Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Calculation of molecular, dielectric and optical properties of 4'-n-pentyl-4-cyano-biphenyl (5CB)

D. Demus; T. Inukai

To cite this Article Demus, D. and Inukai, T.(1999) 'Calculation of molecular, dielectric and optical properties of 4'-n-pentyl-4-cyano-biphenyl (5CB)', Liquid Crystals, 26: 9, 1257 — 1266
To link to this Article: DOI: 10.1080/026782999203922
URL: http://dx.doi.org/10.1080/026782999203922

LIQUID CRYSTALS, 1999, VOL. 26, NO. 9, 1257–1266

Calculation of molecular, dielectric and optical properties of 4′-*n*-pentyl-4-cyano-biphenyl (5CB)†

D. DEMUS*‡§ and T. INUKAI§

‡International Scientific Consulting Office, Veilchenweg 22, 06118 Halle, Germany
§Chisso Corporation, Marunouchi 2-7-3, Chiyoda-ku, Tokyo 100-8333, Japan

(*Received 28 December 1998; accepted 26 March 1999*)

Using the quantum chemical methods *ab initio* (B3LYP/6-31 G(D)) and the semi-empirical MOPAC/AM1, the dipoles and their angle with the molecular long axis and the polarizabilities and their anisotropies, have been calculated for different conformers of 5CB. On the basis of these data the dielectric constants and refractive indices and their anisotropies have been calculated, using the Maier–Meier theory. The poor agreement with experimental data could be improved by use of effective dipoles taking account of Kirkwood's *g* factors, calculated with the theory of Dunmur–Palffy-Muhoray. By calculation of the dispersion of the refractive indices the agreement with the experimental data has been improved. We recommend a procedure for the prediction of dielectric and optical data for nematic compounds, useful for practical application.

1. Introduction

The synthesis of new liquid crystalline compounds is still an important topic for the applications of liquid crystals in displays. The prediction of the physical properties of the compounds, without performing experiments, could save a considerable amount of the manpower and materials needed for the synthesis of new compounds. Among the most important properties of liquid crystals are their dielectric constants and optical refractive indices and their anisotropies. There have been some attempts to calculate these properties. Bremer and Tarumi [1] found a correlation between dipole moments and $\Delta\varepsilon$, as well as between polarizabilities and Δn, with dipoles and polarizabilities calculated by semi-empirical quantum chemical calculations. The observed scattering in the correlations was believed to be due to the limits of the semi-empirical 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 semi-empirical quantum chemical calculations; they set the density of the materials equal to one, and the order parameter equal to 0.7 at room temperature (293 K). Despite these approximations, the agreement between calculated data and experimental data (obtained from extrapolation from 10% solutions of the compounds in a common basic mixture) was very satisfying.

Fujita *et al.* [4] used a similar approach to that of Klasen, but they used molecule-specific densities in relation to 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, but in compounds possessing large dipoles there were systematic differences. Setting the reactive field factors F in the dipole term of the Maier–Meier equations $F=1$, the agreement however became quite satisfying. This points to the important role of association in the polar compounds and the necessity of using effective dipoles for the calculations instead of the dipoles of the free molecules; however it is not satisfying from the theoretical standpoint.

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

---

*Author for correspondence.

†Presented at the Capri Conference held in honour of George W. Gray, FRS, September 1996.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

were performed for a temperature of 25°C. Most compounds are not nematic at this temperature, and only extrapolated data would be available for comparison. Among the few materials which are nematic at room temperature, we chose 4′-*n*-pentyl-4-cyanobiphenyl (5CB), because for this compound reliable experimental data are available in the literature. Also it belongs to the homologous series of the 4′-*n*-alkyl-4-cyanobiphenyls, one of the most important substance classes for practical applications, first synthesized by Gray *et al.* in 1973 [5].

2. Theory of dielectric properties

Onsager developed the equation (1) for the dielectric constant ε of isotropic media [6]

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

where

$$N = N_{\mathrm{A}}/V_{\mathrm{m}} = \text{number density}$$
$$\text{(number of molecules per volume unit).} \tag{2}$$

Here $N_{\mathrm{A}} = 6.02205 \times 10^{23}\ \mathrm{mol}^{-1}$, the Avogadro constant; V_{m} = molar volume; $h = 3\varepsilon/2\varepsilon + 1$, a correction factor for the internal field; $F = (1 - f\alpha)^{-1}$, a 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; $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{J}^{-1}\ \mathrm{C}^2\ \mathrm{m}^{-1}$, the dielectric constant of a vacuum; μ = electric dipole moment; $k_{\mathrm{B}} = 1.38066 \times 10^{-23}\ \mathrm{J\ K}^{-1}$, the 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 [6] derived formulae for the dielectric constants of nematics:

$$\varepsilon_{\parallel} = 1 + (NhF/\varepsilon_0)\{\alpha_{\mathrm{av}} + 2/3\Delta\alpha P_2 + F(\mu^2/3k_{\mathrm{B}}T)[1 - (1 - 3\cos^2\beta)P_2]\} \tag{3}$$

$$\varepsilon_{\perp} = 1 + (NhF/\varepsilon_0)\{\alpha_{\mathrm{av}} - 1/3\Delta\alpha P_2 + F(\mu^2/3k_{\mathrm{B}}T)[1 + 1/2(1 - 3\cos^2\beta)P_2]\} \tag{4}$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, β = angle between molecular long axis and dipole moment, and P_2 = order parameter of the nematic.

