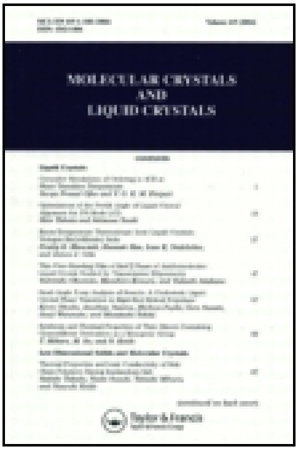

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Optical Anisotropy of Nematic Compounds

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Optical Anisotropy of Nematic Compounds

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The calculation of the principal polarizabilities of nematic compounds with reference to the two approaches using either the Vuks formulae or the Neugebauer's relations is discussed. The polarizabilities and internal field constants have been calculated from the birefringence data in the nematic phase of seven compounds viz., (i) p-azoxyanisole, (ii) p-azoxyphenetole, (iii) anisaldazine, (iv) p-methoxybenzylidene p-butylaniline, (v) 4-n-butyl-4'-ethoxy-α-chlorostilbene, (vi) 4-n-octyl-4'-etnoxy-α-chlorostilbene and (vii) mixture of the isomers of 4-methoxy-4'-butylazoxybenzene. The results support the validity of the Neugebauer's relations rather than the Vuks formulae. The isotropic polarizability and the polarizability $\alpha_{\parallel}$ parallel to the long axis of the molecules are accounted for on the basis that, in the case of the conjugated bonds immediately on either side and in between the benzene rings, the respective bond polarizabilities have values which correspond to their double bond polarizabilities and that the ratio of β_t (the bond polarizability transverse to the bond) to β_l (the bond polarizability parallel to the bond) is zero. The justification for the assumptions is to be sought for in the great mobility of the electron clouds of π bonds in conjugated systems. Also, it emerges that the values of $\alpha_{\parallel}$ given by the Vuks formulae are too large to be accounted for in terms of bond polarizability data. An extrapolation procedure is also discussed for obtaining $\alpha_{\parallel}$ from the effective polarizabilities α_e and α_0 of the nematic phase. The reported diamagnetic ansiotropies in the nematic phase of the above compounds are found to be consistent with their optical anisotropy (α_e-α_0) calculated from Neugebauer's relations. Order parameters are also calculated for anisaldazine and MBBA. The paper also discusses the inherent limitations with regard to obtaining accurate values of the order parameter from birefringence data.

INTRODUCTION

A knowledge of the optical anisotropy of the molecules is essential for calculating the orientational order parameter S from the refractive index data on nematic compounds. In principle, one can obtain the optical anisotropy from the birefringence data in the crystalline phase. Such calculations have been made following either one of the two approaches, viz., (i) the use of the Vuks formulae[1,2] or (ii) the use of the Neugebauer's relations[3-5], the latter involving anisotropic internal field constants. The two approaches lead to values of the order parameter which are in reasonable agreement[1,4] essentially because the anisotropy of the effective polarizabilities (α_e-α_0) in the nematic phase and the anisotropy of the polarizabilities of the molecules ($\alpha_\parallel$-$\alpha_\perp$) are enhanced roughly by the same proportion when one uses the Vuks formulae, as compared with the corresponding values which one obtains from Neugebauer's relations. However, the actual values of the optical anisotropy from the two approaches are quite different. We have gone into this question in detail in the case of seven compounds with similarities in their molecular structure. The compounds are: (i) p-azoxyanisole (PAA), (ii) p-azoxyphenetole (PAP), (iii) anisaldazine, (iv) p-methoxybenzylidene p-butylaniline (MBBA), (v) 4-n-butyl-4′ethoxy-α-chlorostilbene (BECS), (vi) 4-n-octyl-4′-ethoxy-α-chlorostilbene (OECS) and (vii) mixture of the isomers of 4-methoxy-4′butylazoxybenzene (MBAB).

In all these cases the calculations using Neugebauer's relations lead to reasonable and comparable values for the internal field constants in the nematic phase. Further it is found that the Vuks formulae lead to values of the optical anisotropy which are too large and cannot be explained in terms of the additivity of bond polarizabilities even when one makes allowance for the conjugated nature of the structure of the molecules in question. The principal polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ can be estimated also by an extrapolation procedure using the values of α_e and α_0 in a fashion similar to that adopted by Haller *et al.*[6] recently and these values are again consistent with the values from bond polarizability data. It is found that the calculations made from the Neugebauer's relations as well as from bond polarizability data are consistent with the reported measurements of diamagnetic anisotropy in the nematic phase of MBBA, BECS, OECS and MBAB. The present paper also discusses the origin of increasing discrepancies, between the order parameters determined from NMR and birefringence studies, with increasing temperature.

