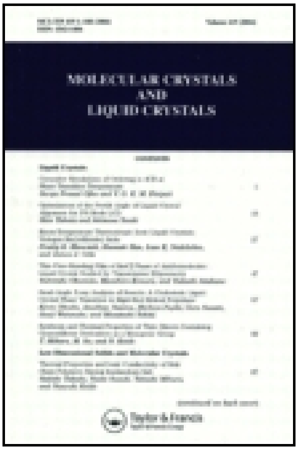

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QUANTUM CHEMICAL CALCULATIONS IN INDUSTRIAL LIQUID CRYSTAL RESEARCH

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In advance to syntheses in the laboratory, it is very useful, to have quick and easy procedures available, allowing the calculation of physical properties of liquid crystal materials without any experimental basis. Using different quantum chemical methods, it is possible to calculate molecular data like electrical dipole moment and polarizability including the anisotropy of these data. By comparison of the results of ab-initio and semiempirical methods it can be shown, that the latter are timesaving and reliable enough for prediction of data for applications. In order to calculate dielectric properties of nematic liquid crystals, the necessary data of molar volumes and order parameters can be obtained by empirical methods without measurements. One major problem is the calculation of effective electrical dipole moments, taking in consideration the association in compounds with large dipole moments. The results of different approaches for this purpose are compared and discussed. Because approaches found in the literature fail in the case of large dipole moments, a new procedure taking in account attractive and repulsive energies of the dipole-dipole interaction has been developed. In order to improve the agreement of calculated optical data with experimental data, the dispersion of the polarizability is taken into account.

Keywords: quantum chemical calculation; dielectric and optical properties; dipole moments; absorption spetrum.

1. INTRODUCTION

The synthesis of new liquid crystalline compounds for the application in displays is still an important topic. The prediction of the physical properties of the compounds, specially the dielectric constants and the optical refractive indices and their anisotropies, without performing experiments, is a useful tool in supporting synthesis groups. There have been some attempts in order to calculate these properties. Bremer and Tarumi [1] observed a correlation between dipole moments and $\Delta\varepsilon$, as well as between polarizabilities and Δn, with dipoles and polarizabilities calculated by semiempirical quantum chemical calculations. The observed scattering in the correlations was believed to be due to the limits of the semiempirical method. Saitoh *et al.* [2] tried to improve these data, by applying the Maier-Meier theory. Klasen *et al.* [3] used the well-known theories of Vuks and Maier-Meier in order to calculate the optical and dielectric anisotropies of nematics. They obtained the necessary data for dipoles, polarizabilities and their anisotropies from semiempirical quantum chemical calculations, by setting generally the density of the materials equal to one, and the order parameter equal to 0.7 at 293 K. Despite these approximations, the agreement between calculated data and experimental data (obtained by extrapolation from 10% solutions of the compounds in a common basic mixture) was very satisfying. Fujita *et al.* [4] used a similar approach as Klasen [3], however they used molecule specific densities calculated from molar volumes obtained from a group contribution method, and individual order parameters evaluated from an empirical relation between clearing temperature and order parameter at room temperature. In the case of compounds with moderate polarity the agreement of calculated and experimental data was good, however in compounds possessing large dipoles there have been systematic differences.

In order to elucidate the role of the data obtained from quantum chemical calculations for the above explained purpose, we used different quantum chemical methods. Further we studied the influence of the different conformations, existing in real liquid crystalline compounds, and the possibilities to calculate effective dipoles. Finally, for the calculation of the optical properties we investigated the role of the dispersion of the polarizabilities and their anisotropies.

2. CALCULATION OF DIELECTRIC AND OPTICAL PROPERTIES

2.1. Theory of Dielectric Properties

The equation for the dielectric constant ε of isotropic media has been derived by Onsager [5]

$$\varepsilon = 1 + (\mathrm{NhF}/\varepsilon_0)[\alpha_{\mathrm{av}} + \mathrm{F}\mu^2/(3\mathrm{k_B T})], \tag{1}$$

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

$N_A = 6.02205 \times 10^{23}$ mol^{-1} Avogadro constant,
V_m = molar volume,
$h = 3\varepsilon/\ 2\varepsilon + 1$ correction factor considering the internal field,
$F = (1 - f\alpha_{av})^{-1}$ correction factor for the reactive field,
$f = (\varepsilon - 1)\ [2\pi\varepsilon_0 a^3\ (2\varepsilon + 1)]^{-1}$,
α_{av} = average polarizability of a molecule,
$\varepsilon_0 = 8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1} dielectric constant of vacuum,
μ = electric dipole moment,
$k_B = 1.38066 \times 10^{-23}$ JK^{-1} Boltzmann constant,
T = Kelvin temperature, a = radius of the spherical cavity.

For calculating a, we use Onsager's approximation: $4/3\pi$ N $a^3 = 1$. Maier and Meier [5] derived formulas for the dielectric constants of nematics:

$$\varepsilon_{\|} = 1 + (\mathrm{NhF}/\varepsilon_0)[\alpha_{av} + 2/3\Delta\alpha\bar{P}_2 + \mathrm{F}(\mu^2/3k_B T)(1 - \{1 - 3\cos^2\beta\}\bar{P}_2)], \tag{3}$$

$$\varepsilon_{\perp} = 1 + (\mathrm{NhF}/\varepsilon_0)[\alpha_{av} - 1/3\Delta\alpha\bar{P}_2 + \mathrm{F}(\mu^2/3k_B T)(1 + 1/2\{1 - 3\cos^2\beta\}\bar{P}_2)], \tag{4}$$

$\Delta\alpha = \alpha_{\|} - \alpha_{\perp}$, $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$, $\overline{P_2}$ = order parameter,
β = angle between molecule long axis and dipole moment.

