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

Orientational Elasticity of Nenatic Dimers

N. V. Tsvetkov [a] , V.V Zuev [b] , I. V. Ksenofontov [a] & V. N. Tsvetkov [b]

[a] Physical Faculty of St. Petersburg State University, Ulianovskaya st. 1, St. Petersburg, 198904, Petrodvoretz, Russia

[b] Institute of Macromolecular Compounds of the Russian Academy of Sciences, 199004, Bolshoi prospect 31, St. Petersburg, Russia

Version of record first published: 04 Oct 2006

To cite this article: N. V. Tsvetkov, V.V Zuev, I. V. Ksenofontov & V. N. Tsvetkov (1999): Orientational Elasticity of Nenatic Dimers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 41-47

To link to this article: http://dx.doi.org/10.1080/10587259908047498

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 41-47
Reprints available directly from the publisher
Photocopying permitted by license only

Orientational Elasticity of Nenatic Dimers

N.V. TSVETKOV[a], V.V ZUEV[b], I.V. KSENOFONTOV[a] and V.N. TSVETKOV[b]

[a]*Physical Faculty of St. Petersburg State University, 198904, Ulianovskaya st.1, St. Petersburg, Petrodvoretz, Russia and* [b]*Institute of Macromolecular Compounds of the Russian Academy of Sciences, 199004, Bolshoi prospect 31, St.Petersburg, Russia*

Using the method of threshold Frederick's transitions in magnetic field were determined the values of splay orientational elastic constants K_{11} of the nematic dimers 4,4'-bis-cyanobiphenyloxyalkanes with the number n of CH_2 groups in their spacers from 2 to 12. The dramatic odd-even effect in the dependence of K_{11} versus n was evaluated. This effect is mainly due to the oscillations of the degree of intermolecular orientational order in the series of the compounds under investigation. The increase of the values of the splay elastic constant K_{11} of both odd and even homologous series of nematic dimers with increase of the spacer length was determined.

Keywords: nematics; dimers; orientational elasticity

INTRODUCTION

The recent considerable interest in the study of dimers and trimers of the «siames twins» type is due to the strong odd-even effect in their thermal [1] characteristics and also to marked oscillations in the degree of orientational order [2], in the entropy and enthalpy of the isotropic liquid - liquid crystal transitions [3, 4] when spacer length in the molecules of these compounds is varied. In our recent investigations dimers (4,4'-bis-cyanobiphenylyloxyalkanes, BCBOA) and trimers (4,4'-bis-[ω-(4-cyanobiphenyl-4'-yloxy)alkyloxy]biphenyls) have been studied in dilute

solutions and nematic melts by the methods of electric birefringence [5] and orientational elastic deformations in electric fields [6, 7]. A strong odd-even effect was detected for these compounds in the optical anisotropy of their nematics (caused by variations of the degree of intermolecular orientational order S) and in the electrical threshold deformational potentials (caused mainly by the conformational-dipolar changes in their intramolecular structure, i.e. the variations in intramolecular orientational-polar order) as a result of change of spacer length in the molecules. In the present work BCBOA nematic dimers were studied by the method of orientational elastic deformations in a magnetic field with the aim of investigating the effect of the length of flexible chain fragments on the elastic characteristics of their mesophase.

EXPERIMENTAL

The number n of CH_2 groups in the spacers of the dimers investigated ranged from 2 to 12. All investigated BCBOA exhibit thermotropic nematic mesomorphism. Their isotropization temperatures T_{NI} determined by polarizing microscopy are given in Table 1. Orientational elasticity of BCBOA nematics was investigated in plane - concave layers up to 10^{-2} cm thick by the procedure described in detail in [8]. The sample temperature was determined with the aid of a thermocouple to within 1°C. Process of nematics reorientation was carried out under the influence of a magnetic field with a strength up to 6 kGs.

