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

Electro-Optical and Dielectric Properties of Nematic Trjmers

N. V. Tsvetkov [a] , V. V. Zuev [a] & V. N. Tsvetkov [a]

[a] 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 & V. N. Tsvetkov (1997): Electro-Optical and Dielectric Properties of Nematic Trjmers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 302:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587259708041826

Mol. Cryst. Liq. Cryst., 1997, Vol. 302, pp. 175–180
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTRO-OPTICAL AND DIELECTRIC PROPERTIES OF NEMATIC TRIMERS

N.V. TSVETKOV, V.V. ZUEV, AND V.N. TSVETKOV
Institute of Macromolecular Compounds of the Russian Academy of Sciences,
199004, Bolshoi prospect 31, St.Petersburg, Russia

Abstract Electro-optical properties of nematics of the trimer series (*bis*-(4-cyanobiphenyloxyalkaneoxy)-4,4'-biphenyls) have been investigated by the method of orientational elastic deformations in electric fields. The number n of CH_2 groups in the oxyalkyl fragment was varied from $n=2$ to $n=10$. A strong odd-even effect was observed in the optical anisotropy Δn and in the values of the threshold potential V_0 for the trimer nematics. These effects are respectively caused by oscillations in the degree of inter- and intramolecular orientational order when n is varied. The great difference in dependencies of Δn and V_0 on n is discussed and compared with dimers data.

INTRODUCTION

The molecules of low molecular weight liquid crystals (LC) usually consist of a rigid core (mesogenic core) and one or two adjoining flexible (often alkyl) terminal groups. However, another class of low molecular weight liquid crystals is also known. Their molecules consist of two (or tree) rigid mesogenic parts joined by flexible spacers. For these liquid crystals the odd-even effect is manifested very dramatically in the periodicity of changes in temperature, enthalpy and entropy of the nematic-isotropic phase transition, as well as in the degree of orientational order of the mesophases.

The properties of dimers (4,4'-*bis*-cyanobiphenyloxyalkanes, BCBOA) have been investigated in solutions[1] and in nematic phase by the methods of NMR spectroscopy and molecular electrooptics.[2] A strong odd-even effect was detected for these compounds. It was manifested in termal and electrooptical characteristics of their melts and solutions as well as in strong oscillations of the degree of intermolecular orientational order S with the variation of the flexible core length in the molecule.

We synthesized liquid crystalline trimers (*bis*-(4-cyanobiphenyloxyalkaneoxy) 4,4'-biphenyls, BCBOAOB)

The number n of CH_2 groups in the spacer of the molecules of BCBOAOB was varied from 2 to 10. All BCBOAOB obtained exhibit termotropic nematic mesomorphism. Their isotropization temperatures T_{NI} determined by polarizing microscopy are shown in Figure 1.

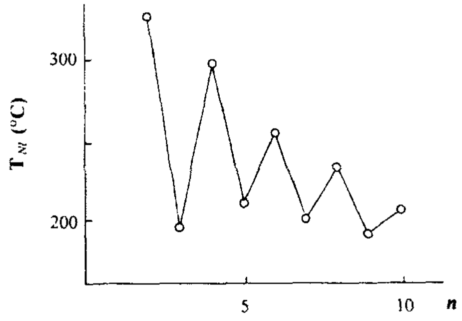

FIGURE 1 Isotropization temperature T_{NI} for BCBOAOB versus number n of methylene groups in oxyalkane spacers.

These compounds were investigated in the nematic phase by the method of orientational elastic deformations in planar concave layers in electric fields described in detail.[2]

RESULTS AND DISCUSSION

Optical characteristics

Figure 2 *a* shows the polarizing micrographs of a planar layer of the BCBOAOB nematic at n=9 in the absence of an electric field at a temperature ΔT=21 °C ($\Delta T = T_{NI}$ - T, T is the measurement temperature) and crossed polarizers. The Figure 2*a* shows a system of concentric interference rings.

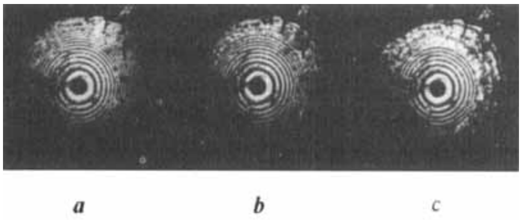

FIGURE 2 Polarizing micrographs of the planar - concave layer of the BCBOAOB nematic at n=9 and ΔT=21 °C; *a*- the initial planar orientation of the director, *b* - *c* is the texture deformed by the electric field $E \times 10^{-3}$ (V/cm) = (*b*) 0.40, (*c*) 0.67.

Analogous patterns were observed for all other BCBOAOB. Using them it is possible to determine the value of birefringence Δn of the nematic. The values of Δn obtained for some BCBOAOB at different temperatures are plotted in Figure 3.