The quantities α_{av}, $\Delta\alpha$, μ and β can be calculated using quantum chemical methods. The molar volume needed for calculation of the number density N is obtained by the group contribution method of Fedors [6]. We derived the empirical relation

$$\overline{P_2} = 0.363 \log T_{NI}, \tag{5}$$

between clearing temperature T_{NI} (°C) and $\overline{P_2}$ at room temperature [4] (25°C).

This determination of $\overline{P_2}$ is suited for single compounds. In mixtures (often basis mixtures with an order parameter of about 0.7) the approximation of Klasen *et al.* [3], using $\overline{P_2} = 0.7$, may be preferable.

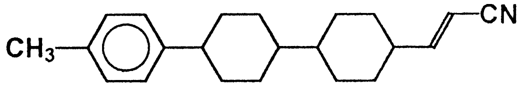
The refractive indices have been calculated by setting $\mu = 0$ in Eqns. (1), (3), and (4) and by using the approximation

$$\varepsilon = n^2. \tag{6}$$

2.2. Calculation of Molecular Data

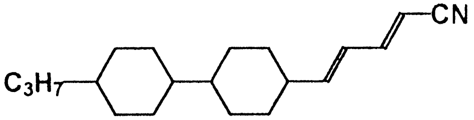
The calculations were performed on known compounds, from which experimental data for comparison have been available. These compounds are shown in the following list:

Fu 6



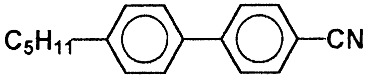
[4]

Fu 3



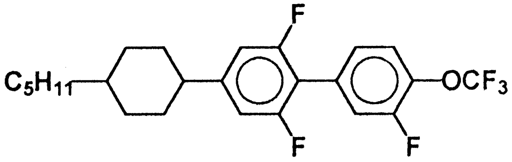
[4]

5CB



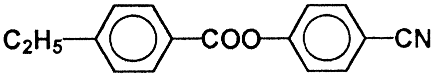
[10]

M 43



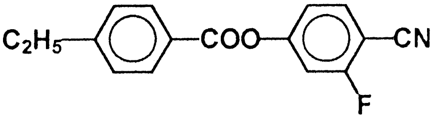
[3]

M 56



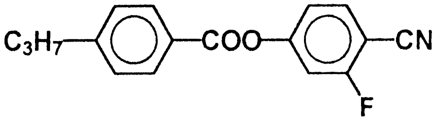
[3]

M 57



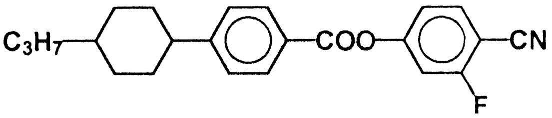
[3]

M 59



[3]

M 53



[3]

The molecular data α_{av}, $\Delta\alpha$, μ and β were calculated using ab-initio (B3LYP/6-31 G(d)) [7] as well as semiempirical methods (MOPAC [8] with AM1 Hamiltonian). In order to demonstrate the suitability of the two methods, we choose the compound 5CB and displayed the results on Table 1. The first column shows the ab-initio data for the most stable conformer, exhibiting the all-trans conformation of the pentyl group. It is well-known, that molecules like 5CB due to their flexibility can exist in several conformations.

TABLE 1 Molecular, Dielectric and Optical Data of 4-n-Pentyl-4′- Cyano-Biphenyl (5CB); $T_{NI} = 35.3°C$ [9]; $\overline{P}_2 = 0.46$ [10]; $V_m = 243.99$ [11]

		ab	Initio	MOPAC	AM1	Exp
	conform[1]	ttt	average	ttt	average	
	Θ^2	44.1		40.2		
1	%[3]	54.69		54.28		
2	α_{av} (a.u.)	207.98	204.61	171.82	171.66	220.06 [10]
3	$\Delta\alpha$ (a.u.)	214.98	204.56	178.50	178.05	183.58 [10]
4	μ (D)	5.949	5.900	4.124	4.117	4.76 [12]
5	β (degrees)	8.07		7.79		
6	$b = 1 - 3\cos^2\beta$	− 1.941	− 1.900	− 1.945	− 1.936	
7	ε_{av}	29.95	29.05	12.98	12.93	10.5 [10]
8	$\varepsilon_{\parallel}$	54.41	52.44	22.99	22.71	18.5 [10]
9	$\varepsilon_{\perp}$	17.72	17.35	7.98	8.04	7.0 [10]
10	$\Delta\varepsilon$	36.69	35.09	15.01	14.67	11.5 [10]
11	$\varepsilon_{av}\,(\mu = 0)$	2.3983	2.3653	2.0685	2.0672	
12	$\varepsilon_{\parallel}\,(\mu = 0)$	2.7445	2.7838	2.3972	2.4066	
13	$\varepsilon_{\perp}\,(\mu = 0)$	2.2251	2.1559	1.9041	1.8974	
14	n_e	1.6566	1.6685	1.5483	1.551	1.71 [10]
15	n_o	1.4917	1.4683	1.3799	1.377	1.53 [10]
16	Δn	0.165	0.200	0.168	0.174	0.18 [10]

[1] Conformations: ttt = all-trans; average = average of 4 most important conformers according to Boltzmann's distribution.

[2] Θ = twist angle of phenyl rings.

[3] Amount (%) according to Boltzmann's equilibrium.

