Vol 18 No 7, July 2009
1674-1056/2009/18(07)/2885-08

Chinese Physics B

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Calculating the dielectric anisotropy of nematic liquid crystals: a reinvestigation of the Maier–Meier theory*

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(Received 19 October 2008; revised manuscript received 24 November 2008)

This paper investigates the average dielectric permittivity ($\bar{\varepsilon}$) in the Maier–Meier theory for calculating the dielectric anisotropy ($\Delta\varepsilon$) of nematic liquid crystals. For the reason that $\bar{\varepsilon}$ of nematics has the same expression as the dielectric permittivity of the isotropic state, the Onsager equation for isotropic dielectric was used to calculate it. The computed $\bar{\varepsilon}$ shows reasonable agreement with the results of the numerical methods used in the literature. Molecular parameters, such as the polarizability and its anisotropy, the dipole moment and its angle with the molecular long axis, were taken from semi-empirical quantum chemistry (MOCPAC/AM1) modeling. The calculated values of $\Delta\varepsilon$ according to the Maier–Meier equation are in good agreement with the experimental results for the investigated compounds having different core structures and polar substituents.

Keywords: dielectric anisotropy, molecule modeling, semi-empirical quantum chemistry, nematic liquid crystals

PACC: 6130B, 3120P

1. Introduction

Liquid crystal displays (LCDs) have dominated flat panel display in the past decade. The increasing performance requirement for LCDs, leads to extremely stringent demands on the liquid crystalline material. The synthesis of new liquid crystal compounds, which have to meet a certain set of physicochemical requirements (e.g., broad nematic phase, moderate dielectric anisotropy, appropriate birefringence, low rotational viscosity, and so on), becomes a challenge and can no longer be fulfilled by conventional trial-and-error approaches.[1] Fortunately, theoretical modeling and calculation methods have been proposed, which aim at predicting the physical properties of nematic liquid crystals (NLCs) without performing time-consuming experiments.[1−3]

Among these important parameters, we focus on the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the permittivity parallel and perpendicular to the director respectively), which is critical for most of the electro-optic applications because it dominates the reorientation of liquid crystal molecules under an external electric field. Bremer and Tarumi[2] first introduced semi-empirical molecular orbit (MO) methods to calculate the dielectric anisotropy. They found a quite reasonable correlation between $\Delta\varepsilon$ and the dipole moment, but some scatter was also found. Saitoh *et al*[4] reported an improved method based on the Maier–Meier theory.[5] Klasen *et al*[6] also took advantage of the Maier–Meier theory to calculate $\Delta\varepsilon$, but they adopted uniform conditions for all molecules, aiming at the comparability. The method[7] of Fujita *et al* is similar to that of Klasen, however, molecular-specific molar volumes are determined by using group contribution methods, order parameters evaluated from an empirical relation to the clearing point were used instead. Demus and Inukai[8,9] compared the results of the *ab initio* method (B3LYPD/6-31 G(d)) with that of the semi-empirical method (MOPAC/AM1), the latter showed better agreement with experiments than the former. Different conformers were also studied and no substantial difference was found. In addition, they employed the effective dipole for the Maier–Meier equation by taking the association effects into account, attempting to improve the

*Project supported by the National Natural Science Foundation of China (Grant Nos 60578035 and 60736042) and the Science Foundation of Jilin Province of China (Grant Nos 20050520 and 20050321-2).

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prediction of strong polar compounds. Recently, Ma *et al*[10] investigated the temperature dependence of ratio between the dielectric anisotropy and order parameter in a series of fluorinated NLCs with the MO methods and Maier–Meier theory.

All these studies have achieved a certain success in predicting the dielectric properties of NLCs, but some condition or assumption in the Maier–Meier theory seems not naturally satisfiable. In order to clarify its impact on the calculated result, we reinvestigate Maier–Meier's original assumption in this paper. Further, we use different methods to evaluate the average permittivity, then compare the reaction field factor F and cavity factor h in the Maier–Meier equation. It turns out that the Onsager equation is more straightforward and convenient for the computation. We also select a batch of commercially important molecules with moderate polar or extremely low polar to test the validity of this method by comparing the calculated values with those of the experiments.

