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Order Parameter and Molecular Polarizabilities of Liquid Crystals with Nematic and Smectic Phases

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In four substances exhibiting nematic and smectic phases the refractive indices n_e, n_o, the density and the order parameter have been measured as a function of the temperature. From the experimental data the molecular polarizability anisotropy was calculated using different internal field models. The results were compared with the data obtained by an extrapolation procedure and by the addition of tabulated bond polarizabilities.

1. INTRODUCTION

The molecular polarizabilities and their anisotropy are important values for the characterization of liquid crystalline substances because the intermolecular interaction energies according to several theoretical models are based on them. Molecular polarizabilities cannot be measured directly, they only can be calculated by the use of different theoretical approaches for the internal field which partly lead to significantly different values. Therefore the situation is somewhat confusing.

In the following we present the most important features of four different theoretical models. We compare the results calculated by the aid of those models in the case of four substances with nematic and smectic phases in order to find out which approaches are more trustworthy.

2. THEORY

In uniaxial liquid crystals the polarizabilities α_e and α_o corresponding to the electric vector parallel and perpendicular to the optical axis, respectively, are given by

$$\alpha_e = \bar{\alpha} + \tfrac{2}{3}(\gamma_{\parallel} - \gamma_{\perp})S \tag{1a}$$

$$\text{and } \alpha_o = \bar{\alpha} - \tfrac{1}{3}(\gamma_{\parallel} - \gamma_{\perp})S \tag{1b}$$

where S is the order parameter and $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the polarizabilities of a molecule parallel and perpendicular to the long molecular axis. The average polarizability $\bar{\alpha}$ may be expressed by

$$\bar{\alpha} = (\alpha_e + 2\alpha_o)/3 = (\gamma_{\parallel} + 2\gamma_{\perp})/3 \tag{2}$$

Combining (1a) and (1b), we obtain

$$S = (\alpha_e - \alpha_o)/(\gamma_{\parallel} - \gamma_{\perp}) \tag{3}$$

Some models are known which relate the main refractive indices n_e, n_o of an uniaxial liquid crystal to the polarizabilities α_e and α_o.

In the Vuks[1] model first applied to nematic liquid crystals by Chandrasekhar and Madhusudana[2] it is assumed that the internal field is isotropic even in an anisotropic crystal. This assumption leads to the following equations:

$$(n_e^2 - 1)/(n^2 + 2) = \tfrac{4}{3}\pi \cdot N\alpha_e \tag{3a}$$

$$\text{and } (n_o^2 - 1)/(n^2 + 2) = \tfrac{4}{3}\pi \cdot N\alpha_o \tag{3b}$$

where N is the number of molecules per unit volume and

$$n^2 = (n_e^2 + 2n_o^2)/3.$$

Considering the anisotropy of the internal field, Neugebauer[3] has derived the following equations first applied to uniaxial liquid crystals by Saupe and Maier[4] and later on by Subramanyam and Krishnamurti[5]:

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

$$n_o^2 - 1 = 4\,\pi \cdot N \cdot \alpha_o\,(1 - \alpha_o\gamma_o)^{-1} \tag{4b}$$

The internal field constants γ_e and γ_o are subjected to the condition $\gamma_e + 2\gamma_o = 4\pi$. Taking the average polarizability $\bar{\alpha}$ in any phase to be independent of temperature

$$\bar{\alpha} = (\alpha_e + 2\alpha_o)/3 = \tfrac{3}{4}\pi N \cdot (n_i^2 - 1)/(n_i^2 + 2) \tag{5}$$

Eqs. (4a), (4b), and (5) can be combined to

$$1/\alpha_e + 2/\alpha_o = \frac{4}{3}\pi \cdot N\left(\frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1}\right) \tag{6}$$

Recently de Jeu and Bordewijk[6] have found that the high-frequency dielectric anisotropy is proportional to the diamagnetic susceptibility anisotropy. Therefore, the internal field of axially symmetric molecules can be taken as independent of the anisotropy of the surroundings of the molecule. Representing the molecules by an anisotropic homogeneously polarizable spheroid in an anisotropic continuum, de Jeu and Bordewijk have derived the following relations[6]:

$$n_e^2 = 1 + \frac{4}{3}\pi \cdot N \frac{\gamma_\parallel(2S + 1)}{1 - 4\pi N\gamma_\parallel A_\parallel} + \frac{\gamma_\perp(2 - 2S)}{1 - 4\pi N\gamma_\perp A_\perp} \tag{7a}$$

$$n_o^2 = 1 + \frac{4}{3}\pi \cdot N \frac{\gamma_\parallel(1 - S)}{1 - 4\pi N\gamma_\parallel A_\parallel} + \frac{\gamma_\perp(2 + S)}{1 - 4\pi N\gamma_\perp A_\perp} \tag{7b}$$

$A_\parallel$, $A_\perp$ are shape factors which depend only on the axial ratio of the spheroid, where

$$A_\parallel = 1 - \omega^2 + \tfrac{1}{2}\omega(\omega^2 - 1)\ln(\omega + 1)/(\omega - 1) \tag{8a}$$

$$A_\perp = (1 - A_\parallel)/2 \tag{8b}$$

with $\omega^2 = a^2/(a^2 - b^2)$, if a and b are long and short axes of the spheroid. According to Ref. 6 a is taken as the length of the most-stretched molecule; b is chosen such that the volume of the spheroid is equal to the volume of a molecule.