We calculated also three conformers containing gauche conformations in the pentyl group. They showed slightly different values. From the 4 conformers we calculated an average according to a Boltzmann distribution (column 2). As the comparison with column 1 proves, the differences are not significant. The semiempirical method MOPAC/AM1 has been applied also to the most stable conformer (column 3) and to the gauche containing conformers, their average is shown in column 4. Both sets of data do not show significant differences. Comparing the semiempirical data with the ab-initio data we see significant differences in α_{av}, $\Delta\alpha$ and μ . All these data are larger in the ab-initio calculations, leading to very unrealistic large dielectric constants. By comparison of the calculated dielectric data with experimental data (column 5) it becomes obvious, that the semiempirical method delivers better results, which nevertheless need corrections.

In order to obtain more realistic dipole moments, we tried to use the COSMO simulation during the calculation with MOPAC/AM1. In the COSMO simulation the molecules are not treated as single molecules in vacuum, but they are surrounded by a dielectric with a certain dielectric constant. The results obtained for 5CB are shown in Table 2. Obviously the dipole

TABLE 2 Dipole Moments μ of 5CB Calculated by MOPAC/AM1 using COSMO Simulation, EPS = Simulated Dielectric Constant

EPS	μ
0	4.124
20	5.566
40	5.635
78.4	5.686

moments are increased by COSMO, and they are even more far from reality than with the ordinary MOPAC/AM1 calculation. The refractive indices calculated on the basis of ab-initio and semiempirical results are not very satisfying. The reason for this will be discussed later.

Summarizing we can say, that calculation of the most stable conformer by semiempirical methods (besides MOPAC/AM1 we also checked in several cases MOPAC/PM3, the former was more satisfying) is an acceptable basis for the evaluation of the dielectric and optical properties of nematics. The ab-initio method is much more time-consuming, can be applied only to small molecules and delivers less useful results.

2.3. Calculation of Effective Dipole Moments

In general, by use of the calculated dipole moments, the dielectric constants and anisotropies obtained by the Maier-Meier theory are too large. This is not mainly due to the approximations inherent in this theory. Instead of the calculated dipole moments, we have to use effective dipole moments μ_{eff}.

In molecules possessing strong dipole moments, by dipole-dipole interaction associates are formed. The associates have dipole moments different from those of the monomers. In the literature this fact is considered by Kirkwood's correlation factor

$$g_i = (\mu_{\mathrm{effi}}/\mu)^2. \tag{7}$$

The index i denotes the possibilities of calculating g from the different dielectric constants $\varepsilon_{\|}$, $\varepsilon_{\perp}$, $\varepsilon_{\mathrm{av}}$ and $\Delta\varepsilon$.
For g_i the relations hold:
dimers with parallel dipoles $g_i > 1$,
dimers with antiparallel dipoles $g_i < 1$,
no association $g_i = 1$.

Generally, the g_i factors are different for the different dielectric constants. Derived from $\varepsilon_{||}$, $\varepsilon_{\perp}$, ε_{av}, $\Delta\varepsilon$ (related to the experimental $\mu = 4.76$ D [12]) we obtained for 5CB:

$g_{||} = 0.625$, $g_{\perp} = 0.629$, $g_{av} = 0.590$, $g_{\Delta\varepsilon} = 0.591$.

In nematic compounds used for applications in many cases only $\Delta\varepsilon$ is known [1,3] . This allows to calculate "experimental" Kirkwood factors $g_{\Delta\varepsilon}$. Since the major correction for the calculation of $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ stems from $\varepsilon_{||}$ including $\mu_{||}$, for the sake of simplicity in the following we restrict our considerations to $\mu_{||}$ and $g_{||}$.

When experimental data are available, it is easy to estimate the g_i factors. A major problem is the calculation of g_i factors, without using experimental data. In the literature only two theoretical approaches have been found, which seemed to be practicable.

For the calculations molecular lengths L are necessary. They have been taken from the calculated molecules, as the distances of the two atomic centers with maximal distance and addition of the respective van der Waals radii ($r_H = 1.20$ Å, $r_N = 1.50$ Å, $r_F = 1.35$ Å). The determination of the molecular breadths B is less straightforward, because the molecules are not simple rods and in principle are biaxial. We have chosen B = 4.5Å according to the lateral intermolecular distance in simple rod-like molecules observed in X-ray investigations. The calculated results are not very sensitive to slight changes of B. All data have been calculated for T = 298.2 K = 25°C.

2.3.1. Theory of de Jeu and Bordewijk

There is an older approach published by de Jeu and Bordewijk [13,14], based on the calculation of the dipole moment of a sphere with the radius a in the field of a central dipole $\mu_{||}$, assuming ideal order ($\overline{P}_2 = 1$). The effective dipole μ_{eff} is given by:

$$\mu_{eff} = \mu_{||}\left[1 - \frac{3\Omega}{4\pi\varepsilon_0 ab^2}\frac{\mu_{||}^2}{k_B T}\right]. \tag{8}$$

The shape factor Ω_a for a prolate spheroid with long axis 2a and short axis 2b is defined by

$$\Omega_a = 1 - w^2 + 1/2w(w^2 - 1)\ln[(w+1)/(w-1)], \tag{9}$$

$$w^2 = a^2/(a^2 - b^2). \tag{10}$$

The shape factor is dependent only on a/b. In calamitic liquid crystalline compounds the relations are valid:

$1 < a/b \leq 5$; $1/3 > \Omega_a \geq 0.05582$.

Using de Jeu's approach, the effective dipole moment was calculated for 5CB:

$\mu_{\mathrm{eff}} = -3.4852\,\mathrm{D}$; μ (AM1) $= 4.124\,\mathrm{D}$; a $= 9.42$ Å; b $= 2.25$ Å; $\boldsymbol{\Omega}_{\mathrm{a}} = 0.0709$.