2. Theory

As an extension of the Onsager theory of the dielectric polarization of isotropic dipolar fluids, Maier and Meier[5] correlate the dielectric anisotropy of NLCs with the anisotropy of molecular polarizability ($\Delta\alpha$), dipole moment (μ) and its orientation relative to the long principal axis (β) in the molecular frame, and the long range orientational order (S),

$$\begin{aligned}
\varepsilon_{\parallel} &= 1+\frac{NhF}{\varepsilon_0}\left\{\overline{\alpha}+\frac{2}{3}\Delta\alpha S+\frac{F\mu^2}{3k_{\mathrm{B}}T}\left[1-\left(1-3\cos^2\beta\right)S\right]\right\},\\
\varepsilon_{\perp} &= 1+\frac{NhF}{\varepsilon_0}\left\{\overline{\alpha}-\frac{1}{3}\Delta\alpha S+\frac{F\mu^2}{3k_{\mathrm{B}}T}\left[1+\frac{1}{2}\left(1-3\cos^2\beta\right)S\right]\right\},\\
\Delta\varepsilon &= \frac{NhF}{\varepsilon_0}\left\{\Delta\alpha-\frac{F\mu^2}{2k_{\mathrm{B}}T}\left(1-3\cos^2\beta\right)\right\}S,
\end{aligned} \tag{1}$$

where N is the molecular number density, ε_0 the vacuum permittivity, and k_{B} the Boltzman constant. The reaction field factor $F=1/\left(1-f\overline{\alpha}\right)$ with $f=\left(\overline{\varepsilon}-1\right)/2\pi\varepsilon_0 a^3\left(2\overline{\varepsilon}+1\right)$, $\overline{\alpha}=\left(\alpha_{\parallel}+2\alpha_{\perp}\right)$ and the cavity factor $h=3\overline{\varepsilon}/\left(2\overline{\varepsilon}+1\right)$. Where a, the radius of the spherical cavity in the Onsager model, can be calculated from $(4/3)\pi Na^3=1$, $\overline{\varepsilon}$ is an imaginary average dielectric permittivity.

2.1. Approximation about $\overline{\varepsilon}$

According to Maier–Meier's approximation, the average dielectric permittivity $\overline{\varepsilon}=\left(\varepsilon_{\parallel}+2\varepsilon_{\perp}\right)/3$, meanwhile it satisfies the inequality $\left|\varepsilon_{\parallel}-\varepsilon_{\perp}\right|\ll\overline{\varepsilon}$. It implies that the values of $\overline{\varepsilon}$, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ should be close to each other to make sure that the errors of the two correction factors (F and h) caused by this approximation are insignificant and the deviation of $\Delta\varepsilon$ is negligible. However, this assumption is not always satisfied for NLCs. One example is 4'-*n*-pentyl-4-cyano-biphenyl (5CB), for which $\overline{\varepsilon}=10.8$, but $\varepsilon_{\parallel}-\varepsilon_{\perp}=18.5-7.0=11.5$ (see Table 1). The contravention with Maier–Meier's original assumption makes it a hidden problem to calculate the dielectric anisotropy of NLC.

Table 1. The calculated dielectric anisotropy $\Delta\varepsilon$ and two correction factors F and h of 5CB, with the assumption that $\overline{\varepsilon}$ equals to $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3$ and ε (the dielectric permittivity in isotropic state, which were measured in Ref.[11]), respectively.

	$\overline{\varepsilon}$	F	h	$\Delta\varepsilon$	$\Delta\varepsilon$(exp)	$\frac{\lvert\Delta\varepsilon-\Delta\varepsilon(\mathrm{exp})\rvert}{\Delta\varepsilon(\mathrm{exp})}$/%
$\varepsilon_{\parallel}$	18.5[a]	1.31	1.46	22.78	21.6[b]	5.5
$\varepsilon_{\perp}$	7.0[a]	1.26	1.40	20.20		6.5
$(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3$	10.8	1.2876	1.4336	21.59		0.0005
ε	10.5[a]	1.2860	1.4318	21.51		0.4

[a] Ref.[11], [b] Ref.[1].

