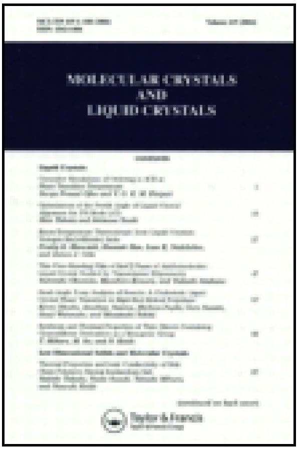

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Raman Spectroscopic Study of Liquid Crystalline N-[4-(4-n-Alkoxybenzoyloxy)-2-Hydroxybenzylidene]-Chloroanilines

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Raman Spectroscopic Study of Liquid Crystalline N-[4-(4-*n*-Alkoxybenzoyloxy)-2-Hydroxybenzylidene]-Chloroanilines

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N-[4-(4-*n*-Alkoxybenzoyloxy)-2-hydroxy-benzylidene]-chloroanilines[nAHmC(n; n=1–8, m; m=2: ortho, m=3: meta, m=4: para)] were synthesized. They exhibited a nematic phase. In addition, 8AH4C exhibited the smectic C and A phases. The temperature dependence of their Raman spectra has been observed in the spectral range of 20–1800 cm^{-1}. In a group of nAHmC, the Raman band at about 980 cm^{-1} decreased in intensity and wavenumber through the solid-liquid crystal phase transition. In the other group, the corresponding band increased through the phase transition. The bands have been assigned to the CH out-of-plane vibration(980 cm^{-1}) of the benzene ring. Such a behavior can be explained by the molecular conformations with different twist angles of the aniline ring to the salicylaldimino part of the molecule in conjunction with information gained in the photochromic studies of N-2-hydroxy-benzylidenanilines. The temperature dependence of the 1190 cm^{-1} band ascribed to the ring-N bond stretching vibration gave support to the result of the CH deformation vibration.

Keywords: nematic; smectic A; salicylidene aniline derivative; chloroanilines; Raman spectroscopy; molecular conformation

1. INTRODUCTION

A number of experimental and theoretical studies have been performed to understand the appearance of liquid crystal phases.[1–3] Nevertheless, some basic problems such as molecular conformations in different phases remain to be elucidated. Raman spectroscopy is a powerful technique for the study of the vibra-

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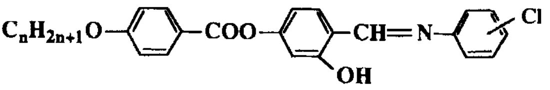
tional dynamics of liquid crystals. The study of the correlation between the Raman spectra and the molecular structures has been performed in order to obtain information on the change of the molecular conformation at phase transitions. Raman spectroscopies have shown that the terminal chains of liquid crystal molecules melt as liquid crystal compounds undergo the first liquid crystal phase transition.[4–7] Raman studies have also shown that the aromatic frame of liquid crystal molecules changes its conformation at liquid crystal phase transitions.[7]

Liquid crystal compounds are mostly composed of two parts, rigid central mesogen and one or two terminal groups. In addition, almost all of the rod-like liquid crystals reported so far had *para*-substituted terminal groups. 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.[8, 9] Consequently, the appearance of the liquid crystal phase is hard to realize. N-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-chloroanilines (nAHmC) having the following structural formula (**1**) were synthesized.



1

n (alkoxy chain length); n = 1–8
m (substituted position of Cl); m =2(-ortho), 3(-meta), 4(-para)

They exhibited a nematic phase. In addition, 8AH4C exhibited the smectic C and A phases. Thus, the 4-chloro-substituted compounds exhibited the liquid crystal phase and also the 2-chloro-and 3-chloro-substituted compounds exhibited that phase.