CALCULATIONS FROM OPTICAL DATA

In our earlier paper[4] we have discussed in detail the calculations for PAA and PAP. For the sake of completeness, the procedure of the calculations is briefly summarized below. The Neugebauer's relation for the crystalline phase is obtained from the equations of the form

$$n_i^2 - 1 = 4\pi N_c \alpha_i \,(1 - N_c \alpha_i \gamma_i)^{-1} \tag{1}$$

and

$$\gamma_1 + \gamma_2 + \gamma_3 = 4\pi, \tag{2}$$

where the n_i's (n_1, n_2, n_3) are the principal refractive indices, the γ_i's $(\gamma_1, \gamma_2, \gamma_3)$ are the corresponding internal field constants, the α_i's $(\alpha_1, \alpha_2, \alpha_3)$ are the principal polarizabilities of the molecules and N_c the number of molecules per unit volume in the crystalline phase. If $\alpha_\parallel$ and $\alpha_\perp$ are respectively the polarizabilities along the long axis and the average value perpendicular thereto, the above relations reduce to

$$\frac{1}{\alpha_\parallel} + \frac{2}{\alpha_\perp} = \frac{4\pi N_c}{3}\left(\frac{n_1^2+2}{n_1^2-1} + \frac{n_2^2+2}{n_2^2-1} + \frac{n_3^2+2}{n_3^2-1}\right) \tag{3}$$

For the nematic phase the effective principal polarizabilities α_e and α_0, the internal field constants γ_e and γ_0 and the extraordinary and ordinary refractive indices n_e and n_0 are related by the equations,

$$n_e^2 - 1 = 4\pi N\alpha_e(1 - N\alpha_e\gamma_e)^{-1}, \tag{4}$$

$$n_0^2 - 1 = 4\pi N\alpha_0(1 - N\alpha_0\gamma_0)^{-1}, \tag{5}$$

and

$$\gamma_e + 2\gamma_0 = 4\pi. \tag{6}$$

where

$$\alpha_e = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp) + \frac{2}{3}S(\alpha_\parallel - \alpha_\perp), \tag{7}$$

$$\alpha_0 = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp) - \frac{1}{3}S(\alpha_\parallel - \alpha_\perp), \tag{8}$$

and S is the orientational order parameter. Combining (4), (5) and (6) we get

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_0} = \frac{4\pi N}{3}\left[\frac{n_e^2+2}{n_e^2-1} + \frac{2(n_0^2+2)}{n_0^2-1}\right] \tag{9}$$

Here N is the number of molecules per unit volume of the nematic phase.

For the liquid phase S = 0 and hence from Eqs. (7) and (8) we have

$$(\alpha_e)_{liq} = (\alpha_0)_{liq} = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp) = \bar{\alpha} = \frac{1}{3}(\alpha_e + 2\alpha_0). \tag{10}$$

Further, in the liquid phase $n_e = n_0 = n$ and hence Eq. (9) reduces to the Lorenz-Lorentz relation viz.,

$$\alpha_\parallel + 2\alpha_\perp = \alpha_e + 2\alpha_0 = 3\bar{\alpha} = \frac{9}{4\pi N_l}\left(\frac{n^2-1}{n^2+2}\right). \tag{11}$$

where N_l is the number of molecules per unit volume of the liquid. Using the refractive index data in the crystalline and liquid phases, $\alpha_\parallel$ and $\alpha_\perp$ are obtained by solving Eqs. (3) and (11). From the index data of the nematic and liquid phases α_e and α_0 are obtained by solving Eqs. (9) and (11). γ_e is obtained from Eq. (4).

