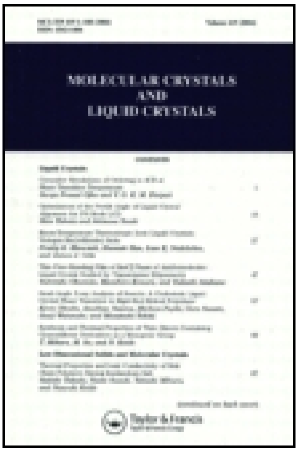

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Goroh Saitoh, Masaharu Satoh & Etsuo Hasegawa (1997): Estimating Dielectric Anisotropy of Liquid Crystal Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 13-18

To link to this article: http://dx.doi.org/10.1080/10587259708041743

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 13-18
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ESTIMATING DIELECTRIC ANISOTROPY OF LIQUID CRYSTAL COMPOUNDS

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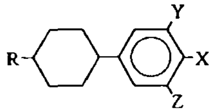
Abstract An applications of the molecular orbital (MO) calculation and Maeir-Meier theory to liquid crystal compounds are investigated for estimating dielectric anisotropy (Δε). The method involves calculating the parameters on MO calculation and substituting these values into Maeir-Meier theory. These calculations are repeated until the calculated Δε saturates. The estimated Δε agree closely with those obtained experimentally for liquid crystal compounds with various skeletons and polarized groups.

INTRODUCTION

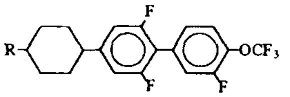
The liquid crystal (LC) compounds should meet many requirements, such as low threshold voltage, quick response time and large operational temperature range. To achieve a low threshold voltage, it is necessary to select the LC compounds with large dielectric anisotropy (Δε). Recently, Bremer et al.[1] estimated the Δε from molecular orbital (MO) calculation and the Maier-Meier theory without applying the anisotropy of polarizability. The results showed the significant discrepancy in Δε between the calculated value and experimentally measured one. Moreover, the difference varies widely from each compounds. In this paper, we report a improved method for the Δε calculation based on the MO calculation and Maier-Meier theory.

METHOD

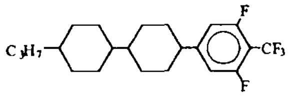
Figure 1 shows the chemical structures for the LC compounds used in this study. The selected compounds covers almost all skeletons and polarized groups.



	R	X	Y	Z
1)	C_3H_7	CN	H	H
2)	C_5H_{11}	CN	H	H
3)	C_3H_7	OCF_3	H	H
4)	C_5H_{11}	OCF_3	H	H
5)	C_5H_{11}	F	H	H
6)	C_5H_{11}	CF_3	H	H
7)	C_5H_{11}	OCH_3	H	H
8)	C_5H_{11}	CN	F	H
9)	C_5H_{11}	CN	F	F



10) R: C_3H_5 11) R: C_5H_{11}



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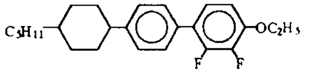

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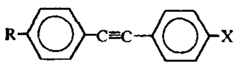
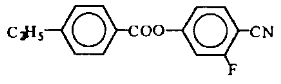
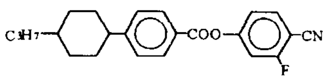


14) R: C_4H_9 X: F
15) R: C_2H_5 X: OCH_3
16) R: C_5H_{11} X: OCF_3



17)



18)

Figure 1. Chemical structures for the liquid crystal compounds

The estimation of Δε involves the calculation of the parameters on MO method, and substituting these values into the Maeir-Meier equations. Namely, the initial ε was supposed from Lorentz-Lorentz equation, and then $\varepsilon_{||}$,$\varepsilon_{\perp}$ and Δε were calculated with Maeir-Meier equations using the initial ε. Next, with using the obtained ε, the calculations of Maeir-Meier equations were repeated until Δε saturates. The Maeir-Meier equations[2,3] are given by

$$\Delta\varepsilon = \frac{NhF}{\varepsilon_0}\left\{\Delta\alpha + \frac{F\mu^2\left(1-3\cos^2\beta\right)}{2K_BT}\right\}S, \tag{1}$$

$$\varepsilon_{\parallel} = 1 + \frac{NhF}{\varepsilon_0}\left[\alpha_{\parallel} + \frac{F\mu^2\left\{1-\left(1-3\cos^2\beta\right)S\right\}}{3K_BT}\right], \tag{2}$$