Those compounds have a core frame of N-2-hydroxybenzylidene-aniline (HBA), which is also known as N-salicylideneaniline(SA). Sometimes HBAs show in the crystalline state photochromism or thermochromism. In recent years, the study on solid photochromic and thermochromic materials has grown because of their possible application in the optical processing of information, in addition to the scientific interest. [10, 11] In the photochromic crystals, the salicylaldimino part of the molecule is planar, but the aniline-ring lies 40–50° out of the plane, and the resulting structure is relatively open with no close face-to-face contacts between molecules.[10, 11] In the thermochromic crystals, the molecules are planar and pack face-to-face with short intermolecular contacts normal to the molecular planes.[11] Therefore, photochromism and thermochromism were generally found to be mutually exclusive properties in the series of crystalline HBAs.[10, 11] Some of nAHmC exhibited the photochromic properties in the solid phase.[12] Through their Raman spectroscopic study, it was found that the band ascribed to the CH deformation vibration and the CCH deformation vibration of the aniline ring closely reflect the molecular conformational change due to the change of the twist angle of the SA part of the nAHmC molecule.[12]

It has been found that the band assigned to the CH out 05-plane deformational vibration of the aniline ring in nAHmC shows an interesting change at the crystalline solid – liquid crystal phase transitions. Through the temperature dependence of the Raman band, we attempted to clarify the change of the molecular conformation related to the liquid crystal core in the different phases in conjunction with information gained in the studies of SAs, as mentioned above.

2. EXPERIMENTAL

4-(4-*n*-Alkoxybenzoyloxy)-2-hydroxybezaldehydes were synthesized by using the method described in an earlier paper.[13] Finally, the substituted benzaldehydes thus obtained were coupled with 2, 3 or 4-chloroaniline 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 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. Furthermore, it should be stressed that the phase-transition temperatures described above based on the texture change are in good accord with those measured from a DSC.

The Raman spectra were obtained with an SPEX 1403 double monochrometor equipped with a photon counting system in a 90° scattering geometry. Radiation of 632.8 nm from a helium – neon laser (NEC GLG 7500) was used to excite the Raman spectra to avoid fluorescence in nAHmCs. A spectral slit width was approximately 6 cm^{-1} and increment was 1 cm^{-1} for the measurement of the internal molecular vibrations (150–1800 cm^{-1}), and a slit width was approximately 1 $cm^{-1}$and increment was 0.5 cm^{-1} for the external vibrations (20–150 cm^{-1}). The powder sample was contained in a glass capillary. The temperature of the sample was controlled to within 0.5°C during the recording of the spectra.

TABLE I Phase transition temperatures of N-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-chloroanilines (nAHmC) /°C

Cl n	4(-para)			3(-meta)			2(-ortho)		
	crystal	nematic	isotropic	crystal	nematic	isotropic	crystal	nematic	isotropic
1	170	298		(127)	173		(149)	157	
2	166	277		(137)	188		140	158	
3	152	285		(118)	150		124	133	
4	127	274		128	131		108	138	
5	120	263		93	123		112	131	
6	117	258		83	127		113	133	
7	116	250		98	122		103	126	
8				103	123		94	126	

8AH4C: crystal-100-smectic-C-153-smectic-A-180-nematic-240-isotropic

The parentheses show the monotropic transitions.

3. RESULTS AND DISCUSSION

The phase transition temperatures of nAHmC are summarized in Table I. In nAH4C, all the homologous series exhibited an enantiotropic nematic phase. 8AH4C also exhibited the smectic C and A phases. In nAH3C, (1–3)AH3C exhibited a monotropic nematic phase. The homologous series with a higher carbon number of the alkoxy group than 3AH3C showed an enantiotropic nematic phase. This characteristic behavior that the enantiotropic nematic phase is observed only for the homologous series with a relatively long alkoxy chain is not unusual as it has frequently been observed as the alkoxy chain length increases in other homologous series of mesomorphic materials.[8] In nAH2C, the first homologue exhibited a monotropic nematic phase. The other homologous series exhibited an enantiotropic nematic phase. Further, a solid-nematic transition temperature for nAH3C or nAH2C is lower than that for nAH4C with the corresponding alkoxy chain. From the comparison of the phase-transition behavior among these homologous series, it is evident that the introduction of a lateral substituent is unfavorable for the appearance of a liquid crystalline phase.

