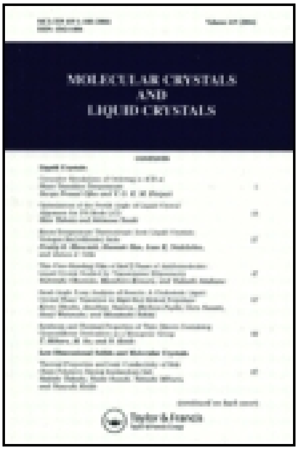

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The Effect of Substituents at Benzoic Ring on the Parameters of Cholesteryl Benzoates Infrared Spectra in Phase Transitions

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Infrared spectra of cholesteryl benzoates, ortho and para Br cholesteryl benzoates, para ethoxy cholesteryl benzoates in crystalline, cholesteric and isotropic states as well as in dilute carbon chloride solutions have been obtained. The behavior of absorption band of carbonyl group ($C=O$) stretching vibrations in cholesteryl benzoates was investigated. The results obtained are indicative of the strengthening of local intermolecular interactions in cholesteric phase.

I. INTRODUCTION

Infrared spectra of liquid crystals, and of cholesteric liquid crystals especially, had been studied insufficiently. As is known,[1] infrared spectra is an informative method of investigation of intermolecular interactions and their different types, in particular, of the so-called specific interactions (hydrogen bonds, donor-acceptor interaction, charge transfer complexes, etc.). In application to liquid crystals, such studies started quite recently. In the previous reports[2,3] we have shown that in binary mixtures of cholesteryl chloride with substituted cholesteryl benzoates a strong shift of the carbonyl ($C=O$) stretching vibration frequency takes place depending on the nature of a substituent and its position at the benzoic ring of the cholesteric molecule. In addition, a strongly pronounced nonlinearity of this shift with concentration was found. A similar nonlinearity (in the same range of concentrations) was observed also in the variation of the supermolecular structural parameter of the cholesteric compositions.[4] These nonlinearities are assumed to be due to specific intermolecular interactions in the cholesteric compositions. We underwent a detailed investigation of the problem. In the present paper, some results obtained for cholesteric substances are given.

II. EXPERIMENTAL METHODS

As objects for the investigation we chose cholesteryl benzoate (CB), para Br cholesteryl benzoate (p-BrCB), ortho Br cholesteryl benzoate (o-BrCB), and para ethoxy cholesteryl benzoate (p-ECB). Infrared spectra were obtained on a double-beam spectrophotometer (Soviet model IKS-14) which provided a recorded spectral range of 600–2000 cm^{-1}. The wavenumber accuracy was ±2.5 cm^{-1}.

The samples were prepared as follows. A drop of the molten substance was placed on the edge of a KBr plate which was covered by another plate slightly shifted tangentially relative the first one. Preliminarily, the plates were thoroughly cleaned and rubbed to ensure a perfect structure of the layer to be obtained. By the capillary forces the molten substance was pulled into the gap between the plates resulting in a monocrystalline layer 10–15 micron thick.

In measuring the ir spectra, the samples were placed in a specially designed thermostat with temperature control accuracy of ±0.5°C.

III. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The comparison of ir spectra of CB, p-BrCB, o-BrCB and p-ECB in the crystalline state shows that the most significant differences are observed for the absorption bands corresponding to the vibrations of carbonyl group ($C{=}O$), $C{=}C$ and $C{-}H$ groups of the benzene ring and $C{-}O{-}C$ group (ester group). Therefore, an analysis of these absorption bands will now be carried out depending on the nature of substituents and their position at the benzene ring.

The absorption bands of the $C{=}C$ skeletal in-plane deformation vibrations in benzene ring of CB, p-BrCB, o-BrCB, and p-ECB are shown in Figure 1. The largest relative intensity is characteristic of the absorption band of p-ECB. In the case of p-BrCB, this absorption band is wider; there is a slight asymmetry on the low-frequency side. The frequencies of the $C{=}C$ skeletal in-plane deformation vibrations in benzene ring of CB,

