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p-Acylphenyl Esters of p-n-Alkoxybenzoic Acids

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p-Acylphenyl Esters of *p*-*n*-Alkoxybenzoic Acids

II. Spectral Features of the Mesomorphic State

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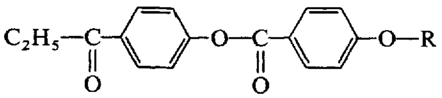
A study is made of the influence of phase states of *p*-propionylphenyl esters of *p*-*n*-alkoxybenzoic acids on IR absorption band parameters. It is shown that the transition from the isotropic melt into the mesophase is accompanied by a change in the absorption band intensity, caused by the benzene ring and polar group vibrations of the molecules. At the phase transition there occurs a shift of the band maximum related to the ester group vibrations. The results obtained are explained by the change of molecular interactions in a liquid crystal as compared with those in the isotropic phase. The degree of molecular orientation depending on temperature and the mesophase type are determined by the IR dichroism method.

INTRODUCTION

The IR spectroscopy method has been used for a study of liquid crystalline materials by a number of workers for example.[1–6] We have made use of this method for investigation of a new class of mesomorphic compounds, *p*-acylphenyl esters of *p*-*n*-alkoxybenzoic acids, in particular a series of *p*-propionylphenyl esters. The majority of homologues of this series are polymorphic and enantiotropic, and have a mesophase with a fairly wide temperature interval.† The molecules of these compounds with the general formula



$R{=}C_4$ through C_{10}

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† The preparation of these compounds and data on phase transitions are reported in I. communication (*Mol. Cryst. Liquid Cryst.*, **29**, 1 (1974)).

contain polar groups which are advantageous in studying the molecular interaction at the phase transitions by IR spectroscopy.

EXPERIMENTAL RESULTS

IR spectra of *p*-propionylphenyl esters of *p*-*n*-alkoxybenzoic acids were recorded on UR-10 spectrometer within the frequency range 700–2000 cm^{-1}. Investigations were carried out in a heating cuvette over the range 35–130°C. An empty heating cuvette is placed in the parallel beam. Samples were prepared in form of unoriented layers between the KBr discs. The thickness of the sample was fixed by Teflon spacers. To prove that the interaction of the substance with KBr does not take place, control spectra were obtained at different temperatures; in this case the samples were isolated by Teflon films. The fact that the spectra in both cases were identical proved that there was no interaction between the substance and the substrate material. To obtain a temperature-phase dependence of the absorption band parameters a sample was kept at each temperature of measurement for 30 minutes. The band intensity was calculated as the product of absorbance and half-width, $\log I_0/I \cdot \Delta\nu_{1/2}$. A correction was made for the final slit width of the monochromator. The thickness of the samples was chosen in such a way that the measured band was over the absorption range of 30–70%. The relative error of $\log I_0/I \cdot \Delta\nu_{1/2}$ value amounted to 5%. The vibration frequencies were measured to an accuracy of 1 cm^{-1}. The intensity change was expressed in the form of the ratio of the band intensity at a measuring temperature to the band intensity at the maximum temperature in an isotropic phase:

$$100 \cdot \left(\log \frac{I_0}{I} \cdot \Delta\nu_{1/2}\right)_T \Big/ \left(\log \frac{I_0}{I} \cdot \Delta\nu_{1/2}\right)_{T\,\max} = I, \%$$

The orientation phenomena in liquid crystals were studied by the IR dichroism method. The preparation of uniformly oriented single-crystal layers of mesophase was carried out as follows. A thin layer of the substance under study was placed between two KBr discs which were preliminarily polished with chromic oxide in one direction. The KBr discs were combined, so that the directions of polishing coincided. On cooling the isotropic melt there was formed an oriented liquid crystal layer with the optical axis parallel to the direction of polishing the KBr discs. The degree of orientational order S in the liquid crystal was quantitatively determined from the known equation $S = 1 - \frac{3}{2}\overline{\sin^2\theta}$, where θ is the angle between the long axis of the molecule and the optical axis of the uniformly oriented liquid crystal layer.

