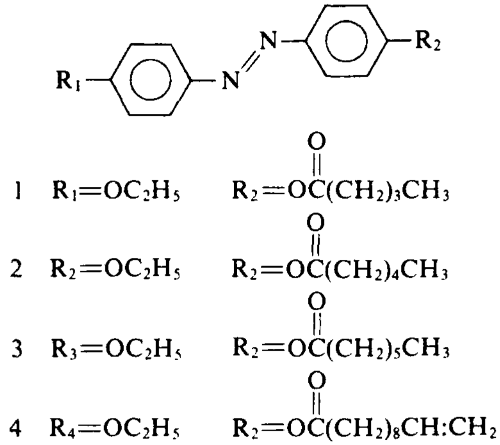
$$n_o^2 - 1 = 4\pi N_n \alpha_o \left[1 - N_n \alpha_o \gamma_o\right]^{-1} \tag{9}$$

Lorenz-Lorentz relation for the liquid phase:

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

In the above N_n, N_l, and N_c refer to the number of molecules per unit volume in the nematic, liquid, and crystalline phases respectively, and α_e and α_o are the effective average polarizabilities of the molecules for the electric vector respectively 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 respectively.

Somashekar *et al.* reported birefringence data for the following four compounds which belong to a homologous series of liquid crystal materials. The structural formulae of the compounds are shown in Figure 1.



$$1 \quad R_1{=}OC_2H_5 \qquad R_2{=}O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_3CH_3$$

$$2 \quad R_2{=}OC_2H_5 \qquad R_2{=}O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_4CH_3$$

$$3 \quad R_3{=}OC_2H_5 \qquad R_2{=}O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_5CH_3$$

$$4 \quad R_4{=}OC_2H_5 \qquad R_2{=}O\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_8CH{:}CH_2$$

FIGURE 1 Structural formulae for the four esters.

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

Using Neugebauer's formulae, we calculated the internal field constants $\gamma_{\|}$ for the crystalline states of the four compounds, and these are tabulated in Table I. For comparison we have put Subramhanyam's data in the fifth and sixth columns of Table I. Subramhanyam[1] *et al.* calculated the internal field constants $\gamma_{\|}$ for the crystalline phases of the mesogens PAA and PAP and found that $\gamma_{\|}$ for PAA and PAP were practically equal. From the first four columns in Table I, we find that the differences between the four $\gamma_{\|}$ values are small, but we also find that from the first liquid crystal to the fourth liquid crystal, the $\gamma_{\|}$ values decrease progressively. This progressive decrease of $\gamma_{\|}$ is equivalent to an increase in the anisotropy of the internal local field. This result can be explained as follows:

The compounds 1,2,3, and 4, have the same central rigid portion (core structure) and differ from one another only in that the end chains are 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, and the longer the molecule is, the more the internal

TABLE I

Compound	1	2	3	4	PAA	PAP
$\gamma_{\|}$	3.26	3.20	3.13	2.97	3.17	3.20

field deviates from that for the isotropic field. So in this case $\gamma_{\parallel}$ is much less than $4\pi/3$.

Using Neugebauer's formula, we then calculated 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 order parameters S_2 are represented graphically in Figures 2 and 3, respectively.