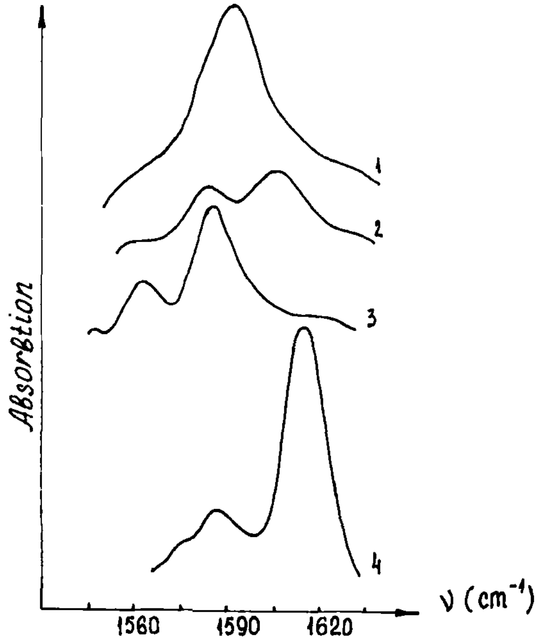

FIGURE 1 Absorption band of C=C skeletal in-plane deformation in benzene in cholesteryl benzoates: (1) para Br cholesteryl benzoate; (2) cholesteryl benzoate; (3) ortho Br cholesteryl benzoate; (4) para ethoxy cholesteryl benzoate.

p-BrCB, o-BrCB and p-ECB are 1605, 1590, 1582 and 1613 cm^{-1}, respectively.

Figure 2 shows C—O—C asymmetric stretching vibrations in the spectra of cholesteryl benzoates. Two remarks can be made here. First, the bands have a clearly pronounced doublet character which can be accounted for by the existence of a set of molecular conformations arising from the rotation about the C—O—C bonds.[5,6] Second, they have a strong relative intensity. This may be due to a significant change of the dipole moment of the C—O—C bonds during vibration.[7]

For the nonsubstituted cholesteryl benzoate the absorption band corresponding to the out-of-plane deformation C—H vibrations of the benzene ring have the frequency 720 cm^{-1}. The C—H vibration frequency increases by 28 and 33 cm^{-1} in p-BrCB and o-BrCB, respectively. The presence of the C_2H_5O group in para position of the benzene ring enhances even more the frequency of deformation vibrations (to 770 cm^{-1}). Thus, the measurements show that the frequency of the out-of-plane deformation

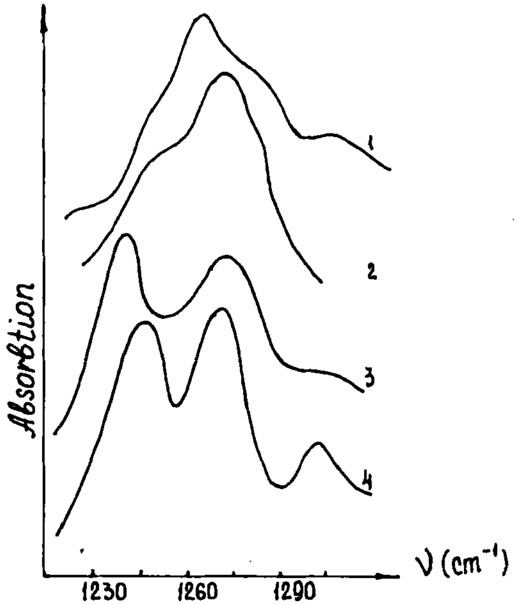

FIGURE 2 Absorption band of C—O—C asymmetric stretching vibration of the ester group in cholesteryl benzoates: (1) para Br cholesteryl benzoate; (2) cholesteryl benzoate; (3) ortho Br cholesteryl benzoate; (4) para ethoxy cholesteryl benzoate.

C—H vibrations of the benzene ring depends on the nature of the substituent very strongly.

Figure 3 presents the absorption band of the carbonyl (C—O) stretching vibrations for CB, p-BrCB, o-BrCB and p-ECB. The frequencies measured are 1720, 1712, 1709 and 1705 cm^{-1}, respectively. It can be seen from Figure 3 that there is a significant difference in the band shapes for these substances which is affected not only by the chemical nature of the substituent but also by its position at the benzoic ring.

We shall attempt to interpret the behavior of only the carbonyl stretching vibration band, since it is of most interest for solving the problem under consideration for the following reasons. First, the carbonyl group is affected by all neighboring groups, due to the redistribution of the electron charge density in the lateral fragment of the cholesteric molecule.[8] Second, in the crystalline state, according to structure data,[5,6,9,10] there is a set of molecular conformations, and an overlapping of C—O groups of adjacent molecules takes place both within the layer and between the neighboring layers of the cholesteric crystal. This appears to provide the possibility of local intermolecular interactions. This state can be expected to retain in the cholesteric phase as well.