RESULTS AND DISCUSSION

The elastic properties of BCBOA were studied in initially planar oriented nematic layers. Under the influence of the external magnetic field the system of interference rings distorted in the range of layer thickness $z \geq z_c$. The resulting deformation is the splay elastic deformation. Measuring the radius r_c of the critical boundary, it is possible to calculate z_c

$$z_c = r_c^2 / 2R \qquad (1)$$

where z_c is the layer thickness corresponding to the critical boundary and R is the radius of lens curvature. The values of z_c make it possible to calculate the ratio of the splay elastic constant K_{11} to the diamagnetic anisotropy of unit volume of the nematic $\Delta\chi$

$$z_c H = \pi (K_{11}/\Delta\chi)^{1/2} \quad (2)$$

where H is the magnetic field strength.

The temperature dependencies of $K_{11}/\Delta\chi$ for some BCBOA are shown in Figure 1. As can be seen from Figure 1, the $K_{11}/\Delta\chi$ rations for all BCBOA decrease with increasing temperature. This fact indicates that the orientational elastic constant K_{11} decreases with temperature more rapidly than $\Delta\chi$ (and, correspondingly, than S [9]). This fact is typical for low molecular weight and polymer nematics. It must be pointed out that the $K_{11}/\Delta\chi$ ratio for BCBOA depends not only on temperature but also on the number n of CH_2 groups in the spacer. It is reasonable to discuss this ratio at the same relative temperature $\tau=\Delta T/T_{NI}$ (ΔT and T_{NI} are presented in units of Kelvin's absolute temperature scale), just as we have done previously in discussing the optical and electrooptical properties of BCBOA nematics [6].

Table 1 lists the values of $K_{11}/\Delta\chi$ for BCBOA nematics at the same relative temperature $\tau=0.057$. The same data are illustrated in Figure 2 in the form of the dependence of $K_{11}/\Delta\chi$ on the number n of CH_2 groups in the spacer.

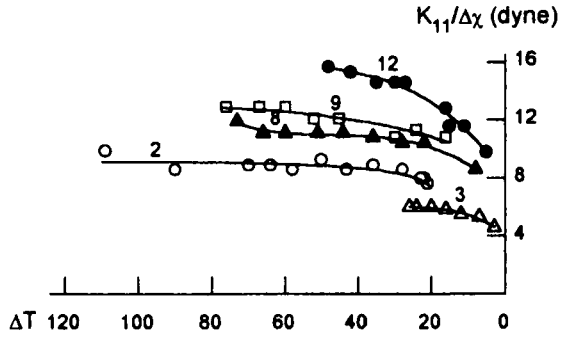

FIGURE 1 The temperature dependencies of $K_{11}/\Delta\chi$ for some BCBOA. The numbers of the curves correspond to the numbers n of CH_2 groups in the BCBOA spacers.

Table 1 and Figure 2 show that the $K_{11}/\Delta\chi$ ratios have a general trend to increasing with increasing n when some oscillations exist (they are particularly noticeable for BCBOA with n= 2 and 7). The increase in $K_{11}/\Delta\chi$ with increasing n may be due both to a decrease in $\Delta\chi$ with decreasing

fraction of aromatic moiety in BCBOA molecules and to the increase in the orientational elastic constant with increasing length of the molecule.

TABLE 1 Isotropization temperatures and characteristics of BCBOA nematics at relative temperature τ=0.057.

n	2	3	4	5	6	7	8	9	10	12
T_{NI}(°C)	270	169	255	186	218	182	205	176	187	171
$K_{11}/\Delta\chi$ (dyne)	8.5	6	7.5	7.6	9	7.6	10.5	11.3	12	14.3
$\Delta\chi\times10^7$	1.51	1.23	1.41	1.1	1.3	1.1	1.27	0.98	1.19	1.14
$K_{11}\times10^7$ (dyne)	12.8	7.4	10.7	8.4	12	8.4	13.3	11.1	14.3	16.3

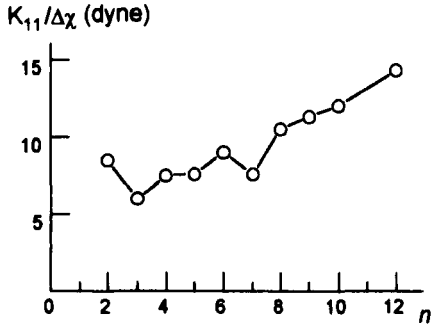

FIGURE 2 The dependence of $K_{11}/\Delta\chi$ on the number n of CH_2 groups in the spacer for BCBOA nematics at the same relative temperature τ=0.057.