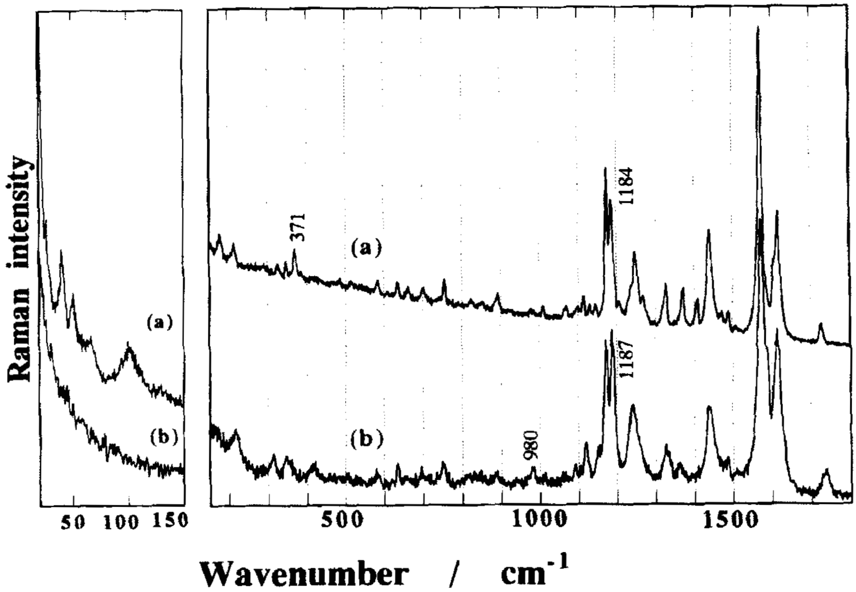


FIGURE 1 Observed Raman spectra of 7AH4C:(a) in the solid (Room temperature) and (b) nematic (129°C) phases

However, it can be clearly recognized that nAH3C and nAH2C exhibit an enantiotropic nematic phase as the end of the long alkoxy chain is lengthened.

The Raman spectra for nAHmC were measured in 20–1800 cm^{-1} at various temperatures. The spectra of (1–3)AH4Cs were not measured because of the high solid-nematic phase transition temperature. The thermal decomposition of nAHmCs began at about 150°C. The spectra of (1–3)AH3Cs and 1AH2C, which were exhibited a monotropic nematic phase, were not measured.

Figure 1 typically shows the Raman spectra of 7AH4C in the nematic(129°C) and solid (room temperature) phases. When 7AH4C undergoes the phase transition from solid to nematic, the Raman bands broaden and some of them decrease in intensity. The solid phase is characterized by three-dimensional order; the molecules move cooperatively. In the liquid-crystal phases, the molecules are loosely coupled to each other and randomly arranged in the direction along the long axis; they move incoherently. Finally, in the isotropic liquid phase, complete disorder prevails, and the molecules undergo a random motion in all dimensions. Furthermore, rotational isomers of the end groups of the liquid crystal molecule appear in the higher-temperature phases.[5, 6] The previous spectroscopic works have been reported that the terminal groups of the liquid crystal molecule melts

