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Temperature dependence of ratio between dielectric anisotropy and order parameter in fluorinated nematic liquid crystals*

Ma Heng(马 恒)[a)†], Sun Rui-Zhi(孙瑞芝)[a)],
Li Zhen-Xin(李振新)[b)], and Liu Yu-Fang(刘玉芳)[a)]

[a)] *College of Physics and Information, Henan Normal University, Xinxiang* 453007, *China*
[b)] *Department of Life Science and Technology, Xinxiang Medical College, Xinxiang* 453003, *China*

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Temperature dependence of ratio between dielectric anisotropy and order parameter of fluorinated nematic liquid crystal is investigated by using a semi-empirical molecular orbital package that can accurately calculate an angle between molecular dipole moment and long axis. We optimize the molecular conformations with three semi-empirical Hamiltonians AM1, PM3 and PM5, and then make a comparison between computational results and experimental measurements. It is shown that the results obtained from AM1 method are in good agreement with the measurements. The present study offers an applicable method to predict the dielectric properties of liquid crystal material.

Keywords: dielectric anisotropy, order parameter, fluorine, nematic liquid crystal
PACC: 6130G

1. Introduction

In recent years, full-colour and flat-screen liquid crystal displays (LCDs), which are almost indispensable to our life in many fields, have aroused much interest. Fluorinated nematic liquid crystals (LCs) are widely utilized in advanced LCDs because of their wider nematic temperature range, high resistivity and birefringence, and modest dielectric anisotropy.[1−4] In order to further improve these features, the evaluation of the physical constants, especially the dielectric anisotropy $\Delta\varepsilon$ and order parameter of the nematic LCs, is necessary, for they are key factors in the development of nematic LC mixtures. On the other hand, the study on the physical property of the LCs can help to further clarify the substitution effect of fluorine atom in molecular structure. Therefore, many groups have already investigated a number of phenylbicyclohexane (PBC) compounds, in which one, two or three hydrogen atoms of the phenyl ring are substituted by the fluorine atoms.[5−10] Particularly, temperature dependences of the physical properties, such as threshold voltage, permittivity, splay elastic constant, birefringence and order parameter have been investigated.

Experimental measurement of the dielectric anisotropy and order parameter is important for the application of LC compounds, but the measurement is always complicated in practice. Therefore, molecular simulation and calculation on the physical parameters are convenient for the material synthesis and prediction of physical property. Xu *et al*[10] and Huh and Kim[11] have evaluated the ratio of dielectric anisotropy to order parameter, $\Delta\varepsilon/s$, for some fluorinated PBC LC compounds using the well-known Maier–Meier theory. However, because of lack of computational program for determining the angle (β) between molecular dipole moment and long molecular axis, it is always difficult to acquire an accurate β value from calculations.

By using the updated version of the molecular orbit package (MOPAC), it is possible to obtain an accurate β value. Furthermore, some new experimental data about physical properties of fluorinated PBC compounds have also been reported recently.[9] In the present paper, we investigate the temperature dependence of the ratio of dielectric anisotropy to order parameter in some fluorinated PBC LC compounds. The molecular structures are optimized with Parametric Method 3 (PM3), Parametric Method 5 (PM5),

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†Corresponding author. E-mail: hengma@htu.cn

and Austin Model 1 (AM1), separately. The computational results are compared with the experimental measurements.

2. Computational process

Quantum chemistry calculation, such as density function and discrete variational method, has been well used in molecular structural optimization and characterization of materials in recent years. In a number of molecular simulations of LCs, the semi-empirical MOPAC is also frequently employed to evaluate the molecular parameters, especially mechanical and electrical properties.[12−15] In the present study, we select five compounds of which the molecular conformation is shown in Fig.1 and structures and phase behaviours are listed in Table 1. According to the Maier–Meier theory,[16] the temperature dependence of the ratio between dielectric anisotropy and order parameter ($\Delta\varepsilon/s$) is given as

$$\Delta\varepsilon/s = \frac{NhF}{\varepsilon_0}\left[\Delta\alpha - F\mu^2\frac{(1-3\cos^2\beta)}{2K_{\mathrm{B}}T}\right], \qquad (1)$$

where N is the number of molecules per unit volume; ε_0 is the dielectric constant in vacuum; $\Delta\alpha = \alpha_{xx} - (\alpha_{yy} + \alpha_{zz})/2$ is the anisotropy of polarizability; μ is the dipole moment; β is the angle between the molecular dipole moment and the long molecular axis; K_{B} is the Boltzmann constant.

