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DETERMINATION OF THE DEGREE OF ORDER OF MESOMORPHIC p-n-ALKOXYBENZOIC ACIDS BY IR DICHROISM METHOD

I. I. KONSTANTINOV, V. L. KHODZHAIEVA, M. V. SHISHKINA and Y. B. AMERIK

Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR Moscow, USSR

Résumé. — On étudie le dichroïsme IR de dix éléments de la série des acides alkoxybenzoïques. On calcule le paramètre d'ordre S dans la phase cristal liquide qui dépend de la température et de la nature de la mésophase. On montre que S est plus grand pour les homologues à nombre pair d'atomes de carbone dans le groupement alkoxy que pour ceux à nombre impair. S est plus grand lorsqu'on prépare la mésophase par refroidissement de la phase isotrope que dans le cas où on l'obtient par fusion du cristal.

Abstract. — Ten homologues of a series of p-n-alkoxybenzoic acids have been studied using the IR-dichroism method. The degree of order, S , in the liquid crystal state, depending on the temperature and the mesophase type, has been calculated. It is shown that the value of S is greater for homologues with an even number of carbon atoms in the alkoxy group than for those with an odd number of carbon atoms. In the mesophase obtained by the cooling of the isotropic phase the value of S is higher than that in the mesophase obtained by heating of solid.

The IR dichroism method is one of the easiest and most convenient methods for the investigation of the liquid crystal structure, in particular, of the degree of molecular order depending on temperature and mesophase type [1]. This method permits also the revelation of structural differences in the homologous series of mesomorphic compounds.

The present paper gives the results on study of ten mesomorphic p-n-alkoxybenzoic acids with the number of carbon atoms from 3 to 10, 12 and 16 in the alkoxy chain, using the IR dichroism method.

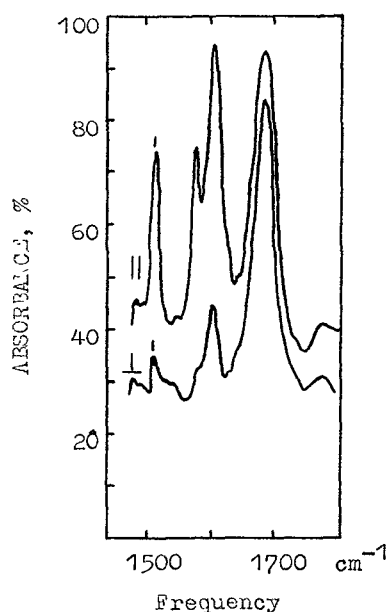


FIG. 1. — The part of IR spectrum of oriented nematic p-n-octyloxybenzoic acid in linearly polarized light.

The preparation of uniformly orientated single-crystal layers of the mesophase was carried out as follows. A thin layer of the substance under study was placed between two potassium bromide discs which were preliminarily polished with chromic oxide in one direction. The KBr discs were combined so that the direction of polishing coincide. The thickness of the sample was maintained by teflon spaces. On cooling the isotropic melt forms an orientated liquid crystal layer with an optical axis parallel to the direction of polishing on the KBr discs. The sample prepared in this way was placed in a heating cell, so that the optical axis of the liquid crystal layer was parallel to the monochromator slit. Changing temperature was carried out at a rate of 0.2-0.4° per minute over the range of 40-160 °C.

As a polarizer, a diffraction lattice replica on polyethylene film with sprayed metal was used. IR spectra were recorded by UR-10 spectrometer over the frequency range of 3 600-400 cm^{-1} .

The degree of order S in the liquid crystal was quantitatively determined from the known equation [2] $S = 1 - \frac{3}{2} \overline{\sin^2 \Theta}$, where Θ is the angle between the long axis of the molecule and the optical axis of the uniformly orientated liquid crystal layer.

The value of $\overline{\sin^2 \Theta}$ was calculated on the basis of the measured dichroic ratio for the absorption band at 1 515 cm^{-1} . This absorption band refers to the skeleton vibration of a 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 acids and has been properly isolated.

In the mesophase obtained by cooling the isotropic phase, the S value is higher (Fig. 2) than that in the

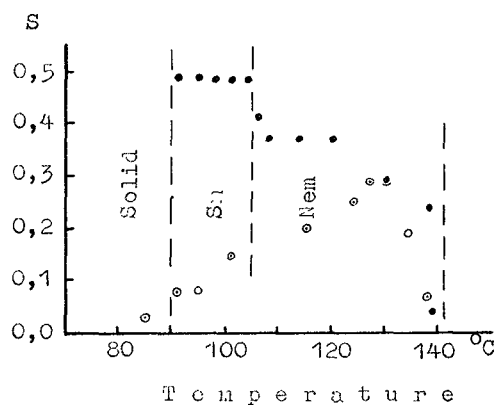


FIG. 2. — The degree of order S vers. temperature for *p*-*n*-nonyloxybenzoic acid in the smectic and nematic phases: ● on cooling of isotropic phase, ○ on heating of solid.

mesophase obtained by heating the solid. The dependence of the S value on the temperature change direction appears to be characteristic of capillary liquid crystal layers and is explained by the fact that in the mesophase obtained by heating the solid there remains partial molecular orientation in the solid polycrystalline sample.

In order to exclude the influence of the solid structure on the molecular orientation in the mesophase,

all the measurements of dichroic ratio were carried out by cooling the isotropic phase. The measurement results of the dependence of the S value on the temperature and phase state for all acids under study are represented in figure 3.

The S value increases gradually over the range of the nematic phase from 0 in the clearing point to values 0.2-0.7, depending on the homologues.

