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Raman spectroscopy of liquid crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-aminopyridines

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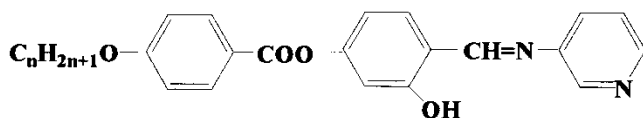
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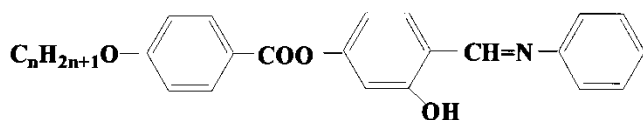
New homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-aminopyridines were synthesized, they exhibited a nematic phase. The temperature dependence of their Raman spectra has been observed in the spectral range 900–1800 cm⁻¹. Some Raman bands show a marked change in their intensity and frequency through the phase transition from crystalline solid to nematic. These bands are ascribed to the vibrational modes related to the core part of the molecule. Such behaviour can be explained by the change of molecular conformation related to the core. Some members of these series exhibited photochromism in the solid state.

1. Introduction

We have previously studied liquid crystalline *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-*X*-anilines [*n*AHXA], in which *X* is Cl, OH or CH₃, by Raman spectroscopy [1–3]. Now, the *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-3-aminopyridines [*n*AHAP (*n* = 1–8)] have been synthesized.



For comparison of phase transition temperatures, the *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]anilines [*n*AHA (*n* = 1–8)] have also synthesized.



In the *n*AHAPs, the aniline ring of the *n*AHAs is replaced by 3-aminopyridine.

A number of liquid crystalline compounds containing a heterocyclic ring have been reported [4–9]. The introduction of heteroatoms causes considerable changes in chemical and physical properties and influences the type of liquid crystal phase, the phase transition temperatures and other properties of the mesogens [9]. The compounds *n*AHAP all exhibited a

nematic phase. Their phase transition temperatures differed appreciably from the corresponding benzene analogues *n*AHA.

Raman spectroscopy is known as a very powerful technique in the study of vibrational dynamics of liquid crystals [10, 11]. The significance of this technique is that the phase transitions in liquid crystals are reflected as variations in measurable parameters of certain vibrational modes [11]. In particular, the measurement and analysis of intensities provide information about the conformation change of the liquid crystalline molecule during phase transitions [10–14]. We have measured the temperature dependence of some Raman bands associated with the core part of *n*AHAP molecules. The Raman bands change in intensity and frequency through the crystalline solid–nematic liquid crystal phase transition. The temperature dependence of the bands can be explained by a change of molecular conformation related to the core.

N-2-hydroxybenzylidene-aniline [HBA], also known as *N*-salicylideneaniline (SA), shows photochromism or thermochromism in the crystalline state [15, 16]. In recent years, the study of solid photochromic and thermochromic materials has grown because of their possible application in the optical processing of information, in addition to their scientific interest. *N*-salicylidene-3-aminopyridines, in which the molecular structure is similar to that of HBA, are weakly thermochromic but not photochromic in the solid state [17]. However, the compounds (4, 6 and 8)AHAP exhibited a weak photochromism in the solid phase.

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The results obtained on this photochromism are described briefly.

2. Experimental

4-(4-*n*-Alkoxybenzyloxy)-2-hydroxybenzaldehydes were synthesized using the method described earlier [18]. The substituted benzaldehydes thus obtained were coupled with 3-aminopyridine by heating under reflux in an ethanol solution. The crude product was purified by repeated 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. Checks on the transition temperatures were made using a Shimadzu differential scanning calorimeter (DSC). Each sample was heated and cooled under a flow of nitrogen to prevent decomposition. The phase transition temperatures based on texture change were in good accord with those measured by DSC.

The Raman spectra and the UV absorption spectra were measured with the same apparatus and techniques as those described in previous reports [1–3].

