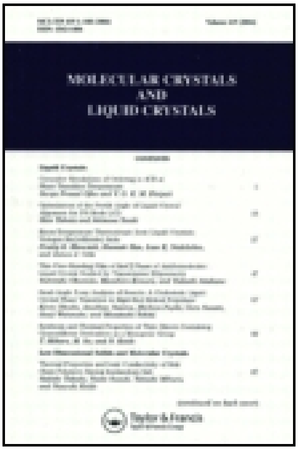

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ORIENTATIONAL ELASTISITY OF 4,4′-BIS-[ω-(4-CYANOBIPHENYL-4′-YLOXY)ALKYLOXY] BIPHENYLS NEMATICS

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Orientational Elastisity of 4,4′-bis-[ω-(4-cyanobiphenyl-4′-yloxy)alkyloxy] biphenyls Nematics

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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 trimers 4,4′-bis-[ω-(4-cyanobiphenyl-4′-yloxy)alkyloxy]biphenyls with the number *n* of CH_2 groups in their spacers from 3 to 10. The dramatic odd-even effect in the dependence of K_{11} versus *n* for trimers 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. Using the values of K_{11} the values of the dielectric anisotropy $\Delta\varepsilon$ of nematic trimers were calculated. The data obtained for trimers were compared with the same characteristics for dimers (4,4′-bis-cyanobiphenyloxyalkanes).

Keywords: nematics; trimers; orientational elasticity

INTRODUCTION

The considerable interest in the study of trimers and dimers is due to the fact that these compounds are the excellent structural analogues of the main chain mesogenic polymers [1]. For a brief but recent review of dimers and oligomers see [2]. These compounds exhibit the strong odd-even effect in their thermal [3] characteristics, in the degree of orientational order [2], in the entropy and enthalpy of the isotropic liquid - liquid crystal transitions [5, 6] when spacer length in their molecules is varied. In our recent investigations dimers (4,4'-bis-cyanobiphenylyloxyalkanes, BCBOA) and trimers (4,4'-bis-[ω-(4-cyanobiphenyl-4'-yloxy)alkyloxy] biphenyls, BCBOAOB) have been studied in dilute solutions and nematic melts by the methods of electric birefringence [7] and orientational elastic deformations in electric [8, 9] and magnetic [10] fields. A strong odd-even effect was detected for these compounds in the optical anisotropy of their nematics, in splay orientational elastic constant (for dimers) and in the electrical threshold deformational potentials as a result of change of spacer length in the molecules. In the present work nematic trimers 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 syntheses of BCBOAOB was described in detail in [9]. The number *n* of CH_2 groups in the spacers of the trimers investigated ranged from 3 to 10. All investigated BCBOAOB 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 [11]. 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 trimers 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 $\Delta\chi$

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

where H is the magnetic field strength.

The $K_{11}/\Delta\chi$ rations for all BCBOAOB decrease with increasing temperature. This fact is typical for low molecular weight and polymer nematics. It must be pointed out that the $K_{11}/\Delta\chi$ ratio for BCBOAOB 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 for BCBOA nematics [10].

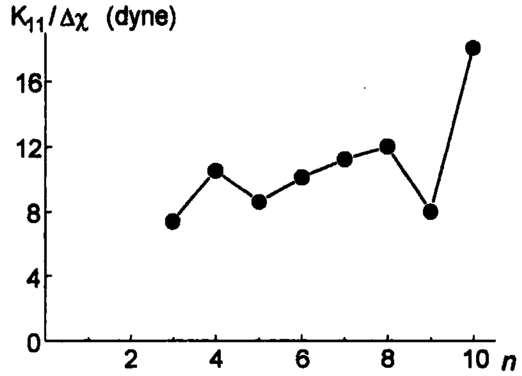

FIGURE 1 The dependence of $K_{11}/\Delta\chi$ on the number *n* of CH_2 groups in the spacer for BCBOAOB nematics at the same relative temperature $\tau=0.04$.

Table 1 lists the values of $K_{11}/\Delta\chi$ for trimers nematics at the same relative temperature $\tau=0.04$. The same data are illustrated in

Figure 1 in the form of the dependence of $K_{11}/\Delta\chi$ on the number *n* of CH_2 groups in the spacer.

Table 1 and Figure 1 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 trimers with *n*= 4 and 9). 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 BCBOAOB molecules and to the increase in the orientational elastic constant with increasing length of the molecule.