Also all other compounds listed on page 5 yielded effective negative dipole moments. This caused us to make model calculations with equation (8). With dipole moments of $\mu \leq 2$ D equation (8) delivered acceptable results, but with dipole moments larger than about 3.5 D the effective dipole moments were negative. From this result we conclude that the approach is not useful for compounds with medium or large dipole moments.

2.3.2. Theory of Dunmur and Palffy-Muhoray [15]

Dunmur and Palffy-Muhoray [15] elaborated a mean field theory of dipole-dipole correlation in nematic liquid crystals by modelling the anisotropic radial distribution functions for two hard ellipsoids. Including the dipole-dipole interaction energy, they were able to calculate the Kirkwood correlation factors. The interaction is order parameter dependent. In the case of uniaxial molecules the model is based on ellipsoids with the length L and the breadth B, while the dipole is parallel to L. Then different g factors parallel respectively perpendicular to the symmetry axis depend on the prolate (elongated) respectively oblate (discotic) shape of the molecules.

If the molecular dipole is parallel to the symmetry axis of the uniaxial molecule, the following equations have been presented:

$$g_{||} = 1 - \frac{4N\mu_l^2\kappa_1(1+2\overline{P}_2)}{45(4\pi\varepsilon_o)k_BT}, \tag{11}$$

$$g\perp = 1 - \frac{4N\mu_l^2\kappa_1(1-\overline{P}_2)}{45(4\pi\varepsilon_o)k_BT}, \tag{12}$$

$$\kappa_1 = 3[\mathrm{L}-\mathrm{B}]/(\mathrm{L}+2\mathrm{B}), \tag{13}$$

μ_{l} = longitudinal molecular dipole, κ_1 depends on the length L and the breadth B , and is a measure for the length-to-breadth ratio, κ_1 is positive in rod-like molecules and negative in discotic molecules. The basis of equations (11) and (12) is an approximation, because in reality the dipoles are not exactly parallel respectively perpendicular to the main axes. Even 5CB has a longitudinal and a lateral dipole component.

In order to check this theory, we calculated the data of several compounds, partly with quite large dipole moments. For the calculations we used the data listed in Table 3 , and in addition B = 4.5 A . The results are also compiled in Table 3. The compounds are listed with increasing dipole moments from left to right, in the range $3.7\Delta < \mu < 7.4\Delta$. It seems that the theory delivers reasonable values of g_{Dunmur} for $\mu < 6$ D. But with larger dipole moments there is a systematic trend to very small values, and even negative values occur in compounds with very large dipole moments. This result was not satisfying for practical applications, in which compounds with very large dipole moments are of special importance.

Because we did not find other suitable approaches in the literature, we tried to elaborate another applicable method for calculation of effective dipole moments.

2.3.3. Approach Considering Attractive and Repulsive Dipole Interaction Energy on the Basis of Coulomb's Law ("Charge Interaction Approach")

In nematic liquid crystals the molecules are in a dense packing. This is, they come so near together, that the repulsive energy plays an important role in determining the structure. In the literature the simple formulas for calculation of the dipole-dipole interaction energy have been derived with the assumption, that the distance of the molecules is large compared with the molecular dimensions. We derived expressions for the dipole-dipole interaction energy using the following simple model. The molecules with length L and breadth B possess a dipole moment μ exactly in longitudinal direction. The quantum chemical calculations deliver the charge distribution in the molecules. Usually the partial charges are distributed over the whole molecule, and not concentrated to certain parts. Then we can assume that the dipole moment of the molecule is extended over the whole length L, and we can connect it with the partial charges q by the equation

$$\mu = \mathrm{qL}. \tag{14}$$

For the calculation of the intermolecular interaction of the molecules we use Coulomb's law ($\mathrm{u} = \mathrm{q}_1\mathrm{q}_2/4\pi\varepsilon_0\,\mathrm{r}$), and the model sketched in Figure 1. Five different molecular configurations are considered.

a) Molecules antiparallel side-to-side

$$u_a = \frac{2q^2}{4\pi\varepsilon_0}\left(\frac{1}{(B^2+L^2)^{1/2}} - \frac{1}{B}\right), \qquad \mu_{\mathrm{a}} = 0. \tag{15}$$

TABLE 3 Data of Several Compounds Calculated with Different Approaches

comp.	Fu6	Fu3	5CB	M43	M56	M57	M59	M53
$V_m(cm^3)$	295.7	300.5	244.0	328.7	196.4	195.4	211.5	289.9
α_{av}(a.u.)	190.5	182.4	171.8	227.9	161.3	163.7	172.7	222.3
$\Delta\alpha$ (a.u.)	138.3	141.9	178.5	173.2	181.6	181.4	185.7	209.5
μ (D)	3.707	4.099	4.124	5.687	6.018	7.149	7.187	7.333
β	5.07	4.51	7.79	8.38	14.27	17.58	17.29	19.06
$1-3\cos^2\beta$	– 1.977	– 1.981	– 1.945	– 1.936	– 1.818	– 1.726	– 1.735	– 1.680
T_{NI}(°C)	295.7	213.7	35.3	45[1]	47	6	18	203
L (A)	20.51	20.89	18.84	23.97	17.44	17.44	18.56	23.09
P_2	0.720	0.713	0.46	0.700	0.700	0.700	0.700	0.700
Data obtained by the theory of Maier-Meier [5] equations (3,4)								
ε_{calc}	8.597	8.55	12.98	17.62	36.53	52.21	47.72	34.67
$\varepsilon_{\|calc}$	18.10	20.43	22.99	38.66	80.29	112.7	103.1	72.98
$\varepsilon_{\perp calc}$	3.84	4.13	7.98	7.10	14.65	21.96	20.03	15.52
$\Delta\varepsilon_{calc}$	14.26	16.30	15.01	31.56	65.65	90.75	83.05	57.46
$\Delta\varepsilon_{exp}$[2]	11.45	15.39	11.5	15.1	37.5	53.7	50.2	37.5
Data obtained by the theory of Dunmur and Palffy-Muhoray [15] equation (11)								
g_{Dunmur}	0.760	0.710	0.731	0.456	0.155	– 0.198	– 0.166	– 0.006
$\mu_{eff\ Dunmur}$	3.232	3.454	3.526	3.841	2.371	—	—	—