In equations (3) and (4) 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 can be approximated using the group contribution method of Fedors [7]. The order parameter P_2 may be taken from an empirical relation between clearing temperature and P_2 at room temperature [4]. For calculation of the refractive indices we have set $\mu = 0$ in equations (1, 3, 4), and we have used the approximation $\varepsilon = n^2$.

3. Calculation of dielectric and optical data

For calculation of the molecular data α_{av}, $\Delta\alpha$, μ and β, we used *ab initio* calculations (B3LYP/6-31 G(D)) [8] as well as semi-empirical methods (MOPAC [9] with AM1 Hamiltonian).

It is well known that molecules like 5CB possess a certain flexibility, and the molecule can exist in several conformations. We investigated the conformers of 5CB systematically by the following procedure. The first thorough conformational study of all-*trans*-pentylbenzene, regarding the stereochemical relation between the pentyl group and the phenyl ring, was made using *ab initio* RHF/6-31G(D). There are two conformers: one is the only predominant conformer in which the all-*trans*-pentyl group extends out of the plane of the phenyl perpendicularly, the other one is much less stable (population about 1%) in which the all-*trans*-pentyl group lies in-plane with the phenyl ring. *Gauche*-containing conformers of pentylbenzene were then examined. Four conformers were found to be retained for consideration. Using these four conformations of *n*-pentylbenzene, four starting conformations of 5CB were constructed by the internal coordinates method, and all the structural parameters were optimized by the *ab initio* B3LYP/6-31G(D) method and MOPAC/AM1 method.

From these calculations, the most stable form of the biphenyl core proved to be that with a twist angle of 40.2° (MOPAC/AM1) or 44.1° (*ab initio*) between the two phenyl rings (table 1). This is near to the angle of 37.6° obtained by an internal coordinate Monte Carlo approach [10]. Clark *et al.* [11] obtained a twist angle of 34° by *ab initio* calculations, but they did not indicate their method in detail. By X-ray investigation of the solid state, an angle of 26.3° has been found [12]. It seems that the solid crystals environment has a substantial influence on these twist angles, since they are: about 1° in 2CB, 42.8° in 3CB and 40.5° in 4CB [12]. In 9CB in the same crystal structure, molecules with different conformations have been found in which the twist angles are 35.97° down to 29.83° [17]. This proves that comparison of the nematic with the solid state can be difficult. The chosen twist angle of 90° between the phenyl ring and the bond between carbons 1 and 2 of the pentyl chain is in good agreement with 89.9° found by Wilson [10].

The four conformers obtained by the calculations are displayed in figure 1. As expected, the all-*trans* (*ttt*) conformer is most stable, followed by $tgt = ttg < gtt$. This is similar to the results of Wilson [10], calculated for the gas phase with an additional nematic mean field. Table 1 presents the molecular data obtained by different quantum chemical methods, considering the 4 conformers mentioned and their averages.

Table 1. Molecular, dielectric and optical data for 4′-*n*-pentyl-4-cyanobiphenyl (5CB). $T_{NI} = 35.3°C$ [13]; $P_2 = 0.46$ [14]; $V_m = 243.99$ [15].

		Column no.[c]											
Line no.	Parameter	1	2	3	4	5	6	7	8	9	10	11	12
	conformation	*ttt*	*gtt*	*tgt*	*ttg*	(average)	*ttt*	*gtt*	*tgt*	*ttg*	(average)	(average, $F = 1$)	(experimental)
	Θ[a]	44.1	44.2	44.1	44.2		40.2	40.2	40.2	40.2			
1	%[b]	54.69	20.54	11.98	12.79		54.28	13.11	16.29	16.32			
2	α_{av}/a.u.	207.98	204.97	207.90	186.54	204.61	171.82	170.61	171.93	171.68	171.66	171.66	220.06 [14]
3	$\Delta\alpha$/a.u.	214.98	193.47	220.79	162.68	204.56	178.50	173.99	180.44	177.52	178.05	178.05	183.58 [14]
4	μ/D	5.949	5.830	5.972	5.988	5.90	4.124	4.058	4.138	4.120	4.117	4.117	4.76 [16]
5	β/deg	8.07	13.74	4.66	9.30		7.79	12.99	4.69	8.93			
6	$b = 1 - 3\cos^2\beta$	−1.941	−1.831	−1.980	−1.922	−1.90	−1.945	−1.848	−1.980	−1.928	−1.936	−1.936	
7	ε_{av}	29.95	28.44	30.16	27.62	29.05	12.98	12.55	13.07	12.95	12.93	10.32	10.5 [14]
8	$\varepsilon_{\parallel}$	54.41	50.45	55.54	50.09	52.44	22.99	21.58	23.18	22.71	22.71	18.11	18.5 [14]
9	$\varepsilon_{\perp}$	17.72	17.43	17.47	16.38	17.35	7.98	8.04	8.01	8.07	8.04	6.69	7.0 [14]
10	$\Delta\varepsilon$	36.69	33.02	38.07	33.71	35.09	15.01	13.54	15.17	14.64	14.67	11.42	11.5 [14]
11	ε_{av} ($\mu = 0$)	2.3983	2.3687	2.3974	2.1966	2.3653	2.0685	2.0584	2.0694	2.0673	2.0672		
12	$\varepsilon_{\parallel}$ ($\mu = 0$)	2.7445	2.7648	2.8525	2.5165	2.7838	2.3972	2.3893	2.4136	2.4057	2.4066		
13	$\varepsilon_{\perp}$ ($\mu = 0$)	2.2251	2.1706	2.1698	2.0365	2.1559	1.9041	1.8928	1.8973	1.8981	1.8974		
14	n_e	1.6566	1.6628	1.6889	1.5863	1.6685	1.5483	1.5457	1.5536	1.5510	1.551		1.71 [14]
15	n_o	1.4917	1.4733	1.4730	1.4271	1.4683	1.3799	1.3758	1.3774	1.3777	1.377		1.53 [14]
16	Δn	0.165	0.189	0.216	0.159	0.200	0.168	0.170	0.176	0.173	0.174		0.18 [14]

[a] Θ = twist angle of phenyl rings.