The Vuks formulae for the crystalline phase are of the form

$$(n_i^2 - 1) / (\overline{n}^2 + 2) = 4\pi N_c \alpha_i / 3 \;, \tag{12}$$

where $\overline{n^2} = \frac{1}{3}(n_1^2 + n_2^2 + n_3^2)$. The polarizabilities can hence be obtained from the index data of the crystal. For the nematic phase analogous sets of relations of the same form as Eq. (12) hold good and from them α_e and α_0 can be calculated. Fuller details may be found in the earlier papers.[1, 3–6]

The polarizabilities calculated for PAA and PAP from the data of Chatelain[7, 8] and for anisaldazine from the data of Madhusudana *et al.*[2] may be seen to be widely different for the two approaches as shown in Table I. The Neugebauer's relations lead to values of $\alpha_\parallel$ and $\alpha_\perp$ which show a normal dispersion i.e., they increase with decreasing wavelength. On the other hand, the values of $\alpha_\perp$ obtained from the Vuks formulae increase with increasing wavelength. None of these compounds has any significant electronic absorption corresponding to $\alpha_\perp$ in the visible region of the spectrum for any such anomalous behaviour to be considered genuine. For example, the colour exhibited by PAA is due to absorption of light polarized parallel to the long axis of the molecules. For light polarized perpendicular to the long axis there is no absorption in the visible region of the spectrum.[9]

In our previous paper[4] we have pointed out that in a nematic medium in which there is anisotropic molecular distribution of an imbricated nature, the internal field constants γ_e should be less than γ_0 and that $\gamma_e \neq \gamma_0 \neq 4\pi/3$. Also, the internal field constants calculated from the refractive index data for different wavelengths (but at the same temperature) should be equal and the reasonable agreement exhibited by the calculated values had already been re-

TABLE I

Polarizabilities calculated from refractive index data of the crystalline and liquid phases.

Compound	Wavelength in A	From Neugebauer's relations		From Vuk's formulae	
		$\alpha_\parallel \times 10^{24}$ (cm^3)	$\alpha_\perp \times 10^{24}$ (cm^3)	$\alpha_\parallel \times 10^{24}$ (cm^3)	$\alpha_\perp \times 10^{24}$ (cm^3)
PAA	5893	49.26	23.61	55.56	20.86
	5461	50.88	23.92	58.42	20.71
PAP	5893	54.55	27.58	60.12	24.99
	4920	59.93	28.13	69.00	24.47
Anisaldazine	5893	55.82	26.84	63.42	23.71
	5461	57.41	27.08	65.98	23.67

TABLE II

Calculated internal field constants from index data for λ 5893 A

Compound	T_c°K	T_c-T	γ_e
PAA	408.2	5.0	3.96
PAP	440.2	2.0	3.79
Anisaldazine	454.0	4.8	3.76
MBBA	318 ± 1	5.0	3.77
BECS	330.8	5.0	3.91
OECS	334.8	5.0	4.02
MBAB	348.0	5.2	3.86

TABLE III

Effective polarizabilities in units of 10^{-24} cm^3, (for λ 5893 A).

	T_c-T	1.0	5.4	9.2	13.8	17.4	20.6	26.7
Anisaldazine	α_e	44.42	45.92	46.57	47.20	47.66	47.92	49.18
	α_o	32.54	31.79	31.47	31.15	30.92	30.79	30.16
	T_c-T	3.0	5.0	7.0	10.0	13.0	16.0	19.0
MBBA	α_e	41.68	42.31	42.83	43.58	43.96	44.17	44.44
	α_o	32.97	32.66	32.40	32.02	31.83	31.73	31.59
	T_c-T	2.1	5.2	10.4	17.4	27.8	34.8	41.8
MBAB	α_e	43.20	43.80	44.59	45.42	46.37	46.88	47.30
	α_o	33.80	33.50	33.10	32.69	32.22	31.96	31.75
	T_c-T	1.3	6.7	13.4	20.1	26.8	33.5	39.0
OECS	α_e	54.01	55.34	56.25	57.08	57.95	58.45	59.22
	α_o	44.73	44.07	43.61	43.20	42.76	42.51	42.13
	T_c-T	0.8	3.3	6.6	13.2	19.9	26.5	37.6
BECS	α_e	46.28	46.76	47.42	48.35	49.01	49.55	50.36
	α_o	37.32	37.08	36.75	36.28	35.95	35.68	35.28