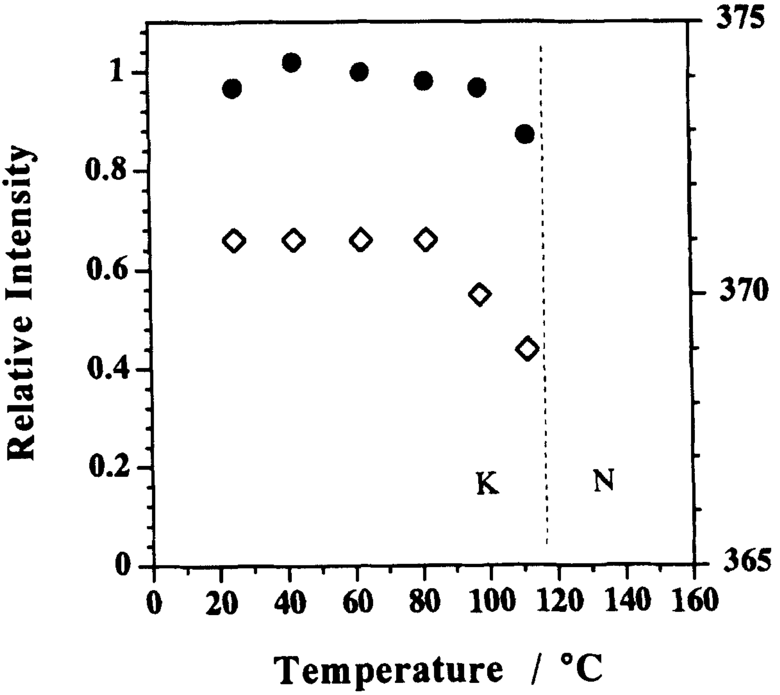


FIGURE 2 Temperature dependence of the intensity and wavenumber of the 371 cm^{-1} Raman band of 7AH4C. The Raman band intensity is measured relative to the 1575 cm^{-1}band. K and N respectively denote solid and nematic phases. ●; intensity, ◊; wavenumber

in the liquid crystal phases, similar to those in the isotropic phase.[5, 6] Thus, the decrease in intensity can be explained by an increase of the degree of randomness in nematic phase. 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 Raman bands due to lattice vibration below 150 cm^{-1}disappear when the three-dimensional order of the crystal lattice is lost by transition to the nematic phase. In the spectral region 150–1800 cm^{-1}, some bands decreased in intensity between the two phases. These decreases can be explained by the increase of the degree of randomness in the nematic phase. The bands in the region of 200 cm^{-1} – 400 cm^{-1} can be assigned to the vibrational modes of the terminal groups.[7] The 371 cm^{-1} band at room temperature can be assigned to the ring-Cl stretching mode.[14] Figure 2 shows the intensity and wavenumber changes of this band as a function of temperature. When 7AH4C undergoes the solid-nematic phase transition, the band

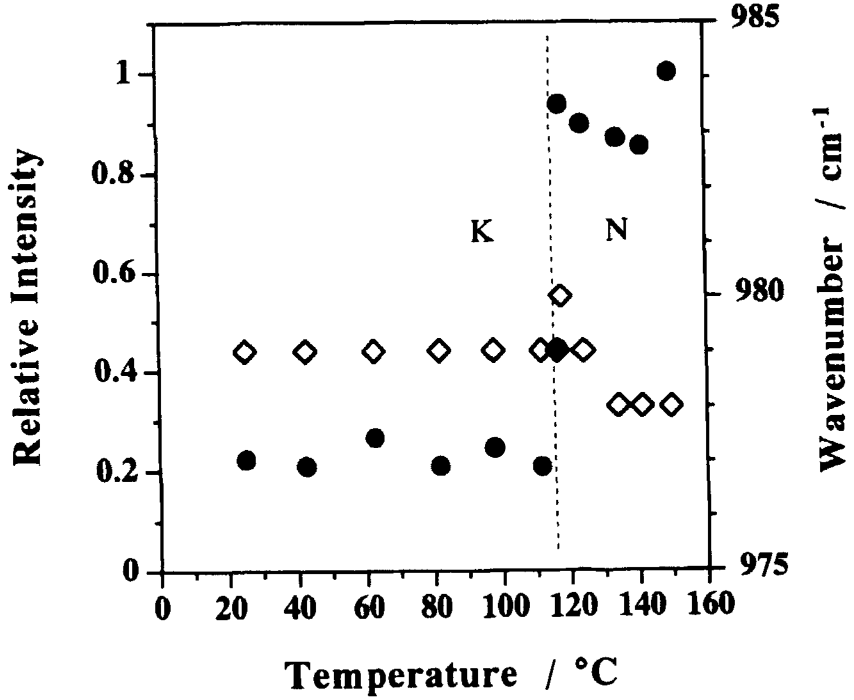


FIGURE 3 Temperature dependence of the intensity and wavenumber of the 979 cm^{-1} Raman band of 7AH4C. ●; intensity, ◊; wavenumber

decreases in intensity and wavenumber and cannot be observed in the nematic phase. In the nematic liquid crystal phase, the molecules are loosely coupled to each other and the end groups randomly rotate.[5, 7] The randomness gives rise to a decrease in the force constant of the ring-Cl bond. Thus, the change of the 371 cm^{-1} band can be explained by an increase of the degree of randomness in the nematic phase. Through the solid-nematic phase transition, the corresponding bands of the other member of nAHmC exhibited similar changes to those bands of 7AH4C. In nAH2Cs and nAH3Cs, a substantial difference in the band between the nematic and isotropic phases was not observed. The band of nAH4Cs in the isotropic phase were not measured because of the high temperature.