[b] Boltzmann distribution.

[c] Columns 1–5, *ab initio* (5, Boltzmann average); columns 6–11, AM1 (10, 11, Boltzmann average; 11, $F = 1$ in dipole terms of equations (1, 3, 4)); column 12, experimental data from literature.

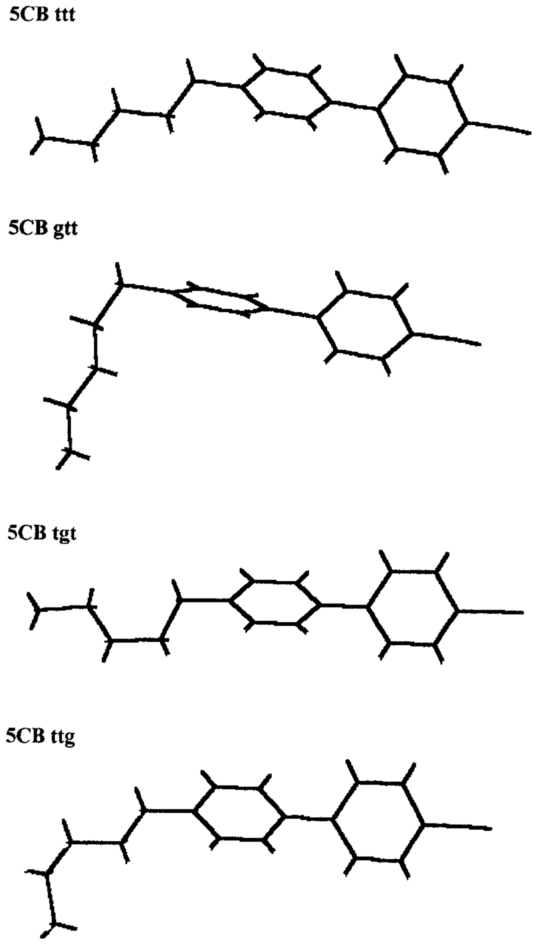


Figure 1. The most stable conformations of 5CB calculated by MOPAC/AM1.

3.1. *Conformers*

The data in table 1 show, that the calculated properties α_{av}, $\Delta\alpha$, μ and β are not very different for the different conformers. The differences between the *ab initio* results (columns 1–5) and the AM1 results (columns 6–10) are much larger than those between the different conformers, using the same quantum chemical method. The average data are not very different from those. Thus, for applicational purposes it is time saving and sufficient to use the data of the all-*trans* conformer.

3.2. *Polarizability data (table 1, lines 2, 3)*

Line 2 of table 1 shows the average polarizability α_{av}. Generally, the data of the *ab initio* calculation are higher than those of the MOPAC AM1 method. The latter data have been calculated for a static electric field. Using alternating fields of high frequency, corresponding to the energy of visible light, the polarizabilities are substantially higher. This effect will be treated separately below. Compared with the experimental value (column 12), all calculated data are too small. Looking at the anisotropy of the polarizability $\Delta\alpha$ (line 3), the data show slightly higher scattering. The experimental data found in the literature are very different (not listed here); therefore any comparison is difficult.

3.3. *Dipoles (table 1, line 4)*

The dipoles μ are given in line 4 of table 1. Using the *ab initio* method, the dipoles (columns 1–5) are much larger than the experimental dipole (column 12, value obtained from diluted solutions of 5CB). The dipoles obtained by MOPAC AM1 (columns 6–10) are smaller than the experimental value, but nearer to it than the *ab initio* data. In general, we find that using the calculated dipoles, in every case the calculated dielectric constants are too large. Instead of the dipoles, we have to use effective dipoles μ_{eff}. The problem of effective dipoles will be treated separately below.

In [4] we used an empirical procedure to obtain better agreement between the calculated dielectric data and the experimental data. We simply set the reactive field factor $F=1$ in the dipole terms of equations (1, 3, 4). As comparison of columns 11 and 12 shows, in fact the agreement is good. However, due to the lack of any theoretical background to this procedure, it is not satisfying.

3.4. *Angle β of the dipole with the molecular long axis (table 1, lines 5, 6)*

This angle is somewhat variable depending on the calculation method and the conformer considered. But the differences are not important, because the factor b (line 6), which occurs in the equations (3, 4) does not show any substantial scattering.

3.5. *Dielectric constants (table 1, lines 7–10)*

Here we find large differences, which are displayed in figure 2. They are not due to different conformers, but the *ab initio* method generally delivers much larger values than the MOPAC AM1 method, which are far from reality. Clearly this is due to the different calculated dipoles. Because the dipoles appear in equations (1, 3, 4) as squares, they are the most critical part. The empirical method with $F=1$ in the dipole terms provides good agreement between calculated and experimental data, and this has been confirmed for several highly polar compounds [4, 18].