The computation of $\overline{\varepsilon}$ is critical for solving the Maier–Meier equation. In order to test the validity of the method while $\left|\varepsilon_{\parallel} - \varepsilon_{\perp}\right| \ll \overline{\varepsilon}$ is not satisfied, we calculated F, h and $\Delta\varepsilon$ of 5CB under the assumption that $\overline{\varepsilon}$ can take the value of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\left(\varepsilon_{\parallel} + 2\varepsilon_{\perp}\right)/3$ and ε (dielectric permittivity of isotropic state) respectively. Table 1 reveals that the values of $\Delta\varepsilon$ is insensitive to the variation of $\overline{\varepsilon}$, and are close to the experimental value in Ref.[1]. We also show the $\overline{\varepsilon}$-dependent properties of F, h and $\Delta\varepsilon$ of 5CB schematically. As in Fig.1, all of them show a similar trend of variation versus $\overline{\varepsilon}$. When $\overline{\varepsilon} > \varepsilon_{\perp}$, a slow change can be found. But in contrast, when $\overline{\varepsilon} < \varepsilon_{\perp}$, they will decrease rapidly. So, as long as the calculated $\overline{\varepsilon}$ is not largely underestimated, there should be no substantial differences between the results of calculation and experiment. However, if the evaluated $\overline{\varepsilon}$ is smaller than $\varepsilon_{\perp}$, a reasonable value can no longer be guaranteed. For positive NLC, it is well-known that $\varepsilon_{\perp} < \overline{\varepsilon} < \varepsilon_{\parallel}$ (it is same for negative NLC except that $\varepsilon_{\parallel} < \overline{\varepsilon} < \varepsilon_{\perp}$), so the Maier–Meier equation should be always applicable for 5CB and other NLCs.

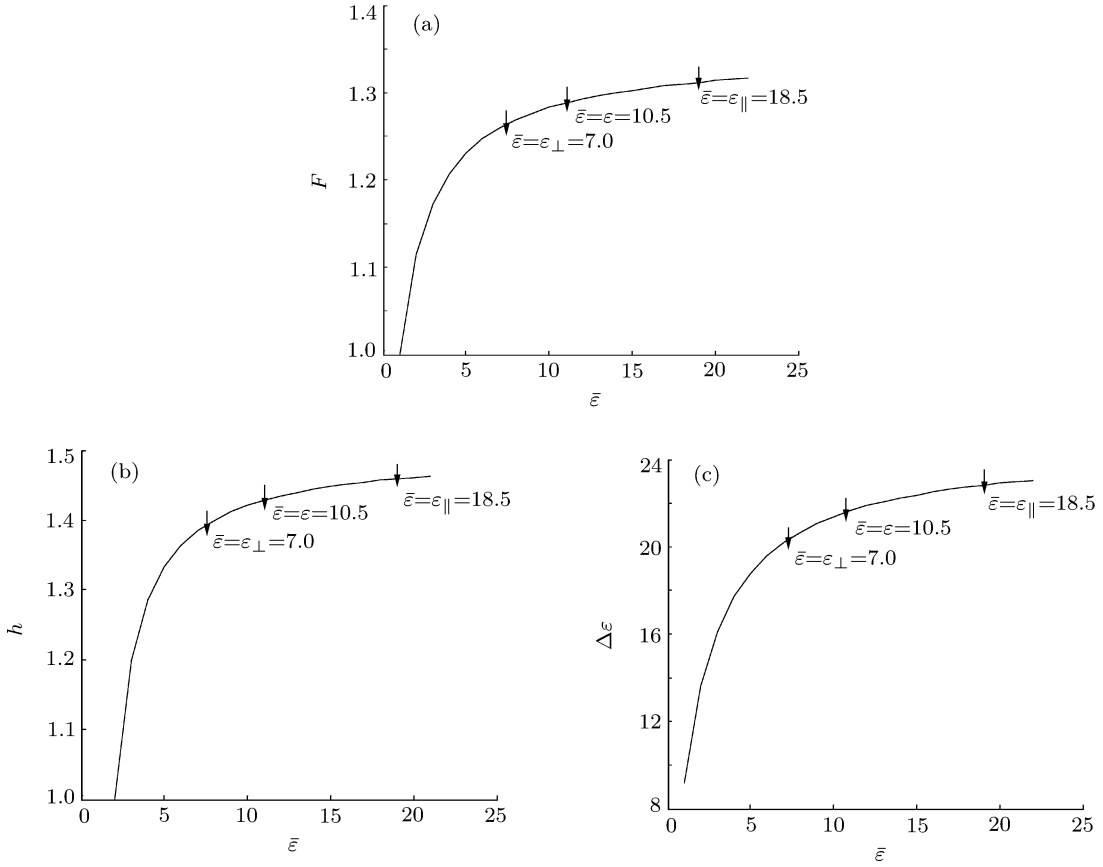


Fig.1. The $\overline{\varepsilon}$-dependent properties of (a) the reaction field factor-F, (b) the cavity factor-h, and (c) the dielectric anisotropy-$\Delta\varepsilon$.