ported by us[4] in the case of PAA and PAP. In the case of the five other compounds also these criteria are found to be satisfied. Also, in all the seven compounds discussed here, all of which have nearly the same effective molecular length (if one ignores the end groups which are capable of free rotation), the internal field constants γ_e may be expected to be very nearly the same. In Table II are shown the calculated internal field constants γ_e for all the seven cases at temperatures a few degrees lower than the nematic-isotropic transition point T_c and their agreement is seen to be remarkably close. Further, the ranges of variation of γ_e in all the cases are also found to be nearly the same (about 0.3) as is to be expected, since the ranges of the density variation in the nematic phase for all the cases are also comparable. Of the seven compounds discussed here, only for the first three, viz., PAA, PAP and anisaldazine, refractive index data in the crystalline phase have been reported. For the others the data are available only for the nematic phase and hence only calculations regarding γ_e, γ_0, α_e and α_0 can be made. We have used the data of Germain[11, 12] for PAA, PAP and MBBA and those of Haller *et al.*[6] for BECS, OECS and MBAB for the above calculations. In Table III are shown the values of α_e and α_0 calculated from the Neugebauer relations in the case of anisaldazine, BECS, OECS and MBAB at different temperatures.

Table IV gives the order parameter S calculated for anisaldazine from the Neugebauer approach using the data of Madhusudana *et al.*[2] and the values here are in good agreement with their calculated values obtained by using the Vuks formulae, as already pointed out. However, the Vuks formulae have no theoretical basis. Essentially, there is no reason to believe that in a medium with anisotropic molecular distribution the local field would be isotropic as assumed in the Vuks formulae. In the liquid phase however, the average local field would be isotropic inspite of the presence of short range order, owing to the fact that the principal directions about which short range order may be present would vary randomly from one volume element to another. γ would not depend on the direction of polarization of the incident light and would be equal to $4\pi/3$.

Haller *et al.*[6], who have determined the refractive indices in the nematic phase of BECS, OECS and MBAB, have justified the use of the Vuks formulae on the basis that the ratio of $(\alpha_e - \alpha_0)$ determined from n_e and n (isotropic) to that determined from n_0 and n (isotropic) is unity and also that $\bar{\alpha}$ is constant. Actually however, the ratio is never exactly equal to unity but slightly more than unity (1.02) over a major portion of the range, and as one approaches the nematic-isotropic transition point, their graphical plots of the ratio as well as of $\bar{\alpha}$ against temperature exhibit a systematic fall starting from about 3° below the transition point.

TABLE IV

Order parameter values of anisaldazine from index data for λ 5893 Å

T_C-T	S (NVM *et al.*)	S (From Neugebauer's relations)
1.0	0.413	0.410
4.8	0.477	0.483
9.2	0.525	0.521
13.8	0.556	0.554
20.6	0.594	0.591
26.7	0.622	0.656

Haller *et al.* have remarked upon the fact that the internal field constant γ_e calculated from Neugebauer's relations shows a feature of a maximum at about 3° below the nematic-isotropic transition point, instead of a monotonic increase with temperature. The maximum exhibited by γ_e is a genuine feature and in the range beyond the maximum γ_e decreases. It must be mentioned here that the value of γ_e very much depends on the molecular distribution within the fictitious spherical cavity. The field due to the dipoles within the cavity is obtained by summing over all the molecules except the one at the centre of the cavity. This sum which consists of both positive and negative terms is a *slowly* convergent one and special mathematical techniques have been developed to calculate it in the case of crystals, (see for example Born and Huang[10]). In the case of liquid crystals the problem of theoretically evaluating γ_e is obviously more complicated. In general, one can expect a decrease in the ansiotropy of molecular distribution with increase of temperature and hence an increase of γ_e. However, one cannot categorically affirm that this feature should systematically persist all the way upto the nematic-isotropic transition point. As one approaches the nematic-isotropic transition point intra and inter molecular motions increase and there may occur changes with regard to the geometry of molecular association between near neighbours. In the absence of any precise knowledge about the nematic structure over short ranges, it is difficult to make an attempt to account for the maximum exhibited by γ_e and the subsequent decrease of γ_e. However, it may be pointed out that the consistent behaviour of γ_e, described earlier in this section for all the seven compounds, clearly establishes the anisotropic nature of the local field.

With regard to the last four compounds MBBA, BECS, OECS and MBAB, the order parameter S cannot be calculated in the absence of data on the refractive indices in their crystalline phase. However, one can arrive at a reasonable estimate of the polarizabilities from bond polarizability data. One has to check initially the values obtained from this approach with the known values of isotropic polarizabilities in all the cases so that one can evolve physically intuitive common guide-lines for such calculations. In the following section we discuss these calculations before passing on later to the question of accounting for the values of $\alpha_\parallel$ in PAA, PAP and anisaldazine and making an estimate of the same in the other cases.