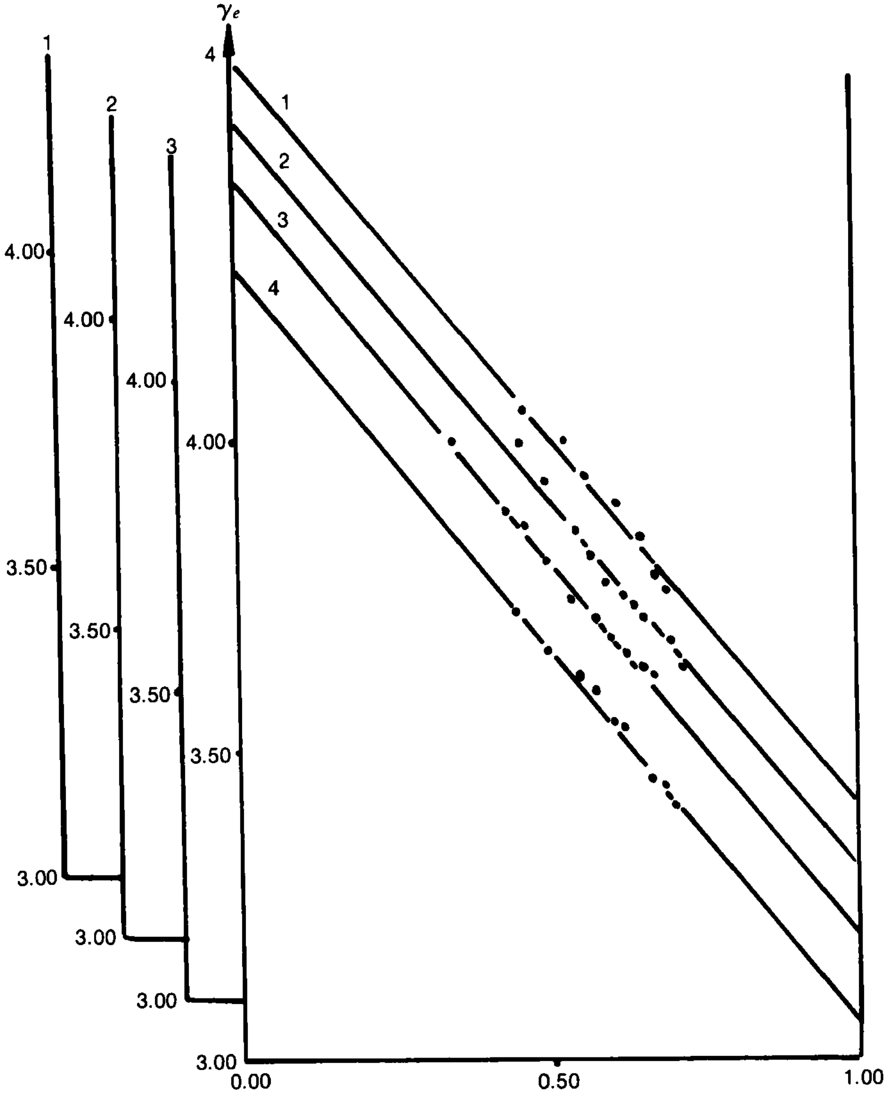


FIGURE 2 Variation of γ_e with the order parameter S_2.

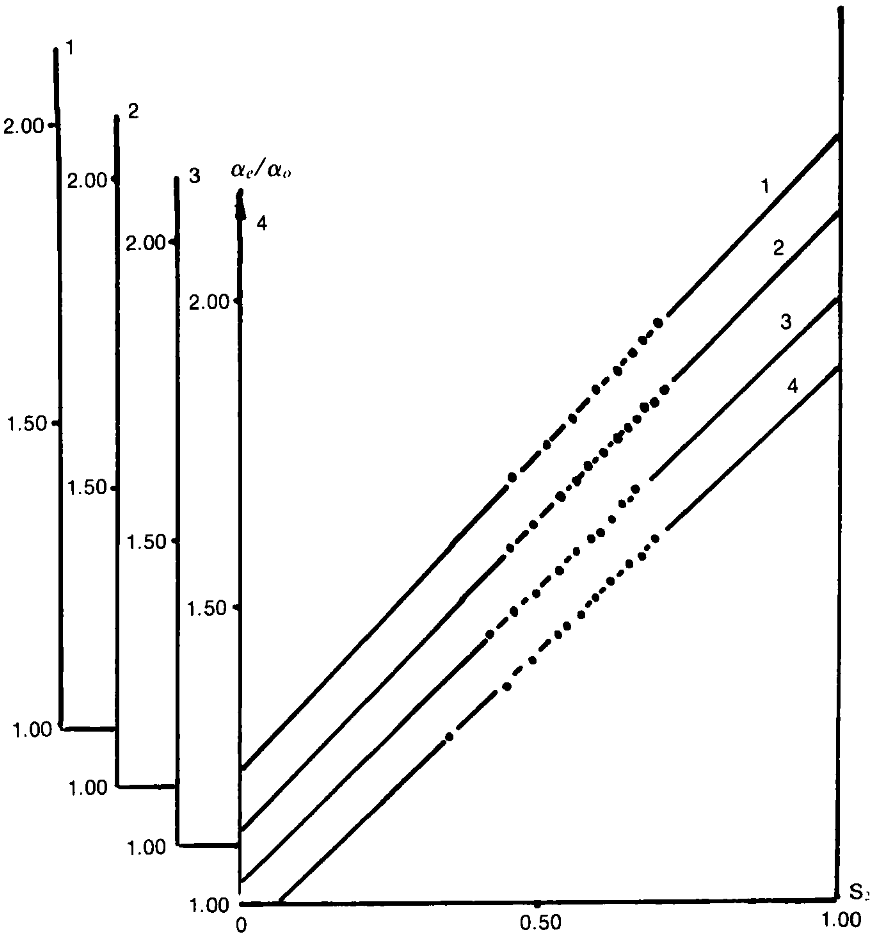


FIGURE 3 Variation of α_e/α_o for 5893 Å with the order parameter S_2.