TABLE 1 Isotropization temperatures and characteristics of BCBOAOB nematics at relative temperature τ=0.04.

n	3	4	5	6	7	8	9	10
T_{NI} (°C)	197	299	210	255	201	233	192	206
$K_{11}/\Delta\chi$ (dyne)	7.4	10.5	8.6	10.1	11.2	12.0	8.0	18.0
S	0.42	0.56	0.39	0.56	0.39	0.56	0.42	0.56
$\Delta\chi\times10^7$	1.02	1.31	0.87	1.21	0.80	1.11	0.80	1.05
$K_{11}\times10^7$ (dyne)	7.5	13.8	7.5	12.2	8.0	13.3	6.4	18.9
$\Delta\varepsilon$	3.8	2.8	5.4	3.6	7.4	5.2	5.9	2.7

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 BCBOAOB nematics, which are not known. However, these values can be determined relatively precisely on the basis of the mass fraction W of aromatic moiety in the molecule. For this purpose it is possible to use the dada in [12] 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 procedure of $\Delta\chi$ determination for BCBOAOB at the same relative temperature τ=0.04 is the same as for BCBOA. The later was described in details in [10].

To calculate the values of $\Delta\chi$ for the BCBOAOB 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 trimers series the values of S (and, hence, that of $\Delta\chi$) experiences strong odd-even oscillations. It is possible to evaluate the values of S for BCBOAOB at τ=0.04 using the data of their optical anisotropy which have been determined previously [9]. The values of S for trimers at τ=0.04 are listed in Table 1. Therefore, the $\Delta\chi$ values for BCBOAOB can be calculated according to the equation:

$$\Delta\chi=(1.74\times10^{-7}\,W\,S)/0.5\,. \qquad (3)$$

In this equation it is taken in to consideration that for low-molecular-weight nematics studied in [12] S at τ=0.04 is close to 0.5. The values of $\Delta\chi$ determined in this way are listed in Table 1. Now it is easy to calculate the orientational elastic constants K_{11} of trimer nematics, which are also listed in Table 1. The same data are plotted in Figure 2 in the form of the dependence of K_{11} on the number *n* of the CH_2 groups in the spacer.

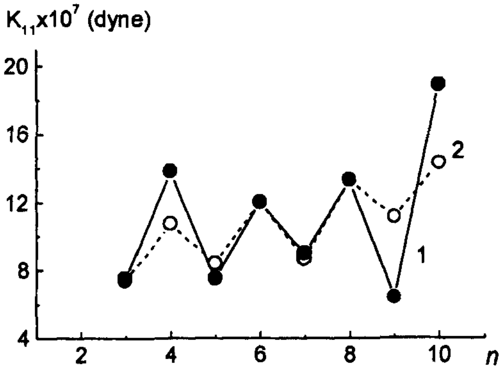

FIGURE 2 The dependence of K_{11} on *n* for (1) trimers (at the same relative temperature $\tau=(T_{NI}-T)/T_{NI}=0.04$) and (2) dimers (at τ=0.057).

It can be seen from Table 1 and Figure 2 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. This result is follows from the fact that 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.

It is of interest to compare the values of K_{11} for trimers with the same data obtained by us previously for dimers [10]. These data are also plotted in Figure 2. The dependencies of K_{11} on *n* for dimers and trimers are similar. Also it should be emphasised that the absolute values of splay elastic constant for dimers are close to that for trimers with the same *n*. This fact leads us to the important conclusion: for LC oligomers the increase in the number of mesogenic groups (from dimers to trimers) in their molecules do not provide the increase in the K_{11} values. That conclusion is in good agreement with the well known fact that elastic constants (K_{11} and K_{33}) of main chain mesogenic polymers are close to that values for their low–molecular–weight structural analogues [11].

Using the values of K_{11} it is possible to calculate from the values of the threshold potential in an electric field V_0 obtained previously [9] the dielectric anisotropy of BCBOAOB nematics according to the equation

$$\Delta\varepsilon=(4\pi^3K_{11})/V_0^2 \quad . \tag{4}$$

The values of $\Delta\varepsilon$ obtained by this procedure are given in Table 1. The same data are illustrated in Figure 3 with the dependence of $\Delta\varepsilon$ on the number *n* of methylene groups in the spacer. This dependence exhibits a strong odd-even effect. This fact is due to the changes in the intramolecular dipolar structure of the compounds under investigation with the variations in the spacer length, and is discussed in detail in our previous paper [9].

