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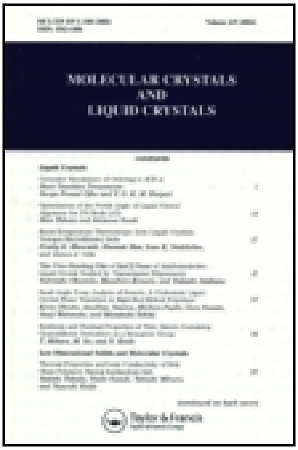

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Infrared Spectroscopic Study of Liquid Crystalline N-[4-(4-n-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-cyanoanilines

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Infrared Spectroscopic Study of Liquid Crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-cyanoanilines

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A homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-cyanoanilines [AHC(*n*; $n = 1-8$, 10, 12)] was synthesized. AHC(4–8, 10) exhibit a monotropic nematic phase. The temperature dependence of infrared (IR) spectra of AHC(4–8) has been observed in the spectral range of 2300–600 cm^{-1}. On cooling, the intensity of the IR band at 2230 cm^{-1} remained unchanged through the phase-transition of isotropic-nematic and increased gradually toward room temperature (solid phase). This band can be assigned to the C≡N stretching vibrational mode. The wavenumber of the band increased slightly (about 1 cm^{-1}) during the temperature from isotropic to solid. In *meta*- CN substituted AHC, it is suggested that the CN group may not play a dominant role in the intermolecular interaction.

Keywords: Nematic; salicylidene aniline derivative; 3-cyano anilines; infrared spectroscopy; molecular conformation

1. INTRODUCTION

A number of investigations have been conducted about the relationship between molecular structure and liquid crystallinity [1, 2]. The vast majority of compounds exhibiting a liquid crystalline phase are composed of a rigid central mesogen and one or two terminal groups. In addition, almost all of the rod-like liquid crystals reported so far have *para*-substituted terminal groups. Much attention has been paid to *N*-salicylideneaniline (SA) and its derivatives because they have thermochromic and/or photochromic properties from the fundamental and optical application viewpoints [3, 4]. While, it

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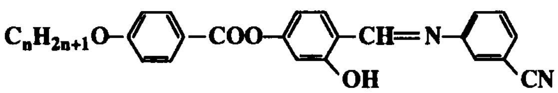
*Corresponding author.

is known that the effect of *ortho*-hydroxy substitution on anil type liquid crystals in general raises the temperatures of both the solid-nematic and nematic-isotropic transitions through the increased stability due to intramolecular hydrogen bonding between the hydroxy group and the nitrogen atom [5, 6]. In order to find a mesomorphic compound having a core frame of SA, a new homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-cyanoanilines having the following structural formula [AHC(*n*; *n* = 1 – 8, 10, 12)] (**1**) was synthesized.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In general, it is well known that the effect of introducing lateral substituents into aromatic rings of core parts of the molecules widens the core and increases the separation between neighboring molecules resulting in reduced lateral interaction. The effect results in a destabilization of the liquid crystal phase [7, 8]. Consequently, the appearance of the liquid crystal phase is hard to realize. Nevertheless, we found that some of AHCs exhibit a nematic phase as the end alkoxyl chain is lengthened.

Infrared (IR) spectroscopy has been used effectively for studying the molecular structure and dynamics of liquid crystals in various phases. We have observed the temperature dependence of the IR spectra of AHCs to clarify the molecular structure in the nematic liquid crystal phase.

2. EXPERIMENTAL

Materials

4-*n*-Alkoxybenzoic acids obtained commercially are converted to acid chlorides by treatment with thionyl chloride in benzene solution as solvent. After the completion of the reaction, the excess of thionylchloride and the solvent were removed. These acid chlorides were esterified by a reaction with 2,4-dihydroxybenzaldehyde in an ether solution including triethylamine. After they had then stood overnight, the triethylamine hydrochloride formed was removed by filtration, the ether was evaporated, and the solid residue was recrystallized from hexane. Finally, the substituted benzaldehydes thus obtained were coupled with 3-cyanoaniline by refluxing in an ethanol solution. The crude product was purified by successive recrystallization from a mixture of ethanol and benzene. The liquid crystalline texture

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and phase-transition temperatures were determined by means of a Nikon polarizing microscope equipped with a Mettler FP-52 microfurnace for sample temperature control. Checks on the transition temperatures were made using a Shimazu differential scanning calorimeter (DSC). Each sample was heated and cooled under a flow of nitrogen gas to prevent the sample from decomposing. The phase-transition temperatures of these homologues are summarized in Table I. On cooling the isotropic liquid under polarizing microscopic observation, so-called nematic droplets appear at the phase transition to the nematic state.