2.2. Calculating $\overline{\varepsilon}$

There are two approaches to evaluate $\overline{\varepsilon}$ in the literature. One is according to the Lorentz–Lorenz formula to determine the initial value of $\overline{\varepsilon}$[4,10,12]

$$\overline{\varepsilon} = \left(3\varepsilon_0 + 2\overline{\alpha}N\right) / \left(3\varepsilon_0 - \overline{\alpha}N\right), \qquad (2)$$

where $\overline{\alpha}$ was obtained from MO modeling and calculation. Then $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\overline{\varepsilon}$ were calculated in sequence by Eq.(1). Next, by using the obtained $\overline{\varepsilon}$, the calculations of Maier–Meier equations were repeated until $\Delta\varepsilon$ saturates.

The other is deduced from the Maier–Meier equation (Eq.(1)), according to its definition $\overline{\varepsilon}$ =

$\left(\varepsilon_{\parallel}+2\varepsilon_{\perp}\right)/3$. The average dielectric constant can be calculated by solving

$$\overline{\varepsilon}-1=\frac{NhF}{\varepsilon_0}\left(\overline{\alpha}+\frac{F\mu^2}{3k_{\mathrm{B}}T}\right) \tag{3}$$

numerically.[6−9] In essence, these two methods are identical to each other and both of them need to iterate several times.

In fact, the average dielectric permittivity $\overline{\varepsilon}$ is a mathematical parameter, which has no concrete physical meaning. We note that while $S=0$, i.e. in isotropic state, it can be concluded that $\varepsilon_{\parallel}=\varepsilon_{\perp}=\varepsilon$ (ε denotes the dielectric permittivity of isotropic state) from Eq.(1) and the expression of ε looks the same as that of $\overline{\varepsilon}$, i.e. $\overline{\varepsilon}=\varepsilon$.[5] Take 5CB for example, the average dielectric permittivity $\overline{\varepsilon}=10.8$ and the measured dielectric permittivity in isotropic state is 10.5. So, we can consider $\overline{\varepsilon}$ as the approximation of ε in physics. Therefore, the Onsager equation[13] is appropriate to take the place of Eq.(3),

$$\frac{\varepsilon_0\left(\varepsilon-n^2\right)\left(n^2+2\varepsilon\right)}{\varepsilon\left(n^2+2\right)^2}=\frac{N\mu^2}{9k_{\mathrm{B}}T}, \tag{4}$$

when $\varepsilon\gg n^2$, we could have

$$\frac{2\varepsilon_0\varepsilon}{\left(n^2+2\right)^2}\approx\frac{N\mu^2}{9k_{\mathrm{B}}T}. \tag{5}$$

On the other hand, for molecules without a strong dipole moment, i.e. μ is close to 0, Eq.(5) will be no longer applicable and Eq.(4) agrees in the first approximation with the Lorentz–Lorenz equation. We readily derive $\varepsilon=n^2$ from Eq.(4) if we assume μ=0. Then, Eq.(2) can be used to evaluate the value of $\overline{\varepsilon}$. In this way, it affords us a simpler route to perform the calculation of $\overline{\varepsilon}$ analytically other than by numerical iteration. We will compare them in next section of this paper.

3. Molecular modeling and calculation

The $\overline{\alpha}$, $\Delta\alpha$, μ and β can be calculated through semi-empirical quantum chemistry modeling. For comparability, we adopt the same conditions as those used by Klasen *et al.*[6] A temperature $T=293$ K, and a density of 1000 kg·m^{-3} were assumed for all molecules in subsequent calculation.