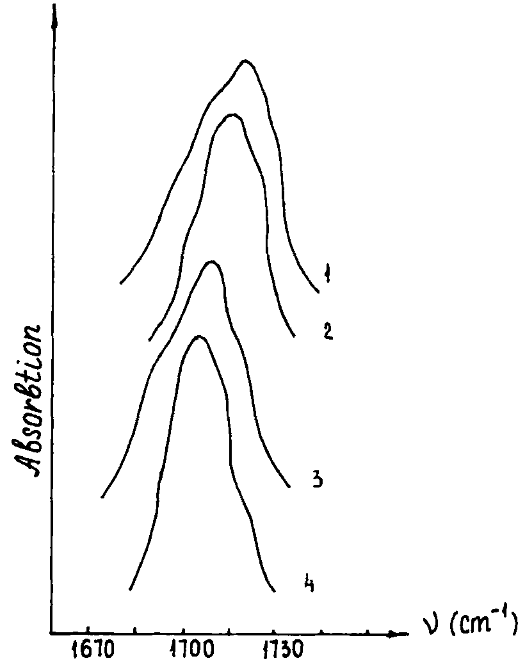

FIGURE 3 Absorption band of carbonyl (C=O) group stretching vibration in cholesteryl benzoates: (a) para Br cholesteryl benzoate; (b) cholesteryl benzoate; (c) ortho Br cholesteryl benzoate; (d) para ethoxy cholesteryl benzoate.

The investigation of the temperature dependence of the carbonyl (C=O) absorption band has shown the following. The frequency of the C=O stretching vibration measured at the absorption band maximum decreases by 7–10 cm^{-1} when going from crystalline to liquid crystalline state, the band shape being changed, too. When passing from liquid crystalline state to isotropic liquid, an asymmetry appears on the high-frequency side of the band. Such a behavior of the carbonyl absorption band at phase transitions is likely to indicate the strengthening of some type of local intermolecular interactions in liquid crystalline state which had already existed in solid crystalline state.

To analyze the carbonyl absorption band behavior in more detail we have employed a computer method of contour separation.[11] The analysis of the absorption band of the carbonyl (C=O) stretching vibration of the o-BrCB reveals the existence of three components with frequencies of 1685, 1707 and 1725 cm^{-1} (Figure 4). We think that these bands are associated with various orientations of C=O group and various types of intermolecular interaction.

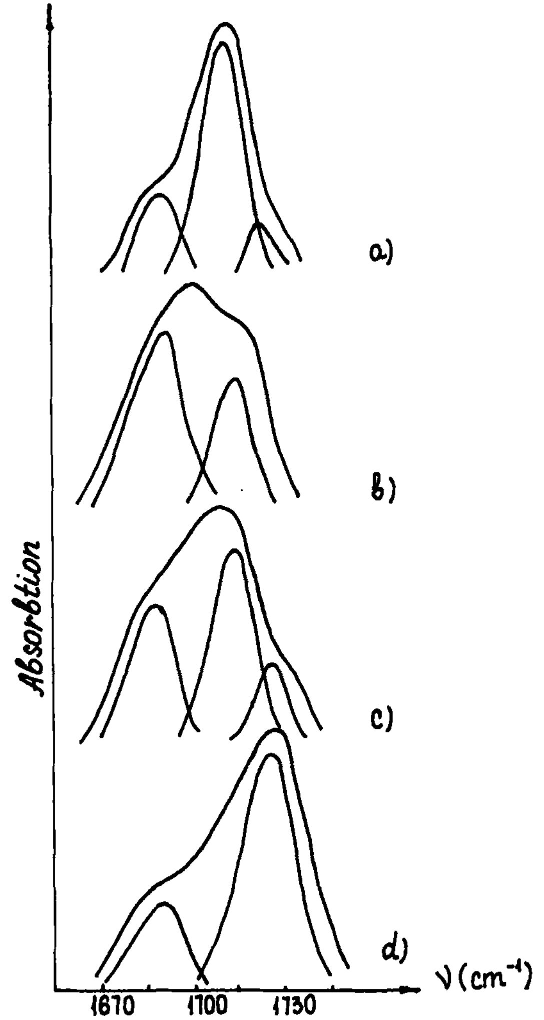

FIGURE 4 Separation of the absorption band of carbonyl group (C=O) stretching vibration in ortho Br cholesteryl benzoate: (a) solid crystalline state; (b) liquid crystalline state; (c) isotropic liquid; (d) solution in carbon tetrachloride.

