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

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S. I. Tatarinov [a]

[a] Department of Physics, N. G. Chernyshevsky State University, Astrakhanskaya str. 83, 410026, Saratov, Russia

Version of record first published: 27 Oct 2006

To cite this article: S. I. Tatarinov (2001): Determination of Molecule Conformations in Liquid Crystal Phase States, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 553-560

To link to this article: http://dx.doi.org/10.1080/10587250108025335

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 553-560
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Determination of Molecule Conformations in Liquid Crystal Phase States

S.I. TATARINOV

Department of Physics, N. G. Chernyshevsky State University, Astrakhanskaya str. 83, 410026, Saratov, Russia

Conformations of liquid crystal molecules by joint application of experimental molecular vibrational infrared spectroscopy and computer simulation of spectra, with correction of force constants and electrooptical data for phase state change were studied.

Keywords: liquid crystal; molecule conformation; infrared vibrational spectra; computer simulation

INTRODUCTION

Polymorphism and physical properties of liquid crystal (LC) depends on conformation of molecules. NMR spectroscopy study of molecule conformations requires replacement of atoms by their isotopes. X-ray diffraction study is limited by an opportunity of reception of crystal samples with perfect structure. LC have imperfect crystal structure. We use the experimental vibrational infrared spectroscopy and computer simulation in study of conformations of LC molecules.

EXPERIMENT, SIMULATION

The LC substances of a series of a asymmetric substituted esters of alkylbenzoic acids an example of 4-*n*-hexyl- and 4-*n*-heptylbenzoic acids -4'-cyanophenyl esters (nABACPE, k=6,7) were investigated. The molecular structure is shown in Figure 1.

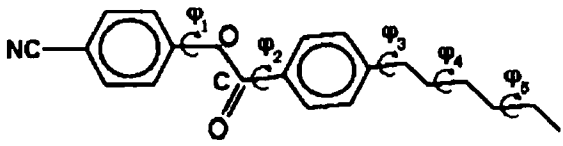

FIGURE 1. The plane trans-conformation of 6BACPE molecule. Hydrogen and carbon atoms of alkyl chain and benzene rings are not shown.

The temperatures of phase transitions solid crystal (SC) - nematic liquid crystal - isotropic liquid (IL) were determined by IR transmission jumps, similarly to [1]. The obtained values 317 K (SC-LC) and 322 K (LC-IL) for n=6, 317 K and 329 K for n=7, respectively, are in agreement with [2]. IR absorption spectra of samples with aligned and disordered molecules were measured in region 400-4000 cm^{-1} in temperature range 290-350 K by temperature-controlled cell [3], grating polarizers and rubbing. The amendments on an imperfection of polarizers were determined according to results of [4]. The thicknesses from 7 up to 30 μm were fixed by teflon spacers.

The feature of studied substances is a molecule asymmetry as a consequence of distinction of substituents in 4- 4'- position of benzene rings and an opportunity to turn for various molecule parts. The asymmetry of molecular structure results in large complexity of IR spectra. In particular, in spectra there are the bands appropriate to vibrations allowed in Raman spectra, and the interaction of the carbon-carbon (C-C) stretching, bending, wagging, rocking and other deformation vibrations results, as a consequence, in a problem of

unequivocal assignment of vibrations between 700 and 1200 cm^{-1}. In known literature the data about molecular conformations of nABACPE is not present. We suppose rod-like molecules with a rigid skeleton and less rigid alkyl chains. The molecules have crossing 4-4'- axes of benzene rings similarly to liquid crystal molecules considered in [5].

The substances with similar structure have in LC and IL smaller barrier of hindered rotation of molecule parts around single bonds than around multiple bonds [6, 7]. Therefore it was supposed, that the molecules conformations of nABACPE in various phase states can differ by turn angles of molecule parts around connecting them C-C and C-O single bonds. The turns of nitrilbenzene ($CN-C_6H_4-$), alkylbenzene ($-C_6H_4-C_nH_{2n+1}$) and alkyl ($-C_nH_{2n+1}$) parts around C_b-O, C_b-C_e, C_{alk}-C_b bonds, where C_{alk}, C_b, C_e are carbon atoms of alkyl chain, benzene rings and central ester group, respectively, (see Figure 1, angles φ_1, φ_2, φ_3) were considered. The probable configurations of alkyl chains were obtained by turns of $-CH_2-$, $-CH_3$ groups around C-C bonds of methylene groups.