The value of $\overline{\sin^2 \theta}$ was calculated on the basis of the measured dichroic ratio for the absorption band 1512 cm^{-1} according to the method described by Maier.[1] This band refers to the skeletal vibration of the benzene ring, with the transition moment being parallel to the long axis of the molecule. The band has the maximum dichroic ratio in the spectrum of the esters and has been sufficiently isolated.

SPECTRAL FEATURES OF SMECTIC AND NEMATIC MESOPHASES

It is seen from Figure 1 that the mesophase spectrum by its frequency composition is nearer to the isotropic liquid spectrum than to the spectrum of the solid. However, the isotropic-mesophase transition is accompanied by a change of the spectral parameters of certain absorption bands.

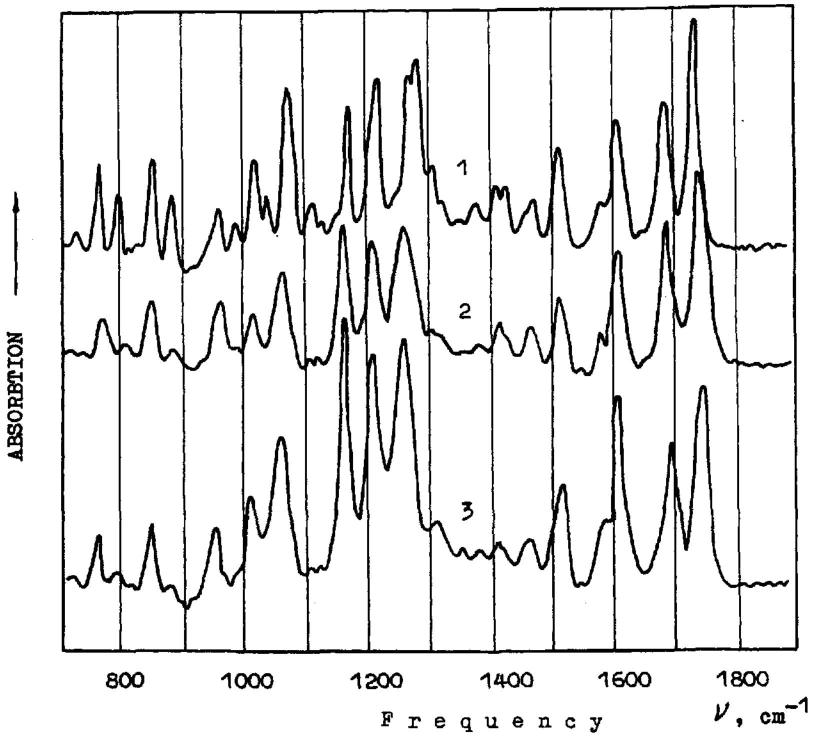

FIGURE 1 IR spectra of the *p*-propionylphenyl ester of *p*-*n*-heptyloxybenzoic acid:

1. solid crystal (35°C)
2. smectic phase (100°C)
3. isotropic liquid (130°C)

Figure 2 shows the temperature-phase dependence of band intensity in the spectra of the homologue C_5. The intensity of a number of absorption bands changes sharply at the isotropic- nematic and nematic-smectic transitions. The most notable intensity changes at the phase transitions are observed for vibrations of the ether and ester group C—O bands (1210 and 1062 cm^{-1} bands), for ν(C═O) of the ketone and ester groups (1688 and 1739 cm^{-1}) and for vibration of the benzene rings (1512 cm^{-1}). The isotropic-mesophase transition does not have a pronounced effect on the intensity of the deformation vibration band of alkyl groups (1470 cm^{-1}).