The fourth model used is a spheroidal model (generalization of the model of Scholte[7]) developed first in 1971 by Derzhanski and Petrov[8] and applied in 1974 for the interpretation of the microwave permittivity data of PAA.[9] The molecule is modelled now as an effective prolate spheroid with the ratio of the short and long axis

$$q = b/a \tag{9}$$

Unlike de Jeu and Bordewijk[6] however, this ratio is determined from the birefringence, not from the molecular shape, so that an optical spheroid instead of geometrical one is used. It is filled with anisotropic dielectric the permittivity tensor of which has its main axes coinciding with the axes of the spheroid with main values $\epsilon_1^m = \epsilon_2^m$ and ϵ_3^m. The main polarizabilities of the spheroid in vacuo are calculated according to the formula:

$$\gamma_i = \frac{V_0}{4\pi} \frac{\epsilon_i^m - 1}{1 + D_i(\epsilon_i^m - 1)} \quad i = 1, 3 \tag{10}$$

$$\gamma_1 \equiv \gamma_\perp \qquad \gamma_3 \equiv \gamma_\parallel$$

where V_0 is the volume of the spheroid. For V_0 we used $V_0 = V_i/N_A$. V_i — molar volume of the isotropic phase. D_i are the depolarizing factors, calculated from expressions, equivalent to Eq. (8)

$$D_3 = \frac{1 - e^2}{2e^3}\left(\ln\frac{1 + e}{1 - e} - 2e\right), D_1 = D_2 = \frac{1}{2}(1 - D_3) \tag{11}$$

where $e = \sqrt{1 - q^2}$ is the excentricity of the spheroid. When this spheroid is placed in the liquid crystal with permittivities

$$\epsilon_\parallel = n_e^2, \qquad \epsilon_\perp = n_o^2, \tag{12}$$

the internal field will depend on the orientation of the spheroid with respect to the optical axis of the liquid crystal. This dependence is neglected by an approximation, similar in sense to the de Jeu-Bordewijk empirical relationship.[6] Namely, at any arbitrary orientation of the spheroid an effective anisotropic environment rotating together with the molecule is introduced, with effective anisotropy smaller than the experimentally measured due to the nonideal uniaxial ordering:

$$\epsilon_1 = \epsilon_2 = \epsilon_\perp + \tfrac{1}{3}(1 - S)\Delta\epsilon \tag{13}$$

$$\epsilon_3 = \epsilon_\parallel + \tfrac{2}{3}(1 - S)\Delta\epsilon$$

Placed in such dielectric, the effective excentricity of the spheroid changes according to

$$e^* = \sqrt{1 - q^{*2}}, \qquad q^* = q\sqrt{\frac{\epsilon_3}{\epsilon_1}} \tag{14}$$

Because of $\epsilon_3 > \epsilon_1$ the spheroid now becomes more prolate. With the new value e^*, corresponding new values of D_i^* and γ_i^* are calculated from Eqs. (11) and (10). Finally the refractive indices are given by:

$$\frac{n_e^2-1}{4\pi} = N\frac{1}{3}[2g_1F_1\gamma_1^* + g_3F_3\gamma_3^* + 2(g_3F_3\gamma_3^* - g_1F_1\gamma_1^*)S] \quad (15)$$

$$\frac{n_o^2-1}{4\pi} = N\frac{1}{3}[2g_1F_1\gamma_1^* + g_3F_3\gamma_3^* - (g_3F_3\gamma_3^* - g_1F_1\gamma_1^*)S]$$

where g_i are the cavity field factors

$$g_i = \frac{\epsilon_i}{\epsilon_i - D_i^*(\epsilon_i - 1)}, \qquad i = 1,3 \quad (16)$$

and F_i are the reaction field factors

$$F_i = (1 - \gamma_i^* f_i)^{-1}, \qquad i = 1,3 \quad (17)$$

where

$$f_i = \frac{4\pi}{V_0}\frac{D_i^*(1 - D_i^*)(\epsilon_i - 1)}{\epsilon_i - D_i^*(\epsilon_i - 1)}, \qquad i = 1,3 \quad (18)$$

The spheroidal parameters V_0, q, and ϵ_1^m, ϵ_3^m are determined from the experimental data as follows: The isotropic permittivity at a given temperature above T_c or its extrapolated value below T_c is expressed by the formula:

$$\frac{n_i^2-1}{4\pi} = N_i\cdot\frac{1}{3}(2g_1^{is}F_1^{is}\gamma_1 + g_3^{is}F_3^{is}\gamma_3^{is}) \quad (19)$$

where g_i^{is} and F_i^{is} are calculated with vacuum values of D_i (because of the isotropic environment), $\epsilon_i = n_i^2$ is put everywhere. At this temperature $N_iV_0 = 1$. It is assumed that the mean micropermittivity of the material in the spheroid is equal to the isotropic permittivity of the whole medium.