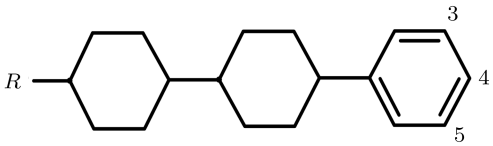


Fig.1. Molecular conformation where hydrogen atoms at positions 3, 4 and 5 of phenyl ring are substituted by fluorine atoms. $R = C_nH_{2n+1}$, $n = 3$ or 5.

Table 1. Phase transition temperature of fluorinated bicyclohexylphenyl compounds corresponding to the molecular conformation in Fig.1.

compounds	3	4	5	T_{CrN}/°C	T_{NI}/°C
3PBC^{34}F$_2$	F	F	H	44.2	118.0
3PBC^{35}F$_2$	F	H	F	50.9	87.9
5PBC^{35}F$_2$	F	H	F	–	94.2
3PBC^{345}F$_3$	F	F	F	37.7	92.7
5PBC^{345}F$_3$	F	F	F	49.1	99.9

The Onsager local field factors are expressed as $h = \dfrac{3\varepsilon}{2\varepsilon+1}$, $F = \dfrac{1}{1-f\alpha_{\mathrm{av}}}$, $f = \dfrac{(\varepsilon-1)}{2\pi\varepsilon_0 a^3(2\varepsilon+1)}$, where α_{av} and ε are the mean values of the polarizability and permittivity, respectively; a is the sphere radius; the density is assumed to be a value of 1000 kg/m^3, i.e. $(4/3)Na^3 = 1$. From the Maier–Meier equation, $\Delta\varepsilon$ is a physical parameter which depends on the molecular structure. Therefore, in order to calculate the dielectric anisotropy, we need to determine the initial value of ε. According to the Lorentz–Lorenz formula,[17] ε is given by

$$\varepsilon = \frac{3\varepsilon_0 + 2\alpha_{\mathrm{av}}N}{3\varepsilon_0 - \alpha_{\mathrm{av}}N}. \qquad (2)$$

The theory considers the molecular anisotropy only with respect to the polarizability, but it neglects the anisotropic shape of molecule. The calculated physical constants of fluorinated LC compounds are listed in Table 2. Giving a series of temperature data, the temperature dependence of $\Delta\varepsilon/s$ for the compounds is calculated using Eq.(1).

Table 2. Calculated physical constants of fluorinated liquid crystal compounds using PM3, PM5 and AM1 methods.

compounds	μ/D	α_{av}/a.u.	$\Delta\alpha$/a.u.	$\beta/(^\circ)$
		PM3		
3PBC^{35}F$_2$	2.063	155.50	70.47	12.2
5PBC^{35}F$_2$	2.066	169.79	72.90	13.5
3PBC^{34}F$_2$	3.187	156.00	76.13	10.9
3PBC^{345}F$_3$	3.717	157.51	75.26	12.4
5PBC^{345}F$_3$	3.721	171.80	77.74	13.8
		PM5		
3PBC^{35}F$_2$	3.322	191.35	93.54	10.7
5PBC^{35}F$_2$	3.327	210.04	99.96	12.4
3PBC^{34}F$_2$	5.056	192.23	98.62	11.5
3PBC^{345}F$_3$	5.971	193.76	98.76	11.0
5PBC^{345}F$_3$	5.980	212.46	105.17	12.7
		AM1		
3PBC^{35}F$_2$	2.159	174.52	76.94	11.1
5PBC^{35}F$_2$	2.163	190.86	80.90	12.1
3PBC^{34}F$_2$	3.230	175.40	85.80	10.8
3PBC^{345}F$_3$	3.766	177.71	84.25	11.5
5PBC^{345}F$_3$	3.771	194.07	88.25	12.4

3. Results and discussion

In order to compare the calculation results with experimental measurements reported in Ref.[9], we adopt PM3, PM5 and AM1 methods to optimize the molecular structures of the compounds. The calculated physical parameters are listed in Table 2, and

the temperature dependence of $\Delta\varepsilon/s$ are shown in Figs.2–4, corresponding to the three different calculation methods: PM3, PM5 and AM1, respectively.

