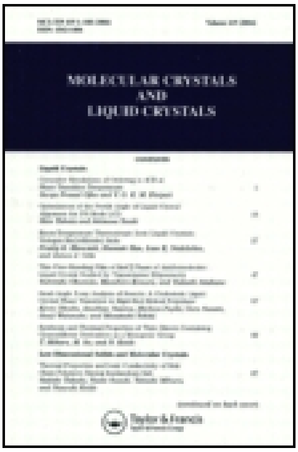

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Igor P. Kolomiets [a] , Alexander M. Ovsipyan [a] & Sergey K. Filippov [a]

[a] Department of Polymer Physics, Saint Petersburg State University, Saint Petersburg, Russia

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NEMATIC BEND-SPLAY ELASTISITY OF CYANOPHENYL COMPOUNDS WITH DIFFERENT TERMINAL GROUPS

IGOR P. KOLOMIETS, ALEXANDER M. OVSIPYAN AND SERGEY K. FILIPPOV
Department of Polymer Physics, Saint Petersburg State University,
Saint Petersburg , Russia

Abstract The elastic properties of nematic compounds with terminal cyanoaromatic and containing cycles alyphatic groups were investigated. The terminal group structure has essential influence on the bend K_3 and splay K_1 elastic constants and their temperature dependences. The ninth and tenth members of 4-cyanophenyl 4'-n-alkyloxybenzoate series (nCPh) and cyanobiphenyl ether with ethylene-butylcyclohexane terminal group show pretransitional divergence of K_3 in the vicinity of the nematic-smectic phase transition. Outside pretransitional temperature region the alternatation from odd to even n in nCPh series is accompanied by positive jumps of the ratio K_3/K_1 and change of the character of its temperature dependence. A striking unmonotonous temperature dependence of the elastic splay constant K_1 was founded for cyanobiphenyl ether with butylcyclohexane terminal group. The occurrence of frozen striped texture in a smectic phase after the nematic-smectic transition in the presence of magnetic field was found for all nematics with the temperature divergence of K_3. Distance between stripes was the less, the more magnetic induction.

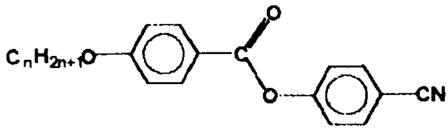
INTRODUCTION

It is known, that values of nematic elastic constants and its ratio are determined by an intermolecular interaction which depends on the form and chemical structure of molecules. The existing molecular theories give expressions for elastic constants through orientational order parameters, potential of interaction and form of molecules, but do not permit to predict an influence of particular structure of molecules on elastic properties of nematic liquid crystals (NLC). Therefore experimental determination of elastic constants of NLC with various structure of molecules remains an urgent problem not only for fundamental research, but also for practical application of liquid crystals. It was established, that the structure of atomic groups on ends of molecule determines conditions of formation and type of mesophase and essentially influences on all physical properties of liquid crystal.

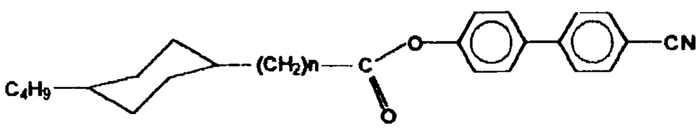
The purpose of this report is to present the results of our study on a nematic bend deformation of compounds with nitryl and containing cycles alyphatic terminal groups.

EXPERIMENTAL

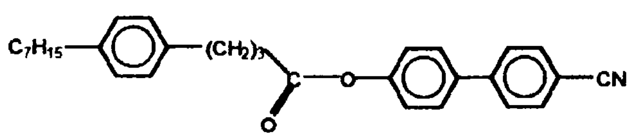
The cyanophenyl and cyanobiphenyl ethers of various carbon acids were investigated:



nCPh: n=5, k 85.8°C n 86.7°C i; n=6, k 71.2°C n 83.2°C i;
n=7, k 70°C n 78.3°C i; n=8, k 74.4°C n 83.9°C i;
n=9, k 40.8°C s_a60.8°C n 86.2 C i; n=10, k 50.1°C s_a 81.8°C n 89.4°C i