The scattering of the dielectric data (indicated by error bars, defined by the lowest and the highest value) due to the scattering of the input data in equations (1, 3, 4) is displayed in figure 3. The dominant influence of the dipole scattering is already visible.

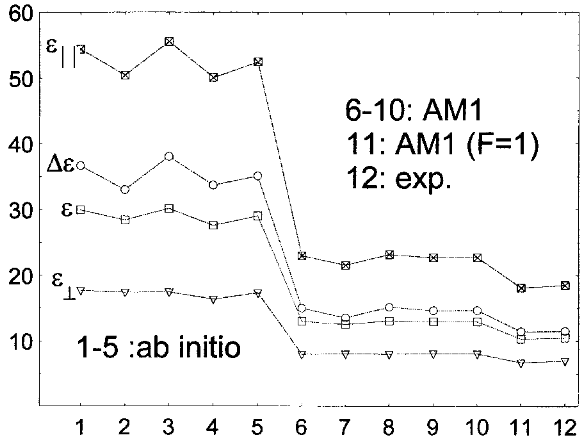


Figure 2. Dielectric data for 5CB, calculated with the Maier–Meier equations (1, 3, 4), using molecular data from *ab initio* and MOPAC/AM1 calculations. 11: calculated using equations (1, 3, 4) with the factor $F = 1$ in the dipole terms; 12: Experimental data from [14].

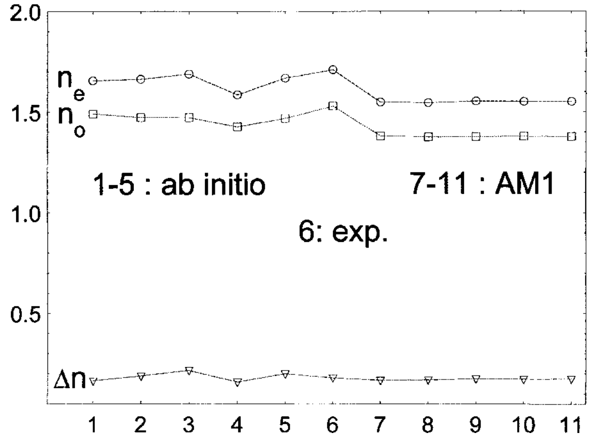


Figure 4. Optical data for 5CB, calculated on the basis of molecular data obtained by *ab initio* and MOPAC/AM1 calculations, in comparison with experimental data from [14].

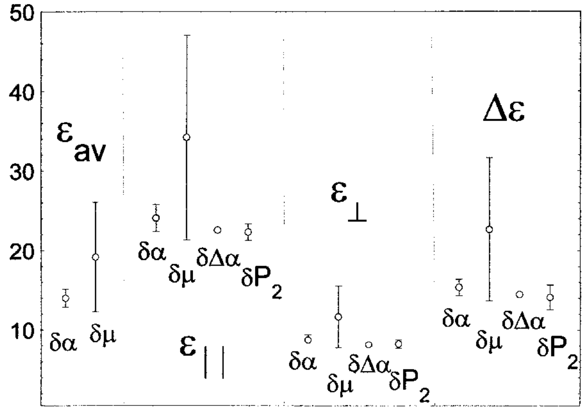
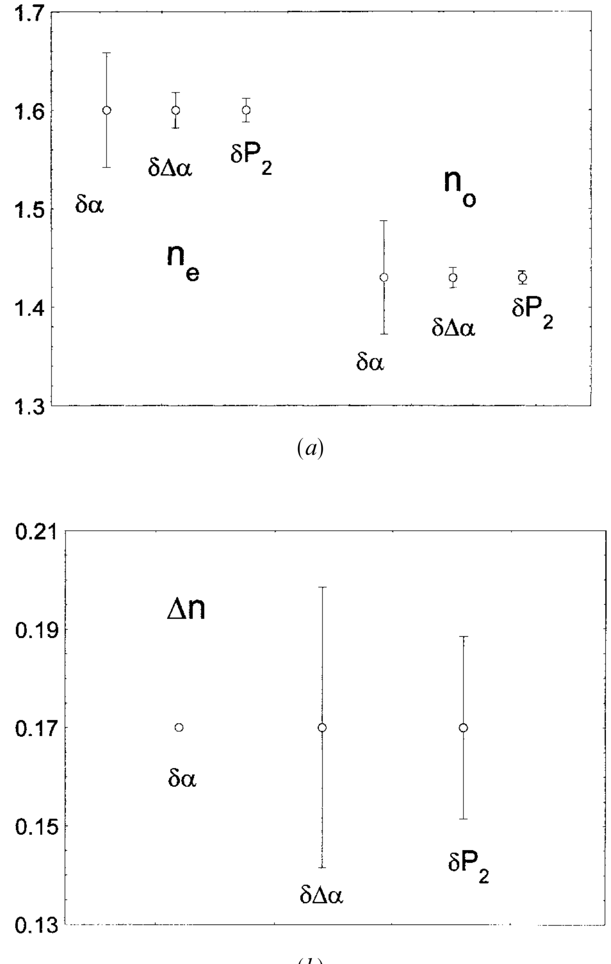


Figure 3. The influence of the scattering δ of the molecular data on the scattering of the dielectric data for 5CB, indicated by error bars.



(*a*)

(*b*)

Figure 5. The influence of the scattering δ of the molecular data on the scattering of the optical data of 5CB, indicated by error bars: (*a*) n_e and n_o; (*b*) Δn.