CALCULATION OF ISOTROPIC POLARIZABILITIES FROM BOND POLARIZABILITY DATA

The isotropic polarizabilities for λ 5893Å in the case of all the seven compounds may be calculated from the Lorenz-Lorentz relation using the refractive index data for the liquid phase reported by the different authors[2, 6, 11, 12]. The calcu-

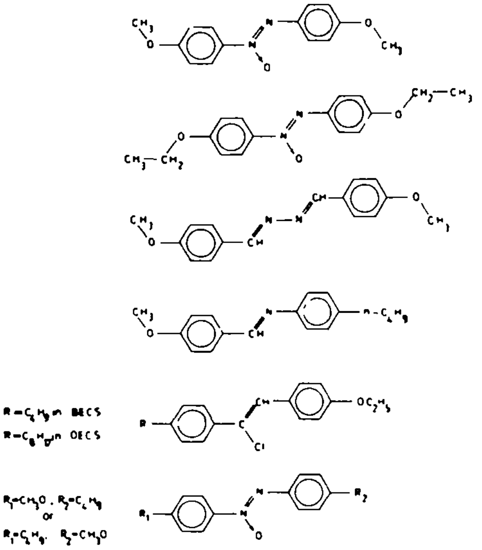

FIGURE 1 Structural formulae: reading from the top, PAA, PAP, anisaldazine, MBBA, BECS and OECS, MBAB.

lations from bond polarizability data were made on the basis of the structural formulae of the seven compounds as shown below in Fig. 1. The relevant bond polarizability data for λ 5893Å available from the literature [9, 13-15] are collected and shown in Table V. β is the isotropic bond polarizability, β_l the polarizability parallel to the bond, and β_t is the polarizability transverse to it. When calculations are made using the principle of additivity of bond polarizabilities, it is found that the values obtained are invariably too low as compared with the values from refractive index data.

The above result is to be anticipated because of the conjugated nature of the molecular structure in the case of all the above compounds. We have here an alternation of single and double bonds involving π bonds. Because of the great mobility of the electron clouds of π bonds, a delocalization of the electrons in all these cases is to be expected [16] and this effect may reasonably be assumed to extend at least from the single bond adjacent to and before the benzene ring on one side of the molecule to the single bond adjacent to the benzene ring on the other side of the molecule. As a result of the delocalization of the electrons it is not correct to consider each one of the bonds as a single bond or a double bond. In fact, theories have been developed with regard to the energy states of electrons in linear systems with alternating carbon-carbon single and double bonds and collective π electron oscillations have been considered for these cases. A

TABLE V

Bond, ionic and molecular polarizability data for λ 5893 Å

Bond	$\beta \times 10^{24}$ (cm^3)	$\beta_\ell \times 10^{24}$ (cm^3)	$\beta_t \times 10^{24}$ (cm^3)	Reference
C–H	0.673	0.82	0.60	9
C–O	0.60	1.46	0.17	9
C=O	1.33	–	–	9
C–C	0.497	0.97	0.26	14
C–C (aromatic)	1.07	2.25	0.48	9
C=C	1.68	2.90	1.07	9
C–N	0.607	1.38	0.22	9
C=S	4.37	7.57	2.77	13
C=N	1.429	–	–	20
C–Cl	2.61	3.67	2.08	9
N–N	0.783	–	–	15
N=N	2.343	–	–	15
N=O	1.576	–	–	15
O^{--}	2.74	–	–	13
C_6H_6	10.32	12.31 (in plane)	6.35 (normal to plane)	13

Note: The single bonds C–C, C–O and C–N exhibit a large optical anisotropy. Further, due to the mobility of the π electrons of the conjugated system, a large optical anisotropy would be associated with the π bonds also, so that effectively for all the bonds of the conjugated region β_ℓ may be expected to be very large compared to β_t.