The computer simulation of IR absorption vibrational spectra was carried out on the basis of the solution of a direct spectral problem of the theory of multinuclear molecular vibrations and fragments method [8] by programs [9], kindly given by Professor L. A. Gribov. The spectra of conformers were calculated with the use of force and electrooptical data from [9] corrected, in the solution of a inverse spectral problem, for the change of a phase state. The interpretation of the IR spectra transformations at variation of angles φ_1-φ_5 was carried out on the basis of calculations of frequencies, intensities, polarizations and potential energy distributions. The molecule conformations were identified by comparison of experimental spectra with results of the solution of mechanical and electrooptical problems for various conformers.

RESULTS AND DISCUSSION

At SC-LC-IL phase transitions of nABACPE the spectra changes are connected, for the majority of bands, with increase of half-width and decrease of peak intensities. Transition to diluted solutions (S) in non-

polar solvents (up to 0.14 mass % in CCl_4) results in decrease of bandwidths and improvement of their resolution in comparison with IL and LC. More spectral changes are observed at SC-LC transition. Figure 2 shows fragments of SC and LC spectra, which have changes in position of bands or redistribution of their intensities, and calculated spectra. The analysis of spectral changes was carried out on bands, which assignment revealed pronounced contribution of vibrations of the appropriate structural groups.

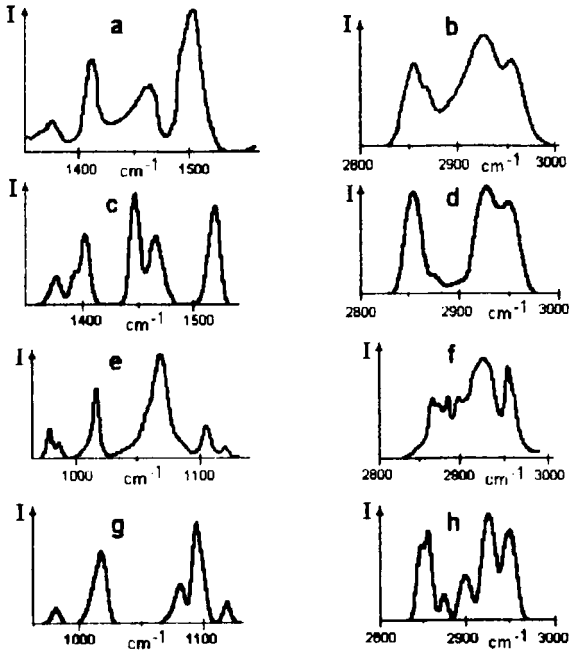

Figure 2. IR absorption spectra of 6BACPE. a-d - LC, e-h - SC; a, b, e, f - experiment; c, d, g, h - theory.

The configuration of alkyl chains was determined by IR bands in 2800-

3000 cm^{-1} region associated with C-H stretching vibrations of methyl and methylene groups, similarly to [10-12]. In experimental spectra of the LC, IL and S two strong (2855 and 2930 cm^{-1}), one middle (2953 cm^{-1}), and two weak (2867 and 2905 cm^{-1}) overlapping bands (Figure 2b) are here observed. In spectra of these phases the relative intensity of bands differs a little. In a solid phase the spectrum becomes more structural: instead of two bands, four occur in 2800-2900 cm^{-1} region, and smooth maximum at 2930 cm^{-1} has in SC spectrum the shape appropriate to four bands (Figure 2f). The theoretical spectra in 2840-2940 cm^{-1} (see Figure 3) demonstrate significant influence of molecule spatial structure changes on frequencies and intensities of IR bands in region of C-H stretching vibrations of methyl and methylene groups at constant force and electrooptical data.

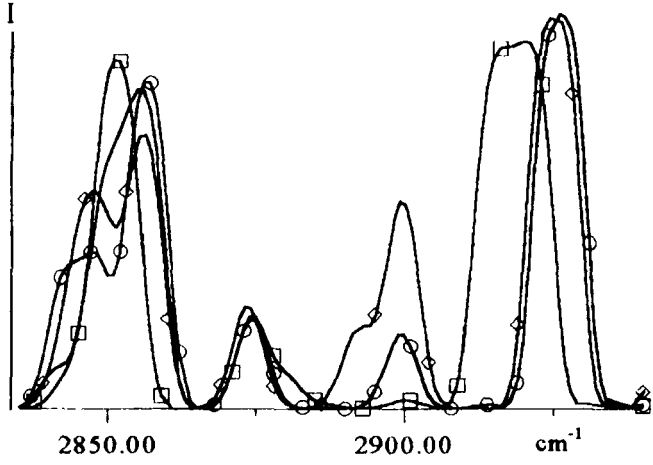

Figure 3. Absorpton spectra for various configuration of alkyl chain: — trans + (φ_4=180^0), -○- trans + (φ_4=180^0) + (φ_5=180^0), -◇- trans +(φ_4=180^0) +(φ_5=90^0), -□- trans +(φ_4=90^0)+ (φ_5=180^0).