3.6. *Optical constants (table 1, lines 11–16)*

In lines 11–13 the dielectric constants obtained from equations (1, 3, 4) with the condition $\mu = 0$ are compiled. In general (except for values based on *ab initio* data, columns 2, 3, 5 in table 1), it seems that the calculated refractive indices and the birefringence are too small, compared with experimental data (see figure 4). This is mainly due to the calculated polarizabilities and their anisotropies, which are smaller than the experimental data. An improvement is to be expected using polarizabilities calculated by AM1 at higher frequencies (see section below). Figures 5(*a*) and 5(*b*) display the influence of the scattering of the input data on the calculated optical constants. We can see that $\alpha_{\|}$ and $\alpha_{\perp}$ dominate the scattering of n_e and n_o, and that $\Delta\alpha$ and P_2 control the scattering of the Δn data.

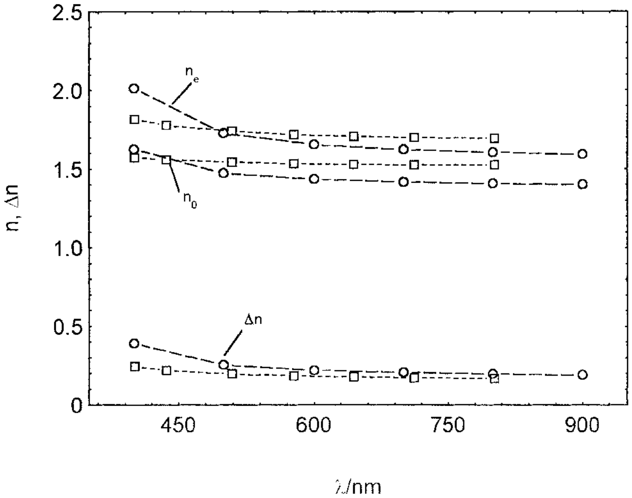


Figure 6. Optical dispersion of 5CB. Circles: calculated; squares: experimental data from [23].

In the literature, an additional factor (considering the relaxation of the contribution of the atomic nuclei) in equation 5 is sometimes [19] used: $\varepsilon = 1.05n^2$. We checked the use of this factor, but it does not deliver substantial improvements in the calculated results.

4. Effective dipoles and correlation factors

It is known that the experimental dipoles of isolated molecules (obtained from diluted solutions or from the gas phase), as well as the dipoles calculated by quantum chemical methods, deliver too high dielectric constants on inserting the dipoles in equations (1, 3, 4). Instead of the dipoles, we have to use effective dipoles μ_{eff}. In molecules possessing strong longitudinal dipoles, they are usually smaller than the dipoles, of the free molecules, due to formation of a considerable degree of association. In the literature this fact is taken account of by the Kirkwood correlation factor

$$g = (\mu_{\mathrm{eff}}/\mu)^2 \tag{6}$$

For g, the following relations hold: dimers with parallel dipoles, $g > 1$; dimers with antiparallel dipoles, $g < 1$; no association, $g = 1$. In our example, 5CB, the g factors are different from the different experimental [16] dielectric constants. Derived from $\varepsilon_\parallel$, $\varepsilon_\perp$, $\varepsilon_{\mathrm{av}}$, $\Delta\varepsilon$ (related to the experimental $\mu = 4.76$ D) we obtain: $g_\parallel = 0.644$, $g_\perp = 0.621$, $g_{\mathrm{av}} = 0.466$, $g_{\Delta\varepsilon} = 0.622$.

When experimental data are available, it is easy to estimate the g factors. A major problem is the calculation of g factors without using experimental data. In the literature only one theoretical approach has been found, which seemed to be practicable (Dunmur, Palffy-Muhoray [20]). The idea of the theory is to calculate the interaction of a molecular dipole with the dipole of a sphere of nearest neighbours, in an anisotropic state. The interaction is order parameter dependent. The uniaxial molecules have ellipsoidal shape with length L and breadth B, while the dipole is parallel to L. Then different g factors parallel and perpendicular to the symmetry axis depend on the prolate (elongated) or oblate (discotic) shape of the molecules.

For the case of the molecular dipole parallel to the symmetry axis of the uniaxial molecules, the following equations have been presented:

$$g_\parallel = 1 - \frac{4N\mu_l^2\kappa_1(1+2P_2)}{45(4\pi\varepsilon_0)k_B T} \tag{7}$$

$$g_\perp = 1 - \frac{4N\mu_l^2\kappa_1(1-P_2)}{45(4\pi\varepsilon_0)k_B T}. \tag{8}$$

If the dipole is oriented perpendicular to the molecular symmetry axis, the equations become:

$$g_\parallel = 1 + \frac{2N\mu_t^2\kappa_1(1-P_2)}{45(4\pi\varepsilon_0)k_B T} \tag{9}$$

$$g_\perp = 1 + \frac{N\mu_t^2\kappa_1(2+P_2)}{45(4\pi\varepsilon_0)k_B T} \tag{10}$$

In these four equations

$$\kappa_1 = 3[\mathrm{L} - \mathrm{B}]/(\mathrm{L} + 2\mathrm{B}) \tag{11}$$

and μ_l and μ_t are the longitudinal and transverse molecular dipoles, respectively. κ_1 depends on the length L and the breadth B, and is a measure of the length-to-breadth ratio; κ_1 is positive in rod-like molecules and negative in discotic molecules.