Furthermore, it should be stressed that the phase-transition temperatures described above on the basis of the texture change are in good accord with those measured from a DSC. The phase transition of AHC(10) has already been reported [9]. The temperature range of the monotropic nematic is narrow (~1°C). AHC(12) did not exhibit the monotropic nematic phase.

IR Spectrometry

IR spectra were measured using a FT-IR spectrometer (Bio-Rad Digilab FTS-60c/d). Samples for IR analysis were prepared in the form of a 10 mm-diameter disc by compressing a mixture of AHC and KBr powder. The temperature of the sample was controlled to within 0.5°C during the recording of the spectra.

3. RESULTS AND DISCUSSION

The IR spectra for AHC(4–8), which were exhibited the nematic liquid crystal phase, were measured in 2300–600 cm^{-1} at various temperatures.

TABLE I Phase transition temperatures of AHC(*n*) (°C)

n	(*nematic*)	*isotropic*
1		200
2		189
3		164
4	(125)	132
5	(120)	125
6	(123)	128
7	(115)	128
8	(118)	127
10	(117)	124
12		124

The parantheses show the monotropic transitions.

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The spectrum for AHC(10) was not measured because the temperature range exhibiting the nematic phase was very narrow.

Figure 1 typically shows the IR spectra of AHC(7) in the isotropic (125°C), nematic (105°C) and solid (39°C) phases on cooling. The spectrum of the solid phase on cooling was similar to that of the initial solid as prepared. When AHC(7) undergoes the phase-transition, some of the IR bands change in intensity (absorption) and wavenumber. Of particular interest are bands that change in intensity and wavenumber in the nematic phase, because the bands are considered to give information on the molecular structure in this phase.

The bands in the spectral range 1150 – 1200 cm^{-1} in Figure 1 appeared to change in intensity and wavenumber through the phase-transitions. In

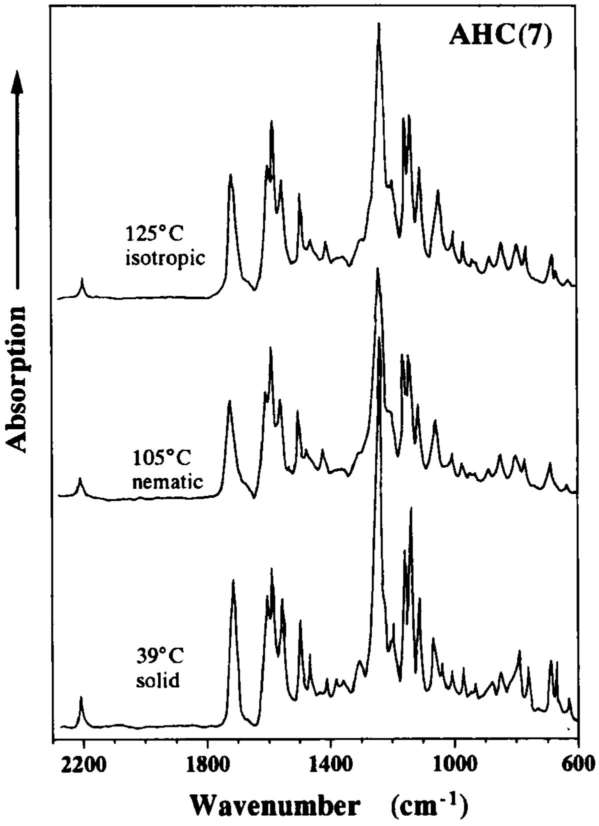

FIGURE 1 Observed IR absorption spectra of AHC(7) in the isotropic (a), nematic (b) and solid (c) phases.