decrease of the electronic frequency with increasing number of double bonds and a consequent increase in the polarizability had been theoretically deduced and also experimentally verified[17]. However, for the molecules in question the alternating single and double bonds involve different atoms and hence a free electron model with a constant potential would not be appropriate. In this connection, it may be pointed out that, even in the case of benzene, the CC (aromatic) bond has a bond polarizability intermediate to that of the single bond C-C and double bond C=C. It may be assumed that, for each of the bonds along the chain immediately on either side of the benzene rings and in between the rings, the bond polarizabilities have values corresponding to the arithmetic means of their respective single and double bond values. Under such an assumption one obtains for the isotropic polarizability, values which are closer to the values from index data although the calculated values are smaller here also in all the cases, as may be seen by comparing columns 2 and 3 of Table VI. For the bonds in question the upper limit of the value of the respective bond polarizabilities may tentatively be taken to be the double bond polarizabilities. If one makes such an assumption, one obtains the values shown in column 4 of Ta-

TABLE VI

Polarizabilities for λ 5893 Å calculated from index data, the bond polarizability data and the extrapolation procedure

Compound	$\bar{\alpha}$ in units of 10^{-24} cm^3			$\alpha_\parallel$ in units of 10^{-24} cm^3			
	From index data	(*a*)†	(*b*)†	From index data using Neugebauer's relations	(*c*)†	(*d*)†	(*e*)†
PAA	32.16	31.5	33.8	49.26	40.7	47.8	48.0
PAP	36.57	35.2	37.5	54.55	45.9	52.9	54.3
Anisaldazine	36.50	32.3	35.8	55.82	44.3	54.8	53.7
MBBA	35.87	34.0	36.3			51.7	48.5
MBAB	36.93	36.5	39.1			54.1	52.4
BECS	40.31	38.6	41.3			57.3	54.9
OECS	47.82	45.9	48.7	-	-	65.3	64.3

† NOTE: (*a*) Assuming average of single and double bond polarizabilities for the bonds of the conjugated region

(*b*) Assuming double bond polarizabilities for the bonds of the conjugated region

(*c*) Assuming double bond polarizabilities for the bonds of the conjugated region and that $\beta_\ell/\beta_t = 2.7$

(*d*) Assuming double bond polarizabilities for the bonds of the conjugated region and that $\beta_t/\beta_\ell = 0$

(*e*) From extrapolation procedure; (for details see text).

ble VI which in the majority of cases are in better agreement with the values shown in column 2 of Table VI. However in most cases they are somewhat higher than the values in column 2. We have verified also that this approach gives a value for the isotropic polarizability within 3% of the value from index data in the case of a considerably shorter conjugated molecule, viz., cinnamaldehyde ($C_6H_5CH = CHCHO$). It may be mentioned here that in all the above and in the following calculations the polarizability contributions due to the two rings of C_6H_4 are obtained by subtracting the values for the C-H groups from the value for benzene.

CALCULATION OF THE POLARIZABILITY $\alpha_\parallel$ FROM THE BOND POLARIZABILITY DATA

The calculations discussed in the previous section clearly indicate that on an average the contributions of the bonds (immediately on either side and in between the benzene rings) to the isotropic polarizability lie close to the respective double bond values. In the calculation of the polarizability $\alpha_{\parallel}$, we take the molecular axis to be along the line joining the centres of the two benzene rings and assume the molecule to be rigid. When a bond makes an angle θ with the molecular axis the effective contribution parallel to the molecular axis due to that bond is given by

$$\beta_{\text{eff}}(\parallel) = \beta_l \cos^2\theta + \beta_t \sin^2\theta. \tag{13}$$

In the case of the rings of C_6H_4 their principal polarizabilities are obtained from the principal polarizability values for the benzene molecule and the optical anisotropy of the C-H bond. There are two principal polarizabilities β_1 and β_2 along two directions perpendicular to one another in the plane of the benzene ring and one another β_3 which is perpendicular to the plane of the ring. The effective contribution of the C_6H_4 group parallel to the molecular axis is given by

$$\beta_{\text{eff}}(\parallel) = \beta_1 \cos^2\theta_1 + \beta_2 \cos^2\theta_2 + \beta_3 \cos^2\theta_3, \tag{14}$$

where θ_1, θ_2 and θ_3 are respectively the angles made by the principal polarizability directions with the molecular axis. In the case of the C-H bonds of the end groups, their effective contributions are assumed to correspond to their isotropic polarizabilities, because (i) the optical anisotropy of the CH group is small and (ii) the different CH groups lie along different directions with respect to the molecular axis. However, for the C-C and C-O bonds of the end groups, their contributions to $\alpha_{\parallel}$ are calculated using Eq. (13). The sum of all the effective contributions parallel to the molecular axis from the different groups and bonds gives $\alpha_{\parallel}$.