Figure 3 shows the dependence of intensity of the 1163 cm^{-1} band (the vibration of the C—O bond of ester group) on temperature for C_4, C_5, C_6 and C_7 homologues. The intensity band changes at phase transitions exceed

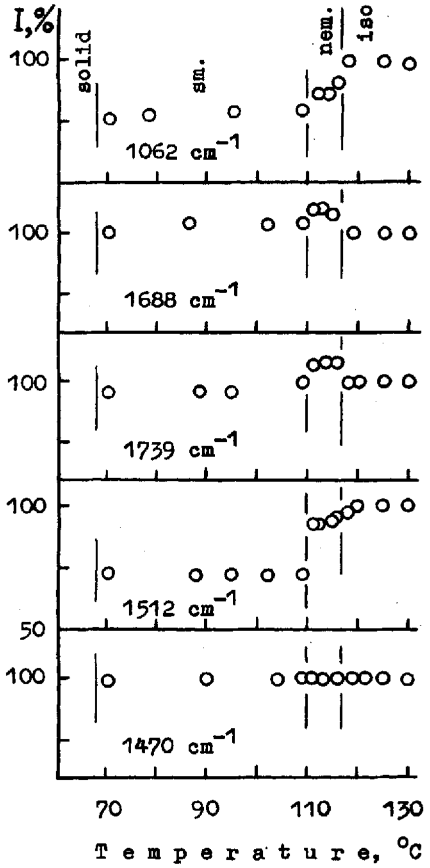

FIGURE 2 Temperature-phase dependence of absorption band intensity for the *p*-propionylphenyl ester of *p*-*n*-amyloxybenzoic acid.

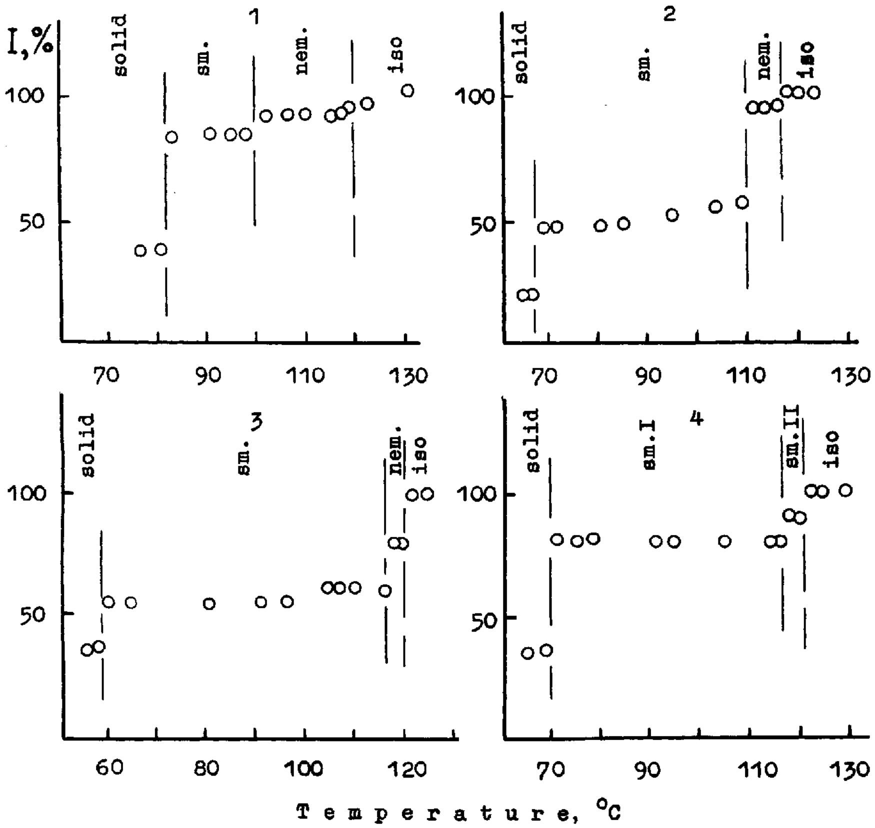

FIGURE 3 Temperature-phase dependence of intensity of the 1160 cm^{-1} band in the spectra of esters:
1. $R = C_4$ 2. $R = C_5$ 3. $R = C_6$ 4. $R = C_7$

the errors of measurement and coincide with the phase transition points of the esters observed by the polarizing microscope.

A mesophase-solid transition is accompanied by significant changes of the IR spectra, all spectral parameters being changed.