$$\tfrac{1}{3}(2\epsilon_1^m + \epsilon_3^m) = n_i^2 \quad (20)$$

Then follows from Eq. (19) that the spheroid's microdielectric anisotropy depends on the excentricity of the spheroid according to:

$$\Delta\epsilon^m = \frac{3(n_i^2 - 1)(1 - 3D_3)}{1 + 3D_3\cdot\frac{1}{n_i^2} + 3D_3^2\frac{(n_i^2 - 1)}{n_i^2}} \quad (21)$$

Now, if such value of $q = b/a$ is chosen that the macroscopic anisotropy calculated from Eq. (15) as

$$\frac{n_e^2 - n_o^2}{4\pi} = (g_3 F_3 \gamma_3^* - g_1 F_1 \gamma_1^*) S \tag{22}$$

becomes equal to the experimentally measured, the problem for simultaneous determination of q, $\Delta\epsilon^m$ and

$$\begin{aligned} \epsilon_1^m &= n_i^2 - \tfrac{1}{3}\,\Delta\epsilon^m \\ \epsilon_3^m &= n_i^2 + \tfrac{2}{3}\,\Delta\epsilon^m \end{aligned} \tag{23}$$

is completely solved.

The calculations were done by means of a computer program. The subroutine RTM I (IBM) is used in order to solve the implicite equation for the determination of q from $\Delta\epsilon$ at each temperature. This equation is given by the function FCT.

The good constancy of q at changing the temperature is considered as a demonstration of the applicability of the model. For n_i the extrapolated value at the highest temperature of the nematic phase is always taken.

We calculated the molecular polarizabilities ($\gamma_\parallel$, $\gamma_\perp$) using the refractive indices (n_e, n_o), the order parameter S and the molar volume V_m by means of the different internal field models established by Vuks,[1] Neugebauer,[3] de Jeu/Bordewijk,[6] and Petrov.[8]

Using the mean polarizabilities (α_e, α_o) from Vuks[1] and Neugebauer[3] we have adopted the extrapolation procedure of Haller *et al.*[10] to estimate the molecular polarizability anisotropy $\gamma_\parallel - \gamma_\perp$ by an independent way. In this method $\gamma_\parallel - \gamma_\perp$ is obtained by extrapolating the linear portion of the curve $\log(\alpha_e - \alpha_o)$ vs $\log(1 - T/T_u)$, where T_u is the nematic-isotropic or smectic-nematic transition temperature. The intercept of the extrapolated straight line section to $T \rightarrow OK$ should yield the molecular polarizability anisotropy.

Furthermore, an attempt has been made to estimate $\gamma_\parallel - \gamma_\perp$ and the average polarizability $\bar{\alpha}$ by addition of the tabulated bond polarizabilities.[11,12,13] The bond angles and bond lengths of the most stretched molecule conformation were taken from the literature.[14,15] The molecule axis is assumed to be along the line joining the centers of the benzene rings. The polarizability parallel to the molecular axis $\gamma_\parallel$ summed for all bonds is given by

$$\gamma_\parallel = \sum \gamma_l \cos^2\varphi + \sum \gamma_t \sin^2\varphi \tag{24}$$

where γ_l and γ_t are bond polarizabilities parallel and transverse to the bond, respectively; φ is the angle between the bond and the molecular axis. This assumption seems to be favorable because according to our estimations in this case the highest values of $\gamma_{\parallel} - \gamma_{\perp}$ are obtained. We used the bond polarizabilities compiled by Prasad.[12] Following Subramanyam *et al.*,[11] the longitudinal polarizabilities γ_l were taken to be equal to three times of the isotropic polarizabilities and the transverse polarizabilities to be zero in the conjugated region of the molecule. γ_l of the terminal —CH_3 group was assumed to be equal to the isotropic polarizability.

In the same way, by addition of the isotropic bond polarizabilities, the average polarizability $\bar{\alpha}$ was determined. In this case we used the average of single and double bond polarizabilities for the bonds of the conjugated region.

The polarizability perpendicular to the molecular axis $\gamma_{\perp}$ was evaluated from $\gamma_{\parallel}$ and $\bar{\alpha}$ using Eq. (2).

3. EXPERIMENTAL

The refractive indices of the liquid crystals were measured by means of Abbe's double prism method. In this method the liquid crystal is used as a homeotropically oriented thin film between the hypotenuse areas of two prisms. If the refractive index of the prisms is greater than the indices in the liquid crystal, the refractive indices of the ordinary (n_o) as well as of the extraordinary ray (n_e) can be measured from the boundary angle of total reflection.[16] The double prism was mounted in an electrically heated hot stage which provided the temperature control. All measurements were made in monochromatic light of wavelength 589 nm. The uncertainty of the refractive indices was in the order of ±0.0005.

Density measurements were carried out in a capillary pycnometer with a volume of about 0.1 cm^3. The pycnometer was held in a thermostate whose temperature could be controlled to 5 mK.

The NMR measurements were performed at 60 MHz with a Bruker pulse spectrometer and Fourier transformations. We used this high field of 1.5 T in order to get a good orientation of the nematic directors. At a lower field of 0.8 T the ordering was not perfect. For the determination of the orientational order parameter S we assumed the dipole splitting at $S = 1$ to be $\Delta\nu_0 = 24.5$.kHz. Then the observed NMR line splitting $\Delta\nu$ allows a direct calculation of S. The experimental errors for the S_B phase are larger due to the poorer resolution of the splitting.