A difficulty is how to determine the order parameter. According to the Maier–Saupe mean field theory,[14−16] the order parameter S is a function of temperature for all NLCs. However, most compounds are not at their nematic phase around 20 °C. Even if it can be extrapolated to this temperature, it is well known that the order parameters of different compounds can be quite different. Fujiata *et al*[7] developed an empirical relation between S and the clearing temperature T_{NI}, but the prediction of T_{NI} itself is not an easy task. Since we want to compare the calculated dielectric anisotropy with the experimental values in Ref.[1], which were measured in a defined solution (usually 10% weight/weight) of the respective single compound in a standardized nematic host mixture and then extrapolated to its pure state, it is reasonable to assume that the order parameter of the expected compound is approximate to that of the host mixture. This has been proved by recent molecular dynamic study of a liquid crystal mixture, which reveals that the order parameters of each component are very close to each other, even if their length to breadth ratio and clearing temperature are remarkably different.[17] Saitoh *et al* and Klasen *et al* used an empirical order parameter $S=0.7$ respectively during the calculation of dielectric anisotropy. Their results show acceptable correlation between the calculated and experimental data. So we adopted this empirical value for all molecules under investigation.

Another question is about the association effects. When the molecules have a large permanent dipole moment, the effective dipole moment in the condensed phase is usually smaller than the total dipole moment obtained in the gas phase or in highly diluted solutions.[18] Kirkwood has introduced the so-called Kirkwood g-factor to take into account the decrease of the effective dipole. A comprehensive study of the association effects of NLC has been carried out by Demus *et al*,[8,9] who brought forward a couple of solutions. However, the evaluation of the effective dipole moment is far from a straightforward work. Besides, the discrepancy of the effective dipoles (and g factors) extrapolated from polar and non-polar basic mixtures shows the weakness of these methods. Because the understanding of molecule interaction, especially in the liquid crystal mixtures, which contain compounds up to 20 or even more, is out of the state-of-the-art knowledge, it is difficult to clarify the dipole–dipole association effects. In practice, most liquid crystal compounds have moderate or extremely low dielectric anisotropy. We focused our attention on these kinds of materials, for which the association effects are not

so strong.

The molecular structure optimization and parameter calculation were implemented by a general semi-empirical molecular orbital package (MOPAC, AM1 Hamiltonian).[19,20] Because there were no substantial differences for various conformers,[8] only the most stable one was chosen.

4. Results and discussion

The modeling results of 5CB are listed in Table 2. $\overline{\alpha}$, $\Delta\alpha$, μ and β were calculated from AM1 method.

Table 2. The average polarizability ($\overline{\alpha}$), anisotropy of polarizability ($\Delta\alpha$), dipole moment (μ) and its orientation in the molecular frame (β) for 4'-*n*-pentyl-4-cyano-biphenyl (5CB) and 4'-*n*-butyl-4-*n*-propyl-bicyclohexyl (BPBCH). (modeled by MOPAC/AM1 method).

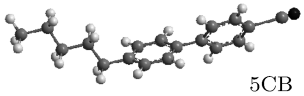
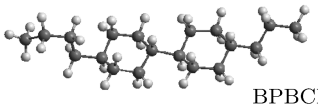
type of molecule (optimized)	$\bar{\alpha}$/a.u.	$\Delta\alpha$/a.u.	$\mu(D)$	$\beta/(^\circ)$
 5CB	171.85	178.84	4.121	7.9
 BPBCH	149.70	26.20	0.066	78.9

Table 3 shows the calculated data of $\overline{\varepsilon}$, F, h and $\Delta\varepsilon$ based on Eqs.(3)–(5) respectively. The results according to Eqs.(3) and (4) are identical, which coincides with our expectation. The calculated $\overline{\varepsilon}$ is a little overestimated than the experimental value 10.5, but the deviation for $\Delta\varepsilon$ is less than 2%. The data according to Eq.(5) is close to that of Eq.(4). This is because the cyano-group makes 5CB have a relative large permanent dipole moment. Therefore, we can depend on the approximation in Eq.(5) to evaluate $\overline{\varepsilon}$ directly.

Table 3. The calculated data of $\overline{\varepsilon}$, F, h and $\Delta\varepsilon$ of 4'-*n*-pentyl-4-cyano-biphenyl (5CB) through Eqs.(3)–(5) respectively.

equation	$\overline{\varepsilon}$	F	h	$\Delta\varepsilon$	$\Delta\varepsilon$(exp)	$\lvert\Delta\varepsilon - \Delta\varepsilon(\text{exp})\rvert$
$\overline{\varepsilon} - 1 = \frac{NhF}{\varepsilon_0}\left(\overline{\alpha} + \frac{F\mu^2}{3k_\mathrm{B}T}\right)$	12.73	1.30	1.443	22.01		0.41
$\frac{\varepsilon_0\left(\varepsilon - n^2\right)\left(n^2 + 2\varepsilon\right)}{\varepsilon\left(n^2+2\right)^2} = \frac{N\mu^2}{9kT}$	12.73	–	–	–	21.6[a]	–
$\frac{2\varepsilon_0\varepsilon}{\left(n^2+2\right)^2} \approx \frac{N\mu^2}{9kT}$	11.54	1.29	1.438	21.77		0.17

[a] Ref.[1].