general, these bands can be assigned to the CCH deformation vibrations of the benzene ring [10, 11]. However, it is difficult to assign these bands to the vibrations of particular benzene ring, respectively. Figure 2 typically shows the changes in intensity and wavenumber of the band at 1149 cm^{-1} (at 125°C) as a function of temperature. In Figure 2, the phase-transition of isotropic-nematic is indicated by a dotted line, but that of nematic-solid is not indicated because the temperature of the phase-transition differs under certain circumstances and is not well-defined. On cooling, the intensity hardly changes as AHC(7) undergoes the phase-transition from isotropic to nematic. Then, the intensity gradually increases to about 60°C and increases abruptly below that temperature. On cooling, the wavenumber of the band does not significantly change through the phase-transition of isotropic-nematic, and increases slightly to about 60°C, and then the wavenumber increases abruptly below that temperature. It is supposed from the above observation of the intensity and wavenumber changes that the phase-transition temperature of nematic-solid is about 60°C under the condition of the IR measurement. The solid phase is characterized by a three-dimensional order. In the nematic phase, the molecules are loosely coupled to each other and randomly arranged in the direction along the long axis. In the isotropic liquid phase, the molecules undergo a random motion in all

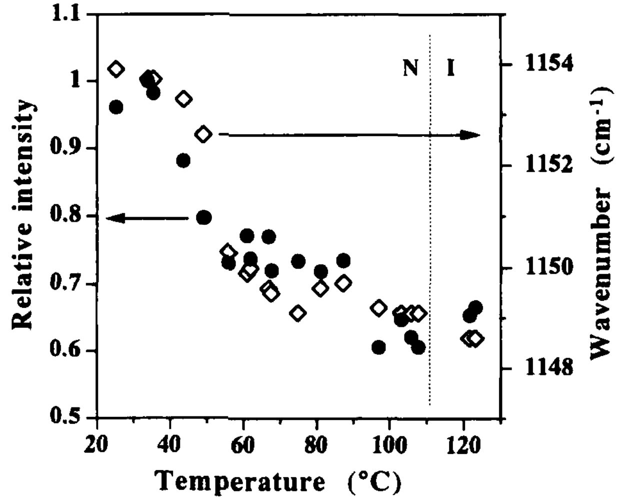

FIGURE 2 Temperature dependence of the intensity and the wavenumber of AHC(7) assigned to the CCH deformation vibration of the benzene ring. The IR absorption intensity is measured relative to the 1603 cm^{-1} band.

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directions. Furthermore, rotational isomers of the end groups of the liquid crystal molecule appear in the higher-temperature phases [12–14]. Thus, the higher temperature phase is characterized by a more random molecular arrangement, molecular conformation and molecular motion. So, the changes in intensity and wavenumber of IR bands are considered to be explained by a change of the degree of randomness in the nematic phase. Practically, from the study of the vibrational spectroscopy, it is well known that the liquid crystal molecule melts in the liquid crystal phases. Namely, the terminal chains of the liquid crystal molecule takes a random molecular conformation similar to that in the isotropic liquid phase and the twist angle between aromatics rings changes through the phase-transition solid–liquid crystals [12–15]. Thus, the changes in intensity and wavenumber of IR bands have been explained by the change of the molecular conformation through the phase-transitions. In *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA), the Raman band at 1170 cm^{-1} due to the CCH deformation vibration of the benzene ring shifts to 1165 cm^{-1} through the phase-transition from solid to nematic. The wavenumber shift has been explained as a result of a change in the twist angle of the aniline ring out of the $C{=}N{-}C$ plane [15]. AHC(7) and MBBA have the common Shiff base as the central core. The explanation of the change of the Raman band may be applicable to that of the IR band in this case. It is reasonably considered that the changes of the 1149 cm^{-1} IR band of AHC(7) can be explained by the change of the molecular conformation, although the band can not assign to the vibration of the particular benzene, as mentioned above. That is, the change of the molecular conformation causes a change in the steric interaction between the intramolecular hydrogen atoms of the benzene ring. Consequently, the CCH vibrational modes may be affected by the change in the force constant of the steric interaction. Thus, when AHC(7) undergoes the phase-transition from nematic to solid, the band increases in intensity and wavenumber. The other bands (1117, 1169 cm^{-1}) ascribed to the CCH vibration showed similar changes in intensity and wavenumber, as those for the 1149 cm^{-1} band.