4. SUBSTANCES

The liquid crystalline substances studied are listed in Table I.

5. DISCUSSION OF THE RESULTS

The refractive indices (n_e, n_o), the molar volume V_m and the order parameter S of the substances investigated are presented in the Tables II–V as function of temperature. It is interesting to compare the order parameter in the different liquid crystalline phases of the four substances (see Figure 1). In the nematic phases the order parameter shows a strong temperature dependence. A relatively low temperature coefficient of S is observed for EEBM, in which the nematic phase possesses a larger existence range compared with the other three compounds.

In the S_A phases of the substances distinct differences of S were found. The order parameter varies between 0.5 and 0.88 depending on the substance and the temperature. It is remarkable that the temperature dependence of S is clearly higher when the substance exhibits an additional S_B phase (see HPHA, HPHC).

In the S_B phase of HBHA the order parameter (0.9) is nearly temperature independent—with exception of the region near to the phase transition $S_B \rightarrow S_A$.

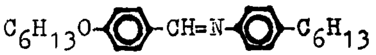
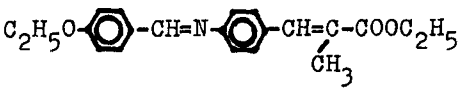
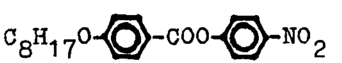
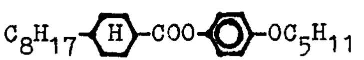
Similar results were observed for the S_B phase of other substances, too.[20] However, in the S_B phase of HPHC relatively low values of S and a stronger temperature dependence of S were found compared with EEBM.

The molecular polarizabilities $\gamma_\parallel$, $\gamma_\perp$, the polarizability anisotropy $\gamma_\parallel - \gamma_\perp$, and the average polarizability $\bar{\alpha}$, calculated from the experimental data by use of different internal field models as well as from the bond polarizabilities are listed in the Tables II–V. For comparison also the $\gamma_\parallel - \gamma_\perp$ values obtained from the Haller extrapolation are given in Table VI.

It is seen from the Tables II–V that $\bar{\alpha}$ is temperature independent for all internal field models in all substances studied. The $\bar{\alpha}$ values obtained from the Vuks model,[1] the Neugebauer model,[2] and from the

TABLE I

Transition temperatures of the substances studied

Substance formula		*Cr*		S_G		S_B		S_A		*N*		*Is*
 [17]	HBHA	·	15	·	33	·	61.3	·	75.5	·	79.0	·
 [16]	EEBM	·	94	—		—		(·	77)	·	123	·
 [18]	NPOB	·	49	—		—	—	·	60.5	·	67.1	·
 [19]	HPHC	·	51	—		·	58.5	·	65	·	73.5	·

Cr: solid crystal
S_A, S_B, S_G: smectic *A*, *B*, *G*
N: nematic
Is: isotropic liquid
The numbers between the phase symbols are the transition temperatures (°C).
The bracket denotes a transition in the supercooled state.

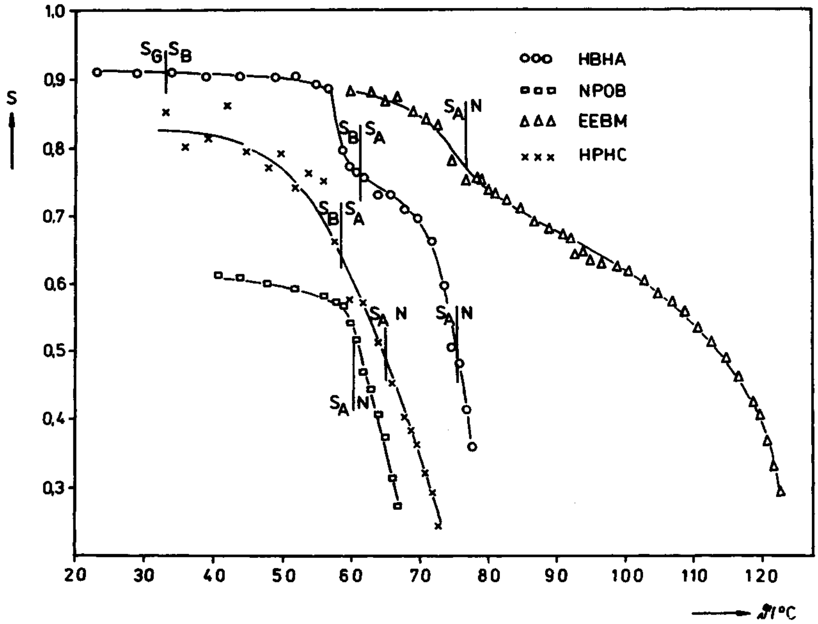


FIGURE 1 The order parameter S of the nematic and smectic phases of HBHA, EEBM, NPOB, and HPHC as function of the temperature.

bond polarizabilities agree very well, whereas the de Jeu/Bordewijk model[6] and the Petrov model[8] give higher resp. lower values. The values are constant within the experimental errors which can be seen from the calculated standard deviations. On the other side, $\gamma_{\parallel}$ and $\gamma_{\parallel} - \gamma_{\perp}$ show a more or less pronounced change with temperature. Provided that the experimental errors of n_e, n_o or V_m are relatively small, two reasons could be responsible for the inconstancy of the calculated polarizability anisotropies: Firstly, the order parameter S can show a systematic error because in NMR measurements S is connected with the orientation of benzene rings, but the refractive indices of the liquid crystals are related to the orientation of the polarizability ellipsoids. Secondly, the internal field can differ in the nematic and smectic phases, so that the same model gives different $\gamma_{\parallel} - \gamma_{\perp}$ in different phases.