The Raman bands at 900–1200 cm^{-1} appeared to change in intensity and wavenumber through the phase transition, as shown in Fig. 1. Figure 3 shows the intensity change and the frequency shift of the 979 cm^{-1} band at room temperature. The intensity and wavenumber of the band increase through the phase tran-

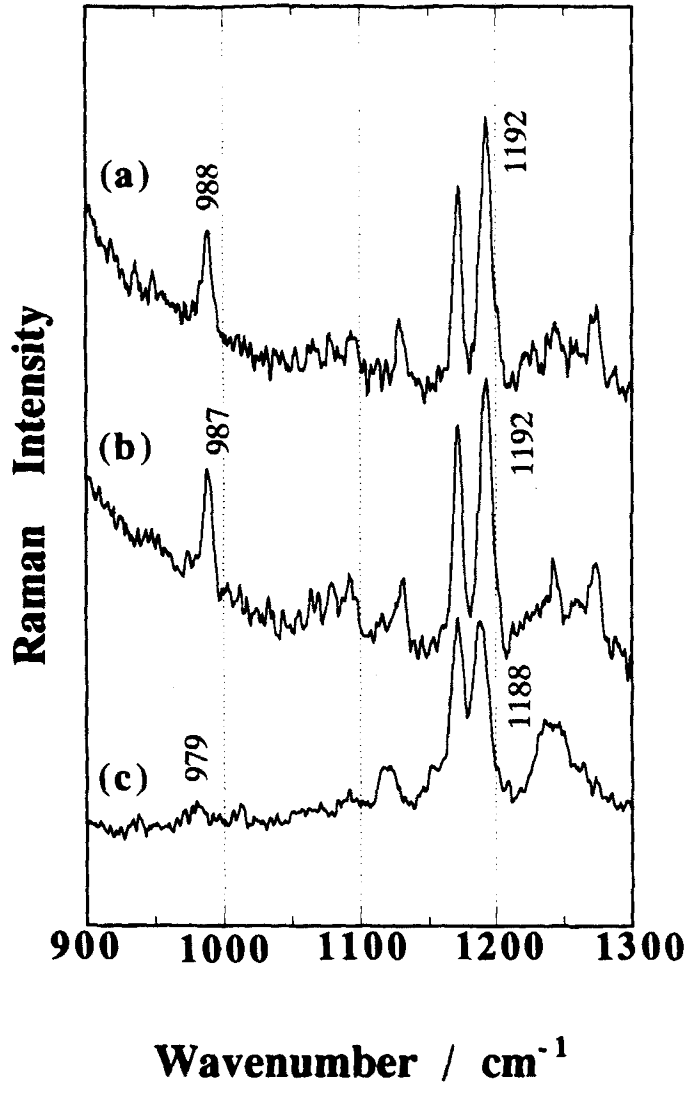


FIGURE 4 Observed Raman spectra of 8AH4C:(a) in the solid (room temperature; 25°C), (b) solid (60°C) and (c) smectic C (108°C) phases

