The influence of the surface on conformational equilibrium in thin layers of nematic liquid crystal

L. B. Boinovich★ *and A. M. Emelyanenko*

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 5308. E-mail: ame@serv1.phyche.ac.ru

Changes in the conformational equilibrium in thin layers of the nematic liquid crystal 5CB between fluorite plates were studied by IR spectroscopy. A decrease in the thickness of the liquid crystalline layer symmetrically confined by poorly wettable fluorite surfaces is accompanied by the shift of conformational equilibrium toward rotamers characterized by a higher energy and the spatial structure preventing dense packing of molecules in the interlayer.

Key words: liquid crystals, thin layers, surface, conformational equilibrium, IR spectroscopy.

The interaction of the liquid with the adjacent phases results in a substantial change in its properties in thin layers as compared to the volume parameters.[1] In the case of liquid crystals (LC), the influence of surface forces is manifested much more strongly than in layers of isotropic liquids. This is due to the fact that in thin layer the fields of surface forces of the phases that bound this layer overlap.[1] In addition, LC are characterized by the long-range orientation.[2] The specific features of the structure in thin layers of nematic LC were examined in many works (see, *e.g.*, Refs. 3—5 and references cited therein[6,7]). However, in the most cases, molecules are presented as rigid rods, and the specific features of intermolecular interactions are ignored. An attempt to understand the character of the influence of the metallic substrate on both the orientation behavior of the molecule as a whole and the conformational structure of the alkyl tail of cyanobiphenyls has been made previously.[8] However, the influence of the layer thickness on the character of conformation changes of LC molecules was not studied. In this work, the main attention was given to the influence of the layer thickness on the conformation equilibrium in the thermotropic LC 4-pentyl-4-cyanobiphenyl (5CB).

Experimental

4-Pentyl-4′-cyanobiphenyl, $CN(C_6H_4)_2(CH_2)_4Me$, (BDH) (5CB) was used as received. This liquid crystal exists in the nematic state at 24±1 °C (temperature of experiment).

Plates of crystalline CaF_2, which belongs to the cubic syngony, were used as phases that restrict the LC layer and simultaneously serve as optical windows. The plates were prepared by grinding and fine polishing followed by washing with organic solvents. The height of microroughness in the plates did not exceed 5 nm.

Transmission IR spectra were recorded on a Perkin—Elmer-2000 Fourier spectrometer with a mercury-cadmium-tellurium detector cooled with liquid nitrogen (resolution 2 cm^{-1}). The number of scans was selected in such a way to provide the signal/noise ratio for thin layers not worse than 100 : 1 accumulating up to 8000 scans for films 25 nm thick.

To record transmission spectra of thin layers of LC, we used the cell designed by us, which made it possible to obtain films with a thickness from several tens of microns to tens of nanometers.[9—10] The thickness of the LC layer (thinner than at least 250 nm) was accepted to be equal to the thickness of the air gap between the optical windows (until the latter was filled with the liquid crystal) and determined from the position of interference maxima in the IR, visible, and near-UV spectral regions. UV spectra were recorded on a Specord M40 instrument. The gap thickness was maintained during filling monitoring the thickness of the air bubble between the optical windows, which was slowly displaced by the LC front. Thinner thicknesses were estimated by absorption bands of symmetrical and asymmetrical stretching vibrations of the CH_3 groups in the framework of the two-fraction model with a fast angle according to the procedure described previously.[11]

To reduce the number of errors related to changes in the atmospheric composition, the cell compartment of the spectrometer was continuously blown through with anhydrous nitrogen, and scanning was performed in the Shuttle mode, which allows detection of changes in the atmosphere. To exclude the influence of dynamic effects related to the establishment of equilibrium orientations of the molecules inside the thin LC layer, all analyzed spectra were obtained after the transorientation equilibrium in the system was established. As a rule, the time of establishment of this equilibrium was several h.[11]

Results and Discussion

Plentiful calculations on the dynamics of polymethylene chains[12,13] made it possible to pick out the region of wave numbers from 1400 to 1300 cm^{-1} in which vibrations related to the presence of *gauche*-rotamers in the chain are well detected. Therefore, to study the redistribution of statistic weights of different rotamers of the alkyl tail during thinning of the LC

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 305—307, February, 2001.

layer, we will mainly examine precisely this region of deformation vibrations. The difference absorption spectra of the 5CB layers obtained by the subtraction of the normalized spectrum for the layer 50 μm thick from the normalized spectrum referred to the lower thickness are presented in the same scale in Fig. 1, *a*. The thickness of the layers used to obtain the difference spectrum is indicated in Fig. 1 near the curves. Since the changes in the conformation composition of LC increase dramatically for the layers with the thickness <100 nm, in the scale of Fig. 1, *a* the changes that occur at the first stages of thinning for the layers several microns thick and thicker are insufficiently discernible. To illustrate these changes, we present in Fig. 1, *b* some differential spectra for the layers with the micron thickness in the enlarged scale.