$$\varepsilon_{\perp} = 1 + \frac{NhF}{\varepsilon_0}\left[\alpha_{\perp} + \frac{F\mu^2\left\{1+0.5\left(1-3\cos^2\beta\right)S\right\}}{3K_BT}\right], \tag{3}$$

where

$$F = \frac{1}{1-f\alpha}, \tag{4}$$

$$f = (\varepsilon-1)\left\{2\pi\varepsilon_0 a^3(2\varepsilon+1)\right\}^{-1}, \tag{5}$$

$$\frac{4}{3}\pi N a^3 = 1, \tag{6}$$

$$h = \frac{3\varepsilon}{2\varepsilon+1}, \tag{7}$$

where N is the molecular number per unit volume, μ is the dipole moment, K_B is the Bolzman constant, ε_0 is the dielectric constant for vacuum, $\Delta\alpha$ is the anisotropy of polarizability, β is the angle between μ and the main axis of polarizability, S is the order parameter of LC. The Lorentz-Lorenz Equation is given by

$$\alpha = \frac{3\varepsilon_0(\varepsilon-1)}{N(\varepsilon+2)} \tag{8}$$

In the course of our calculations, the density and S were chosen to be 1.0×10^3 kg/m^3 and 0.7, respectively. $\Delta\alpha$, μ and β were obtained by MO calculation using the AM1 method[4], which was performed with MOPAC ver.6.03.[5] The geometies of the basic component of LC were assumed as follows: (a) Phenylcyclohexane takes a most stable geometry, in which phenyl ring is parallel to the iso-hydrogen atom of cyclohexane ring[6]. (b) For phenybenzoate skeleton and biphenyl moiety, only the dihedral angles of phenyl rings are optimized. (c) The carbon of OCH_3, OC_2H_5 or OCF_3 group and phenyl ring are placed on the same plane.

RESULTS AND DISCUSSION

Table 1 summarizes the calculated parameters and experimental Δε. Figure 2 shows the relationship between the calculated and experimental values for Δε. The calculated Δε values agree closely with those obtained experimentally, with the correlation coefficient of 0.99. The calculated Δε values for liquid crystal compounds are slightly smaller than the experimental values. It should be originated from the inaccuracy of MO calculation. Indeed, the calculated μ is smaller than the experimental value (ex. μcal.=3.44 and μexp.=4.18 for cyanobenzene, μcal.=1.51 and mexp.=1.60 for fluorobenzene).[11]

TABLE 1 Calculated parameters and experimental Δε values for LC compounds

Compound	Δα(Å^3)	μ(D)	β(deg.)	Δε cal.	Δε exp.
(1)	9.4	3.9	0.8	16.8	21.1[1)]
(2)	8.8	3.9	5.0	14.6	18.0[1)]
(3)	6.6	2.6	4.7	4.6	7.1[1)]
(4)	5.8	2.5	0.6	4.0	5.6[1)]
(5)	3.6	2.1	5.9	3.4	3.2[7)]
(6)	3.0	3.1	4.3	6.6	10.9[7)]
(7)	5.6	1.3	78.4	-0.4	-0.5[7)]
(8)	8.3	4.8	8.4	21.4	22.0[1)]
(9)	8.1	5.4	4.7	26.0	30.0[1)]
(10)	16.8	5.3	17.0	15.0	16.7[1)]
(11)	16.7	5.3	11.4	15.0	15.0[1)]
(12)	3.7	4.8	3.7	13.3	16.3[1)]
(13)	18.5	3.9	84.2	-4.8	-4.1[8)]
(14)	26.4	2.4	3.9	6.4	9.9[9)]
(15)	29.2	1.2	80.5	0.3	1.6[1)]
(16)	30.8	2.5	3.3	4.9	10.0[10)]
(17)	19.3	7.0	20.0	44.9	53.7[1)]
(18)	22.1	7.5	18.4	37.9	37.5[1)]