Data obtained by the charge interaction approach								
Two configurations								
ΔU	258	303	387	427	962	1358	1194	772
x_d	0.526	0.531	0.539	0.543	0.596	0.634	0.618	0.577
g	0.899	0.882	0.850	0.836	0.653	0.537	0.583	0.715
$\mu_{eff \neq \Delta}$	3.514	3.849	3.803	5.198	4.865	5.238	5.489	6.200
Five configurations								
x_a	.2766	.2914	.2871	.3363	.5004	.6182	.5771	.4545
x_b	.2246	.2283	.2276	.2383	.2302	.2068	.2201	.2439
x_c	.1365	.1267	.1294	.1003	.0402	.0177	.0237	.0518
x_d	.1680	.1617	.1632	.1415	.0874	.0528	.0622	.0965
x_e	.1943	.1921	.1927	.1836	.1418	.1045	.1170	.1534
g	0.840	0.814	0.822	0.741	0.466	0.306	0.366	0.555
$\mu_{eff \neq \Delta}$	3.397	3.698	3.739	4.895	4.108	3.956	4.345	5.461
Calculated using experimental data								
g_{exp}	0.821	0.936	0.805	0.501	0.581	0.599	0.613	0.662
$\mu_{effexp \neq \Delta}$	3.359	3.965	3.699	4.024	4.588	5.535	5.625	5.965

[1] estimated by comparison with molecules of related structure.

[2] Experimental data from: Fu3[4], Fu6 [4], 5CB[10], M43-M59[1].

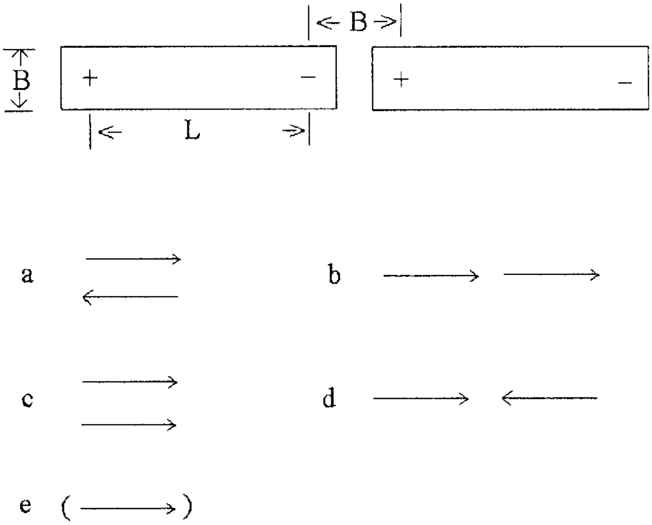


FIGURE 1 Definition of length and breadth in the dipolar molecules and the 5 molecular configurations (a - e) in the Coulomb approach.

b) Molecules parallel end-to-end

$$u_b = \frac{q^2}{4\pi\varepsilon_0}\left(\frac{2}{L} - \frac{1}{B} - \frac{1}{2L}\right), \quad \mu_{\mathrm{b}} = 2\mu. \tag{16}$$

c) Molecules parallel side-to-side

$$u_c = \frac{2q^2}{4\pi\varepsilon_0}\left(-\frac{1}{(B^2+L^2)^{1/2}} + \frac{1}{B}\right) = -u_a, \quad \mu_{\mathrm{c}} = 2\mu. \tag{17}$$

d) Molecules antiparallel end-to-end

$$u_d = \frac{q^2}{4\pi\varepsilon_0}\left(-\frac{2}{L} + \frac{1}{B} + \frac{1}{2L}\right) = -u_b, \quad \mu_{\mathrm{d}} = 0. \tag{18}$$

e) Molecules without interaction (monomers)

$$\mathrm{u}_{\mathrm{e}} = 0, \quad \mu_e = \mu. \tag{19}$$

The effective dipole moments can be calculated as the sum of the molar fractions of the configurations with non-zero dipole moments:

$$\mu_{\mathrm{eff}} = 2\mathrm{x}_b\mu + 2\mathrm{x}_c\mu + \mathrm{x}_e\mu. \tag{20}$$

The molar fractions $\mathrm{x_b}$, $\mathrm{x_c}$ and $\mathrm{x_e}$ can be calculated as existence probabilities in a Boltzmann equilibrium of the 5 different configurations:

$$\mathrm{x_i} = \frac{N_i}{N} = \frac{\exp(\frac{-u_i}{k_B T})}{\sum_i \exp(\frac{-u_i}{k_B T})}. \tag{21}$$

We calculated the molar fractions of the 5 configurations. The g factors and the effective dipole moments of the investigated compounds have been calculated in a first approach using only configurations a and b ("Two configurations approach"), and in another step using all 5 configurations ("Five configurations approach"). The results are compiled in Table 3.