At transition to a smectic phase increases the degree of order sharply and remains practically unchanged in the entire smectic interval.

In the vicinity of the clearing point the S value is approximately equal for all the homologues. In the low temperature range of the nematic phase the degree of order depends on the alkoxy chain length. The lowest value of S is observed for *p*-*n*-propoxybenzoic acid. This is presumably due to the fact that the nematic phase of this homologue exists at a higher temperature. For this reason the mutual orientations of molecules are considerably disturbed because of their intensive thermal motion. Besides, as we have earlier shown [3], the molecular association of this homologue is partially broken, which also hinders the molecular orientation. For the highest homologue — *p*-*n*-hexadecyloxybenzoic acid — there is observed a decrease of the S value. This can be explained by the violation of the linear shape of the molecule

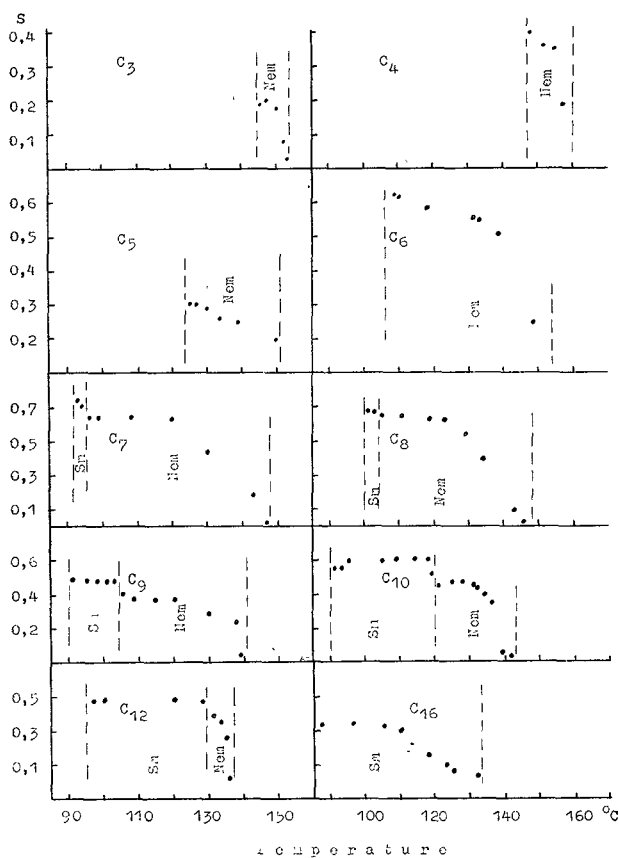


FIG. 3. — The degree of order S vers. temperature for *p*-*n*-alkoxybenzoic acids in mesomorphic state.

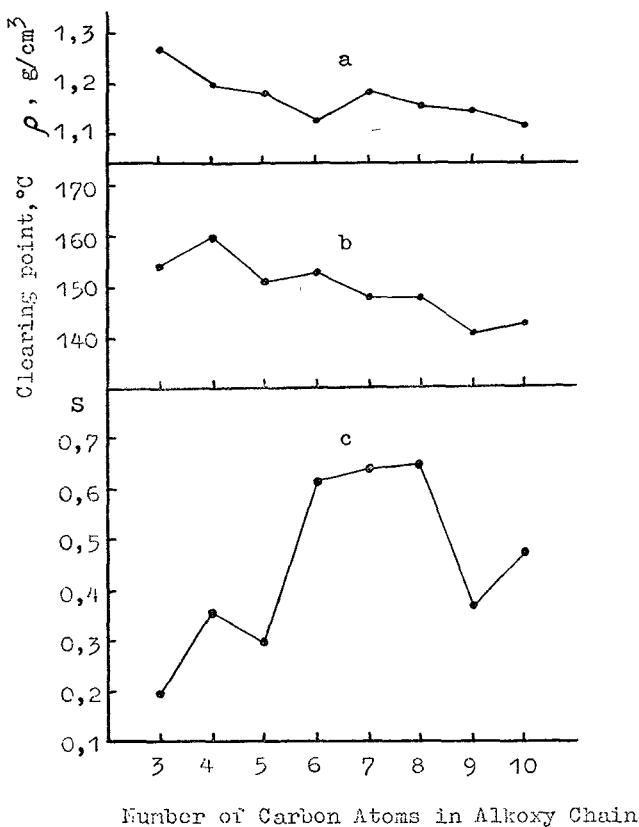


FIG. 4. — The effect of alkoxy chain length on: a) density of solid [5]; b) clearing point; c) degree of order S in nematic phase for *p*-*n*-alkoxybenzoic acids.

when the normal paraffin chain is a set of rotational isomers, as is usually the case in isotropic phase [4].

As shown in figure 4, the degree of order in the nematic phase depends on the even or odd number of carbon atoms in the alkoxy chain. The S value for all homologues was taken within 5-7° before the low temperature transition. It is higher for even homologues than for odd homologues. This depen-

dence is similar to the characteristic alternation of clearing points in the acid series.

The deviation of the S value for p-n-heptyloxybenzoic acid from the common pattern is correlated with deviation of density for this acid in the solid [5] (Fig. 4a). The high density of this homologue was explained by approaching the critical balance between the effect of aliphatic and aromatic parts of molecules on their packing.

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Editorial Comment

The S values quoted are anomalously small (e. g. 0.25 near a clearing point instead of 0.43). This may reflect either a chemical complication specific of these materials, or some uncertainty in the calibration of the IR results.