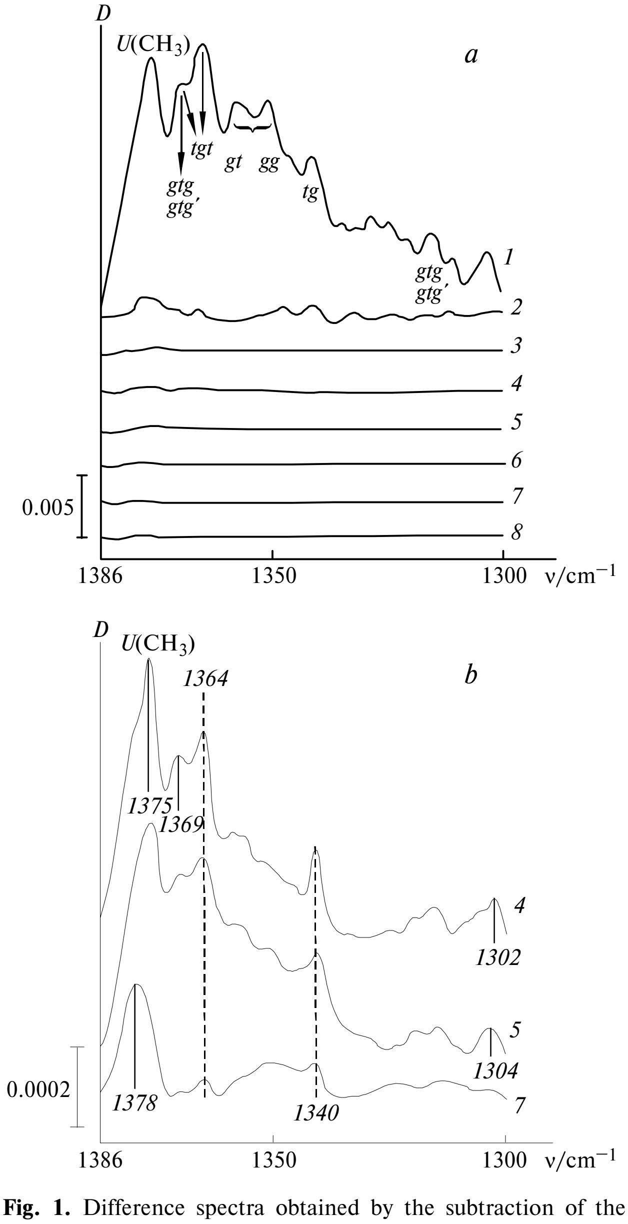

Fig. 1. Difference spectra obtained by the subtraction of the normalized spectrum for the LC layer of 5CB 50 μm thick from the normalized spectrum referred to a smaller thickness: *a*, thicknesses of the layers used to obtain the difference spectrum (in μm): 0.025—0.050 (*1*), 0.096—0.050 (*2*), 4—50 (*3*), 6—50 (*4*), 10—50 (*5*), 22—50 (*6*), 27—50 (*7*), and 46—50 (*8*); *b*, amplified scale for layers (in μm): 6—50 (*4*), 10—50 (*5*), and 27—50 (*7*).

As follows from analysis of the experimental data, the changes in the conformation composition with the LC layer thinning down to the micron thickness are characterized, first, by an increase in the intensity of the bands attributed to deformation vibrations of the terminal *tg*- and *tgt*-conformers (see Fig. 1, *b*). The previous examination[11] of the plots of the orientation of transition moments of the stretching $C\equiv N$ and valent symmetrical C—H vibration in the CH_3 group *vs.* layer thickness indicates that a change in the slope angle of the director of the molecule relative to the normal to the layer surface is not a reason for an increase in the intensity of the considered bands. According to the model approach,[8] the observed changes in intensities can be explained by an increase in the fraction of the terminal *tg*- and *tgt*-conformers. As can be judged from the frequencies of the appeared bands (see Fig. 1, *a*), the fraction of folded conformers, such as *gtg*, *gg*, and terminal *gt*, increases substantially with further thinning.[13,14]

The influence of the temperature, phase state, chain length, and intermolecular interaction on the conformation composition has repeatedly been discussed.[8,14—16] The data[15] obtained for 5CB by Raman resonance spectroscopy indicate that the transplanar (*ttt*)-conformations predominate not only in the nematic, but also in the isotropic state. Their fraction in the nematic phase reaches 23%, and according to the published data,[16] it is 33%. In addition, the statistical weights of other conformers extended along the axis of the biphenyl fragment (*tgt*, *ttg*, *etc.*) exceed substantially those for the folded conformation of the *ggt*, *tgg*, and other types. In this connection, it is essential that the conformation equilibrium can be displaced due to the interaction of LC with the phases that confine it, which was established in this work.