In the "Five configurations approach" we find quite good agreement for compounds Fu6, 5CB, M56 and M53, this is for compounds with moderate up to very large dipole moments. The agreement is moderate in compounds Fu3 and not good in M43, M57 and M59.

Using the "Two configurations approach", there is reasonable agreement in all cases except M43. When we check the chemical structure of M43, we recognize that the dipole moment has several quite large lateral partial moments that are concentrated on the two benzene rings of the molecule, and thus does it not fulfill the suppositions of the present model.

We find that the results of the Dunmur-Palffy-Muhoray theory agree reasonably with the experimental data in the case of dipole moments up to about 6 D (compounds Fu6, Fu3, 5CB and M43), but with larger dipole moments there are large systematic deviations, which finally arrive at negative g factors.

Comparing the different approaches for the whole spectrum of dipole moments, we see that the "Two configurations charge interaction approach" works best. This is surprising, because it is the most simple approach. For compounds with pronounced longitudinal dipole moments it seems to be a satisfying approximation but it should not be used for a sophisticated discussion of the dipole association phenomena.

In model calculations we have checked the "Two configurations charge interaction approach". Figures 2–4 present the dependence of the g factor on μ, L and B. We can see that g is very sensitive to μ, but much less sensitive to L and B. For the further calculations we have chosen $\mathrm{B} = 4.5\text{Å}$.

L has been chosen as the distance of the atomic nuclei of the most distant atoms in longitudinal direction. This gave better results than the complete molecular length including the van der Waals radii of the most distant atoms.

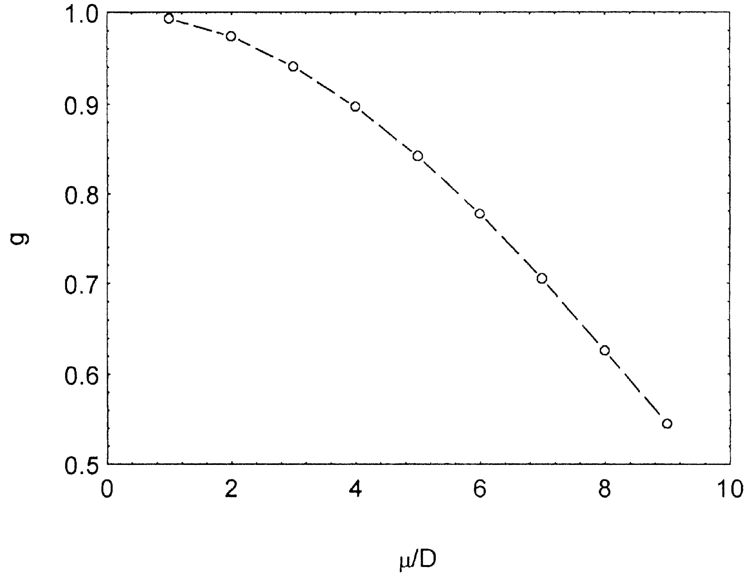


FIGURE 2 g factors calculated with the "Two configurations charge interaction approach"; L = 20Å; B = 4.5Å.

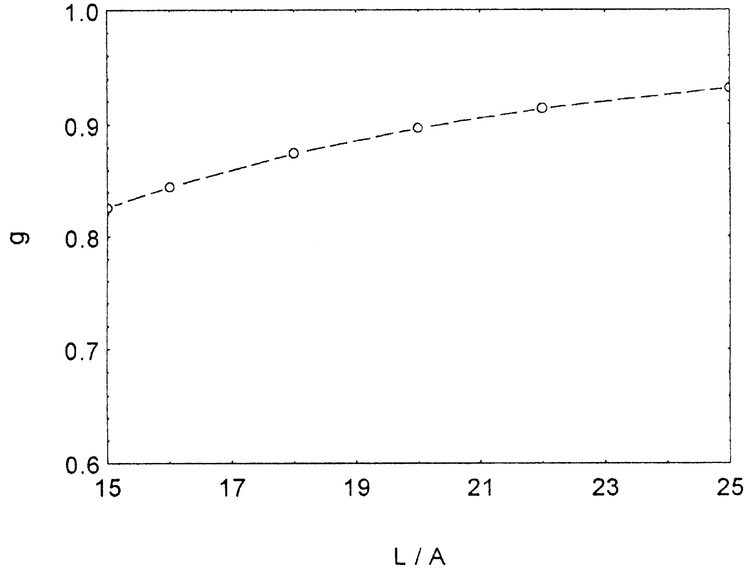


FIGURE 3 g factors calculated with the "Two configurations charge interaction approach"; $\mu = 4.0$ D; B = 4.5 Å.

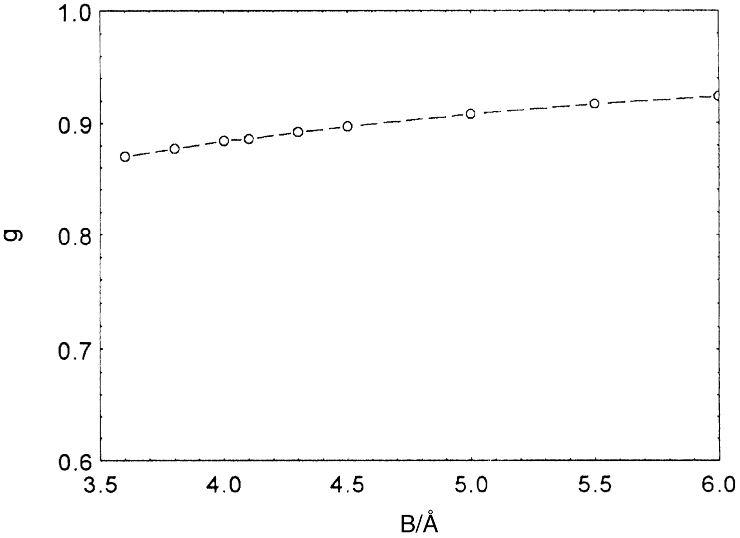


FIGURE 4 g factors calculated with the "Two configurations charge interaction approach", $\mu = 4.0\,\mathrm{D}$; $\mathrm{L} = 20.0\,\text{Å}$.

