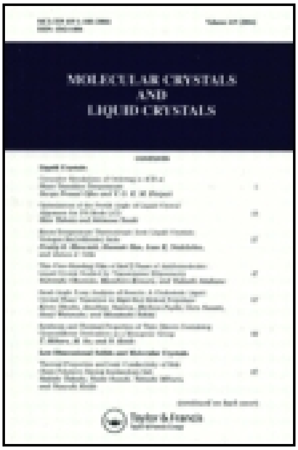

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Calculation of Dielectric and Optical Anisotropy of Nematic Cyanoethylene and Cyanobutadiene Derivatives

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Calculation of Dielectric and Optical Anisotropy of Nematic Cyanoethylene and Cyanobutadiene Derivatives

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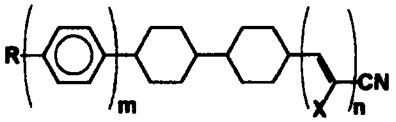
We have synthesized compounds with the general chemical structure



m = 0,1

n = 1,2 X = H, F

R = alkyl

By quantum chemical methods the polarizability and its anisotropy, the electrical dipole moment and its angle with the molecular long axis have been calculated. The molar volumes have been determined using group contribution methods. For the determination of the order parameter an empirical relation to the clearing temperature has been developed. Using these data, by the theory of Maier and Meier the dielectric and optical anisotropy have been calculated. The comparison with experimental data shows, that the method works with an accuracy acceptable for industrial application.

Keywords: dielectric constants; refractive indices; order parameter; semiempirical calculations; nematics

INTRODUCTION

For the development of new nematic liquid crystals, it would be advantageous to be able to calculate important properties of compounds in advance, without the necessity to do experiments. Bremer and Tarumi[1] made an attempt to correlate the results of semi-empirical quantum chemical calculations with $\Delta\varepsilon$ and Δn, and they found quite reasonable correlation between computed dipole moments and $\Delta\varepsilon$, as well as between computed polarizabilities and Δn. Significant scatter in the correlations was believed to be due to the limits of the semiempirical method. Their method does not allow to calculate directly these quantities.

Considering the theory of the dielectric properties of nematics, elaborated by Maier and Meier[2], we found that using some approximations the prediction of $\Delta\varepsilon$ and Δn is possible with an accuracy, acceptable for applications.

THEORY

According to Onsager the dielectric constant ε of isotropic media is given by[3]

$$\varepsilon = 1 + (NhF/\varepsilon_0)[\alpha_{av} + F\mu^2/(3k_BT)] \qquad (1)$$

$$N = N_A/V_m = \text{number density (number of molecules per volume unit)} \qquad (2)$$

$N_A = 6.02205\text{x}10^{23}\ \text{mol}^{-1}$(Avogadro's constant) ; V_m = molar volume
$h = 3\varepsilon/2\varepsilon + 1$ correction factor considering the internal field
$F = (1 - f\alpha)^{-1}$ correction for the reactive field; $f = (\varepsilon - 1)[2\pi\varepsilon_0 a^3(2\varepsilon + 1)]^{-1}$
α_{av} = average polarizability of a molecule; μ = electric dipole moment
$\varepsilon_0 = 8.854\text{x}10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}$(dielectric constant of vacuum)
$k_B = 1.38066\text{x}10^{-23}\ \text{JK}^{-1}$ (Boltzmann's constant); T = Kelvin temperature
a = radius of the spherical cavity,with Onsager's approximation: $4/3\pi\ N\ a^3 = 1$

Maier and Meier[2] derived formulas for the dielectric constants of nematics :

$$\varepsilon_{||} = 1 + (NhF/\varepsilon_0)[\alpha_{av} + 2/3\Delta\alpha\, P_2 + F(\mu^2/3k_BT)(1 - \{1 - 3\cos^2\beta\}\, P_2)] \qquad (3)$$

$$\varepsilon_{\perp} = 1 + (NhF/\varepsilon_0)[\alpha_{av} - 1/3\Delta\alpha\, P_2 + F(\mu^2/3k_BT)(1 + 1/2\{1 - 3\cos^2\beta\}\, P_2)] \qquad (4)$$

$\Delta\alpha = \alpha_{||} - \alpha_{\perp}$. $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$; P_2 = order parameter of the nematic

β = angle between molecule long axis and dipole moment

In equations (3) and (4) the quantities α_{av}, $\Delta\alpha$, μ and β can be calculated using quantum chemical methods. For calculating F and h the average dielectric constant ε and the number density N are needed. In equations (3) and (4) further the order parameter P_2 is needed.