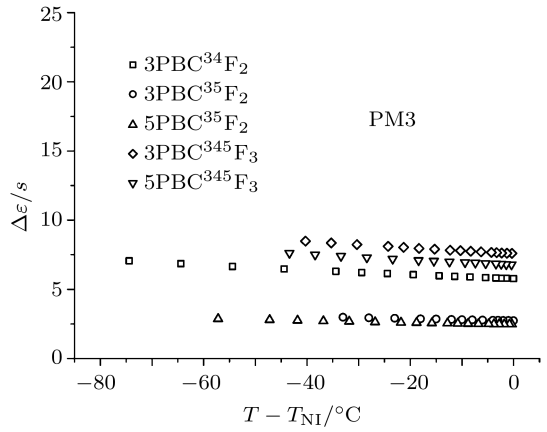


Fig.2. Temperature dependence of $\Delta\varepsilon/s$ calculated by substituting the molecular parameters into the Maier–Meier equation with PM3 method. The temperature is expressed as $T - T_{NI}$.

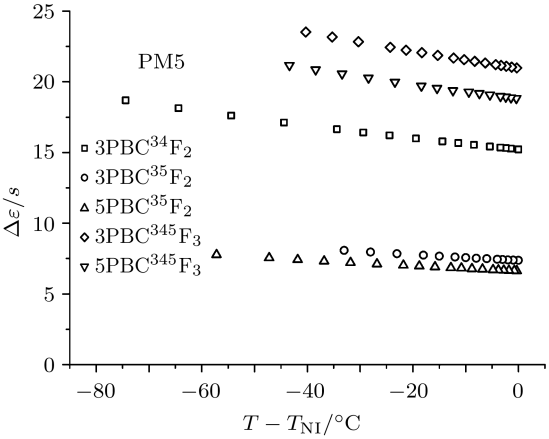


Fig.3. Temperature-dependent $\Delta\varepsilon/s$ calculated by using the PM5 method. The temperature is expressed as $T - T_{NI}$.

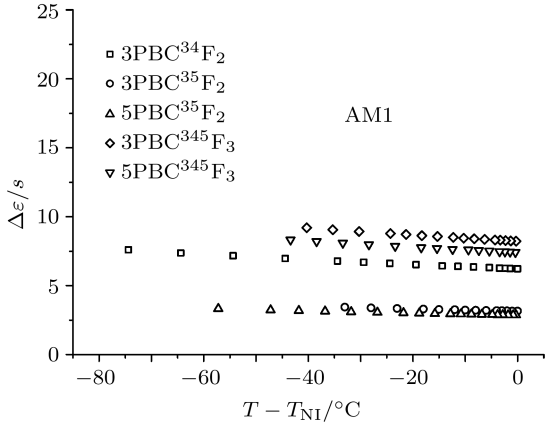


Fig.4. Temperature-dependent $\Delta\varepsilon/s$ calculated by using the AM1 method. The temperature is expressed as $T - T_{NI}$.

No matter which of the three calculation methods is used, all the calculated values of $\Delta\varepsilon/s$ show the following order: $3PBC^{345}F_3 > 5PBC^{345}F_3 > 3PBC^{34}F_2 > 3PBC^{35}F_2 > 5PBC^{35}F_2$.

By investigating the experimental data of the anisotropic dielectric constant published in Refs.[5, 8, 9], the experimental temperature dependence of $\Delta\varepsilon$ is shown to be also in the above value order. This can be attributed to two causes: one is that a number of the substituted strong polar fluorine atoms strongly contribute the dielectric to the molecule; the other is that the angle β, which is chiefly determined by fluorine atoms,[6] can also exert an influence on the value of $\Delta\varepsilon$ markedly. On the other hand, the alkyl radicals give a slight influence on $\Delta\varepsilon$, i.e. the longer the radical, the smaller the dielectric constant. As the value order of the measured temperature dependence of $\Delta\varepsilon$ is identical with that of the computed temperature dependence of $\Delta\varepsilon/s$, one can estimate roughly that all the temperature properties of the order parameter for those compounds do not markedly differ from each other.[9]

In order to observe the above order property quantitatively, we select a representative middle temperature range of $T - T_{NI} = -25$°C to compare the $\Delta\varepsilon/s$ value which is listed in Table 3. The experimental data are presented by Ma *et al.*[9] No matter which data are adopted: measured or computed, the above rule always holds true that compounds $3PBC^{345}F_3$ and $5PBC^{345}F_3$ show the largest value, and compounds $3PBC^{35}F_2$ and $5PBC^{35}F_2$ show the smallest value, while the value from the $3PBC^{34}F_2$ mediates between them.