The molecular structures of many of these substances have not yet been determined. In these calculations, for the sake of uniformity and simplicity the bond angles are assumed to be 109° for the bonds involving tetrahedral linkage and in all other cases as 120°. Standard values of the bond lengths are assumed, and the angles, which the molecular axis makes with the different bonds, were determined by drawing a figure of the molecule. In crystalline PAA the two benzene rings are not found to be in the same plane, but are twisted so that the normals to the two benzene rings make an angle of 22.6°.[18] Calculations based on (i) a planar *trans* conformation for the structure and (ii) the slightly twisted conformation do not give very different values for the polarizability $\alpha_{\parallel}$. Hence, in all cases it is assumed, for purposes of calculation of the principal polarizability $\alpha_{\parallel}$, that the two benzene rings lie in the same plane. Also, in the case of PAA and PAP for the bond N → 0, a polarizability equivalent to that of the O^{--} ion is assumed. If one assumes the value corresponding to N = O, the value of $\alpha_{\parallel}$ would turn out to be somewhat smaller.

Although one can adopt the respective values of the double bond polarizabilities for the bonds adjacent to the benzene rings and in between them, there arises the question of how the anisotropy of the polarizability of each one of these bonds is altered due to the delocalization of the electrons. The ratio of β_l to β_t is nearly equal to 2.7 in the cases of the bonds C = C and C = S. If this ratio is assumed, then the values of $\alpha_\parallel$ in the case of PAA, PAP and anisaldazine turn out to be quite low in comparison with the value obtained from the Neugebauer's relations (see, columns 5 and 6 of Table VI) and are considerably lower when compared with the values from Vuks formulae. Only by making the drastic assumption that the ratio, β_l/β_t associated with each of the bonds immediately on either side of the benzene rings and in between the rings, is very large, or in other words that $\beta_t = 0$, it is possible to account for the high value of $\alpha_\parallel$. The only justification which one can think of for such an assumption is the great mobility associated with the electron cloud of π bonds in conjugated systems, parallel to the chain of conjugation. As a consequence of this property the displacements of the electrons parallel to the bonds (or along the chain of conjugation) due to an applied electric field may be very large and that comparatively the displacements perpendicular to the bonds may be negligible, so that $\beta_l >> \beta_t$, i.e., $\beta_l = 3\beta$. The values of $\alpha_\parallel$ calculated under such assumptions for all the cases are shown in column 7 of Table VI and there exists reasonable agreement with the values obtained from Neugebauer's relations in the case of PAA, PAP and anisaldazine. It must also be mentioned here that the above calculations indicate that it is practically impossible to account for the considerably larger values of $\alpha_\parallel$ obtained through the Vuks formulae.

AN EXTRAPOLATION PROCEDURE

Haller *et al.*[6] have found that a plot of log $(\alpha_e\text{-}\alpha_0)$ versus log $(T_c\text{-}T)$, where T_c is the nematic-isotropic transition point, gives a straight line at lower temperatures. They have extrapolated the straight line to log T_c (T_c in °K) in order to find the limiting value of $(\alpha_e\text{-}\alpha_0)$ which is assumed to correspond to $(\alpha_\parallel\text{-}\alpha_\perp)$ at $T = 0\,°K$. They find that the values of $(\alpha_e\text{-}\alpha_0)$ obtained through the Vuks formulae give a limiting value which is in deficit of what one expects from the data of the refractive indices in the crystalline phase through the use of the Vuks formulae. We have adopted the slightly different procedure of using the values from Neugebauer's relations and plotting log (α_e/α_0) versus log $(T_c\text{-}T)$, which also gives a straight line at the lower temperatures. By extrapolating this straight line to log T_c the ratio $\alpha_\parallel/\alpha_\perp$ is found. Using the result that $(\alpha_\parallel + 2\,\alpha_\perp) = 3\,\bar{\alpha}$, $\alpha_\parallel$ and $\alpha_\perp$ can be evaluated. The values of $\alpha_\parallel$ so evaluated are shown for all the seven cases in column 8 of Table VI. There is reasonable agreement between columns 7 and 8 in the different cases.

