Mesogenic-molecule conformation change induced by phase transitions in uniaxial liquid crystals

E. M. Aver'yanov, V. A. Zhuikov, and P. V. Adomenas

Institute of Physics, Siberian Division, USSR Academy of Sciences

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A new method for studying the conformation of mesogenic molecules in phase transitions to liquid crystals is experimentally realized. It is based on the use of polarization spectroscopy of infrared absorption induced by the mesomer effect. A change in the conformation of the aromatic skeleton of the molecules was observed in four liquid crystals of the alkylcyanobiphenyl class in transitions between the isotropic-liquid, nematic, and smectic-*A* phases. It is established that the conformation of the molecules depends on their orientational and translational order in the mesophase.

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INTRODUCTION

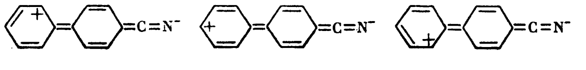
Recent investigations have shown that the phase transitions in liquid crystals (LC) have, in addition to the known features that have caused them to be extensively studied experimentally and theoretically, a number of other interesting properties. The use of independent physical methods has revealed a noticeable change of the internal mobility of flexible aliphatic fragments of the molecules in transitions between different phases, as well as a substantially different temperature dependence of the fragment ordering compared with a subsystem of the relatively rigid aromatic fragments of the molecules.[1-3] Whereas the investigations of the conformational transformations of flexible alkyl chains by the NMR method[1,4,5] have already served as a basis for a theoretical generalization,[6] the changes of the conformation of the aromatic skeleton of molecules in phase transitions in LC have been very little investigated. Isolated results obtained in this direction with the aid of various modifications of the NMR method[7,8] are as yet rare. The complexity of such experiments, due to the need of selective doping of the molecules with deuterium and with the isotopes ^{13}C and ^{15}N leads to a strong discrepancy between the results obtained for the same objects,[7,8] and to conflicting interpretations.[1,4] It is not yet clear how the conformation of the aromatic skeleton of the molecules changes in transitions between phases of unlike symmetry (nematic—isotropic liquid) and like symmetry (nematic—smectic-*A*), and how it depends on the orientational order of the molecules in the presence or absence of translational order of their mass centers. To answer these questions it is necessary to develop new research methods based on different physical principles, and to choose objects that are sufficiently simple from the point of view of interpretation of the experiment.

To solve the foregoing problems, we propose in this paper a method for polarization spectroscopy of infrared (IR) absorption induced by the mesomer effect. The objects chosen for the investigation were crystals of the homologic series of 4-*n*-alkyl-4′-cyanobiphenyls. The reason is that biphenyl and polyphenyl fragments are present in many mesogenic molecules. On the other hand, biphenyl is a classical example for the consideration of the influence of intermolecular interaction on the conformation of a molecule: its dihedral angle φ between the benzene rings is 42, 30, and 0° in the gas phase, isotropic solution, and crystal, respectively.[9]

In the first part of the paper we describe the theory of the proposed method as applied to the oriented liquid-crystal phase of cyanobiphenyls. The experimental technique is described in the second part. The third part contains the results of the experiment and their discussion.

§1. IR ACTIVITY INDUCED BY THE MESOMER EFFECT, AND CONFORMATION OF A MOLECULE

In the biphenyl molecule, the valent characteristic vibration of the *C–C* (α) bond between the benzene rings is not active in IR absorption in accordance with the selection rules. In cyanobiphenyl, the π-electron conjugation of the strong electron-acceptor group $C\equiv N$ with the biphenyl fragment leads to appearance of resonant valent structures of the type



where the signs + and – denote respectively a shortage and an excess of electron density. The result is polarization of the π-electron system of the molecule in the ground state (the mesomer effect).[10] The dipole moment $\mu(r)$ of the π-system of the molecule (mesomer moment) in benzene and biphenyl substitutes varies linearly with length r of the π-conjugation chain,[11] and its increment $\Delta\mu$ on going from benzonitryl to cyanobiphenyl depends on the twist angle φ of the benzene rings around the bond α (Ref. 12):

$$\Delta\mu=\Delta\mu_{max}\cos^2\varphi.$$

From the experimental data[11] for μ and from the ratio of the lengths of the π-electron conjugation chain in these substances (solution in benzene) we obtain $\Delta\mu=0.28$ D, $\Delta\mu_{max}=0.37$ D, and $\varphi\approx 30°$ in accordance with the known value for the non-substituted biphenyl molecule.[9] Owing to the isomer effect, the vibration of the α bond now causes a change in the length of the conjugation chain and in the mesomer moment $\Delta\mu_{max}$, and therefore becomes active in the IR absorption.