In all substances studied the molecular polarizability anisotropy obtained by the relation of de Jeu/Bordewijk[6] is markedly higher than that determined by the Vuks,[1] Neugebauer[3] or Petrov[8] relations. With one exception (HBHA) the data of the Vuks approximation are some-

TABLE II

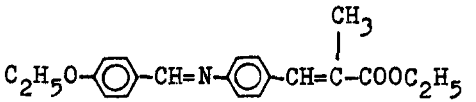
The refractive indices (n_e, n_o), the molar volume V_m, and the order parameters S in the nematic and smectic phases as function of temperature. The molecular polarizabilities $\gamma_\parallel$, $\gamma_\perp$; the polarizability anisotropy $\gamma_\parallel - \gamma_\perp$ and the mean polarizability $\bar{\alpha}$ calculated by the relations of Vuks (V), Neugebauer (N), de Jeu/Bordewijk (J/B), Petrov (P), and by the addition of bond polarizabilities.

(HBHA)

				V_m			$\gamma_\parallel \cdot 10^{24}\text{cm}^{-3}$				$\gamma_\perp \cdot 10^{24}\text{cm}^{-3}$				$(\gamma_\parallel - \gamma_\perp) \cdot 10^{24}\text{cm}^{-3}$				$\alpha^{-} \cdot 10^{24}\text{cm}^{-3}$		
phase	ϑ/°C	n_e	n_o	$\text{cm}^3\text{mol}^{-1}$	S	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P
N	77.5	1.6333	1.5110	387.11	0.385	72.2	77.6	93.9	60.5	37.4	35.1	36.6	36.9	34.8	42.5	57.2	23.6	49.1	49.2	55.7	44.8
	77	1.6379	1.5101	386.82	0.41	71.9	76.7	93.5	60.3	37.8	35.5	36.8	37.2	34.1	42.2	56.7	23.1	49.1	49.2	55.7	44.9
	76	1.6527	1.5076	385.94	0.48	71.4	77.0	93.1	60.0	38.3	35.3	37.1	37.7	33.1	41.4	55.9	22.3	49.3	49.2	55.8	45.1
	74	1.6610	1.5020	383.55	0.55	69.9	73.9	89.5	59.5	38.5	36.8	37.7	38.4	31.4	37.1	51.8	21.1	48.9	49.2	55.0	45.4
S_A	73.7	1.6802	1.4897	383.00	0.61	71.4	70.5	93.3	60.0	37.5	38.5	36.4	37.8	33.9	32.0	56.9	22.2	48.8	49.2	55.4	45.2
	68	1.6873	1.4890	380.12	0.712	68.7	69.6	90.0	58.8	38.6	39.1	37.1	39.3	30.1	30.5	52.8	19.5	48.6	49.2	54.7	45.8
	65	1.6904	1.4894	378.51	0.735	68.0	70.2	89.5	58.6	38.7	38.4	37.1	39.6	29.3	31.8	52.4	19.0	48.5	49.0	54.6	45.9
	60.3	1.6942	1.4900	376.50	0.77	67.3	70.4	88.6	58.3	38.9	38.2	37.2	40.0	28.4	32.2	51.3	18.3	48.3	48.9	54.3	46.1
S_B	58.6	1.7050	1.4880	372.03	0.82	66.6	71.9	88.1	58.1	38.6	37.4	36.9	40.3	28.0	34.5	51.2	17.8	47.9	48.9	54.0	46.2
	55	1.7064	1.4889	370.16	0.893	64.9	70.7	85.9	57.3	39.2	37.8	37.3	41.3	25.7	32.9	48.5	16.0	47.8	48.8	53.5	46.6
	44.8	1.7121	1.4918	365.34	0.903	64.3	72.6	85.4	57.2	39.0	36.7	37.0	41.4	25.3	35.9	48.3	15.8	47.4	48.7	53.1	46.7
	36.4	1.7165	1.4939	361.24	0.905	63.9	74.0	85.0	57.1	38.7	35.6	36.7	41.4	25.3	38.2	48.3	15.7	47.1	48.5	52.8	46.6
	26	1.7220	1.4968	356.20	0.91	63.4	75.5	84.6	57.1	38.3	34.8	36.5	41.5	25.0	40.7	48.2	15.6	46.7	48.3	52.5	46.7
		mean value				68.0	73.1	89.3	58.7	38.4	36.9	36.9	39.5	29.6	36.3	52.3	19.2	48.3	48.9	54.4	45.8
		standard deviation				3.1	2.7	3.3	1.2	0.5	1.4	0.3	1.6	3.5	4.1	3.3	2.9	0.8	0.3	1.1	0.7
		bond polarizabilities					61.7				44.1				17.55				50.0		

TABLE III

The refractive indices (n_e, n_o), the molar volume V_m, and the order parameters S in the nematic and smectic phases as function of temperature. The molecular polarizabilities $\gamma_\parallel$, $\gamma_\perp$; the polarizability anisotropy $\gamma_\parallel - \gamma_\perp$ and the mean polarizability $\bar{\alpha}$ calculated by the relations of Vuks (V), Neugebauer (N), de Jeu/Bordewijk (J/B), Petrov (P), and by the addition of bond polarizabilities.