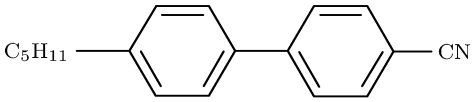
Furthermore, we modeled a non-polar liquid crystalline compound[1] (the results also listed in Table 2), with the same procedure and conditions for 5CB. BPBCH carries a dipole moment only 0.066 Debye, which is almost two orders of magnitude lower than 5CB. Table 4 shows us that the results according to Eqs.(3) and (4) are still consistent with each other. When the Lorentz–Lorenz equation is used, the calculated values of $\overline{\varepsilon}$, F, h and $\Delta\varepsilon$ agree well with those of Eq.(4).

Table 4. The calculated data of $\overline{\varepsilon}$, F, h and $\Delta\varepsilon$ of BPBCH through Eqs.(3)–(5) respectively.

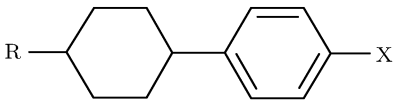
equation	$\overline{\varepsilon}$	F	h	$\Delta\varepsilon$	$\Delta\varepsilon$(exp)	$\lvert\Delta\varepsilon - \Delta\varepsilon(\text{exp})\rvert$
$\overline{\varepsilon} - 1 = \frac{NhF}{\varepsilon_0}\left(\overline{\alpha} + \frac{F\mu^2}{3k_{\mathrm{B}}T}\right)$	1.8063	1.0798	1.1748	0.0975		0.4975
$\frac{\varepsilon_0\left(\varepsilon - n^2\right)\left(n^2 + 2\varepsilon\right)}{\varepsilon\left(n^2 + 2\right)^2} = \frac{N\mu^2}{9kT}$	1.8063	–	–	–	–0.4[a]	–
$\varepsilon = \frac{3\varepsilon_0 + 2\overline{\alpha}N}{3\varepsilon_0 - \overline{\alpha}N}$	1.8046	1.0797	1.1746	0.0975		0.4975

[a] Ref.[1].

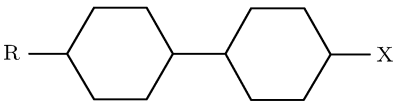
Besides 5CB and BPBCH, a selection of 26 compounds with representatives of the most important core structures and polar substituents were investigated. The chemical structures for these liquid crystal compounds are shown in Fig.2. Table 5 summarizes the parameters from molecular modeling and the values of $\Delta\varepsilon$ from calculation and measurement. Figure 3 shows the relationship between the calculated and measured values. Although the applied theories and the semi-empirical calculations imply a lot of assumptions and simplifications, the calculated $\Delta\varepsilon$ values agree well with those obtained experimentally for all investigated molecules, with the correlation coefficient of 0.98.



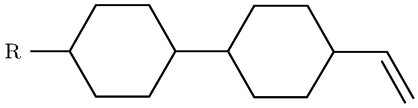
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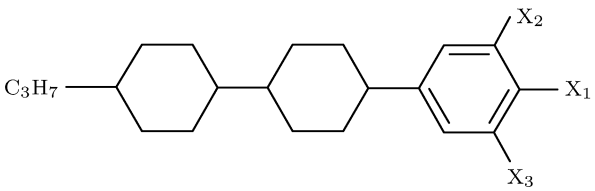
X = CN	$R = C_5H_{11}$	2
X = F	$R = C_5H_{11}$	3
$X = CF_3$	$R = C_5H_{11}$	4
$X = OCF_3$	$R = C_3H_7$	5
$X = OC_2H_5$	$R = C_3H_7$	6



$X = C_3H_7$	$R = C_4H_9$	7
$X = C_3H_7$	$R = C_5H_{11}$	8
$X = OC_2H_5$	$R = C_5H_{11}$	9
$X = CF_3$	$R = C_5H_{11}$	10
$X = OCF_3$	$R = C_5H_{11}$	11
$X = OCH{=}CF_2$	$R = C_5H_{11}$	12