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The integrated optical density of the sample in the IR absorption band of the α vibration is

$$I_\alpha \sim \left\langle \left(\frac{\partial \Delta\mu}{\partial r} \right)^2 \right\rangle \sim \langle \cos^4 \varphi \rangle,$$

where the brackets ⟨. . .⟩ denote statistical averaging. Thus, by watching the change of the integrated intensity of this band we can track the variation of the average angle $\bar{\varphi}$, defined by the relation

$$\cos \bar{\varphi} = \langle \cos^4 \varphi \rangle^{1/4}.$$

To perform a polarization IR experiment on a homogeneously oriented LC sample, it is convenient to use thin LC films in sandwich cells with homeotropic orientation of the molecules.

When the beam is incident normal to the wall of the cell, it propagates along the optical axis of the LC. Thus, it becomes possible to obtain a sample IR-absorption spectrum polarized normal to the director, without using polarizers, which are usually imperfect in the IR region of the spectrum. In such an experimental geometry, the depolarizing influence of the multiple scattering of the light by the director fluctuations, which are always present in polarization measurements on LC, is reduced to a minimum. Since the α bond is oriented along the long molecular axis, it follows that by using the results of Ref. 13 we can show that the ratio $N_\alpha = I_{\alpha\perp}/I_{\alpha i}$ of the optical densities of the α-band in the uniaxial-mesophase spectral component normal to the director ($\perp$) and in an isotropic liquid (i) is connected with the parameter of the orientational order S and with the angle φ by the relation

$$N_\alpha = \frac{1-S}{g_\alpha} \frac{\langle \cos^4 \varphi \rangle}{\langle \cos^4 \varphi_i \rangle}, \quad g_\alpha = \frac{\rho_i n_{\alpha\perp}^\Phi}{\rho n_{\alpha i}^\Phi} \left(\frac{f_{\alpha i}^\Phi}{f_{\alpha\perp}^\Phi} \right)^2. \tag{1}$$

Here ρ and ρ_i are the densities of the phases, $n^b_{\alpha\perp,i}$ and $f^b_{\alpha\perp,i}$ are the background values of the refractive indices and of the components of the tensor of the local field in the α absorption band, and φ_i is the value of the angle φ in the isotropic liquid. For the valent characteristic vibration of the $C\equiv N(\beta)$ bond, which is also oriented along the long axis of the molecule, the following relation is valid[13]

$$N_\beta = (1-S)/g_\beta.$$

Since the difference between the frequencies ν_α (1287 cm^{-1}) and ν_β(2222 cm^{-1}) is much less than their distance to the lowest band of the electron spectrum, which makes the principal contribution to the values $n^1_{\perp i}$, the difference between g_α and g_β can be neglected. Taking this into account, we ultimately obtain from (1) the connection of the experimentally measured N_α and N_β with the angle $\bar{\varphi}$:

$$\bar{\varphi} = \arccos \left[(N_\alpha/N_\beta)^{1/4} \cos \varphi_i \right]. \tag{2}$$

§2. INVESTIGATED OBJECTS AND EXPERIMENTAL TECHNIQUE

In the experiments we used the crystals 4-n-C_nH_{2n+1} – 4'-cyanobiphenyl (nCB) crystals with $n = 5$, 6, 7, and 8. The temperatures (°C) of the phase transition between the solid-crystal (smectic-A (SmA), nematic (N) and isotorpic-liquid (I) phases were: Cr 22.5° N 35° I (5CB), Cr 14.4° N 28.5° I (6CB), Cr 29.1° N 41.4° I (7CB), and Cr 20.9° SmA 35.5° N 40° I (8CB). The choice of these objects, in addition to the reasons noted in the introduction, is convenient also because the structural organization of the molecules in the different phases of the homologs has been investigated in detail (with the exception of 6CB) by x-ray diffraction.[14,15]