From Figure 2, we find that for the liquid crystal materials the curve of $\gamma_e \sim S_2$ is nearly a straight line, and the slopes of the four $V_e \sim S_2$ lines are nearly equal. For example, if we take $S_2 = 0.5$, we find from the four curves that the corresponding $\gamma_e^1 S$ values are $\gamma_e^1 = 3.71$, $\gamma_e^2 = 3.70$, $\gamma_e^3 = 3.70$, and $\gamma_e^4 = 3.67$. Consequently, corresponding to $S_2 = 0.5$, the γ_e values for the four compounds are nearly equal. We then extrapolated the $\gamma_e \sim S_2$ straight line to $S_2 = 1$, which is assumed to correspond to $\gamma_{\parallel}$ for the crystalline phase. From the extrapolation, we find four values of $\gamma_{\parallel}^1$, and these values can be compared with the $\gamma_{\parallel}$ values calculated from the birefringence data for the crystalline phase; these are tabulated in Table II. In Table II, we see that the discrepancy between $\gamma_{\parallel}^1$ and $\gamma_{\parallel}$ for a given compound is small.

TABLE II

Compound	1	2	3	4
Calculated $\gamma_{\|}$	3.26	3.20	3.12	2.98
Extrapolation $\gamma'_{\|}$ to $S_2 = 1$	3.12	3.10	3.14	3.04
$\gamma = \frac{4\pi}{3}$	4.18	4.18	4.18	4.18
Extrapolation γ' to $S_2 = 0$	4.29	4.30	4.26	4.28

We can also extrapolate the straight line to $S_2 = 0$, which is assumed to correspond to $\gamma = 4\pi/3$ in the isotropic liquid phase. From the extrapolation procedure we find four γ^1 values, which can be compared with the value of $4\pi/3$. We have tabulated these values in the third and fourth rows of Table II, and find that the $\gamma^1 S$ values are slightly larger than $4\pi/3$.

From Figure 3, we find 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 $\alpha_{\|}/\alpha_{\perp}$ in the crystalline phase. From the extrapolation procedure we find four $(\alpha_{\|}/\alpha_{\perp})'$ values. We have tabulated these values in Table III, and have also listed in this Table the $(\alpha_{\|}/\alpha_{\perp})$ values which are calculated from the birefringences of the crystalline phases of the four compounds. We see that the values of $(\alpha_{\|}/\alpha_{\perp})'$ are in agreement with the values of $(\alpha_{\|}/\alpha_{\perp})$ for each compound.

We have also extrapolated the straight line to $S_2 = 0$, so that we find four $(\alpha_{\|}/\alpha_{\perp})'$ values, and we have tabulated these in Table III. The values of $(\alpha_{\|}/\alpha_{\perp})'$ for $S_2 = 0$ correspond to the isotropic liquid values of $(\alpha_{\|}/\alpha_{\perp}) = 1$, but from the extrapolation procedure the values $(\alpha_{\|}/\alpha_{\perp})'$ are slightly smaller than 1.

TABLE III

Compound	1	2	3	4
$\alpha_{\|}/\alpha_{\perp}$ Calculated	2.01	1.98	1.94	1.95
$(\alpha_{\|}/\alpha_{\perp})'$ Extrapolation to $S_2 = 1$	1.97	1.94	1.90	1.89
$\alpha_e/\alpha_o = 1$ For liquid	1	1	1	1
$(\alpha_e/\alpha_o)'$ Extrapolation to $S_2 = 0$	0.92	0.93	0.94	0.93

From the above discussion we can reach the following conclusion:

The Neugebauer relation is applicable to the nematic and the crystalline phases of liquid crystal materials, but the basic approximations involved in this point dipole model are of a simplified nature. Actually the molecules are of finite size, have irregular shapes, and consist of groups which are polarizable to different extents.

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