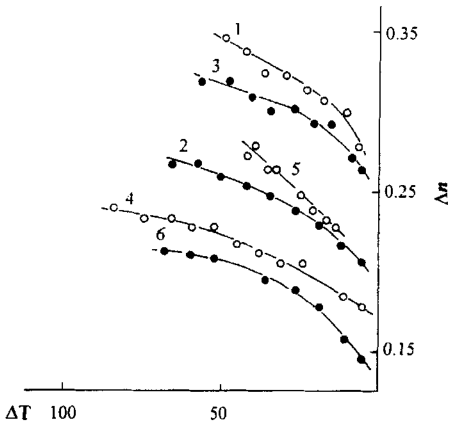

FIGURE 3 Birefringence Δn versus temperature for BCBOAOB at n= (1) 2, (2) 3, (3) 4, (4) 5, (5) 8, and (6) 9.

Figure 3 show that for all BCBOAOB Δn increases monotonically with increasing ΔT. This dependence is mainly related to temperature changes in the degree of intermolecular orientational order S (according to Equation (1))

$$\Delta n=(2\pi/3n_{av})(n_{av}^2+2)N_A(\Delta\alpha/M)\rho S, \qquad (1)$$

where M is the molecular weight of the nematic, ρ is its density, $\Delta\alpha$ is the polarizability anisotropy of the molecule, and n_{av} is the average refractive index of the substance. Figure 3 show that the value of Δn for BCBOAOB depends on both the temperature and the alkyl spacer length. Therefore, it is correct to discuss the dependence of Δn on the number n of CH_2 groups in a flexible fragment of the molecule at the same relative temperature $\tau=\Delta T/T_{NI}$ (here ΔT and T_{NI} are presented in units of Kelvin absolute temperature scale). The anisotropies Δn of BCBOAOB at a relative temperature $\tau=0.04$ and, correspondingly, at the absolute temperatures of the nematics $T=T_{NI}(1-\tau)=0.96\times T_{NI}$ K are plotted in Figure 4.

The curve 1 in Figure 4 demonstrates a pronounced odd-even effect in optical characteristics of BCBOAOB nematics. These large periodical changes in Δn reflect the change in the degree of orientational order S of the mesophase with the variation of alkyl chain length.

The dependence of optical anisotropy .on spacer length for BCBOAOB is virtually identical to the similar dependence obtained for BCBOA.[2] A characteristic feature of the dependencies of Δn on n for BCBOAOB and BCBOA is the absence of a marked extinction in the oscillations of optical anisotropy (and, correspondingly, in the degree of intermolecular orientational order S) with increasing length of the alkyl chain fragment. This property is a specific feature of compounds the molecules of which consist of *several* mesogenic cores joined by flexible fragments.

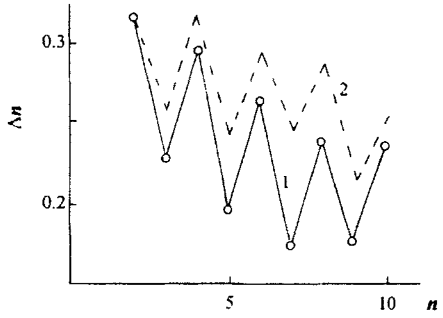

FIGURE 4 Birefringence Δn versus n for (1) BCBOAOB and (2) BCBOA at relative temperature τ=0.04.

Figure 4 shows that the value of optical anisotropy Δn for BCBOAOB in the series of both even and odd n has a tendency to decrease with increasing spacer length. This tendency for dimers was explained by us previously.[2]

Elastic deformations and electrooptical characteristics

The results obtained for BCBOAOB by the method of elastic deformations in electric fields are illustrated in Figure 2*b* - 2*c*. This deformation is the splay elastic deformation, and the sign of dielectric anisotropy $\Delta\varepsilon$ of this nematic is positive. Similar results were obtained for all other BCBOAOB. Using these patterns it is possible to calculate the value of the threshold potential V_0 of BCBOAOB. At constant temperature V_0 depends nonmonotonically on the length of alkyl spacers in BCBOAOB molecules. Let us apply the expression relating the values of V_0 and $\Delta\varepsilon$ for nematics:

$$V_0 = 2\pi^{3/2}(K_1 / |\Delta\varepsilon|)^{1/2}. \qquad (2)$$

It is reasonable to explain the oscillations of the value of V_0 mainly by the nonmonotonic dependence of $\Delta\varepsilon$ on n. The values of V_0 for BCBOAOB nematics with different n values should be compared at the same temperature τ. The values of $1/V_0$ obtained in this way are plotted in Figure 5 (curve 1).

Curve 1 in Figure 5 clearly illustrates the periodicity of changes in $1/V_0$ (and, hence, in that of $\Delta\varepsilon$) when n is varied. The dielectric anisotropy of the nematic $\Delta\varepsilon$ not only depends on S but also to a considerable extent determined by the dipolar architecture of the molecules. For a molecular model with axial symmetry of dielectric polarizability, the value of $\Delta\varepsilon$ can be expressed in the form of an approximate relationship

$$\Delta\varepsilon = 4\pi N_A PQXS, \qquad X = \Delta\delta + (\mu^2/2kT)(3\cos^2\vartheta - 1) \qquad (3)$$

where P and Q are the internal field multipliers. The function X characterizing the dipolar anisotropic structure of molecules and their intramolecular orientational polar order[2] ; $\Delta\delta$ is the anisotropy of electric polarizability of the molecule and μ is its dipole moment forming an angle ϑ with the axis of symmetry of the molecule.