The calculated IR spectrum of 6BACPE with trans- configuration of C_6H_{13} chain has in this region a set of bands with frequencies and shapes close to experimental for IL and S at any orientation of a chain with respect to the plane of molecule skeleton. The some spectra difference in Figure 2b, d can be associated with the use, in the program, of Gauss shaped bands for depicturing calculated spectra, instead of dispersion or convolution shaped bands characteristic for liquid phases. The theoretical spectrum, closest to SC experimental spectrum in this region (Figure 2f, h), was obtained with twisted non-planar configuration of a hexyl chain, in which the methyl group is turned through 90^0 around last C-C bond of methylene groups. Earlier such twisted alkyl chain with similar length was observed in SC of 4-n-pentyloxy-4'-cyanobiphenyl by X-ray diffraction [13]. In the same work, as it follows from a resulting figure, analogous displacement of methyl group out from a methylene groups plane in SC of 4-n-propoxy-4'-cyanobiphenyl is observed.

Similar results were obtained by us for heptyl chain [9]. The analysis of experimental and theoretical spectra in 2800-3000 cm^{-1} region results in a conclusion about a realization of planar completely extended (all-trans) configuration of heptyl chain in LC. The theoretical spectrum of twisted non-planar configuration of molecule chain corresponds in the best way to an experimental spectrum of SC. In SC molecule, $-C_4H_9$ fragment of a hexyl chain turns around corresponding C-C bond through the angle of 180^0, and $-CH_3$ group through 90^0.

The skeleton conformation of nABACPE and its mutual orientation with the alkyl chain were identified by spectra changes in 400-1800 cm^{-1} region (see Figure 2a, c, e, g). The analysis of spectra at variation of φ_1, φ_2 in nABACPE molecules has allowed us to make a conclusion about correlation of spectral transformations in low-frequency regions with the turn of benzene rings at phase transitions. The best conformity of theoretical and experimental spectra of SC 6BACPE was obtained for the conformation with ester group turned around C_b-O bond through 90^0 with respect to plane of nitrilbenzene fragment. In addition, the benzene ring with alkyl group is turned around C_b-C_{ak} bond through 180^0. The metylene groups lay in a plane of the nearest benzene ring. The best conformity of theoretical and experimental spectra of LC, IL and S was obtained for the conformation with the plane of ester group turned

through 210^0 with respect to plane of nitrilbenzene fragment, the benzene ring with alkyl group turned around C_b-C_e bond through 90^0, and alkyl chain having a trans configuration in a plane of its benzene ring. The best conformity of theoretical and experimental spectra in 400-1800 cm^{-1} region of SC 7BACPE was obtained for the conformation with the ester group turned around of C_b-O bond through 55^0 with respect to plane of nitrilbenzene fragment, in addition the benzene ring with alkyl group turned around C_b-C_e bond through 10^0, the alkyl group turned around C_b-C_{alk} bond with respect to plane of its benzene ring, in addition through 75^0. The best conformity of theoretical and experimental spectra of LC, IL and S was obtained in these regions for the conformation with the ester group that lay in a plane of nitrilbenzene fragment, the benzene ring with alkyl group turned around C_b-C_e bond through 50^0, and trans configuration of alkyl chain extended in perpendicular plane of its benzene ring. The analogous increase of angle φ_2 at LC - IL phase transition was discussed for 4-n-methoxybenzylidene -4'-butylaniline in [14]. These data are confirmed by the analysis of angles of orientation of vibrational moments of molecular structural groups by the use the dichroic ratios of the appropriate bands, calculated in similar way [1].

CONCLUSIONS

In all phases nonplanar conformations of a molecule are found. The turn angles of benzene rings of a rigid skeleton are different. In LC, IL and S there are trans, and in SC the twisted nonplanar configurations of alkyl chains.

It is shown, that the alkyl chain configuration in different phases can be determined by computer simulation of IR experimental spectra in 2800-3000 cm^{-1} region assigned to C-H stretching vibrations of methyl and metylene groups.

The efficiency of joint application of experimental molecular vibrational infrared spectroscopy and computer simulation of spectra, with correction of force constants and electrooptical data for phase state change, for study of conformations of liquid crystal molecules is shown.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (RFBR). Grant 97-03-32175.

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