Summarizing we can say, that besides the results of quantum chemical calculations , the knowledge of N and P_2 at room temperature (25^0 C) is necessary. For both quantities approximations are available, which will be explained in the next sections.

APPROXIMATION OF THE NUMBER DENSITY N

According to eq. (2), N depends on the molar volume V_m. The molar volumes at a reference temperature of 25^0 C of organic liquids can be approximated by a method of „group contributions“, proposed by Fedors [4]. The method uses partial volumes for each group or atom of a molecule, derived from a vast amount of organic simple liquids. We checked about 20 nematics with different chemical structures. We found that the calculation mostly delivers volumes smaller than the experiments, however, in all cases the difference being less than 10 %.

APPROXIMATION OF THE ORDER PARAMETER

According to the Maier-Saupe theory, the order parameter P_2 is a universal temperature function for all nematics[3]. In fact, however, the Maier-Saupe theory is an oversimplification and it is well known, that the order parameters of different compounds can be quite different. Since our further calculations are to be done for room temperature, we need order parameters at 25^0 C . In most cases P_2 data only for higher temperatures are available, which must be extrapolated to 25^0 C.

The temperature dependence of the order parameters of nematics in acceptable approximation follows the universal function (Pohl et al. [5])

$$P_2 = S_0\,(1 - yT/T_{NI})^{\beta} \qquad (5)$$

$S_0 = 1$ $\beta = 0.13 - 0.18$ depending on the specific material $y = 0.98$

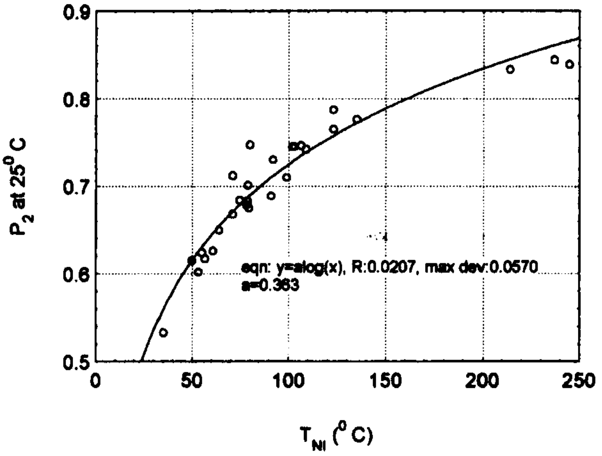
This formula is equivalent to that of Hanson and Shen [6], which was proposed by Haller et al. [7]. It is frequently used for the „Haller extrapolation“ for evaluation of $\Delta\alpha/\alpha$ and P_2 from the temperature dependence of refractive indices.

Specially Tough and Bradshaw [8] point at the fact, that equ. (5) has several failings. Near to T_{NI} it cannot represent the temperature dependence of P_2, and therefore we avoided to use it in this temperature region. The range for β indicated in [5] is not sufficient, and it must be extended to about 0.35 in order to describe small order parameters. In most cases β is 0.20 to 0.23.

We extracted from 25 references P_2 data and extrapolated them to room temperature by use of equ. (5). The data are plotted versus the clearing temperatures T_{NI} of the compounds in Fig. 1. There is a clear dependence of P_2 on the clearing temperature, which can be described well by:

$$P_2 = 0.363 \log T_{NI} \qquad (6)$$

Fig.1
Order Parameter versus clearing temperature



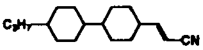
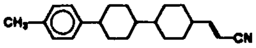
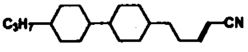
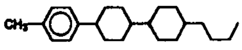
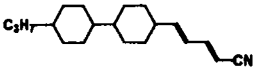
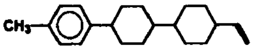
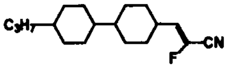
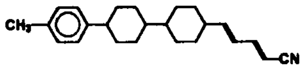
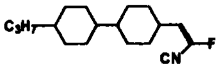
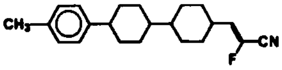
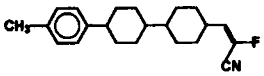
Using this relation, order parameters of arbitrary compounds at 25^0 C can be calculated, when the clearing temperatures T_{NI} are known. When data for T_{NI} are lacking, they can be approximately evaluated by the procedure included in the data base „LIQCRYST"[9], or for two ring compounds by the method of Vill[10].