COMPARISON WITH MEASUREMENTS ON DIAMAGNETIC ANISOTROPY

The diamagnetic anisotropy $(\chi_e\text{-}\chi_0)$ in the liquid crystalline phase of MBBA has been reported for different temperatures by Rose[19]. Haller *et al.* have also reported the values for BECS, OECS and MBAB at different temperatures in the nematic phase. Rose has assumed that the diamagnetic anisotropy of MBBA in the crystalline phase has a value close to that of PAA and hence calculated the order parameter S for different temperatures. The order parameter S is given by

$$S = (\chi_e\text{-}\chi_0)/(\chi_\parallel\text{-}\chi_\perp) = (\alpha_e\text{-}\alpha_0)/(\alpha_\parallel\text{-}\alpha_\perp), \qquad (15)$$

where $\chi_\parallel\text{-}\chi_\perp$ is the diamagnetic anisotropy in the crystalline phase. Hence it follows that $(\chi_e\text{-}\chi_0)/(\alpha_e\text{-}\alpha_0)$ should be independent of temperature. Using the values of $(\alpha_e\text{-}\alpha_0)$ calculated from the Neugebauer's relations and the values of $(\chi_e\text{-}\chi_0)$ reported by Rose, we find that there is reasonable constancy of $(\chi_e\text{-}\chi_0)/(\alpha_e\text{-}\alpha_0)$ as shown in Table VII. Similar constancy is obtained in the other three cases also. Table VII also shows the values of S calculated by us using the value of $(\alpha_\parallel\text{-}\alpha_\perp)$ for MBBA obtained from bond polarizability data. There is reasonable agreement between the order parameters calculated by us and those calculated by Rose.

CONCLUDING REMARKS

The foregoing discussions clearly indicate that the values of $\alpha_\parallel$ and $\alpha_\perp$ obtained from Neugebauer's relations are to be preferred over those calculated from the Vuks formulae. However, we have to mention here that the values of the internal field constants are rather sensitive to small experimental errors in the determination of the refractive index; however, small inaccuracies in the internal field

TABLE VII

Order parameter values for MBBA

T_c-T	$\dfrac{(\chi_e - \chi_0)}{(\alpha_e - \alpha_0)} \times 10^6$	S (Rose)	S^a
4	4.37	0.37	0.39
8	4.23	0.43	0.46
12	4.18	0.46	0.51
15.9	4.24	0.50	0.54
19.9	4.36	0.52	0.55

[a] Using $(\alpha_e\text{-}\ \alpha_0)$ calculated from Neugebauer's relations and $\alpha_\parallel$ calculated from bond polarizability data.

constants do not alter the polarizability values significantly. Where there are no data available with regard to the refractive indices in the crystalline phase owing to difficulties of growing single crystals as in the case of MBBA, the bond polarizability approach discussed above may be expected to give reasonable values for $\alpha_\parallel$ and $\alpha_\perp$ the errors in their estimates being about 5%.

Finally, as already pointed out earlier[4] small differences exist between the order parameters calculated from birefringence data and from NMR studies, the values from the former being invariably lower. Also, the discrepancies increase with increasing temperature. These facts may be explained as follows. The order parameter S is given by the relation

$$S = (3\,\overline{\cos^2\theta}\text{-}1)/2 = (\alpha_e\text{-}\alpha_0)/(\alpha_\parallel\text{-}\alpha_\perp), \tag{16}$$

where θ is the angle made by a molecule in the nematic phase with the direction of the optic axis. If one goes into the derivation of the above equation it may be realised that $(\alpha_\parallel\text{-}\alpha_\perp)$ refers to the optical anisotropy of the molecules in the liquid crystalline phase rather than in the crystalline phase. If the molecules were rigid, then the conformation of the molecules and hence their anisotropies in the two phases would be identical. But, in most cases, motions of parts of the molecule, e.g., free rotation about the single bonds (as in the case of the CH_2 and CH_3 groups at the ends of the molecule), are always possible in the liquid crystalline phase. The fractional number of molecules in which such motions take place and the amplitudes of such motions increase with increasing temperature. As a result there should be a small but systematic decrease in the optical anisotropy with increasing temperature. Clearly, when one uses the optical anisotropy from the refractive index data in the crystalline phase for calculating the order parameter S, it would be smaller than the true value. Order parameter data with reproducible accuracy from NMR studies are preferable to those from birefringent data, since calculations from the latter inherently involve a certain amount of inaccuracy.

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