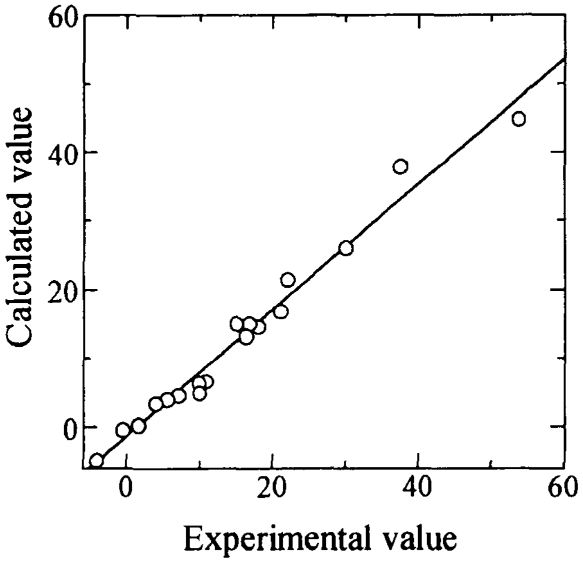


FIGURE 2 Calculated $\Delta\varepsilon$ versus experimental $\Delta\varepsilon$

Although the compound (18) consist of compound (17) with chemical similarity, both of the experimental and estimated $\Delta\varepsilon$ values of compound (18) are extremely smaller than those of compound (17). The small N in compound (18) should be the reason for the small $\Delta\varepsilon$. It indicates that the molecular weight affects the $\Delta\varepsilon$. On the other hand, there observed little discrepancy between the calculated $\Delta\varepsilon$ values and the experimental values for the tolane compounds (15) and (16) with the OCF_3 or OCH_3 group. It is may be due to complex effect of the tolane skeleton and OCH_3 or OCF_3 groups. Table 2 summarizes the results of the another (perpendicular) confomer having the carbon of OCH_3 or OCF_3 group placed on the perpendicular plane to the phenyl ring.

TABLE 2 Calculation results for the perpendicular confomer

Compound	$\Delta\alpha$(Å^3)	μ(D)	β(deg.)	$\Delta\varepsilon$ cal.	$\Delta\varepsilon$ exp.
(14)	28.7	1.8	54.0	1.1	1.6
(15)	31.5	3.2	3.5	8.0	10.0

The estimated Δε values for perpendicular confomer of compounds (15) and (16) agree with the experimental values. As the compounds with tolane skeleton and alkoxy derivatives have large π conjugation and lone electrons, the μ and β for perpendicular confomers are different from those for the parallel (same plane) ones. For the compounds having large π conjugation and lone electrons, it should be examine the several possible confomers for Δε calculation.

CONCLUSION

An improved method of estimating dielectric anisotropy (Δε) for liquid crystal compounds is developed. The estimated Δε agree closely with those obtained experimentally for various liquid crystal compounds. Some confomers are considered for estimating Δε on the compounds having large π conjugation and lone electrons. The estimating method is useful for molecular design for liquid crystal compounds.

REFERENCES

1. M. Bremer and K. Tarumi, Adv. Mater., 5, 842(1993)
2. W. Maier and G. Meier, Z. Naturforsch, 16a, 262 (1961)
3. C. J. F. Böttcher and P. Bordewijk, THEORY OF ELECTRIC POLARIZATION (Elsevier Scientific Publishing Company, Amsterdam, 1978) Chap.15, p.469
4. M.J.S. Dewar, E.G.Healy and J.J.P.Stewart, J.Am.Chem.Soc.,107,3902(1985)
5. MOPAC Ver.6,J.J.P.Stewart, QCPE Bull., 9, 10(1989); Revised as Ver.6.01 by T. Hirano, University of Tokyo, for HITAC and UNIX machine, JCPE Newsletter, 6, 25(1995); Revised as Ver.6.02 by T. Noguchi, NEC Software Kansai Co. for EWS-UX/V. JCPE Newsletter, 6, 88(1995); Revised as Ver.6.03 by present authors for increasing calculable atoms.
6. N. L. Allinger and M. T. Tribble, Tetrahedorn Lett., 3259(1971)
7. LIQUID CRYSTAL APPLICATION AND USES, Edited by B. Bahadur (World Scientific, Singapore, 1993), 1, Chap.3, pp.149-153
8. V.Reiffenrath, J. Krause, H. J. Plach and G. Weber, Liq. Cryst., 5, 159(1989)
9. Y. Chen, S. Wang, S. Lung and C. Hsu, Proc. SPIE Int. Soc. Opt. Eng., 1815, 268(1992)
10. V. Reiffenrath, U. Finkenzeller, E. Poetsch, B.Rieger and D. Coates, Proc. SPIE Int. Soc. Opt. Eng., 1257, 84(1990)
11. HANDBOOK of CHEMISTRY and PHYSICS, Edited by D.R. Lide, 72nd Edition (CRC Press, Inc., Boca Raton, 1991)