sition solid-nematic. In general, the band can be assigned to the CH out-of-plane deformation vibrational mode of the benzene rings.[16–18] For the convenience of assignment of the vibrational band, N-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxy-benzylidene]-anilines in which hydrogen of the aniline ring was replaced by deuterium was examined. In the deuterated compound, the corresponding band shifted to about 960 cm^{-1}. Hence this band is confirmed to relate to the vibrational mode of the aniline ring. The temperature dependence of the 979 cm^{-1} band can be explained by the change of the twist angle of the aniline ring out of the Shiff base plane.[4, 12] That is, the change of the molecular conformation causes a change in the steric interaction between the hydrogen of the Schiff base and the hydrogen atoms of the aniline ring. A further explanation will be described below. In (2–8)AH2Cs, the temperature dependence of the corresponding band was similar to that of 7AH4C described above. These compounds were non-photochromic in the solid phase.[12] The CH out-of-plane deformation vibrational modes of the other member of nAHmCs showed different behavior from the member described above. Figure 4 shows the Raman spectra of 8AH4C in the smectic C (116°C) and solid(53°C) phases. The 988 cm^{-1} band disappeared through the phase transition crystalline solid-smectic C(SmC). A weak shoulder band appeared at lower wavenumber side of the 988 cm^{-1} band with increasing temperature. The weak band remained in the smectic C phase. The band is presumably assigned to the CH out-of-plane deformation vibrational mode of the aniline ring. However, it is difficult to explain exactly the behavior of the band at this stage because of the very weakness in intensity. Figure 5 shows the temperature dependence of the 988 cm^{-1} band. The corresponding band at about 990 cm^{-1} in (4–8)AH3C and (4–6)AH4C exhibited the temperature dependence similar to that of 8AH4C. These compounds were more or less photochromic in the solid phase.[12]

It is of interest that the different temperature dependence of the band ascribed to the same vibrational mode has been observed between two groups of nAHmCs. In the photochromic crystals, the salicylaldimino part of the molecule is planar, but the aniline ring lies 40–50° out of the plane.[10, 11] Therefore, the aniline ring in those groups of nAHmCs is considered to adopt a non-planar conformation with respect to the other part of the molecule, whereas, in the non-photochromic group of nAHmCs, the molecule adopts a planar conformation. Such difference in conformation causes a change in the steric interaction between the hydrogen of Schiff base(-CH=N-) and the hydrogen of the aniline ring.[4] Consequently, the CH out-of-plane deformation vibrational modes may be affected by the change in the force constant of the steric interaction. Mizuno and Shinoda have reported [4] that the twist angle of the aniline ring out of the C=N-C plane of MBBA (4-methoxybenzylidene-4-*n*-butylaniline) changes at phase transition. The CH in-plane deformation vibrational mode at 1160–1170 cm^{-1} is affected by the change in the force constant of the steric interaction. The mode have different frequencies depending on the twist angles. Here, it is considered that in the non-planar conformation the band ascribed to the CH out-of-plane deformational

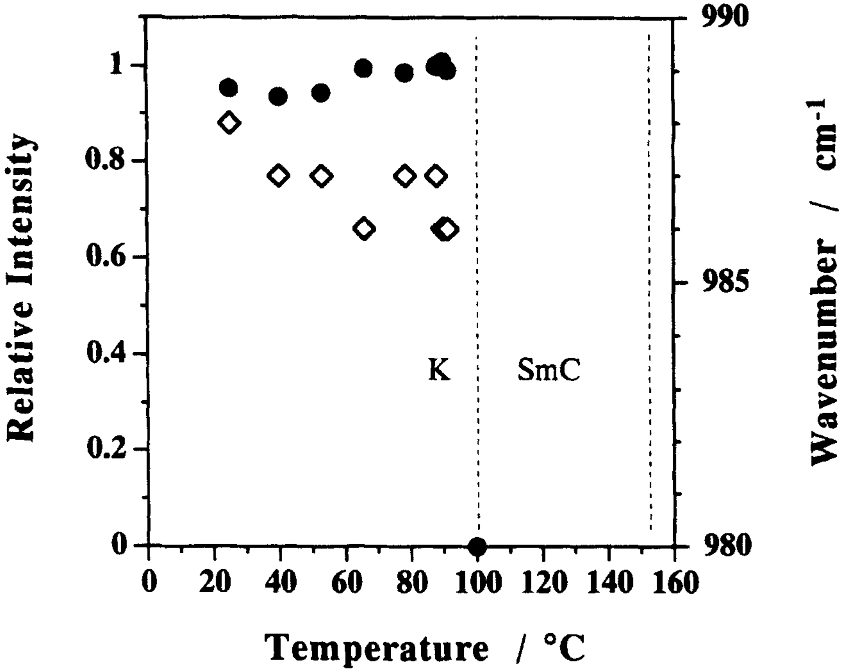


FIGURE 5 Temperature dependence of the intensity and wavenumber of the 988 cm^{-1} Raman band of 8AH4C. K and SmC respectively denote solid and smectic C phases. ●; intensity, ◊; wavenumber