The basis of equations (7–10) is an approximation, because in reality the dipoles are not exactly parallel or perpendicular to the main axes. Even 5CB has a longitudinal and a lateral dipole component (see table 1). Inserting the longitudinal dipole component in equation (6), we obtain $g_\parallel < 1$. However, the calculated value is smaller than the experimental $g_\parallel$. When we use equation (9), and insert the lateral dipole component, we obtain $g_\perp > 1$. This does not correspond to reality.

We have slightly modified equations (7) and (8), by inserting in both the longitudinal and lateral dipole components, and calculating g_{av} for the isotropic case:

$$g_\parallel = 1 - 4N\kappa_1[\mu_l^2(1+2P_2) + \mu_t^2(1-P_2)]/45(4\pi\varepsilon_0)k_B T \tag{12}$$

$$g_\perp = 1 - 4N\kappa_1[\mu_t^2(1+2P_2) + \mu_l^2(1-P_2)]/45(4\pi\varepsilon_0)k_B T \tag{13}$$

$$g_{\mathrm{av}} = 1 - 4N\kappa_1[\mu_t^2 + \mu_l^2]/45(4\pi\varepsilon_0)k_B T \qquad P_2 = 0. \tag{14}$$

The total dipole moment μ consists of the components: $\mu^2 = \mu_l^2 + \mu_t^2$, with $\mu_l = \mu\cos\beta$, $\mu_t = \mu\sin\beta$.

We then used equations (12–14) for further calculations of the g factors. The second term in these equations depends on the square of μ. This dipole can be the dipole of the compound itself, or the average dipole of a mixture in which the dielectric data are measured. Then it is to be expected that the dielectric constants, the effective dipoles and the g factors will be different when a given compound is investigated as a component in a polar and a non-polar basic mixture. We made such an experiment with 5CB in a polar mixture A (MiA) and a non-polar mixture B (MiB); the data are compiled in table 2. In fact, the extrapolated $\varepsilon_{\parallel}$ and $\Delta\varepsilon$ are very different in the two cases, pointing out 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.

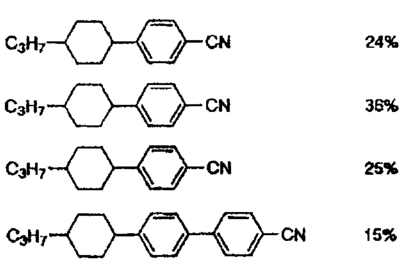
In table 3 we have compiled the results of calculations of effective dipoles and g factors. In the first column we show data from the literature [16]. The g factors have been obtained by use of Bordewijk's equations containing factors taking account of the shape anisotropy of the molecules, therefore complete agreement with the g factors calculated with equation (6) cannot be expected. In columns 2 and 3, the dipole data were calculated by use of the experimental dielectric data of ref. [14] (table 1) and the equations (1, 3, 4), inserting the molecular data from the AM1 and the *ab initio* calculation, respectively. In columns 4 and 5 we used the dielectric data extrapolated from the mixtures, and in equations (1, 3, 4) the molecular data from AM1 calculation. In all cases the 'experimental' g factors were calculated with equation (6). Line 4 presents μ_{ref}, the dipoles which are used in the denominator of equation (6).

We see in table 3 that the effective dipoles depend on the method of quantum chemical calculation, because data from the latter are inserted in equations (1, 3, 4) and the dipoles are fitted to the experimental data. In

Table 2. Dielectric and optical data for 5CB, extrapolated from a polar and a non-polar basic mixture.

Component	Contents/wt %			
Mixture A	100	85		
Mixture B			100	85
5CB		15		15
Parameter				
T_{NI}/°C	72.3	65.0	74.0	66.8
T_{NI}/°C extrapol.		23.7		26.0
$\varepsilon_{\parallel}$	14.4	14.9	3.0	6.7
$\varepsilon_{\parallel}$ extrapol.		17.73		27.66
$\Delta\varepsilon$	10.0	10.3	– 1.4	2.1
$\Delta\varepsilon$ extrapol.		12.0		21.80
$\varepsilon_{\perp}$ extrapol.		5.73		5.86
$\varepsilon_{\mathrm{av}}$ extrapol.		9.73		13.13
n_{e}	1.6293	1.6448	1.563	1.5885
n_{e} extrapol.		1.7326		1.7326
n_{o}	1.4914	1.4962	1.4777	1.4848
n_{o} extrapol.		1.5233		1.5253
Δn	0.1379	0.1486	0.0876	0.1037
Δn extrapol.		0.2093		0.2073

Mixture A



Mixture B

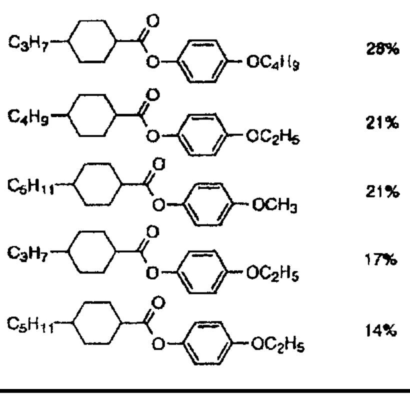


Table 3. Dipoles and g-factors for 4′-*n*-pentyl-4-cyanobiphenyl (5CB).