Disagreements with experimental data are partly due to the uncertainty in the order parameters of compounds, whose data are extrapolated from mixtures. Table 4 elucidates this on the hand of two M compounds. Table 4 contains the order parameters obtained by equation (5) using the clearing temperatures and the data calculated with them, in comparison to data

TABLE 4 Data Calculated with Different Values of the Order Parameter

	M 57			M 53		
	$\overline{P}_2$ 0.283		$\overline{P}_2$ 0.700	$\overline{P}_2$ 0.838		$\overline{P}_2$ 0.700
$\Delta\varepsilon_{\mathrm{calc}}$[1]	82.38		204.11	121.79		101.78
$\Delta\varepsilon_{\mathrm{exp}}$[2]		53.7			37.5	
μ_{calc}[3]		7.149			7.333	
μ_{ex}[4]	6.01		3.756	4.189		5.394
g_{ex}[5]	0.707		0.276	0.326		0.451

[1] calculated by the theory of Maier-Meier, equations (3,4).

[2] experimental data from Klasen *et al.* [3], obtained by extrapolation from mixtures.

[3] calculated by MOPAC/AM1.

[4] calculated from $\Delta\varepsilon_{\mathrm{exp}}$[2] using the indicated order parameter.

[5] calculated using μ_{calc}[3] and μ_{ex}[4].

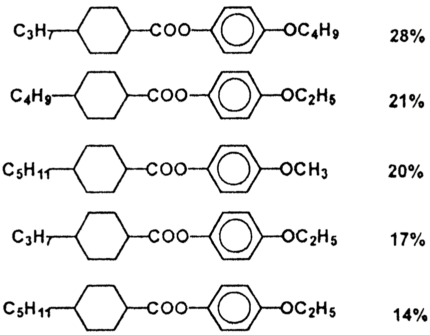
calculated with $\overline{P}_2$=0.7. There are very large differences, also in the "experimental" data. We may assume, that neither the $\overline{P}_2$ calculated for the pure compound nor the $\overline{P}_2 = 0.7$ of the mixture is correct, the true $\overline{P}_2$ should be intermediate between these two.

There is another problem in extrapolating data from mixtures. The dielectric constants, the effective dipoles and the g factors are different when a given compound is investigated in a polar and a non polar basic mixture, because the formation of associated molecular pairs is dependent on the dielectric constant of the medium. We made experiments [16] with 5CB in the polar mixture A (Mixture A) and the non polar mixture B (Mixture B) and compiled the data in Table 5. In fact, the extrapolated ε_{av} and $\Delta\varepsilon$ are very different in the two cases, pointing at the large differences in the effective dipoles and the g factors. It should be emphasized, that the optical constants extrapolated from both mixtures are nearly equal.

TABLE 5 Dielectric and Optical Data for 5CB, Extrapolated From a Polar and a Non Polar Basic Mixture

Component	Contents weight %			
Mixture A	100	85		
Mixture B			100	85
5CB		15		15
T_{NI}(°C)	72.3	65.0	74.0	66.8
T_{NI}(°C) extrapol.		23.7		26.0
$\Delta\varepsilon$	10.0	10.3	− 1.4	2.1
$\Delta\varepsilon$ extrapol.		12.0		21.80
ε_{av} extrapol.		9.73		13.13
Δn	0.1379	0.1486	0.0876	0.1037
Δn extrapol.		0.2093		0.2073

Mixture B



Mixture A

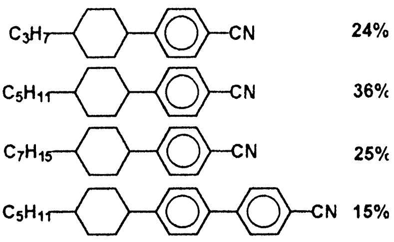


TABLE 6 Effective Dipoles μ_{eff} and Kirkwood g_i Factors of 5CB Calculated With Equs. 1,3,4 Using Data From AM1 Calculation: $\alpha_{av} = 171.66$ $\Delta\alpha = 178.05$ and $\mu_{\exp} = 4.76$ D

	$\mu_{\mathrm{eff\ i\Delta}}$		g_i	
	mixt. A	mixt. B	mixt. A	mixt. B
from $\varepsilon_{\parallel}$	3.630	4.599	0.582	0.933
from $\varepsilon_{\perp}$	3.263	3.247	0.470	0.465
from ε_{av}	3.499	4.151	0.540	0.760

Of course, the g and μ_{eff} calculated from the data of both mixtures are also quite different (Table 6).

2.4. Refractive Indices

Using the molecular data presented in Table 3, we calculated the refractive indices and the birefringence of 5CB (Table 7). The calculated results are smaller than the experimental data.