The general tendency to increasing $\Delta\varepsilon$ with increasing *n* is due to the weakening of correlation in the orientations of strongly polar cyanobiphenyl groups in the electric field with increasing spacer length. The values of $\Delta\varepsilon$ for BCBOAOB with $n=10$ seem excessively small. This is possibly caused by the existence of fluctuation nuclei of the smectic phase in nematic. Their existence can lead to an increase in the value of elastic constant K_{11} of the trimer nematic with $n=10$ (see Figure 2) and also to a decrease in its positive dielectric anisotropy $\Delta\varepsilon$ [13].

It is at interest to compare the dielectric properties of BCBOAOB and BCBOA nematics. For comparison, Figure 3 (curve 2) shows the dependence of $\Delta\varepsilon$ on *n* for BCBOA. It can be seen that the shapes of curves 1 and 2 are largely identical: both dependences exhibit

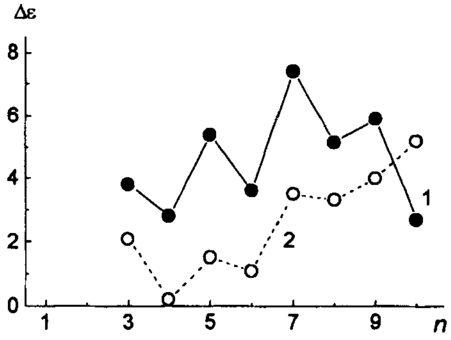

FIGURE 3 The dependence of Δε on *n* for (1) trimers at τ=0.04 and (2) dimers at τ=0.057.

considerable oscillations on the background of a general tendency towards increasing with increasing *n*. For both dimers and trimers the maxima of the values of Δε are observed at odd *n* and the minima at even *n*. However, Δε values for trimers are higher than for dimers at the same *n*. This fact is not fortuitous. As we report in our previous papers [8, 9] for both dimers and trimers intramolecular orientational polar order decreases with increasing spacer length, i.e. with increasing distance between strongly polar cyan groups. At the same number of CH_2 groups in spacers, in trimers the length of flexible fragments between cyan groups is twice as large as that in dimers. This is the explanation of the higher values of Δε for trimers than for dimers at the same *n*.

CONCLUSIONS

It was shown that the splay orientational elastic constant of a series of BCBOAOB 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. It was shown that for LC oligomers nematics the increase in the number of mesogenic groups (from dimers to trimers) in their molecules do not provide the increase in the K_{11} values. The values of dielectric anisotropy $\Delta\varepsilon$ for trimers are higher than for dimers at the same n.

Acknowledgments

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References

[1] D.Y. Yoon, P.J. Flory, *Mat. Res. Symp. Proc., 134*, 11 (1987).
[2] C.T. Imrie, G.R. Luckhurst in *Handbook of Liquid Crystals*, ed. by D. Demus, J. Goodby, G.W. Gray, H.-W. Spies, V. Vill (Wiley-VCH, Weinheim, 1998), V. 2B, p. 801.
[3] D. Vorlander, *Z. phys. Chem., A*, **126**, 449 (1927).
[4] J.W. Emsley, G.R. Luckhurst, and G.N. Shilstone, *Mol. Phys.*, **53**, 1023 (1984).
[5] J.W. Emsley, G.R. Luckhurst, G.N. Shilstone, and I. Sage, *Mol. Cryst. Liq. Cryst. (Letters)*, **102**, 223 (1984).
[6] C.T. Imrie, F.E. Karasz, and G.S. Attard, *Macromolecules*, **26**, 3803 (1993).
[7] N.V. Tsvetkov, V.N. Tsvetkov, V.V. Zuev, and S.A. Didenko, *Mol. Cryst. Liq. Cryst.*, **265**, 487 (1995).
[8] V.N. Tsvetkov, N.V. Tsvetkov, S.A. Didenko, and V.V. Zuev, *Mol. Cryst. Liq. Cryst.*, **265**, 341 (1995).
[9] N.V. Tsvetkov, V.V. Zuev, and V.N. Tsvetkov, *Liquid Crystals*, **22**, 245 (1997).
[10] N.V. Tsvetkov, V.V. Zuev, I.V. Ksenofontov, and V.N. Tsvetkov, *Liquid Crystals*, **25**, 727 (1998).
[11] V.N. Tsvetkov, and I.P. Kolomiets, *Europ. Polymer J.*, **24**, 379 (1988).
[12] V.N. Tsvetkov, and A.A. Sosnovsky, *Acta physicochimica U.R.S.S.*, **18**, 359 (1943).
[13] W.H. De Jeu, *Physical Properties of Liquid Crystalline Materials*(Gordon and Breach, New York, 1980), p. 152.