Parameter	Dunmur *et al.* [16]	AM1, all *trans*	*Ab initio*, all *trans*	Extrapol. from MiA	Extrapol. from MiB	Urban [21]
$\mu_{\mathrm{av,eff}}$	3.178[a]	3.657	3.339	3.499	4.151	
$\mu_{\mathrm{eff},\parallel}$		3.699	3.408	3.630	4.599	
$\mu_{\mathrm{eff},\perp}$		3.699	3.408	3.263	3.247	
μ_{ref}	4.76[b]	4.124	5.949	4.76[b]	4.76[b]	
g_{av} exper.	0.4444[c]	0.786	0.315	0.540	0.760	
calc.		0.898[e]	0.788[e]			≅ 0.7[h]
$g_{\parallel}$ exper.	0.2713[d]	0.805	0.328	0.582	0.933	
calc.		0.807[f]	0.598[f]			
$g_{\perp}$ exper.	0.5628[d]	0.805	0.328	0.470	0.465	
calc.		0.942[g]	0.880[g]			

[a] Calculated from Maier–Meier theory, using anisotropic internal field.
[b] Extrapolated from isotropic diluted solution.
[c] Calculated with equation (6), μ_{eff} from Maier–Meier theory.
[d] Calculated with the equations of Bordewijk [16].
[e] Calculated with equation (14) and the condition $P_2 = 0$.
[f] Calculated with equation (12).
[g] Calculated with equation (13).
[h] Calculated with $\Delta\varepsilon$, using a modified Maier–Meier equation [21].

the case of extrapolation from mixtures, they strongly depend on the polarity of the mixtures. The *g* factors, however, do not depend only on the effective dipoles, but also on the chosen μ_{ref}. In most cases experimental data for the dipoles of the free molecules are not available. In this situation, according to our experience, the dipoles calculated with the AM1 method are preferable.

When we look at the *g* factors in table 3, they are very different, depending on the method of their evaluation. Our aim is to calculate, without the need for experiments, data which are as near as possible to reality. It seems that $g_{\parallel}$ calculated with equation (12) in the case of AM1 shows good agreement with the 'experimental' $g_{\parallel}$. The calculations for g_{av} and $g_{\perp}$ are less satisfying. It seems, that the calculated $g_{\parallel}$ shows better agreement with the 'experimental' g_{av} and $g_{\perp}$. Insertion of the total dipole μ in equation (7) delivers a similar result, so that this procedure might be recommended for practical applications.

5. Dispersion of the refractive indices

Similarly to all aromatic compounds, 5CB has optical absorption bands in the UV region. According to [22, 23] these are: one $\sigma \rightarrow \sigma^*$ transition at about 120 nm, and two $\pi \rightarrow \pi^*$ bands at 200 and 282 nm, respectively. These bands cause an anomalous increase of the refractive indices and the birefringence with decreasing wavelength.

The method MOPAC/AM1 allows us to calculate the polarizabilities α and their anisotropics $\Delta\alpha$ at different wavelengths. Using the procedure described above, we calculated from these data the corresponding refractive indices and the birefringence for the all-*trans*-conformers. These data are compiled in table 4. The dispersion of the data is clearly recognizable.

The calculated data were compared with experimental data from [23]. Except for n_{e} and Δn at 400 nm, there seems to be fairly good agreement. However, the more detailed figure 7 indicates systematic deviations of the calculated and measured data for Δn. The calculated n_{e} and n_{o} are too small, but their difference Δn is too large in comparison with the experiments. Usually, refractive

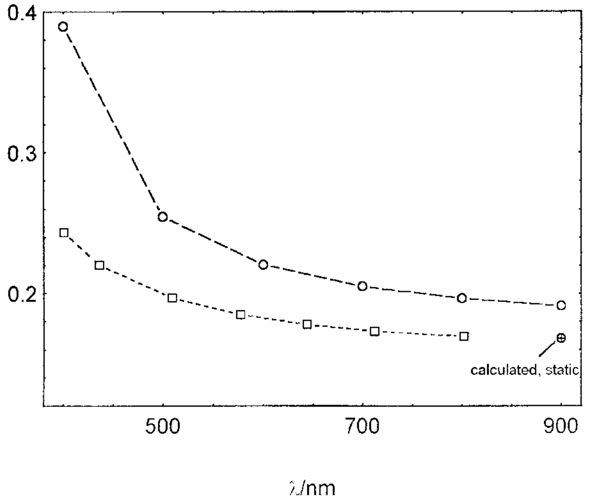


Figure 7. Dispersion of the birefringence of 5CB. Circles: calculated; squares: experimental data from [23].

Table 4. Calculation of the optical dispersion of 5CB. Method: AM1 at different wavelengths; $V_m = 243.99\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$; $P_2 = 0.46$; $T = 298.2$ K.

Parameter	Wavelength/nm						
	static	900	800	700	600	500	400
α/a.u.	171.821	181.257	184.087	188.520	196.212	212.303	270.604
$\Delta\alpha$	178.497	196.069	201.535	210.278	225.969	260.867	394.407
$\varepsilon_\parallel\ (\mu=0)$	2.3972	2.5310	2.5690	2.6298	2.7390	2.9842	4.0619
$\varepsilon_\perp\ (\mu=0)$	1.9041	1.9590	1.9775	2.0067	2.0582	2.1696	2.6432
$\varepsilon\ (\mu=0)$	2.0685	2.1497	2.1747	2.2144	2.2852	2.4412	3.1162
n_e (exp)[a]	1.71						
n_e (calc)	1.5483	1.5909	1.6028	1.6217	1.6550	1.7275	2.0154
n_o (exp)[a]	1.53						
n_o (calc)	1.3799	1.3996	1.4062	1.4166	1.4346	1.4730	1.6258
Δn_{exp}[a]	0.18						
Δn_{calc}	0.168	0.1913	0.1966	0.2051	0.2204	0.2545	0.3896

[a] experimental data for wavelength 589 nm from [14].

indices are determined at 589 nm. It seems, that the data calculated for 900 nm come nearest to the experimental data at 589 nm (table 4).