To discuss the dependence of the orientational elastic constant K_{11} on spacer length, it is necessary to know the values of diamagnetic anisotropy $\Delta\chi$ of BCBOA nematics, which are not known. However, these values can be determined relatively precisely on the basis of the mass fraction of aromatic moiety in the molecule. For this purpose it is possible to use the dada in [10] in which the values of molar anisotropy's $\Delta\chi_m$ have been determined for a number of nematic liquid crystals. The values of $\Delta\chi$ of unit volume of the nematics were calculated from the known values of their molecular weights and also assuming their densities to be ρ=1 g/cm^3. In further discussion we will be interested only in values of $\Delta\chi$ for BCBOA at the same relative

temperature τ=0.057. Therefore, the values of $\Delta\chi$ obtained at the same relative temperature for nematics investigated in [10] will be used.

Figure 3 shows the dependence of $\Delta\chi$ on the mass fraction W of the aromatic moiety in the molecule for a number of nematics investigated in [10] at the same relative temperature τ=0.057.

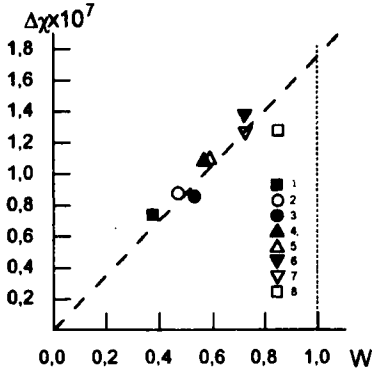

FIGURE 3 The dependence of $\Delta\chi$ on the mass fraction W of the aromatic moiety in the molecule for a number of nematics at the same relative temperature τ=0.057. (1) methoxycinnamic acid, (2) *p*-acetoxybenzalazine, (3) azoxyphenetole, (4) anisaldazine, (5) azoxyanisole, (6) *di*-anisalbenzidine, (7) anisal-*p*-amynoazobenzene, (8) *di*-benzalbenzidine.

The points in Figure 3 may be approximated by a straight line which is also shown in this figure. If this dependence is extrapolated to W=1 (i.e. to a molecule consisting only of benzene rings), then the value of $\Delta\chi$ obtained will be twice smaller than that for crystalline benzene with respect to the axis lying in the plane of the phenyl ring [11, 12]. This result means that at the predetermined relative temperature τ the degree of orientational order S of nematics investigated in [10] is close to 0.5.

To calculate the values of $\Delta\chi$ for the BCBOA nematics studied by us, it is necessary, first, to calculate the values of W and, second, to take into account the fact that for nematics of dimer series the values of S (and, hence, that of $\Delta\chi$) experiences strong odd-even oscillations. It is not very difficult to take into account the latter fact because the values of S for BCBOA at τ=0.057 have been determined previously [6] proceeding from data on the

optical anisotropy of these compounds in the crystalline phase. It should be borne in mind that the values of S obtained by us were in good agreement with the corresponding values measured at the isotropization temperature by NMR spectroscopy [2]. Therefore, the $\Delta\chi$ values for BCBOA can be calculated from the tangent of the slope of the linear dependence in Fig. 3 and the value of S at τ=0.057 according to the equation:

$$\Delta\chi=(1.76\times10^{-7}\ \text{W S})/0.5 . \quad (3)$$

Using the values of $\Delta\chi$ determined in this way, it is easy to calculate the orientational elastic constants K_{11} of BCBOA nematics, which are listed in Table 1. The same data are plotted in Figure 4 in the form of the dependence of K_{11} on the number n of the CH_2 groups in the spacer.

