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Anisotropy of Lorentz field factors in two symmetric homologous series

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Abstract : In this paper, we report the results of our calculations on the orientational order parameters and anisotropic Lorentz field factors from refractive index data in the nematic phase for the following two different homologous series :

1. p, p'-di-n-alkyl azoxybenzene (series 1)

2 p, p'-di-n-alkoxy azoxybenzene (series II)

It emerges from these calculations for both the series I and series II, that there is a linear variation of L_e and $(L_o - L_e)$ with S, the orientational order parameter, which is in good agreement with the existing model of the nematic phase. Secondly, it has been observed that the values of $(L_o - L_e)$ and S evaluated at any temperatures below nematic-isotropic transition temperature for both the series show alternation with the molecular length, and in general, the value of $(L_o - L_e)$ decreases

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Anisotropic properties of liquid crystalline materials in relation to the birefringence and dielectric measurements have been studied by earlier investigators [1-4]. A knowledge of local field experienced by a molecule in the medium is necessary to interpret the birefringence and dielectric measurements in terms of molecular properties. On the basis of a simple lattice model of oriented nematic liquid crystals, Dunmur [5] has shown the anisotropy in the local field is important in understanding the properties of liquid crystalline materials. Averyanov *et al* [6] have shown for various uniaxial liquid crystals that there is a strong dependence of the local field tensor and Lorentz factor tensor in the specific features of the molecular structure. Subramhanyam and Krishnamurti [7] and Xue-Hua He and He-Yi Zhang [8] have pointed that Neugebauer relations lead to consistent results and at the same time provide indirect information regarding the anisotropic nature of the molecular distribution in the nematic phase. In this paper, we examine the following two symmetric homologous series of compounds which exhibit nematic phase on the basis of Lorentz field factors, calculated using Neugebauer relations.

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Series I :
$$C_m H_{2m+1} C_6 H_4 N:N (:O) C_6 H_4 C_m H_{2m+1}$$
(m=3-7)Series II : $C_{m-1} H_{2m-1} OC_6 H_4 N:N (:O) OC_6 H_4 C_{m-1} H_{2m-1}$ (m=4-9)

Calculation of Lorentz field factors and orientational order parameters

Using the refractive index and density data reported by de Jeu and his coworkers [9,10] and employing Neugebauer relations [11] the Lorentz field factors L_e and L_o , and the orientational order parameter S at various relative temperatures $(T_e - T)$ in the nematic phase were calculated. The Lorentz field factors L_e and L_o satisfy the condition $L_e + 2L_o = 1$. The calculated values of S are in agreement with those estimated by others [9, 12] using different methods and hence in this note we have used our S values only for the interpretation of the temperature dependence of anisotropy of molecular distribution in

different members of series I and II.

The anisotropic molecular distribution is generally expected in the case of molecules which are long and lath-shaped and in all such cases the effect of the molecular distribution is manifested as a difference between the Lorentz field factors $(L_o - L_e)$ or $(L_\perp - L_{\parallel})$. As may be found from our calculations, the value of L_e increases with increase of temperature and the difference between the Lorentz field factors $(L_o - L_e)$ decreases with increase of temperature. The anisotropy of molecular distribution is zero at the nematic-isotropic transition temperature. The decrease in the anisotropy of Lorentz field factors is consistent with the expectation that the molecular distribution should be less anisotropic with increase of temperature. It may also be seen from our calculations that in both the series, there is a linear variation of the Lorentz field factors L_o and L_e with the orientational order parameter S. The values L_{\parallel} and L_{\perp} correspond to the case when S = 1 are given in Table 1. It is

Series I						
m	3	4	5	6	7	
L _{II}	0.268	0.270	0.273	0.273	0.268	
L	0.366	0.365	0.364	0.364	0.366	
$L_{\perp}-L_{\parallel}$	0.098	0.095	0.091	0.091	0.098	
			Serie	es H		
m	4	5	6	7	8	9
L _{II}	0.258	0.258	0.255	0.255	0.260	0.260
L_{\perp}	0.371	0.371	0.373	0.373	0.370	0.370
LL	0.113	0.113	0.118	0.118	0.110	0.110

Table 1. Lorentz field factors of series I and II at S = I

evident from our calculations that the anisotropy of the Lorentz field factors $(L_o - L_e)$ increases with increase in S, which is in confirmity of the nematic model suggested by Saupe and Maier theory [13]. It should be mentioned here that $(L_o - L_e)$ at any particular (T_e-T) when plotted against the number of carbon atoms (m) for both the series, shows odd-

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even effect (see Figure 1) as observed by Marcelja [14]. It is interesting to note that in general $(L_o - L_e)$ in the nematic phase decreases with increase in the chain length and this is due to the fact that the pseudo-pair potential seen by the molecule increases with the increase in chain length [15]. From Table 1, it is clearly seen that the variation of L_{\parallel} , L_{\perp} and $(L_{\perp} - L_{\parallel})$ with the chain length is almost constant showing that when methylene groups are added symmetrically on either side of the central rigid portion, the change in Lorentz field factors is almost negligible. This is not surprising since numerous configurations are possible for the end chains.



Figure 1. Variation of anisotropy of Lorentz field factors $(L_0 - L_c)$ with m at $(T_c - T) = 10^{\circ}$ C.

Following are some of the conclusions which emerge from the above calculations.

1. The orientational order parameter S at a given (T_c-T) was found to be higher in those substances which show smectrc and nematic phases, when compared with substances exhibiting only nematic phase.

2. The trend in the variation of the anisotropy of Lorentz field factors $(L_o - L_e)$ with $(T_e - T)$ for all members of the series I and II is similar.

3. The value of anisotropy of Lorentz field factors $(L_o - L_c)$ increases linearly with increase in the value of the orientational order parameter S.

4. The value of $(L_o - L_e)$ at any given relative temperature alternate as the number of methylene groups in the end chain is increased.

5. The presence of C-O group on either side of the central rigid portion in series II does not affect much the values of L_{\parallel} and L_{\perp} observed in series I (see Table 1).

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