In AHC(4–6, 8), the similar changes of IR bands due to the CCH vibrations were observed with decreasing temperature. Their changes can be explained in a similar manner to those of AHC(7).

Figures 3 and 4 show the changes in intensity and wavenumber of the IR bands at 1737 cm^{-1} and 1247 cm^{-1} (at 125°C) as a function of temperature on cooling, respectively. When AHC(7) undergoes the phase-transition from isotropic to nematic, their intensities remain unchanged. Then, they increase to room temperature on cooling. With decreasing temperature, the wavenumber of the 1737 cm^{-1} band decreases slightly with decreasing

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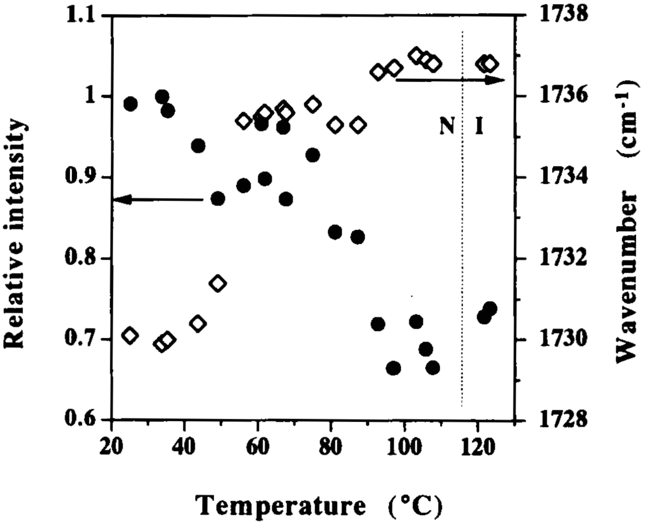

FIGURE 3 Temperature dependence of the intensity and the wavenumber of AHC(7) assigned to the C=O stretching vibration of the COO group.

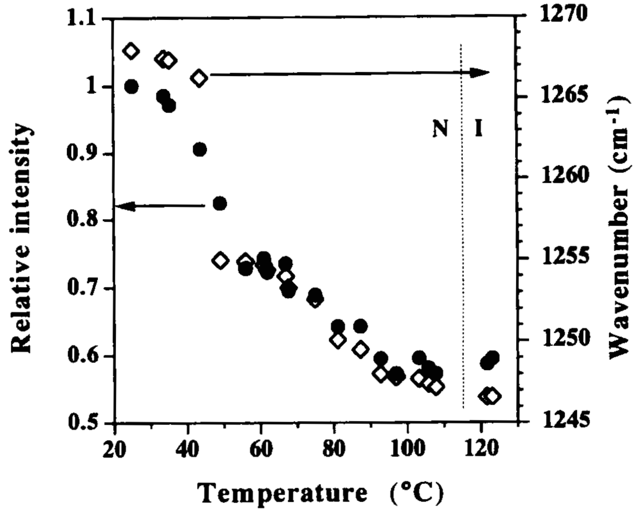

FIGURE 4 Temperature dependence of the intensity and the wavenumber of AHC(7) assigned to the C—O stretching vibration of the COO group.

temperature and decreases rapidly at about 60°C. The wavenumber of the 1247 cm^{-1} band increases slightly on cooling and increases rapidly at about 60°C. The 1737 cm^{-1} band can be assigned to the C=O stretching vibrational mode of the carboxyl group and the 1247 cm^{-1} band to the C—O stretching vibrational mode of the carboxyl group [16, 17]. It is known that the carboxyl group changes molecular conformation at the phase-transition of solid–liquid crystals [12]. The changes in intensity and wavenumber can be explained in terms of the change of the molecular conformation of the carboxyl group through the phase transitions. Of interest is that the wavenumber of C=O stretching mode abruptly decreases at the phase-transition from nematic to solid. The other bands studied increase in wavenumbers at the phase-transition nematic-solid. The unique behavior of the 1737 cm^{-1} band may be explained by the change of the molecular conformation. However, it is difficult to explain exactly the behavior of the band at this stage.