vibration is strong in intensity and high in wavenumber because of a weak (or little) steric interaction due to the long distance between the hydrogen of the Schiff base and the hydrogen of the aniline ring. On the other hand, the band in the planar conformation is weak in intensity and low in wavenumber because of steric hinderance due to the short distance between the hydrogen of the Schiff base and the hydrogen of the aniline ring. Thus, in two groups, the different behavior of temperature dependence of the band at about 990 cm^{-1} can be explained by the different internal rotation of the aniline ring out of the other part in the solid phase. In the non-photochromic group, the non-planar conformation with a large twist angle is presumably increased through the solid-liquid crystal phase transition. On the other hand, the degree of randomness in the molecule increases with increasing temperature. In this case, the effect of the change of conformation is considered to be larger than that of the randomness. Hence the intensity and the frequency of the band increase in the liquid crystal phase. In the photochromic group, the planar conformation with a small twist angle is increased. In addition to this change of conformation, the randomness increases in the nematic phase. Hence the band decreases in intensity and wavenumber in liquid crystal phases.

The band at 1185 cm^{-1} in 7AH4C increased through the phase transition crystalline solid-nematic, as shown in Figure 6. The band has been assigned to the benzene ring-N (ϕ-N) bond stretching vibrational mode.[16, 17, 19] In the deuterated compound, the corresponding band shifted to about 1160 cm^{-1}. Hence this band is confirmed to relate to the vibrational mode of the aniline ring. In (2–8)AH2Cs, the temperature dependence of the corresponding band was similar to that of 7AH4C described above. These compounds were not photochromic and the molecule adopted a planar conformation in crystalline solid phase, as mentioned above.

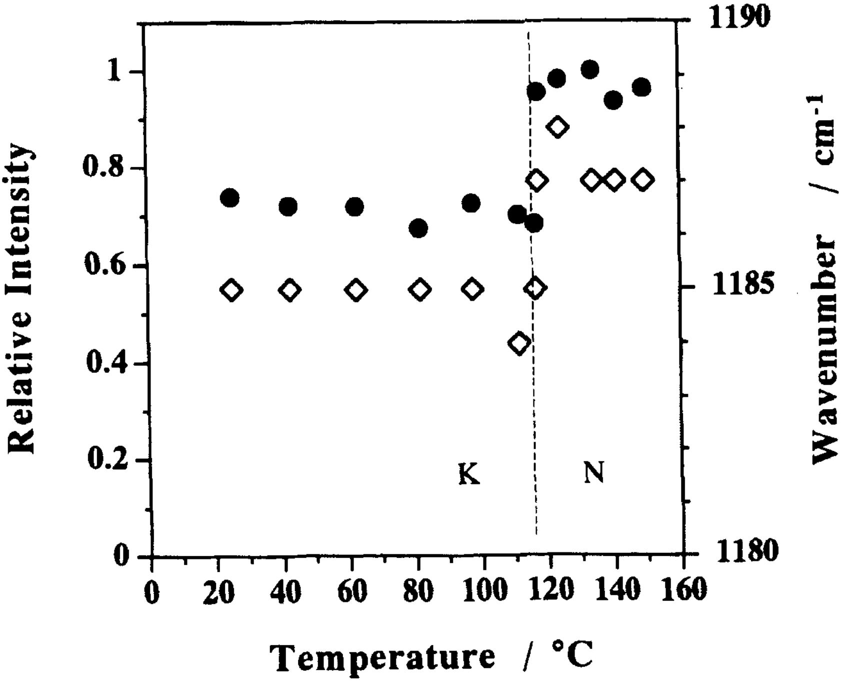


FIGURE 6 Temperature dependence of the intensity and wavenumber of the 1184 cm^{-1} Raman band of 7AH4C. ●; intensity, ◊; wavenumber

The 1192 cm^{-1} band in 8AH4C decreased in intensity and wavenumber through the phase transition solid-SmC, as shown in Figure 7. This band is assigned to the ϕ-N stretching vibration. The corresponding band at about 1190 cm^{-1} in (4–7)AH3C and (4, 6)AH4C exhibited the temperature dependence similar to that of 8AH4C. There was not a substantial difference in the band between the nematic and the isotropic phases for (4–7)AH3Cs. These compounds were photochromic and the molecule adopted a non-planar conformation, as mentioned above.