4-Chx-nCB: n=0 k 80°C n 242°C i
n=2 k 71°C s_a 125°C n 174°C i



7-Ph-3CB k 55°C n 69°C i

The compounds of homologous series nCPh were synthesized by P. Adomenas in Vilnius University, the compounds 4Chx-nCB and 7-Ph-3CB were synthesized in Institute of Organic Semiproducts and Dyes (Moscow).[1]
The bend K_3 and splay K_1 elastic constants were determined by the Freedericksz method [2], photographing the interference picture in parallel beam of polarized light through homeotropic layer deformed by magnetic field between flat and spherical surfaces of quartz glasses. The diameter of the dark central circle d_o in the picture, when polaroids are crossed, corresponds to critical thickness z_k of the undeformed area of the layer. The value of z_k was determined by the substituting of measured value of d_o in the formula

$$z_k = R - (R^2 - d_o^2 / 4)^{1/2} \quad , \qquad (1)$$

where R - radius of the spherical surface. The value of ratio $K_3/\Delta\chi$ ($\Delta\chi$- diamagnetic anisotropy) was calculated by the Freedericksz formula

$$z_k=\pi(K_3/\Delta\chi)^{1/2}/H \qquad (2)$$

from the slope of linear dependence of z_k on reverse magnetic induction 1/H.

An inclination of a nematic axis to direction of light flow in deformed area of the layer causes a birefringence and an occurrence of interference rings. The angle θ of inclination of a nematic axis has maximum value θ_m in the middle of the layer and grows with increasing thickness, i.e. along radial directions in the layer. The growth of θ followed by radial increase of extraordinary refractive index n'_e and, hence, birefringence n'_e-n_o. The diameters of dark interference rings correspond to the value z, where optical path difference is multiple of the wave length λ=632.8 nm for crossed polaroids or of $\lambda/2$ for parallel polaroids. The relation of n'_e-n_o with a diameter of the ring d_i is expressed by the formula

$$n'_e - n_o = i(\lambda/2)/[R - (R^2 - d_i^2/4)^{1/2}], \qquad (3)$$

where i is a number of dark ring by way of the increase of d_i. The formulas (3) and (1), in which values d_i were substituted for d_o, were used in order to get a dependence n'_e-n_o on a layer thickness.

The control tests of an influence of a layer curvature on experimental data were carried out on samples with different values of radius R. There was no appreciable influence on measuring values, when R was varying from 10 mm up to infinity (flat - parallel layer).

To describe n'_e-n_o as a function of the layer thickness z the following theoretical relations were used [3]

$$n'_e - n_o = (n_e - n_o)(K/E) - n_o(1 - K/E), \qquad (4)$$

where

$$K=\int_0^{\pi/2}\{(1-\kappa\sin^2\theta_m\sin^2\psi)/[(1+\nu(1-\sin^2\theta_m\sin^2\psi)](1-\sin^2\theta\ \sin^2\psi)\}^{1/2}d\psi,$$

$$E=(z/2z_k)=\int_0^{\pi/2}[(1-\kappa\sin^2\theta_m\sin^2\psi)/(1-\sin^2\theta_m\sin^2\psi)]^{1/2}d\psi,$$

θ_m - maximum angle of inclination of optical axis in the middle of the layer,
$\psi = \arcsin(\sin\theta/\sin\theta_m)$, $\nu = (n_e^2 - n_o^2)/n_o^2$, $\kappa = (K_3-K_1)/K_3$.

For comparison of the theory with experiment, the computer program was made. Experimental dependence n'_e-n_o from z_k/z, approximated by cubic splain, was compared with calculated dependence using formula (4) by fitting of parameters K_3/K_1 and n_e-n_o. Optimum values of fitting parameters were determined by minimization of the sum squares of differences between experimental and theoretical values n'_e-n_o at the same thickness z. The minimum root-mean-square deviation of measured values n'_e-n_o from calculated ones had order 10^{-3}. The fitting error did not exeed a few percent for n_e-n_o and 15 % for K_3/K_1.

The testing of the mesuring method and the procedure of data processing on the most complete investigated pentylcyanobiphenyl has shown, that obtained values of $K_3/\Delta\chi$, K_3/K_1 and n'_e-n_o coincide with the literature data within the limits of experimental error.