Table 3. Comparison of $\Delta\varepsilon/s$ between measured and calculated values at $T - T_{NI} = -25°$ using AM1, PM3 and PM5 methods.

compounds	Exp.	AM1	PM3	PM5
$5PBC^{35}F_2$	4.18	3.04	2.62	7.08
$3PBC^{35}F_2$	4.63	3.36	2.92	7.89
$3PBC^{34}F_2$	6.75	6.62	6.14	16.67
$5PBC^{345}F_3$	11.20	7.91	7.23	20.09
$3PBC^{345}F_3$	13.90	8.79	8.11	22.48

By comparing the calculated values in Figs.2–4 and Table 3, it is found that the $\Delta\varepsilon/s$ obtained by using PM5 method attains at a maximum value, and the AM1 method produces a minimum value. From Table 2, one can find that there exist the differences among the three methods due to that the PM5 method produces a larger polarizability than the PM3 and AM1

methods.

It is found from Ref.[9] that the calculation from the AM1 method is the closest to the measurement. Therefore, for comparison, we fit the AM1 calculation data to a function of temperature indicated by solid lines in Fig.5, where the measurements are also indicated by symbols. For compounds $3PBC^{34}F_2$, $3PBC^{35}F_2$ and $5PBC^{35}F_2$, which are possessed of a small dipole moment, their calculations are in good agreement with the measurements. Conversely, because of their large dipole moment, the compounds of $3PBC^{345}F_3$ and $5PBC^{345}F_3$ reveal computational values smaller than the measurements.

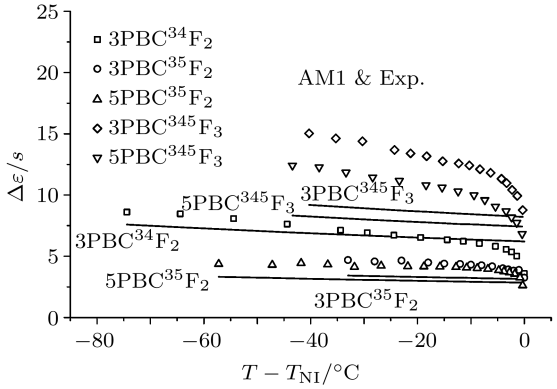


Fig.5. Comparison between values of $\Delta\varepsilon/s$ measured and calculated by using the AM1 method. Measurement results are represented with symbols, and the calculation results are denoted by fitting lines. The temperature is expressed as $T - T_{NI}$.

All the calculations from the three methods show that they are weakly temperature-dependent, furthermore, the $\Delta\varepsilon/s$ presents a negative linear correlation with temperature increasing. We have also fitted the $\Delta\varepsilon/s$ to a linear function of temperature, which indicates that all the absolute values of the relevant coefficients of the fitting functions are extremely close to 1, or rather, they are in a range of 0.99985–0.99996. This demonstrates that the Maier–Meier equation can describe the temperature dependence of the $\Delta\varepsilon/s$, partly and inaccurately only, for the actual experimental results appear to manifest quadric, tridric or more upper functional correlations. This is due to the fact that the calculations, or the Maier–Meier equation, did not take into consideration the temperature dependence of the molecular parameters, such as density, polarizability, dipole moment, furthermore the molecular conformation deformation. Particularly, closing to the nematic/isotropic phase transition range, the molecule will change its own physical parameters more easily and markedly. Therefore, more accurate and comprehensive calculation is expected.

4. Conclusions

In fluorinated phenylbicyclohexane LCs, the temperature dependence of ratio $\Delta\varepsilon/s$ is studied numerically using the Maier–Meier equation and MOPAC. In the calculation of molecular physical parameters, the methods of AM1, PM3 and PM5 are employed, separately. By comparing the calculation results and experimental measurements, it is found that the AM1 method is an applicable way to calculate an actual $\Delta\varepsilon/s$ ratio. The Maier–Meier equation cannot describe a quadric function for the temperature dependence of $\Delta\varepsilon/s$, and it seems that only for a smaller molecular dipole moment, can the equation give a good theoretical description.

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