	$R = C_3H_7$	13
	$R = C_5H_{11}$	14



X_1 = F	$X_2 = X_3$= H	15
$X_1 = X_2$= F	X_3=H	16
$X_1 = X_2 = X_3$ = F		17
$X_1 = OCF_3$	X_2 = F X_3= H	18
$X_1 = OCF{=}CF_2$	$X_2 = X_3$= F	19

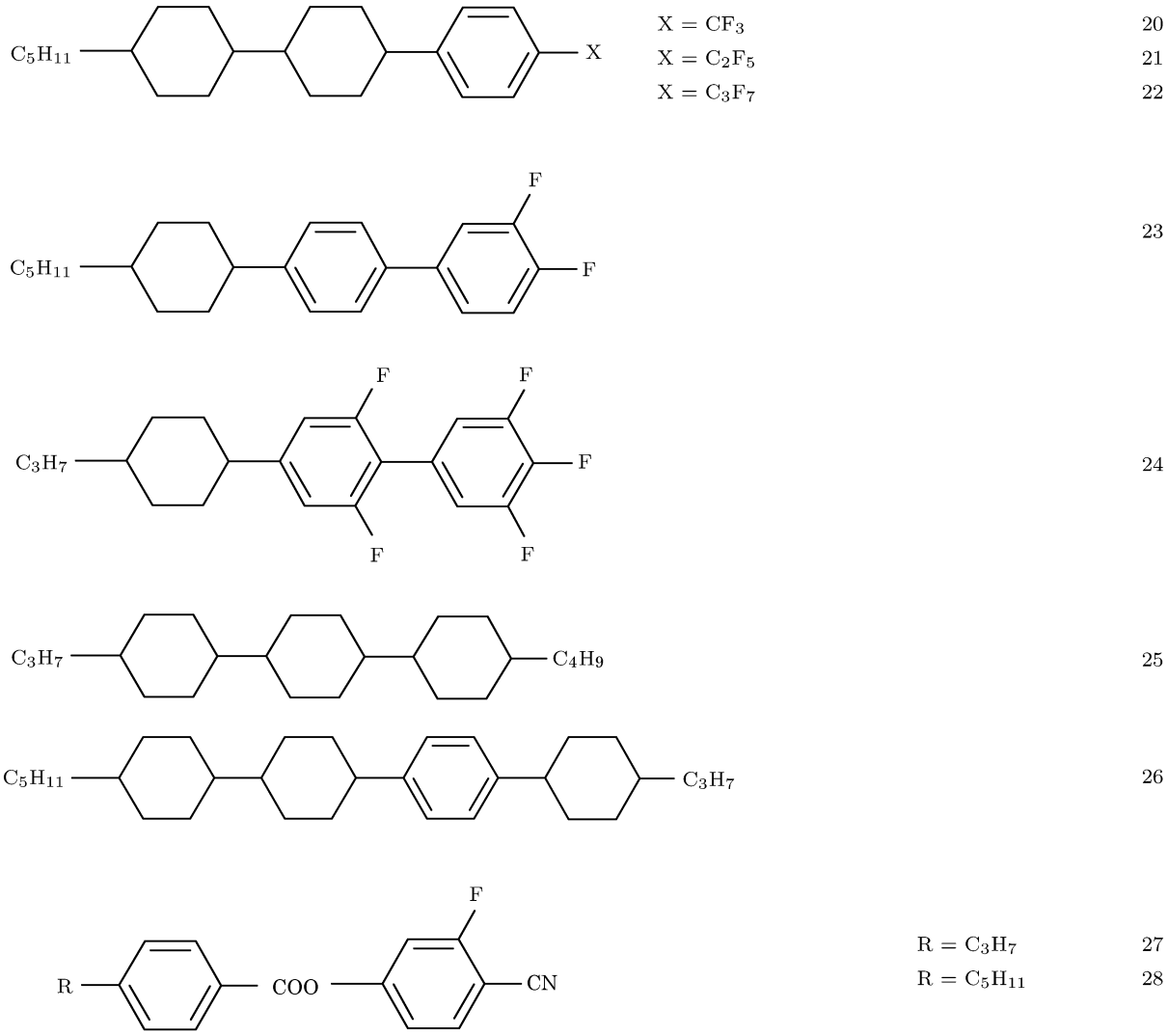


Fig.2. The chemical structures of the investigated liquid crystal compounds.