In AHC(4–6, 8), the similar changes of IR bands due to the vibrational modes of the carboxyl group were observed with decreasing temperature. Their changes can be explained in a similar manner to those for AHC(7).

Figure 5 shows the changes of the band at 2230 cm^{-1} (at 125°C) in intensity and wavenumber as a function of temperature on cooling. This band has been assigned to the vibrational mode of C≡N stretching [11, 17, 18]. The IR band shows hardly any notable change in intensity at the phase transition of isotropic-nematic on cooling. That band gradually increases toward room temperature. An abrupt change in intensity was not observed at about 60°C as observed in the bands ascribed to the CCH deformation,

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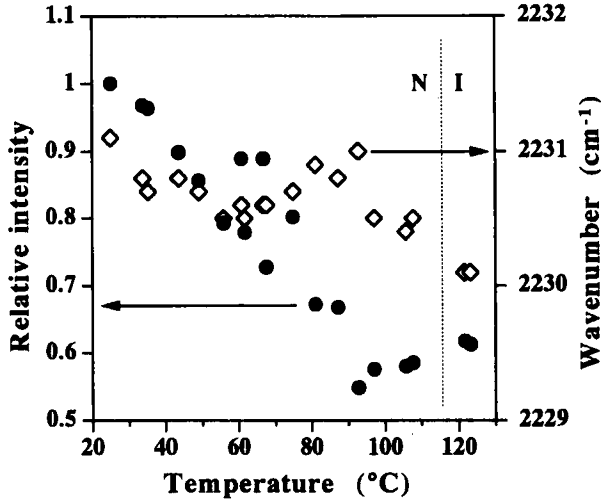

FIGURE 5 Temperature dependence of the intensity and the wavenumber of AHC(7) assigned to the C≡N stretching vibration.

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C═O stretching and C—O stretching modes. It has been considered that in dodecylcyano biphenyl (DCB) the cyano group may play a dominant role in the intermolecular interaction as short and also at relatively long distances [19]. Consequently, *para*-cyano substituted compounds form antiparallel molecular associations owing to the large dipoles associated with the nitrile bond [19]. On increasing temperature, the extent of the interaction has been decreased through the phase-transition solid-smectic A. This change influences the intermolecular interaction through the nitrile, and consequently the C≡N stretching vibration. The band decreases abruptly in intensity and wavenumber near the phase-transition of solid-smectic A. The temperature dependence of the C≡N stretching vibration for AHC(7) is presumably explained in a similar manner to that of DCB, although the CN group is substituted on the *meta*-position. However, in AHC(7), an abrupt change was not observed but gradual change, as mentioned above. It may be suggested that a role of the CN group at the phase-transition is not dominant compared with that of DCB. The wavenumber of that band increases slightly by about 1 cm^{-1} in the temperature range between the solid and isotropic phases, as shown in Figure 5. In DCB, the wavenumber has been increased by 3 cm^{-1} at the phase-transition of solid-smectic A [19]. The difference in wavenumber shift between both compounds may be correlated to the alternation of position of the CN group substituted for the aromatic ring. The small shift in AHC(7) may reflect an undominant role of the CN group in the intermolecular interaction at the phase-transition. Thus, in *meta*-CN substituted AHC(7), the CN group may not play the dominant role in the intermolecular interaction compared to that in the para-substituted compound. This may result in the appearance of the monotropic nematic phase in AHC(7).

In AHC(4–6, 8), the band ascribed to the C≡N stretching vibration showed similar changes in intensity and wavenumber to those for AHC(7). Thus, this CN group may not play the dominant role in the intermolecular interaction in a similar mannar to AHC(7) above.

All AHCs exhibited photochromism in the solid phase. The photochromic properties will be reported elsewhere.

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