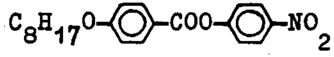


$C_2H_5O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}CH{=}C(CH_3){-}COOC_2H_5$ (EEBM)

phase	ϑ/°C	n_e	n_o	V_m cm^{3}mol^{-1}	S	$\gamma_\parallel \cdot 10^{24}$cm^{-3}				$\gamma_\perp \cdot 10^{24}$cm^{-3}				$(\gamma_\parallel - \gamma_\perp) \cdot 10^{24}$cm^{-3}				$\bar{\alpha} \cdot 10^{24}$cm^{-3}			
						V	N	J/B	P	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P
N	122	1.7100	1.5620	321.66	0.325	71.8	67.7	86.9	55.6	30.6	32.9	31.4	29.7	41.2	34.8	55.5	25.9	44.3	44.5	49.9	38.3
	120	1.7275	1.5572	320.87	0.4	70.1	64.4	85.4	55.1	31.6	34.4	32.1	30.8	38.5	30.0	53.3	24.3	44.4	44.4	49.9	38.9
	115	1.7555	1.5460	319.30	0.485	70.4	65.4	85.8	55.0	31.4	33.9	31.9	30.9	39.0	31.5	53.9	24.1	44.4	44.4	49.9	38.9
	105	1.7875	1.5377	317.25	0.58	70.3	64.4	85.9	54.8	31.5	34.4	32.0	31.3	38.8	30.0	53.9	23.5	44.4	44.4	50.0	39.1
	78	1.8465	1.5260	311.22	0.76	69.4	63.7	85.5	54.3	32.0	34.6	32.3	32.4	37.4	29.1	53.2	21.9	44.5	44.3	50.0	39.7
S_A	77	1.8593	1.5165	310.30	0.795	69.7	65	85.8	54.3	31.5	33.9	32.0	32.3	38.2	31.1	53.8	22.0	44.2	44.3	49.9	39.6
	72.5	1.8645	1.5145	309.20	0.832	68.9	65	85.0	54.0	31.7	34.1	32.1	32.8	37.2	30.9	52.9	21.2	44.1	44.4	49.7	39.9
	65	1.8715	1.5135	307.30	0.87	68.1	64.9	84.3	53.7	31.9	34.1	32.2	33.3	36.2	30.8	52.1	20.4	44.0	44.4	49.6	40.1
	51	1.8830	1.5143	304.00	0.885	67.9	65.3	84.2	53.7	31.7	33.7	31.9	33.4	36.2	31.6	52.3	20.3	43.8	44.2	49.3	40.2
		mean value				69.6	65.1	85.4	54.5	31.5	34.0	32.0	31.9	38.1	31.1	53.4	22.6	44.2	44.4	49.8	39.4
		standard deviation				1.1	1.0	0.8	0.6	0.4	0.5	0.3	1.2	1.5	1.5	0.9	1.8	0.2	0.1	0.2	0.6
		bond polarizabilities					61.3				35.5				25.8				44.1		

TABLE IV

The refractive indices (n_e, n_o), the molar volume V_m, and the order parameters S in the nematic and smectic phases as function of temperature. The molecular polarizabilities $\gamma_\parallel$, $\gamma_\perp$; the polarizability anisotropy $\gamma_\parallel - \gamma_\perp$ and the mean polarizability $\bar{\alpha}$ calculated by the relations of Vuks (V), Neugebauer (N), de Jeu/Bordewijk (J/B), Petrov (P), and by the addition of bond polarizabilities.



(NPOB)

				V_m		$\gamma_\parallel \cdot 10^{24}\text{cm}^{-3}$				$\gamma_\perp \cdot 10^{24}\text{cm}^{-3}$				$(\gamma_\parallel - \gamma_\perp) \cdot 10^{24}\text{cm}^{-3}$				$\bar{\alpha} \cdot 10^{24}\text{cm}^{-3}$		
phase	ϑ/°C	n_e	n_o	$\text{cm}^3\text{mol}^{-1}$	S	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P
N	67	1.5933	1.5238	335.71	0.27	58.5	52.6	74.7	50.6	34.1	37.0	32.8	33.4	24.4	15.6	41.9	17.2	42.2	42.2	46.8	39.1
	66	1.6012	1.5210	335.11	0.31	58.7	56.4	75.0	50.7	33.9	35.1	32.7	33.3	24.8	21.3	42.2	17.4	42.2	42.2	46.8	39.1
	64	1.6146	1.5144	334.41	0.405	57.8	55.5	74.0	50.2	34.3	35.5	33.0	33.9	23.5	20.0	41.0	16.3	42.2	42.2	46.7	39.3
	61	1.6310	1.5085	333.51	0.515	57.2	54.5	73.4	49.9	34.7	36.0	33.2	34.4	22.5	18.5	40.2	15.5	42.2	42.2	46.6	39.6
S_A	60	1.6360	1.5058	333.15	0.54	57.3	55.0	73.5	49.9	34.5	35.8	33.1	34.3	22.8	19.3	40.5	15.6	42.1	42.2	46.6	39.5
	56.5	1.6417	1.5040	332.23	0.577	57.1	55.6	73.4	49.8	34.5	35.5	33.1	34.5	22.5	20.1	40.4	15.3	42.0	42.2	46.5	39.6
	44	1.6523	1.5052	328.99	0.605	57.1	55.7	73.9	49.8	34.4	35.4	32.9	34.5	22.6	20.3	41.1	15.3	42.0	42.2	46.5	39.6
	34	1.6597	1.5067	326.44	0.62	57.0	55.6	73.6	49.9	34.2	35.1	32.7	34.4	22.8	20.6	40.9	15.5	41.8	42.0	46.4	39.6
		mean value				57.6	55.1	73.9	50.1	34.3	35.7	32.9	34.1	23.2	19.5	41.0	15.9	42.1	42.2	46.6	39.4
		standard deviation				0.7	1.0	0.6	0.3	0.3	0.6	0.2	0.5	0.8	1.7	0.7	0.8	0.14	0.07	0.14	0.21
		bond polarizabilities					55.3				38.5				16.8				44.1		