FIGURE 4 The dependence of K_{11} on the number n of the CH_2 groups in the spacer for BCBOA nematics at the same relative temperature τ=0.057.

It can be seen from Table 1 and Figure 4 that the dependence of K_{11} on n exhibits a pronounced odd-even effect, the maxima in K_{11} values corresponding to even n and the minima to odd n. Note that oscillations in the K_{11} values are almost completely determined by oscillations in $\Delta\chi$ on S when n is varied (the $K_{11}/\Delta\chi$ ratio does not exhibit the odd-even effect with the exception of n=2 and 7). This result is not fortuitous. In fact, the orientational elastic constant is determined by forces of intermolecular interaction in the nematic (nematic potential). The same forces induce the long-range orientational order in the liquid-crystalline medium, which is characterised by the parameter S.

The analysis of the dependence in Figure 4 also suggests that the value of K_{11} in the series of both odd and even n tends to increase with increasing n. In other words, for BCBOA nematics the value of K_{11} increase with the length

of the molecules, which agrees qualitatively with the predictions of the theories of orientational elasticity [13].

CONCLUSIONS

It was shown that the splay orientational elastic constant of a series of BCBOA nematics exhibits a strong odd-even effect when the length of the oxyalkane spacer is varied. The oscillations of the dependence of K_{11} on n are mostly determined by the odd-even effect in the dependence of the degree of intermolecular orientational order on n in the nematics investigated. An increase in the orientational elastic constant K_{11} with increasing elongation of the molecule is detected in the series of both even and odd BCBOA homologues.

Acknowledgments
This work was supported by the Russian Foundation for Fundamental Research (grants No. 96-03-33863a, and 96-15-97335) and Federal Program «Integration» (project No. 326.38). The travel grant programme "Integration" and the Organising Committees of 16th ILCC (Kent, USA) and 17th ILCC (Strasbourg, France) are also gratefully acknowledged for the financial support.

References

[1] D. Vorlander, *Z. phys.Chem., A, 126,* 449 (1927).

[2] J.W. Emsley, G.R. Luckhurst, and G.N. Shilstone, *Mol. Phys., 53,* 1023 (1984).

[3] J.W. Emsley, G.R. Luckhurst, G.N. Shilstone, and I. Sage, *Mol. Cryst. Liq. Cryst. (Letters), 102,* 223 (1984).

[4] C.T. Imrie, F.E. Karasz, and G.S. Attard, *Macromolecules, 26,* 3803 (1993).

[5] N.V. Tsvetkov, V.N. Tsvetkov, V.V. Zuev, and S.A. Didenko, *Mol. Cryst. Liq. Cryst., 265,* 487 (1995).

[6] V.N. Tsvetkov, N.V. Tsvetkov, S.A. Didenko, and V.V Zuev, *Mol. Cryst. Liq. Cryst., 265,* 341 (1995).

[7] N.V. Tsvetkov, V.V. Zuev, and V.N. Tsvetkov, *Liquid Crystals, 22,* 245 (1997).

[8] V.N. Tsvetkov, and I.P. Kolomiets, *Europ. Polymer J., 24,* 379 (1988).

[9] V.N Tsvetkov, *Acta physicochimica U.R.S.S., 16,* 132 (1942).

[10] V.N. Tsvetkov, and A.A Sosnovsky, *Acta physicochimica U.R.S.S., 18,* 359 (1943).

[11] M.V. Volkenstein, *Molecular Optics* (State Sci. Publ., Moskow, Russ., 1951), p. 744.

[12] W.H. De Jue, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach, New York, 1980), p. 152.

[13] R.B. Meyer in *Polymer Liquid Crystals,* edited by A. Ciferri, W.R. Krigbaum, and R.B. Meyer (Academic Press, New York, 1982), pp. 133–163.