An isotropic-mesophase transition has a marked influence on the maximum frequency. As shown in Figure 4 the isotropic-mesophase transition is characterized by a shift of the vibration frequency $\nu(C{=}O)$ of the ester group. The frequency at this phase transition shifts by 4 cm^{-1} towards the lower frequencies; within the mesophase the frequency remains constant and on crystallization it undergoes again a further shift by 7 cm^{-1}, also towards the lower frequencies. It will be noted that the vibration frequency of the C—O bond of the ester group at the phase transitions changes in the

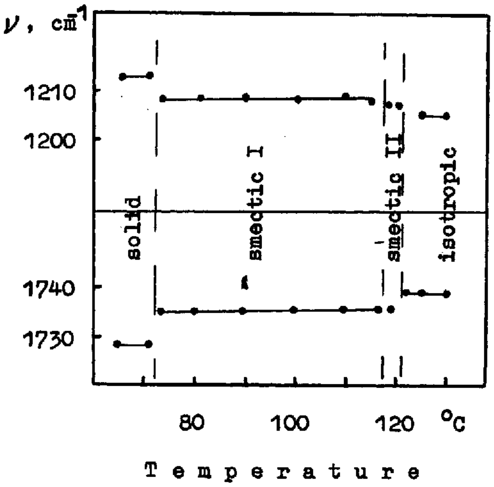

FIGURE 4 Temperature-phase dependence of the absorption band maximum of *p*-propionylphenyl ester of *p*-*n*-heptyloxybenzoic acid.

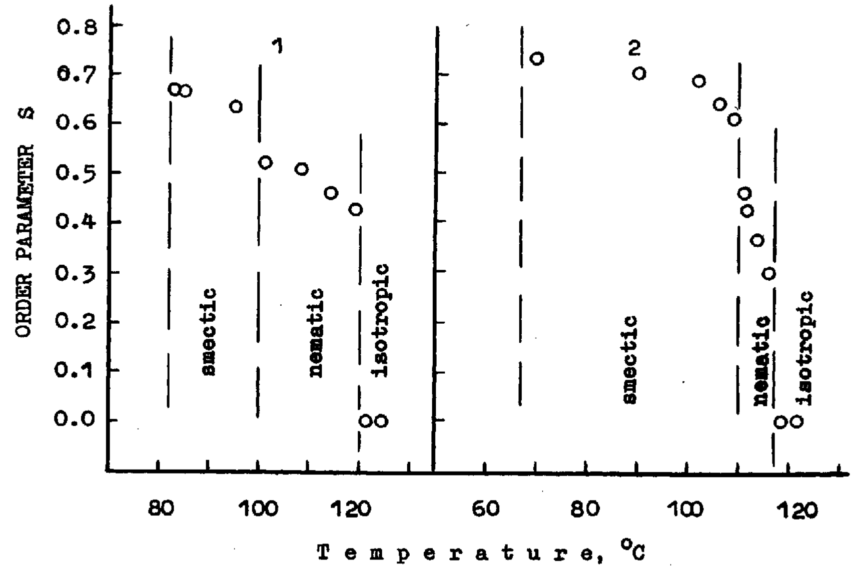

FIGURE 5 Degree of order *S* vs temperature for *p*-propionylphenyl esters of butyloxy- (1-) and amyloxybenzoic (2) acids.

opposite direction, increasing from 1205 cm^{-1} in the isotropic phase to 1209 cm^{-1} in the smectic phase, and then it increases to 1214 cm^{-1} at the transition into solid (Figure 4). Phase transition within the liquid phases—isotropic, nematic and smectic—do not have any significant influence on the frequencies of the other vibrations.

DETERMINATION OF THE DEGREE OF ORIENTATIONAL ORDER

Figure 5 shows the dependence of the degree of orientational order S on temperature for C_4 and C_5. The curves were obtained on cooling from the isotropic melt. The order parameter S increases sharply from 0 in an isotropic phase to 0,3–0,4 values in a nematic phase. The value of S then increases gradually over the range of the nematic phase as the temperature decreases and increases sharply at the transition to a smectic phase. The S value increases slightly with a temperature decrease over the smectic range, achieving the maximum value of about 0.7.