RESULTS

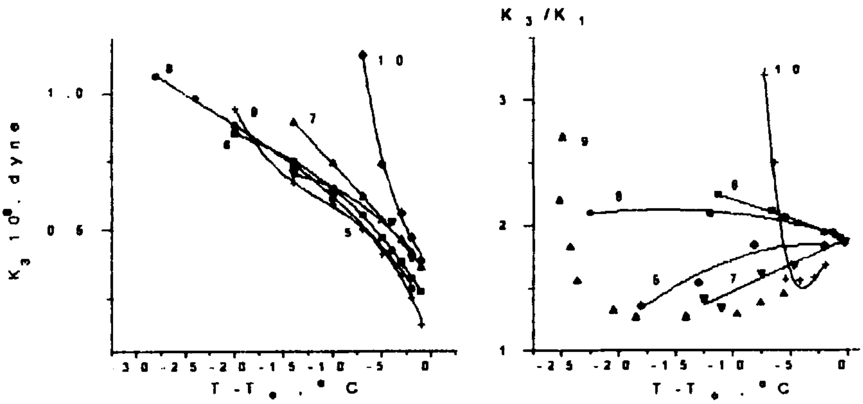
The dependence of critical thickness z_k on reverse magnetic induction 1/H for all samples was well approximated by straight line according to the formula (2).

Elastic properties of homologous series nCPh.

Values of the birefringence n_e-n_o received by comparison experimental and theoretical (4) dependences of n'_e-n_o on z_k/z for nCPh coincides with the difference of refractive indices n_e and n_o, measured earlier.[5] To determine elastic constants of nCPh from values $K_3/\Delta\chi$ and K_3/K_1 magnetic susceptibility of 9CPh in the nematic $\chi_{\shortparallel}$ and isotropic χ_{is} phases was measured by the original absolute method [4]. Specific diamagnetic anisotropy $\Delta\chi/\rho$ was calculated by formula $\Delta\chi/\rho = 3(\chi_{\shortparallel} - \chi_{is})/2$. Using values of density ρ [5] and the order parameter S [6] measured earlier for nCPh, molar diamagnetic anisotropy of molecules 9CPh $\Delta\chi_m=\Delta\chi M/\rho S$ was calculated. Assuming that the main contribution in $\Delta\chi_m$ of molecules nCPh is brought by aromatic cycles, and neglecting the influence of the other atomic groups on magnetic anisotropy, we used the value $\Delta\chi_m=4.40\ 10^{-5}$ $mole^{-1}$ for 9CPh to calculate the elastic constants of other homologues from the ratios $K_3/\Delta\chi$ and K_3/K_1.

The nematics 9CPh and 10CPh when cooled below melting point show abnormal increase K_3, leading to monotropic transition in smectic liquid crystal (SLC). The change of refractive indices, density and the order parameter at monotropic transition NLC-SLC occurs smoothly without appreciable jumps. That is an indication of a second-order phase transition. The temperature divergence K_3 is caused by fluctuations of the smectic order parameter. The rather large K_3 of 10CPh, which has narrow temperature region of existence, can be explained by the influence of fluctuations.

The measured temperature dependences of elastic constants of nCPh outside the pretransition anomalous region do not correspond to molecular theory of the nematic elasticity which predict square-law dependence of the elastic constants on the order parameter. The ratio of K_3/K_1 (Figure 1) depends on temperature; the character of a temperature dependence is influenced by the parity of the number of carbon atoms n in terminal chain. K_3/K_1 of odd homologues is decreasing but K_3/K_1 of even homologues is increasing as a temperature grows. The influence of the number n on values of elastic constants K_3 and K_1 is illustrated by Figure 2.



(a) (b)

FIGURE 1 The temperature dependence of the bend elastic constant K_3 (a) and the ratio of K_3 to the splay elastic constant K_3/K_1 (b) of homologous series nCPh.

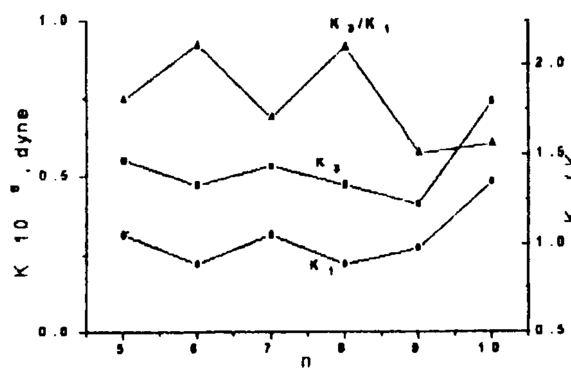


FIGURE 2 The elastic constants K_3, K_1 and their ratio K_3/K_1 versus the number of carbon atoms n in terminal group of homologous series nCPh at T_0-T = 5 °C.