In our experiments, a perfect homeotropic orientation of the molecules in LC layers of thickness 20 μm (measurement of N_β) and 40μm (N_β) was induced by the walls of a sandwich cell of fluorite (CaF$_2$) without special chemical treatment or mechanical texturing of the walls. Qualitatively, the orientation was monitored with a polarization microscope in parallel and converging light beams. Multiple passage through the point T_{NI} of the nematic—isotropic liquid (N—I) transition did not change the quality of the orientation of the molecules in the nematic phase.~~—When the nematic~~ phase of 8CB was cooled, the homotropic orientation of the molecules remained perfect also in the smectic-A-phase without an additional shift of the cell walls relative to each other. Multiple passage through the point T_{SN} of the smectic-A-nematic (SmA—N) transition did not change the orientation order of the molecules in these phases. Homeotropic orientation of these molecules in fluorite cells was observed by us also for other LC containing a terminal benzonitryl fragment: for the homologs of the series 4-n-alkoxy-4-cyanobiphenyl, 4-heptyloxy-4'-cyanotolane, and 4-cyanophenyl ester of 4-heptylcynnammic acid. The sample temperature was maintained constant and monitored during the experiment accurate to 0.1° C.

The isolated IR absorption bands corresponding to the α and β vibrations in the investigated samples were recorded in a parallel radiation beam using a SPECORD 75 IR two-beam spectrophotometer. The spectrum scanning velocity v, of the slit width s, and the time

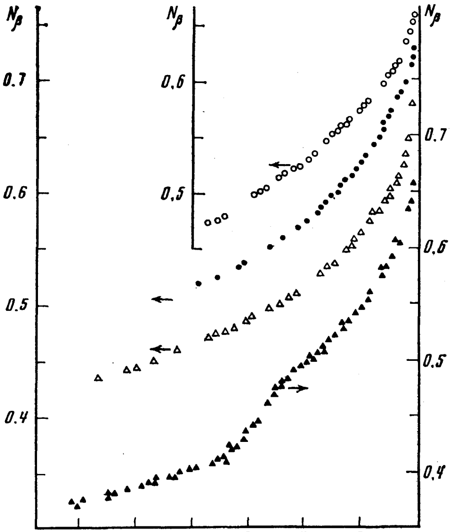

FIG. 1. Temperature dependence of N_α in liquid crystals 5CB (○), 6CB(●), 7CB(△), and 8CB(▲). T_{NI}—temperature of the transition between the nematic phase and the isotropic liquid.

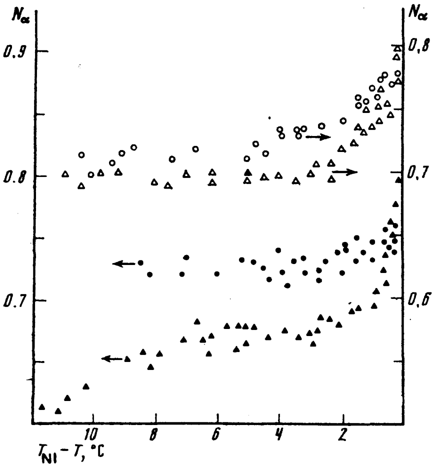

FIG. 2. Temperature dependence of N_α in liquid crystals 4-n-alkyl-4′-cyanobiphenyls. The symbols are the same as in Fig. 1.

constant τ of the instrument were chosen so as to minimize the distortion of the shape of the recorded band: $v\tau/s=0.21$ (Ref. 16). The observed integrated optical density $I_{\alpha,\beta}$ in the mesophase and in the isotropic liquid was corrected for the finite width of the instrument slit to obtain the true value. The temperature dependences of the values of $N_{\alpha,\beta}$ of the investigated crystals, obtained in this manner, are shown in Figs. 1 and 2.