Table 5. The parameters from molecular modeling (AMI) and the calculated and measured values of $\Delta\varepsilon$.

	$\mu(D)$	$\overline{\alpha}$/a.u.	$\Delta\alpha$/a.u.	$\beta/(^\circ)$	$\Delta\varepsilon$(calc.)	$\Delta\varepsilon$(meas.)
1	4.121	171.85	178.84	7.9	21.773	21.6
2	3.901	155.99	105.25	13.5	16.231	18.0
3	1.961	141.57	69.78	12.6	3.172	4.0
4	3.893	151.42	72.27	11.6	12.510	9.2
5	2.634	141.25	80.61	10.5	5.335	7.1
6	1.251	149.19	86.46	86.5	–0.134	–0.1
7	0.066	149.70	26.20	78.9	0.097	–0.4
8	0.003	158.68	34.13	29.9	0.122	–0.5
9	1.224	156.65	43.21	75.4	–0.136	–0.4
10	3.189	145.33	31.54	14.8	7.112	5.3
11	2.804	150.01	41.70	11.9	5.070	6.9
12	3.604	165.05	74.69	31.7	6.375	5.6
13	0.226	136.63	49.91	8.0	0.252	–0.7
14	0.224	153.06	54.19	7.4	0.241	0.3
15	1.989	173.03	83.82	11.4	2.583	3.0
16	3.231	175.46	85.74	12.0	7.770	6.4

Table 5. (*Continued*).

	$\mu(D)$	$\overline{\alpha}$/a.u.	$\Delta\alpha$/a.u.	$\beta/(^\circ)$	$\Delta\varepsilon$(calc.)	$\Delta\varepsilon$(meas.)
17	3.768	177.76	84.23	11.1	10.289	8.3
18	4.088	191.98	100.95	9.6	10.569	9.0
19	4.356	210.58	114.78	9.0	11.370	10.7
20	3.945	199.15	90.79	13.5	9.699	9.1
21	4.032	212.06	96.85	12.8	8.688	6.3
22	4.341	225.15	107.33	8.5	9.280	7.5
23	3.388	207.26	157.26	30.5	5.898	6.3
24	5.478	196.18	148.48	6.1	22.189	20.5
25	0.011	197.84	49.98	82.3	0.144	–0.1
26	0.095	262.93	113.80	63.5	0.263	–0.3
27	7.160	172.58	184.92	18.7	48.936	50.2
28	7.184	189.79	195.72	20.0	43.522	43.0

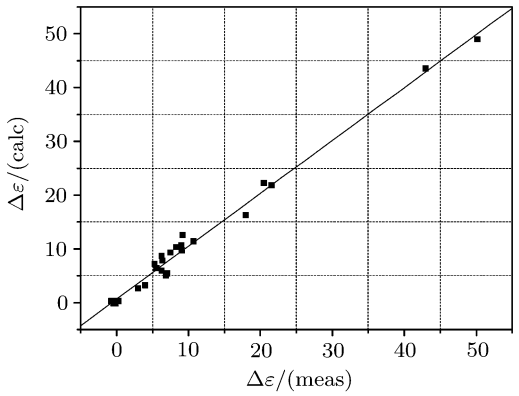


Fig.3. Calculated dielectric anisotropy $\Delta\varepsilon$ versus measured values and least-squares fit.

5. Conclusion

We have explored the $\overline{\varepsilon}$-dependent properties of the dielectric anisotropy $\Delta\varepsilon$ of NLCs according to the Maier–Meier equation. Under the framework of Maier–Meier theory, $\overline{\varepsilon}$ has the same expression with the isotropic dielectric permittivity of NLC. The average permittivity $\overline{\varepsilon}$ plays an important role in calculating $\Delta\varepsilon$. Usually it is determined by numerical methods, which will iterate several times until the value of $\overline{\varepsilon}$ is saturated. We apply the Onsager approximation and Lorentz–Lorenz equation to evaluate $\overline{\varepsilon}$ for polar and non-polar NLC respectively. This solution is more straightforward and shows reasonable agreements with those numerical methods.

The calculated dielectric anisotropy $\Delta\varepsilon$ through semi-empirical quantum chemistry modeling and the Maier–Meier equation shows good correlation with the experimental values. The estimating method is useful for the molecular design of liquid crystal compounds.

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