what higher than the data calculated by the Neugebauer relation. This result agrees with the measurements of other authors.[21,22,23,24,25]

We applied Haller's extrapolation procedure[10] based on the Vuks[1] as well as the Neugebauer[3] relation. In Table VI these values are listed obtained by the extrapolation from different phases (N, S_A, S_B). For comparison the mean values of $\gamma_{\parallel} - \gamma_{\perp}$ are given calculated from the Vuks[1] relation and the Neugebauer[3] relation, respectively. In the nematic phase of HBHA and NPOB the extrapolation procedure leads to unreasonable results, because the nematic region is small (contrary to EEBM), so that the Haller extrapolation[10] does not yield linear curves. In HPHC the nematic region is also relatively small, but the temperature dependence of $\alpha_e - \alpha_0$ is not so different in the nematic and smectic phases.

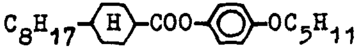
Generally (with exception of the Petrov model[8]) the polarizability anisotropy determined from the bond polarizabilities is distinctly lower than that calculated from the refractive indices (Tables II–V). This is obviously the result of polarizing effects which occur along the conjugated region of the molecule and which are not sufficiently considered by the addition of bond polarizabilities. It is not surprising that in the cyclohexane derivative HPHC the data determined from the bond polarizabilities agree very well with the other values.

The polarizability anisotropy in Petrov's model[8] is the lowest. Comparing it with the de Jeu/Bordewijk model, which is also spheroidal, the reasons of this difference is clear. Geometrical values of the ratio $b/a = q$ in the de Jeu/Bordewijk model[8] are markedly lower so that the spheroid is more prolate than the optical spheroid used in Petrov's model. Above all, in the Petrov model the isolated spheroid, representing the polarizability of a single molecule, is even less prolate than the spheroid embedded in the liquid crystal phase, because of $n_e^2 - n_o^2 > 0$ and the dielectric transformation of the internal field equations.[26] Thibault *et al.*[27] have proved that in the case of the Scholte model[7] of isotropic liquids a correct value of the polarizability anisotropy requires a value of q which differs from the geometrical value. Petrov's model[8] being a generalization of the Scholte model[7] determines similarly to Thibault's procedure,[27] q from the value of the birefringence.

Comparing the polarizability anisotropy of the four liquid crystal substances studied it is plausible that the azomethines exhibit the largest anisotropy because the —CH = N— group favors the conjugation between the benzene rings whereas —COO— is a much less rigid bridging group giving rise to relatively small conjugative interactions. On the other side, on replacing one benzene ring by the cyclohexane

TABLE V

The refractive indices (n_e, n_o), the molar volume V_m, and the order parameters S in the nematic and smectic phases as function of temperature. The molecular polarizabilities $\gamma_\parallel$, $\gamma_\perp$; the polarizability anisotropy $\gamma_\parallel - \gamma_\perp$ and the mean polarizability $\bar{\alpha}$ calculated by the relations of Vuks (V), Neugebauer (N), de Jeu/Bordewijk (J/B), Petrov (P), and by the addition of bond polarizabilities.



(HPHC)