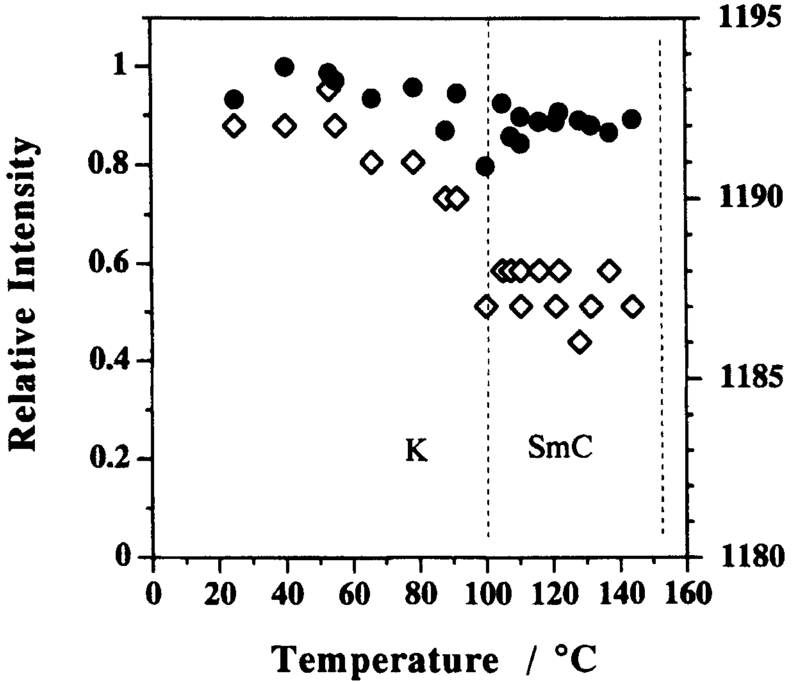


FIGURE 7 Temperature dependence of the intensity and wavenumber of the 1192 cm^{-1} Raman band of 8AH4C. ●; intensity, ◊; wavenumber

The temperature dependence of the ϕ-N bond stretching vibrational mode can be explained by the change of the twist angle, in analogy with the CH deformation vibration. It has been reported in the study of N-benzylideneaniline, which aromatic frame is similar to nAHmC, that the increase in non-coplanarity of the aniline ring provides for effective participation of the nitrogen lone pair.[17] The participation results in the shift of the ϕ-N band to a higher wavenumber. In 7AH4C, the increase of the ϕ-N band in intensity and wavenumber through the phase transition can be explained by an increase of the non-planar molecular conformation. On the other hand, in 8AH4C, the band decreases in intensity and wavenumber by an increase the planar molecular conformation. This gives support to the discussion of the CH deformation vibration mentioned above. The corresponding band in 5AH4C and 8AH3C. which were photochromic, remained unchanged through the phase transition. Thus, the ϕ-N bond stretching mode is considered to be less sensitive to the change of molecular conformation than the CH deformational mode.

The difference in conformation described above is considered to affect the vibrational modes related to the Schiff base. However, such the interest behavior found in the CH out-of-plane deformation vibrational mode and the ϕ-N bond stretching mode was not observed for the modes related the Schiff base for all nAHmCs studied. For example in 7AH4C, the band around 1620 cm^{-1} slightly increased in intensity with increasing temperature. This band has assigned to the coupling mode of the C=N stretching and the vibrational mode of the benzene ring(ν_8).[20] Accordingly, it is considered that the influence of the change of conformation does not explicitly appear in the band. With regard to this feature, a detailed study is in progress.

In nAH2Cs and nAH3Cs, there is not a substantial difference between the nematic and isotropic liquid phases on the CH out-of-plane deformation vibrational mode and the ϕ-N bond stretching mode. Hence a difference of the molecular structure between the nematic and isotropic phases was not observed from Raman scattering study.

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