6. Conclusions

We have shown that the equations of Maier and Meier [6] can be used for the calculation of dielectric and optical data for 5CB. For evaluation of the necessary molecular data α_{av}, $\Delta\alpha$, μ and β we used *ab initio* calculations (basis set 6-31 G) [8], as well as semi-empirical methods (MOPAC [9] with AM1 Hamiltonian). In the calculations the four conformers of 5CB possessing the highest Boltzmann probability have been considered. The calculated dielectric and optical data based on AM1 calculations show better agreement with experiment than those based on *ab initio* calculations. The different conformers do not yield substantially different dielectric and optical data, and therefore it is sufficient to use the most stable (all-*trans*) conformer for the calculations.

In strongly polar compounds the agreement of the calculated dielectric data with experimental values is unsatisfactory. This is mainly due to association effects, which in compounds with strong longitudinal dipoles cause a partial cancellation of the dipoles. The effective dipoles to be inserted in the Maier–Meier equations can be obtained by calculating Kirkwood factors [$g = (\mu_{\mathrm{eff}}/\mu)^2$] using the theory of Dunmur and Palffy-Muhoray [20]. This theory allows us to calculate g factors $g_\parallel$, $g_\perp$ and g_{av}. In 5CB it seems that the value of $g_\parallel$ provides the best correction of the dipoles for calculation of $\varepsilon_\parallel$, $\varepsilon_\perp$ and $\varepsilon_{\mathrm{av}}$.

The agreement of the calculated optical data with experimental values can be improved, when the dispersion of the polarizability and its anisotropy (calculated with MOPAC/AM1) are considered.

In summary, we propose a method for the calculation of dielectric and optical data for nematic compounds, without the need for experimental data, and with an accuracy acceptable for practical applications.

We thank Dr E. Nakagawa for making available experimental data.

References

[1] Bremer, M., and Tarumi, K., 1993, *Adv. Mater.*, **5,** 842.

[2] Saitoh, G., Satoh, M., and Hasegawa, E., 1997, *Mol. Cryst. liq. Cryst.*, **301,** 13.

[3] Klasen, M., Bremer, M., Götz, A., Manabe, A., Naemura, S., and Tarumi, K., 1998, *Jpn. J. appl. Phys.*, **37,** L 945.

[4] Fujita, A., Ushioda, M., Takeuchi, H., Inukai, T., and Demus, D., 1998, in Proceedings of the 17th International Liquid Crystal Conference, Strasbourg 1998; *Mol. Cryst. liq. Cryst.* (to be published).

[5] Gray, G. W., Harrison, K. J., Nash, J. A., Constant, J. Hulme, D. S., Kirton, J., and Raynes, E. P., 1974, *Liquid Crystal and Ordered Fluids*, Vol. 2, edited by J. F. Johnson and R. S. Porter (New York: Plenum), p. 617.

[6] Maier, W., and Meier, G., 1961, *Z. Naturforsch.*, **16a,** 262; see also De Jeu, W. H., 1980, *Physical Properties of Liquid Crystals* (New York: Gordon & Breach).

[7] Fedors, R. F., 1974, *Polym. Eng. Sci.*, **14,** 147.

[8] Gaussian 94 W, Gaussian Inc., Pittsburgh PA, (1995).

[9] Stewart, J. J. P., 1993, MOPAC 93, Fujitsu Limited, Tokyo, Japan.

[10] Wilson, M. R., 1996, *Liq. Cryst.*, **21,** 437.

[11] Clark, S. J., Adam, C. J., Cleaver, D. J., and Crain, J., 1997, *Liq. Cryst.*, **22,** 477.

[12] Hanemann, T., Haase, W., Svoboda, I., and Fuess, H., 1995, *Liq. Cryst.*, **19,** 699.

[13] BDH: Product Information 1986.

[14] Cummins, P. G., Dunmur, D. A., and Laidler, D. A., 1975, *Mol. Cryst. liq. Cryst.*, **30,** 109.

[15] Sen, S., Brahma, P., Roy, S. K., Mukherjee, D. K., and Roy, S. B., 1983, *Mol. Cryst. liq. Cryst.*, **100,** 327.

[16] Dunmur, D. A., Manterfield, M. R., Miller, W. H., and Dunleavy, J. K., 1978, *Mol. Cryst. liq. Cryst.*, **45,** 127.

[17] Manisekaram, T., Bamezai, R. K., Sharma, N. K., Shashidhara Prasad, S., 1997, *Liq. Cryst.*, **23,** 597.

[18] Inukai, T., and Demus, D., unpublished results.

[19] Schad, H., and Osman, M. A., 1981, *J. chem. Phys.*, **75,** 880.

[20] Dunmur, D. A., and Palffy-Muhoray, P., 1992, *Mol. Phys.*, **76,** 1015.

[21] Urban, S., 1995, *Z. Naturforsch.*, **50a,** 826.

[22] Wu, S.-T., 1991, *J. appl. Phys.*, **69,** 2080.

[23] Wu, S.-T., Wu, C.-S., Warenghem, W., and Ismaili, M., 1992, *Proc. SPIE*, **1815,** 179.