§3. EXPERIMENTAL RESULTS AND DISCUSSION

The change of N_β with the temperature of the mesophase reflects the change of the parameter of the orientational order of the molecules, inasmuch as $S=1-N_\beta g_\beta$, and the values of g_β for the crystals considered here lie in the interval 0.94—0.88. In the scale of the relative temperature $\Delta T=T_{NI}-T$, the values of S for 6CB are noticeably lower than for the other homologs (Fig. 1). In the nematic phase of 8CB there is observed a strong pre-transition increase of S near the transition temperature T_{SN}. The jump $\Delta S\approx 0.01$ at the point T_{SN} points to a weak first-order phase transition. Taking into account the g_β factor, the absolute values of S for 5CB are in good agreement with the previously measured ones[8] in samples with planar orientation of the molecules in NaCl cells. For the smectic-A phase of 8CB, the values of S agree with the x-ray measurement data.[15]

The accuracy of the measurement of N_α is lower than that of N_β (Fig. 2) because of the weakness of the α band. In an isotropic liquid, at a fixed sample thickness, experiment yields $I_{\alpha i}/I_{\beta i}=0.08$. The joint influence of two non-linear processes, namely the change of the orientational order and the π-conjugation between the benzene rings, leads to a complicated temperature dependence of N_α in the mesophase of the investigated substances, especially 8CB.

From the experimental values of $N_{\alpha,\beta}$, the values of the angle $\bar{\varphi}$ in the mesophase of cyanobiphenyls were determined from formula (2) (Fig. 3), with the angle $\bar{\varphi}_i$ assumed to be 30°, as obtained earlier (§ 1). For all the investigated crystals one observes in the $N—I$ transition a jumplike decrease of the angle $\bar{\varphi}$, but for 6CB it is quite insignificant and lies within the experimental error. With increasing S, the angle $\bar{\varphi}$ decreases both when the temperature of the nematic phase of each of the crystals is lowered, and on going from 6CB to other homologs at a fixed value of ΔT. The absolute value of $\bar{\varphi}$ in the nematic phase of the investigated crystals is comparable with the same value for the nematic LC 4-MBBA, investigated by the NMR method.[7] The accuracy of our present experiment near T_{NI} is not worse than in Ref. 7, and is higher than in Ref. 8. A comparison of Figs. 1 and 3 shows that close values of S in the nematic phase of the homologs 5CB, 7CB, and 8CB correspond also to close values of the angle $\bar{\varphi}$.

The change of $\bar{\varphi}$ reflects also the pre-transition increase of S in the nematic phase of 8CB near the N—SmA transition. The one-dimensional translational ordering of the molecules in this transition also influences strongly the conformation of their aromatic skeleton, just as the change of S in the nematic phase. In the smectic-A phase of 8CB, the change of $\bar{\varphi}$ is negligible. It is of interest to note that according to an x-ray structure analysis[14,15] binary association of aromatic fragments of molecules with antiparallel orientation of the dipole moments takes place in the nematic phase of the substances investigated here. A possible cause of this may be the interaction of the $C\equiv N$ group with the benzene ring of the neighboring molecule, due to the presence of the resonant valent structures considered in §1. The nematic phase of cyanobiphenyls has a local layered packing of the molecules of smectic-A type[14] with correlation radii $\xi_{\parallel,\perp}$ of the order of several intermolecular distances. With increasing number of the homologs, the values of $\xi_{\parallel,\perp}$ increase. On going into the isotropic phase, the short-range order of the molecules is preserved.[14] Comparison of these data with our present results (Fig. 3) shows that the change of the conformation of the molecules depends on the long-range orientational and translational order of the mesophase and has

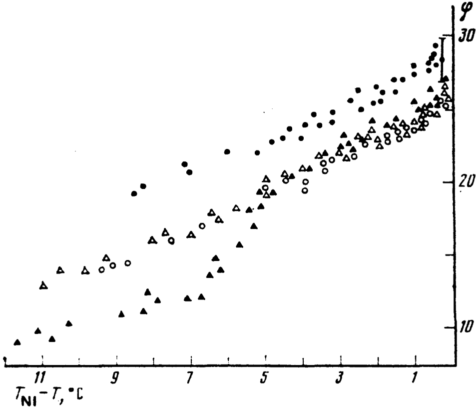

FIG. 3. Change of the dihedral angle $\bar{\varphi}$ between the benzene rings of the biphenyl fragments of 4-n-alkyl-4′-cyanobiphenyl molecules in the mesophase. The symbols are the same as in Fig. 1.

therefore a cooperative character. The role of these conformation transformations in the singularities of the phase transitions between different LC phases is still unclear and calls for a special theoretical investigation. The same holds also for the establishment of the functional dependence of $\overline{\varphi}$ on S. One can hope that the experimental results presented in the present article, together with the available NMR data[7] will stimulate this research.

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