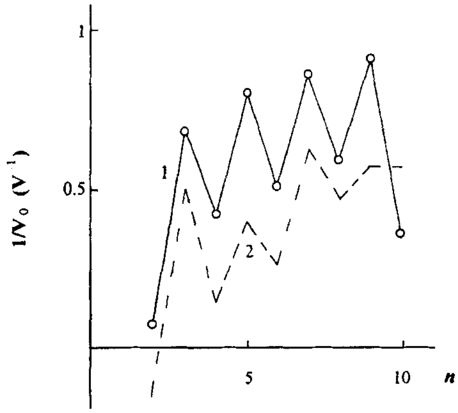

FIGURE 5 $1/V_0$ for (1) BCBOAOB and (2) BCBOA nematics versus *n*.

The results obtained in this work show that the odd-even effect observed in dielectric characteristics of BCBOAOB nematics is determined by oscillations of function X with the variation in *n*. In order to explain this fact (at least qualitatively) let us consider Figure 6.

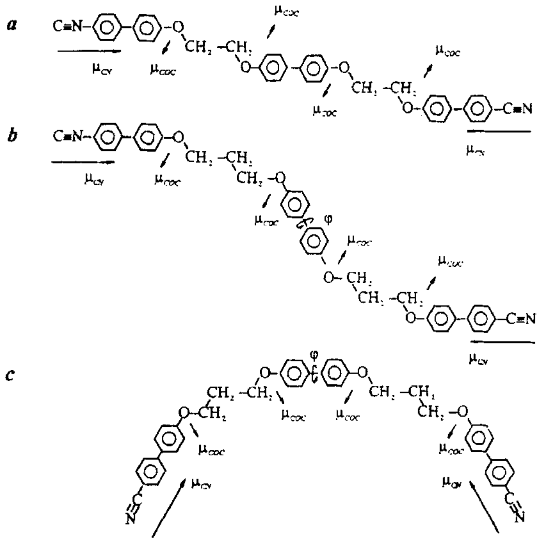

FIGURE 6 Conformations of BCBOAOB molecules at *n*= (*a*) 2 and (*b*, *c*) 3 in the case of a planar trans-form of the spacer. Angle φ = (*b*) 0 and (*c*) 180°.

The conformations of BCBOAOB molecules represented at Figure 6 (*a* and *b*) are such that at both odd and even *n* all dipoles in the molecules of these compounds are compensated in the approximation used. Therefore, for these conformations of the molecules the value of X should change only slightly with a variation in *n*. In this case it is difficult to expect a strong odd-even effect in the dielectric properties of BCBOAOB nematics. However, in the nematic phase of BCBOAOB at odd *n*, molecules can exist the conformation of which is close to that sown in Figure 6 *c* (this conformation is obtained from the conformation shown in Figure 6 *b* by rotation of one half of the molecule about the central *para*-aromatic axis by an angle $0<\varphi\leq 180°$). The peculiar feature of these conformations is the large non-compensated molecular dipole leading to a change in the value of $\Delta\varepsilon$ of BCBOAOB when even *n* is replaced by odd *n*.

CONCLUSIONS

It was shown that the electrooptical properties of nematic mesophases of dimers and trimers exhibit a strong odd-even effect when the number *n* of CH_2 groups in spacers is varied. The maxima of the values of optical anisotropy Δn determined by intermolecular orientational order are observed at even *n*. It was found that oscillations in the dependence of Δn on *n* for dimers and trimers under investigation are not extinguished with increasing *n*. This is a characteristic feature of the compounds the molecules of which consist of two or more mesogenic cores joined by flexible spacers.

The maxima in the values of dielectric anisotropy $\Delta\varepsilon$ which is mainly determined by intramolecular orientational-polar order, are observed at odd *n*. The general shape of the dependencies of $1/V_0$ on *n* for dimers and trimers is largely identical. However, for dimers this dependence is accompanied by a change in the sign of $\Delta\varepsilon$, which is not observed for trimers. This phenomenon is caused by a greater distance between strongly polar CN groups in trimer molecules than that in dimers. As a result, their orientational correlation in the electric field is weakened. This weakening of correlation with increasing length of alkyl spacers also leads to an increase in $1/V_0$ for dimers and trimers in the series of both odd and even *n*.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation of Fundamental Researches (Grant 96-03-33863a).

REFERENCES

1. N.V. Tsvetkov, V.N. Tsvetkov, V.V. Zuev, and S.A. Didenko, Mol. Cryst. Liq. Cryst., 265, 487 (1995).
2. V.N. Tsvetkov, N.V. Tsvetkov, S.A. Didenko, and V.V. Zuev, *Mol.* Cryst. Liq. Cryst., 265, 341 (1995).