Let us consider the change in the shape of the band assigned to the umbrella vibration $U(CH_3)$ of the CH_3 group. For the films with a thickness of tens of μm, the absorption maximum is observed at 1378 cm^{-1}. This position of the maximum indicates mixing of the umbrella vibration with the wagging vibrations of the methylene chain.[13] The decrease in the thickness is characterized by both an increase in the intensity of this band and the appearance of a shoulder at 1375 cm^{-1} (the umbrella vibration undisturbed by the wagging vibrations of the methylene chain[13,17]). The first circumstance is resulted by an increase in the orientation angle of the axis of the CH_3 group relatively to the normal to the support,[11] and the second fact is stipulated by a change in the environment of the terminal CH_3 group due to a change in the conformation composition. Thus, a decrease in the thickness of the symmetrical, *i.e.*, restricted by similar phases from the both sides, LC layer between the fluorite surfaces is accompanied by the shift of the conformation equilibrium toward rotamers, which possess, on the one hand, a higher energy,[13] and on the other hand, as shown in Ref. 14, the spatial structure preventing the dense packing of the molecules in the layer. The transformation of some transplanar conformations into *gauche*-structures increases the distance between the planes of the phenyl rings[14] and, hence, decreases the density in the LC layer. This behavior agrees well with the experimentally observed decrease in the density of the liquid near the poorly wettable wall,[1] which is the fluorite toward 5CB.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32732).

References

1. B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces*, Consultant Bureau, New York—London, 1987.
2. P. G. de Gennes, *The Physics of Liquid Crystals*, Eds. W. Marshall and G. Wilkinson, Claredon, Oxford, 1984, 329 p.
3. S. Herminghaus, *Science*, 1998, **282,** 916.
4. G. P. Crawford, R. Stannarius, and J. W. Doane, *Phys. Rev. A.*, 1991, **44**, 2558.
5. F. Vandenbrouck, S. Bardon, M. P. Valignat, and A. M. Cazabat, *Phys. Rev. Lett.*, 1998, **81**, 610.
6. L. M. Blinov, E. I. Kats, and A. A. Sonin, *Usp. Fiz. Nauk*, 1987, **152**, 449 [*Sov. Phys. Uspekhi*, 1987, **30**, 604 (Engl. Transl.)].
7. A. S. Sonin, *Vvedenie v fiziku zhidkikh kristallov* [*The Introduction into Physics of Liquid Crystals*], Nauka, Moscow, 1983, 320 pp. (in Russian).
8. A. Kaito, *Mol. Cryst Liq. Cryst. Science and Technology. Sect. A-Mol. Cryst Liq. Cryst.*, 1995, **269**, 111.
9. L. B. Boinovich and A. M. Emelyanenko, *Surf. Interface Anal.*, 1991, **17**, 764.
10. L. B. Boinovich and A. M. Emelyanenko, *Yacheika dlya issledovaniya spektrov propuskaniya zhidkikh veshchestv* [*A Cell for Studying Transmission Spectra of Liquid Substances*], A. c. USSR No. 1807320 (in Russian).
11. L. B. Boinovich, A. M. Emelyanenko, and E. I. Kochetkova, *Kolloid. Zh.*, 2001, **63**, in press [*Colloid J.*, 2001, **63**, in press (Engl. Transl.)].
12. G. Zerbi, *Adv. in Infrared and Raman Spectroscopy*, Wiley, New York, 1984, **23**, 301.
13. R. G. Snyder, *J. Chem. Phys.*, 1967, **47**, 1316.
14. E. Galbiatti and G. Zerbi, *J. Chem. Phys.*, 1986, **84**, 3509.
15. T. Kobayashi, H. Yoshida, A. D. L. Chandani, S. Kobinata, and S. Maeda, *Mol. Cryst. Liq. Cryst.*, 1986, **136**, 267.
16. J. W. Emsley, G. R. Luckhurst, and C. P. Stockley, *Proc. Roy. Soc. London*, 1982, **A381**, 117.
17. G. Zerbi, R. Magni, M. Gussoni, K. H. Moritz, A. Bigotto, and S. Dirlikov, *J. Chem. Phys.*, 1981, **75**, 3175.

Received July 12, 2000;
in revised form November 17, 2000