The occurence of even-odd effect in the nematic elastisity was found early for another homologous series.[7-10] At increasing n the tendency to the vanishing of the difference between K_3 ank K_1 of nCPh is observed.

<u>Elastic properties of 4-Chx-nCB and 7-Ph-3CB containing the cycles in terminal groups.</u>

The temperature dependences of $K_3/\Delta\chi$ and K_3/K_1 of 4-Chx-nCB and 7-Ph 3CB (Figures 3) have unusual character.

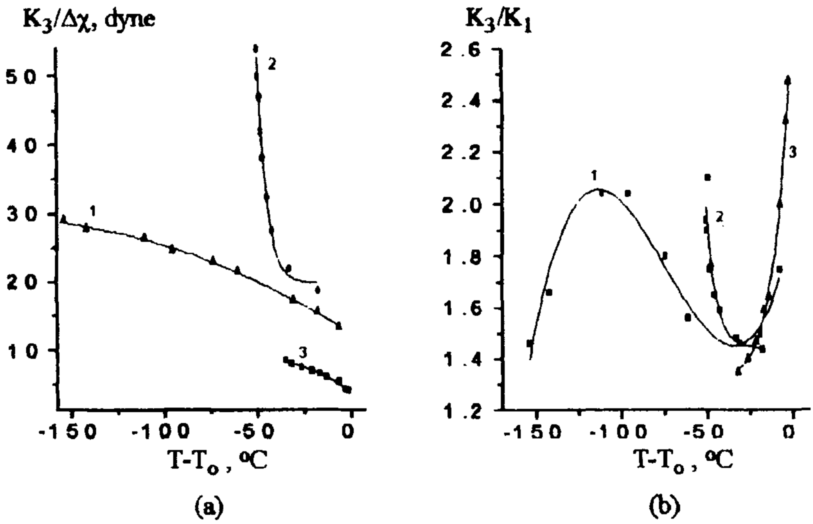


FIGURE 3 The temperature dependence of the ratio of the bend elastic constant to diamagnetic anisotropy $K_3/\Delta\chi$ (a) and the ratio of elastic constants K_3/K_1 (b) for 4-Chx-0CB (1), 4-Chx-2CB (2), 7-Ph-3CB (3).

4-Chx-2CB has smectic A phase and shows the temperature divergence of the bend elastic constant K_3 near to the NLC-SLC transition. The ratio K_3/K_1 and, hence, the splay elastic constant K_1 of 4-Chx-0CB have unmonotonous temperature dependence, which has no analogues. The peculiarity of 7-Ph-3CB is the unusual combination of value and character of the temperature dependence of the ratio of K_3/K_1. When the value of K_3/K_1 is greater than 1 it usually decreases as the temperature increases whereas K_3/K_1 of 7-Ph-3CB increases.

<u>The abnomal deformation at the nematic-smectic phase transition in magnetic field.</u>

For all investigated liquid crystals with the temperature divergence of K_3, the occurrence of the frozen striped texture in the smectic phase (Figure 4) was observed, during the nematic-smectic phase transition in presence of magnetic field.

FIGURE 4 Photos of the striped texture in the layer of 4-Chx-2CB. H=5200 Gs (a), H=12300 Gs) (b)

The stripes were parallel to magnetic field. The distance between stripes became the less, the more magnetic induction. It is known that the reason for the occurrence of the striped texture is instability of the bend deformation at large values of the ratio K_3/K_1 in the vicinity of the NLC-SLC transition, when it is close to the second-order phase transition. A similar phenomenon has been observed earlier [11]. The discovered phenomenon can be explained by supposing that in the vicinity of phase transition on the side of the smectic phase there are strong fluctuations of the orientational order parameter, resulting in the reduction of the elastic constant of the interlayer compression or stretching. Just the relatively small rigidity of SLC near to transition in NLC makes for appearence and safety of deformation caused by weak magnetic field.

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