DISCUSSION

For mesomorphic *p*-propionylphenyl esters there are definite spectral indications of the liquid crystal state, change of the parameters of a number of IR absorption bands with respect to both the isotropic and solid states. As was shown both in early works[1,2,4,5] and in the present work, sharp changes in the spectra of unoriented samples are observed at a solid-mesophase transition. But there are differences in the spectra of the mesophase and the isotropic melt. These differences are exhibited first of all in the change of intensity of certain absorption bands at this transition. Moreover, in the case of *p*-propionylphenyl esters the mesophase-mesophase transitions are also accompanied by a change of intensity of the same absorption bands. Thus, one can determine the modification of smectic transition points by a change of an absorption band intensity in the spectra of unoriented sample. These transitions are sometimes difficult to determine by the texture change observed in the microscopic studies as in the case of C_7 (Figure 3.4). Decreased intensity is observed for the majority of bands at the isotropic-nematic and nematic-smectic transitions; consequently the observed effect cannot be explained by change of density, as this would result in increased intensity at transition into the denser liquid crystal medium.

All these facts suggest that the change of the intensity of bands is caused by the change of the electrooptic parameters of the molecules due to characteristic molecular interaction in the liquid crystal.

Together with the intensity change at an isotropic-mesophase transition, there is observed a shift of the ester vibration bands. The shift of the 1210 cm^{-1} maximum may be an apparent shift caused by a superposition of vibrations, but the shift of the carbonyl vibration band (1740 cm^{-1}) seems to be real as this band is isolated and characterized. The shift appears to be explained by the change in the intermolecular interaction in the liquid crystal as compared with those in the isotropic phase. Redistribution of electron density in the ester group causing the shift of the carbonyl valent vibration band is known to be connected with a rotational isomerization.[7] In this connection the shift of the band of ν(C=O) at phase transitions in studied materials may be supposed to be caused by rotation round the C—O bond of the ester group. It will be noted that the shift of the band maximum is unusual for an isotropic-mesophase transition. However, it has been observed in the Raman spectral study of PAA.[8]

It was shown that the degree of orientational order of the oriented *p*-propionylphenyl esters in smectic and nematic phases increases with temperature decrease, but the increase exhibited in the nematic is smaller than in a smectic. These results are in accord with the data obtained by different methods on the other mesomorphic compounds.[1,2,9–11]

References

1. W. Maier and G. Englert, *Zeitsch. Elektrochemie*, **64**, 683 (1960).
2. A. Saupe, *Mol. Cryst. and Liq. Cryst.*, **16**, 87 (1972).
3. V. D. Neff, L. W. Gulrich, and G. H. Brown, *Mol. Cryst. Liquid Cryst.*, **1**, 225 (1966).
4. B. J. Bulkin, D. Grunbaum, and A. V. Santoro, *J. Chem. Phys.*, **51**, 1602 (1969).
5. A. S. Ljvova and M. M. Sushchinsky, *Optika i spectroscopiya, Sb. statey*, **2**, 266 (1966); *Trudi commissii po spectroscopii AN SSSR*, **I**, 611 (1963).
6. N. Kirov and P. Simova, Abstracts of Vth International Liquid Crystal Conference, June 17–24, 1974, Stockholm, Sweden, p. 211.
7. L. J. Bellamy, *Advances in Infrared Group Frequencies*, Methuen & Co. Ltd., Bungay, Suffolk, 1968.
8. H. Itoh, H. Nakatsuka, and M. Matsuoka, *J. Phys. Soc. Japan*, **34**, 841 (1973).
9. N. V. Madhusudana, R. Shashidhar, and S. Chadrasekhar, *Liquid Crystals*, part 1, Ed. G. H. Brown and M. M. Labes, (1972) p. 115.
10. B. Deloche and B. Cabane, *Mol. Cryst., Liquid Cryst.*, **19**, 25 (1972).
11. I. G. Chistijakov, Dissertation, Moscow-Iwanowo, 1970.