				V_m		$\gamma_\parallel \cdot 10^{24}$cm^{-3}				$\gamma_\perp \cdot 10^{24}$cm^{-3}				$(\gamma_\parallel - \gamma_\perp) \cdot 10^{24}$cm^{-3}				$\bar{\alpha} \cdot 10^{24}$cm^{-3}			
phase	ϑ/°C	n_e	n_o	cm^{3}mol^{-1}	S	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P	V	N	J/B	P
N	73.4	1.4989	1.4662	429.9	0.24	59.2	54.1	76.6	55.0	42.7	45.1	39.8	42.2	16.5	9.0	36.8	12.8	48.1	48.1	52.1	46.5
	73	1.5036	1.4649	429.5	0.265	60.0	53.3	77.6	55.4	42.3	45.5	39.5	41.8	17.7	7.8	38.1	13.6	48.2	48.1	52.2	46.3
	71	1.5105	1.4631	427.86	0.34	59.3	56.9	76.8	55.1	42.5	43.6	39.6	42.1	16.8	13.3	37.2	13.0	48.1	48.0	52.0	46.7
	69	1.5191	1.4621	425.75	0.45	58.2	53.0	75.6	54.4	43.0	45.4	39.9	42.7	15.2	7.6	35.7	11.7	48.1	47.9	51.8	46.6
	66	1.5210	1.4618	425.2	0.475	57.9	53.3	75.4	54.3	43.0	45.3	39.9	42.9	14.9	8.0	35.5	11.4	48.0	48.0	51.7	46.7
S_A	65	1.5310	1.4592	423.6	0.495	59.6	56.3	77.4	55.2	42.2	43.7	39.4	42.0	17.4	12.6	38.0	13.2	48.0	47.9	52.1	46.4
	64	1.5320	1.4595	423.15	0.515	59.2	55.5	77.0	55.0	42.4	44.1	39.5	42.2	16.8	11.4	37.5	12.8	48.0	47.9	52.0	46.5
	62	1.5338	1.4600	422.1	0.565	58.3	54.9	76.0	54.5	42.8	44.4	39.7	42.7	15.5	10.5	36.3	11.8	48.0	47.9	51.8	46.6
	60	1.5353	1.4604	421.2	0.605	57.7	54.5	75.2	54.1	43.0	44.5	39.8	43.0	14.7	10.0	35.4	11.1	47.9	47.8	51.6	46.7
	59	1.5360	1.4608	420.7	0.625	57.4	54.0	74.9	53.9	43.1	44.7	39.9	43.2	14.3	9.3	35.0	10.7	47.9	47.8	51.6	46.8
S_B	58.4	1.5422	1.4613	417.0	0.66	57.3	57.2	74.9	54.0	42.9	43.1	39.7	43.2	14.4	14.1	35.2	10.8	47.7	47.8	51.4	46.8
	56	1.5440	1.4622	415.6	0.725	56.5	56.4	73.9	53.4	43.2	43.4	39.8	43.7	13.3	13.0	34.1	9.7	47.6	47.7	51.2	46.9
	54	1.5449	1.4630	414.6	0.75	56.1	56.0	73.5	53.3	43.3	43.5	39.9	43.8	12.8	12.5	33.6	9.5	47.6	47.7	51.1	47.0
	50	1.5462	1.4639	412.98	0.785	55.6	55.7	73.0	53.0	43.4	43.5	39.9	44.1	12.2	12.2	33.1	8.9	47.5	47.6	50.9	47.1
	45	1.5480	1.4657	411.3	0.82	55.1	54.5	72.5	52.8	43.4	44.0	39.9	44.3	11.7	10.5	32.6	8.5	47.4	47.5	50.8	47.1
	35	1.5518	1.4686	408.3	0.825	54.7	52.7	72.5	52.8	43.2	44.5	39.9	44.3	11.5	8.2	32.6	8.5	47.4	47.2	50.8	47.1
		mean value				57.6	54.9	75.2	54.1	42.9	44.3	39.8	43.0	14.7	10.6	35.4	11.1	47.8	47.8	51.6	46.7
		standard deviation				1.6	1.4	1.7	0.8	0.4	0.8	0.2	0.8	1.9	2.1	1.7	1.7	0.26	0.22	0.46	0.25
		bond polarizabilities					61.5				48.8				12.7				53.0		

TABLE VI

The polarizability anisotropies of HBHA, EEBM, NPOB, and HPHC determined by Haller's extrapolation procedure from the nematic and smectic phases using the Vuks and Neugebauer relation.
For comparison the calculated values are listed.

substance	phase	$(\gamma_\parallel - \gamma_\perp)\cdot 10^{24}\text{cm}^{-3}$				bond polarizabilities
		Haller extrap.		mean values calc.		
		V	*N*	*V*	*N*	
EEBM	*N*	42.3	31.2	39.0	31.1	25.8
	S_A	32.9	29.7	37.0	31.1	
HBHA	*N*	49.3	54.0	33.3	40.8	17.55
	S_A	22.5	27.7	30.2	31.6	
	S_B	22.8	40.1	25.9	36.4	
NPOB	*N*	36.9	52.2	23.8	18.8	16.8
	S_A	15.8	14.4	22.7	20.1	
HPHC	*N*	11.5	7.1	16.2	9.1	12.7
	S_A	9.4	5.5	15.7	10.8	
	S_B	9.6	7.3	12.7	11.8	

ring the conjugated region of the molecule is markedly shortened and therefore the polarizability anisotropy becomes relatively small as found for HPHC.

We cannot decide from our investigations which internal field model is the best. Such decision would be possible only by measurements in the gaseous state in which the problem of internal field is avoided. We believe that all methods applied are relatively rough approximations. We can suppose that the de Jeu/Bordewijk model[6] generally gives too high values because in the less polarizable substance HPHC there is a relatively good agreement between the data calculated from the Vuks,[1] Neugebauer,[3] and Petrov[8] internal field models and the data obtained from the bond polarizabilities. The increment method obviously yields too low values for molecules exhibiting an extended conjugated region. Haller's extrapolation method[10] leads to different results depending on the internal field used and depending on the liquid crystalline phase in which the extrapolation is carried out.

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