In confirmation, the X-ray diffraction data can be used. The cholesteric liquid crystals have layer structures.[6,12] The introduction of a substituent to the benzene-ring fragment markedly affects the structure of the asymmetrical molecule unit.[5,6] The rotation of the lateral fragment of the CLC molecule about the C—O—C bond of the ester group yields various conformations of the cholesteryl benzoate molecules.[5,6,9]

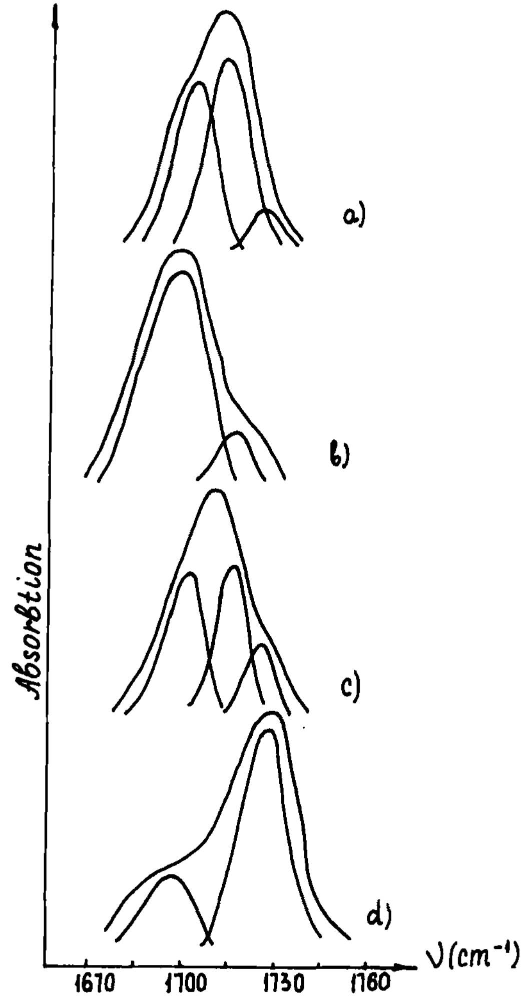

FIGURE 5 Separation of the absorption band of carbonyl group (C$=$O) stretching vibration in para ethoxy cholesteryl benzoate.

From energy considerations, the component with frequency 1725 cm^{-1} on the high-frequency side can be assigned to free vibrations, while the one with frequency 1707 cm^{-1}, to vibrations of carbonyl groups taking part in interlayer interactions (Figure 4). Then the band on the low-frequency side corresponds to local interactions of carbonyl groups within a layer.

The temperature variation confirms the validity of the assignment suggested. As the temperature increases, a redistribution of band intensities occurs still in solid crystalline state. The intensity of bands associated with free vibrations or interactions between layers decreases, while the intensity of the band on the low-frequency side increases. In liquid crystalline state, the whole band shifts towards lower frequencies. An enhancement of local interactions within layers occurs due to possible conformation reconstructions. In an isotropic liquid state, the existence of various conformations is of equal probability, which is revealed in leveling the band intensities (Figure 4). In a dilute carbon tetrachloride solution, the free vibration band strengthens sharply, and a weak band is retained which is likely due to a residual association. Such an association is known, and was studied earlier, in nonliquid-crystal substances.[13]

The absorption bands of stretching vibration of C=O group in CB, p-BrCB and p-ECB (Figure 5) behave similarly, like the one in o-BrCB.

The experimental data obtained permit us to suppose that in cholesteric phase of cholesteryl benzoates a strengthening of local intermolecular interactions occurs which takes place already in solid-crystalline state. It is these local intermolecular interactions that are likely to be responsible for the nonlinear behavior of the supermolecule-structure parameter (the helical pitch) in binary mixtures based on substituted cholesteryl benzoates.[4] In our further work we intend, using the computer method of contour separation, to investigate in detail the temperature and concentration behavior of C=O bond in such systems.

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