The correlation between P_2 and T_{NI}, which has been derived empirically, is supported by theoretical considerations. The hard-rod [11]as well as the van-der-Waals theories[12] predict increasing P_2 at T_{NI} for increasing length-to-breadth ratios, in the same sense, in which T_{NI} is increasing. On the other hand, in the case of dyes dissolved in nematic basic mixtures a vaste experimental evidence is available, proving the increasing order parameters of the guest dyes with increasing molecular length-to-breadth ratios[13].

RESULTS

The compounds have been synthesized according to the instruction of Fujita et al.[14] .The experimental data of the compounds listed in Tab. 1, are compiled in Table 2.

Table 1

No.	Compound	No.	Compound
1		6	
2		7	
3		8	
4		9	
5		10	
		11	

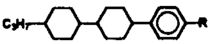
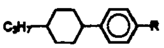
Mixture A	R	weight %
	$-CH_3$	15
	$-OCH_3$	5
	$-C_3H_7$	15
	$-OC_2H_5$	35
	$-OC_4H_9$	30

Table 2

Comparison of calculated and experimental data

comp.	1	2	3	4	5	6	7	8	9	10	11
V_m	273.5	305.7	300.5	282.0	282.0	295.7	307.2	284.8	320.8	303.7	303.7
α_{av}	151.9	167.6	182.4	153.6	151.3	190.5	188.8	174.7	221.4	192.3	189.9
$\Delta\alpha$	80.96	83.6	141.9	78.7	48.7	138.3	88.14	98.53	194.4	136.8	94.29
μ	3.697	3.688	4.099	3.300	3.096	3.707	0.075	0.202	4.103	3.306	3.084
β	3.89	8.61	4.51	18.31	48.49	5.072	67.34	21.21	4.26	16.86	47.7
T_m	38.9[1]	74.7[2]	75.3	38.4[3]	51.3	98.0	59.5[4]	63.5	104.2	116.0	105.4
T_{NI}	162.2	136.9	213.7	124.1	<51	295.7	174.9	159.0	<300	248.1	66[5]
T_{NI}:M	81.5	80.0	90.8	74.2	57.0	95.3	86.7	87.0	101.6	88.9	72.9
P_2	0.696	0.693	0.713	0.681	0.639	0.720	0.705	0.706	0.731	0.709	0.678
ε_{exp}	8.06	7.71	8.82	7.40	8.28	6.037	1.797	1.637	7.150	5.660	6.617
ε_{calc}	6.63	5.89	8.55	6.71	6.01	8.597	1.894	1.905	9.976	6.903	6.15
ε_{calc}:F	6.19	5.55	7.57	5.95	5.39	7.207	1.797	1.637	8.160	5.921	5.383
$\varepsilon_{\|exp}$	16.54	14.68	19.08	13.75	8.54	13.67	2.01	2.07	16.61	11.34	6.21
$\varepsilon_{\|calc}$	16.83	14.84	20.43	12.38	6.97	18.10	2.088	2.157	21.55	13.07	7.60
$\varepsilon_{\|calc}$:F	14.35	12.76	16.86	10.61	6.14	14.74	2.09	2.15	17.13	10.90	6.56
$\varepsilon_{\perp exp}$	3.82	4.22	3.69	4.22	8.15	2.22	1.69	1.42	2.42	2.82	6.82
$\varepsilon_{\perp calc}$	3.79	3.54	4.13	3.87	5.54	3.84	1.80	1.77	4.19	3.82	5.42
$\varepsilon_{\perp calc}$:F	3.46	3.27	3.69	3.51	4.92	3.44	1.80	1.78	3.68	3.43	4.74
$\Delta\varepsilon_{exp}$	12.72	10.46	15.39	9.53	0.39	11.45	0.32	0.65	14.19	8.52	-0.61
$\Delta\varepsilon_{calc}$	13.04	11.30	16.30	8.51	1.43	14.26	0.29	0.38	17.36	9.25	2.18
$\Delta\varepsilon_{calc}$:F	10.89	9.49	13.17	7.10	1.22	11.30	0.29	0.38	13.45	7.47	1.82
n_e(exp)	1.542	1.542	1.575	1.555	1.569	1.635	1.536	1.551	1.536	1.572	1.583
n_e(calc)	1.406	1.396	1.484	1.394	1.361	1.510	1.445	1.458	1.576	1.496	1.455
n_o(exp)	1.458	1.464	1.444	1.464	1.511	1.467	1.469	1.475	1.447	1.461	1.508
n_o(calc)	1.299	1.297	1.310	1.295	1.304	1.336	1.339	1.331	1.348	1.331	1.345
Δn_{exp}	0.084	0.078	0.131	0.091	0.058	0.168	0.067	0.076	0.089	0.111	0.075
Δn_{calc}	0.107	0.099	0.174	0.099	0.057	0.174	0.106	0.127	0.228	0.165	0.110