Similar to all aromatic compounds, 5CB has optical absorption bands in the UV region. There are: one $\sigma \rightarrow \sigma^*$ transition at about 120 nm, and two $\pi \rightarrow \pi^*$ bands at 200 resp. 282 nm [17,18]. These bands are responsible for the anoma-lous increase of the refractive indices and the birefringence with decreasing wavelength [17,18]. The absorption spectrum of 5CB has been calculated by MOS-F on the basis of a structure optimized by MOPAC/AM1. The result is shown in Figure 5. The two lines with the largest oscillation strength correspond well with the experimental $\pi \rightarrow \pi^*$ bands at 200 resp. 282 nm.

The method MOPAC/AM1 allows to calculate the polarizabilities α and their anisotropies $\Delta\alpha$ at different wavelengths. Using our procedure described above, we calculated from these data the corresponding refractive indices and the birefringence for the all-trans conformers of 5CB. In Figure 6 the calculated birefringence data are compared with experimental data [18]. The figure points at systematic deviations of the calculated and measured data of Δn. The calculated n_e and n_0 are too small, however, their difference

TABLE 7 Optical Data of 4-n-Pentyl-4′-cyano-biphenyl (5CB) $T_{NI} = 35.3°C$ [9]; $\overline{P}_2 = 0.46$ [10]; $V_m = 243.99$ [11]

	ab-initio	AM1	experim.
n_e	1.6566	1.5483	1.71 [10]
n_o	1.4917	1.3799	1.53 [10]
Δn	0.165	0.168	0.18 [10]

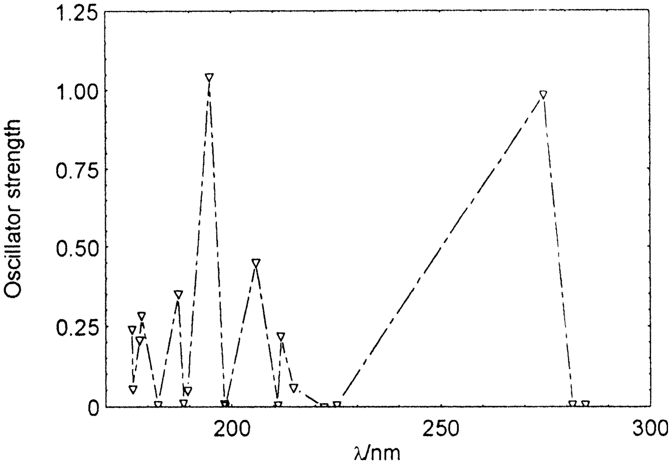


FIGURE 5 Optical transitions in 5CB calculated with MOS-F.

Δn is too large in comparison with the experiments. Usually, refractive indices are determined at 589 nm. It seems, that the data calculated for 900 nm come nearest to the experimental data at 589 nm.

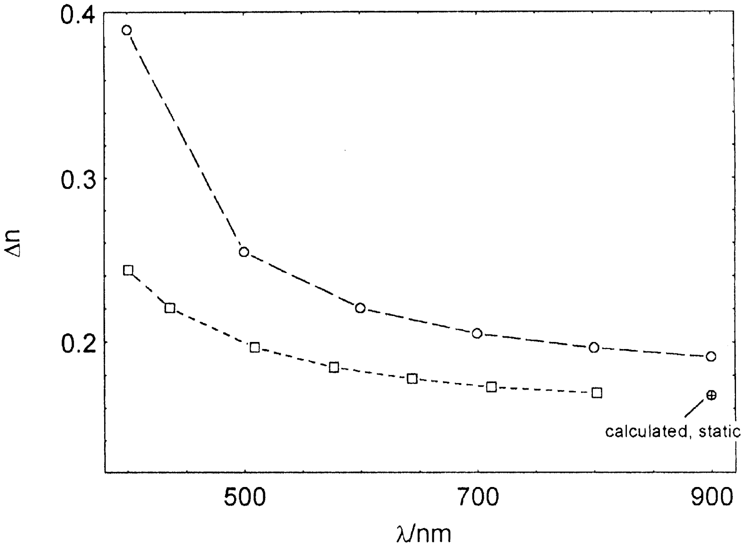


FIGURE 6 Dispersion of the birefringence of 5CB. Circles: calculated; squares: experimental [18].

3. CONCLUSIONS

The calculation of properties of nematic liquid crystals without need of experimental investigations is an important goal in industrial research.

The equations of Maier and Meier can be used for the calculation of dielectric and optical data of nematic compounds. The necessary molecular data α_{av}, $\Delta\alpha$, μ and β can be calculated by ab-initio (B3LYP/6-31 G(d)) as well as semiempirical methods (MOPAC with AM1 Hamiltonian). The consideration of different conformers does not substantially improve the results. The necessary molar volumes can be obtained by a group contribution method proposed by Fedors, and for the evaluation of order parameters we found an empirical dependence on the clearing temperature. The calculated dielectric and optical data based on AM1 calculations show better agreement with the experiments than those based on ab initio calculations.

In strongly polar compounds because of dipole-dipole association effects the agreement of the calculated dielectric data with experimental values is not satisfying. Instead of the calculated dipole moments, effective dipole moments must be used. For the calculation of effective dipoles de Jeu and Bordewijk as well as Dunmur and Palffy-Muhoray proposed procedures, which, however, fail with large dipoles. Considering attractive and repulsive energies for the dipole-dipole interaction, we elaborated the "Two configurations charge interaction approach" for calculation of effective dipole moments as well as for Kirkwood's g factors. This method delivers useful values also in the case of very large dipole moments.

The agreement of the calculated optical data (refractive indices and birefringence) with experimental values can be improved, when for the calculation instead of static polarizabilities the calculated dispersions of the polarizability and its anisotropy are applied. The optical absorption, which controls the dispersion, can be approximately calculated by methods like MOS-F on the basis of structures optimized with MOPAC/AM1.

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