V_m : cm^3/mol ; α , $\Delta\alpha$: atomic units; μ : Debye ; T_{NI} : clearing temperature of pure compound; T_{NI}:M = clearing temperature of the mixture ; all temperatures in ^{0} C; P_2 : order *parameter calculated with equ. (6) using the T_{NI} of the mixtures; F : in the dipole terms of* equs. (1,3,4) we set F=1 . The molecular data have been calculated with MOPAC/AM1 for most stable confor-mations including all-trans conformations of the alkyl chains.

Some compounds have additional phase transitions: [1] sm3 57.4 sm2 59.3 sm1 65.5 N [2] sm2 101.2 sm1 101.4 N [3] sm 65.6 N [4] smB 135.7 N

[5] extrapolated from a blend with mixture A of Table 1

The dielectric and optical data have been extrapolated from blends, containing 85 weight % of the basic mixture A and 15 weight % of the respective compound.

For calculation of the molecular data α_{av}, $\Delta\alpha$, μ and β we used ab-initio calculations [15] as well as semiempirical methods (MOPAC [16] with AM1 and PM3 Hamiltonians). The most critical point is the estimation of the effective dipole moment μ_{eff}, which due to association effects in liquids is smaller than the total dipole moment μ, obtained in the gas phase or in highly diluted solutions [17]. The decrease of the effective dipole can be expressed by the factor $g = (\mu_{eff}/\mu)^2$, which can become as small as 0.45 [18]. The quantum chemical calculations deliver data for the gas phase, this is for compounds without intermolecular interactions. We found, that the ab-initio calculations deliver higher μ values than use of AM1. Therefore in Tab. 2 only data obtained by AM1 are listed (those obtained by PM3 are similar). Using equs. (2) (3) and (4) too high values are obtained for $\varepsilon_{||}$, $\varepsilon_{\perp}$ and $\Delta\varepsilon$. By calculation of conformers, which do not have the all-trans conformation, we tried to improve the agreement, but without success. When we set the factor F = 1 in the dipole terms of equs. (1), (2), (3), surprisingly we obtained better agreement between the calculated data with those extrapolated from mixtures. This procedure is not theoretically founded, however, reflects the effective decrease of the dipoles in nematics.

The calculated optical data mainly depend on α_{av} and $\Delta\alpha$. Using different quantum chemical methods or consideration of different conformers did not improve substantially the results. In selected examples we found, that the calculated α_{av} and $\Delta\alpha$ are considerably lower than the experimental data, calculated from the refractive indices. Using MOPAC7 it is possible to calculate the polarisability data for higher frequencies, which delivers larger α_{av} and $\Delta\alpha$ and may simulate the dispersion, however, only small improvements could be achieved.

The order parameter has influence on $\Delta\varepsilon$ and Δn . From mixtures for the guest-host effect it is well known, that guest molecules can have P_2 values different from those of the host mixtures. In our calculations, however, we found better agreement with the experiments, when we used the P_2 derived by equ. (6) from the clearing temperatures of the mixtures.

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