3. Results and discussion

3.1. Phase transitions

The phase transition temperatures of the *n*AHAPs are summarized in table 1. Included in the table for comparison are the phase transition temperatures of the *n*AHAs. In the *n*AHAPs, all of the homologous series exhibited an enantiotropic nematic phase. A crystalline solid (Cr)–nematic (N) transition temperature for *n*AHAPs is lower than that for *n*AHAs with the corresponding alkoxy chain, except for 1AHAP. That of 1AHAP is 30°C higher than that of 1AHA. Furthermore, the N–isotropic (I) transition temperature for *n*AHAPs is higher than that for *n*AHAs with corresponding alkoxy chain, except for 1 and 2 AHAs. The N–I transition temperature of 1AHAP is equal to that of 1AHA, while that of 2AHAP is slightly lower than that of 2AHA.

Table 1. Phase transition temperatures (°C) of *n*AHAP and *n*AH compounds.

<i>n</i>	<i>n</i> AHAP		<i>n</i> AHA	
	Nematic	Isotropic	Nematic	Isotropic
1	157	197	127	197
2	143	198	171	202
3	137	183	155	179
4	110	195	130	182
5	107	189	127	170
6	114	173	123	161
7	99	176	114	160
8	105	174	110	159

The thermal stability of the liquid crystal state depends on the anisotropy of the molecules forming the state [5]. The anisotropy of such molecules is largely determined by the polarizability along their major axis. The presence of a nitrogen atom in the ring in no way changes the molecular geometry in comparison with the corresponding benzene analogue [5]. However, it may change the polarizability along the long axis, depending on its position in the aromatic ring, since the nitrogen atom has a higher electron density relative to the carbon atoms of the ring. As a result, it reduces polarizability in this direction. Thus, the replacement of the benzene ring by a pyridine ring decreases the thermal stabilities of the liquid crystal phase. In the studies of 2-alkoxy-5-(4-alkoxy-4-benzylidene)aminopyridine and 2-alkyl-5-(4-alkoxy-4-benzylidene)aminopyridine [6, 7], it has been reported that N–I transition temperatures were lower for the heterocyclic compounds than for the corresponding benzene analogues. This explains the decrease in Cr–N phase transition temperatures for *n*AHAPs. However, in 3–8AHAPs, the N–I phase transition temperatures were higher than for the corresponding benzene analogues, as described above. This behaviour is difficult to explain and more work is needed to understand it. Moreover, the unusual behaviour of 1AHAP is difficult to explain at this stage.

3.2. Raman spectra

The Raman spectra for *n*AHAPs were recorded in the 20–1800 cm⁻¹ range at various temperatures. The spectra of (1–3)AHAPs were not measured because of the high Cr–N phase transition temperature. The spectra of (4–8)AHAPs in the isotropic liquid phase were also not measured because of high temperatures; thermal decomposition of *n*AHAPs began at about 130°C.

It has been realized that pyridine and benzene have a remarkably similar set of fundamental frequencies [19]. The presence of a nitrogen atom in the ring in no way change the molecular geometry in comparison with the corresponding benzene analogue [5], as mention above. It could be expected that the spectrum for *n*AHAP would not differ greatly from that for *n*AHA with the corresponding alkoxy chain. The Raman spectrum of *n*AHAP was similar to that of *n*AHA; hence, the assignment of vibrational modes between the pyridine derivative and benzene derivative cannot be considered to differ greatly.

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 along the molecular 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 [14]. Hence, lattice mode Raman bands disappear as the three-dimensional order of crystal lattice is lost by transition to higher temperature phases [20, 21]. The alkyl chain of the liquid crystal molecule melts in the liquid crystal phases, similar to those in the isotropic phase [10–14]. The decrease in intensity in the alkyl chain mode region can be explained by an increase of the degree of randomness in liquid crystal phases. The temperature dependence of Raman bands in these two regions is not reported here, because these bands showed a similar behaviour to those reported previously.

We now report the temperature dependence of prominent Raman bands of *n*AHAPs in the 900–1800 cm^{-1} spectral region (mainly associated with the core part of the molecule). It is interesting to correlate the change in the Raman bands associated with the core part of the molecule as a function of temperature with intra/inter molecular interactions and the resulting dynamics of the core. The Raman bands around 1250 and 1720 cm^{-1} are ascribed to the vibrational modes of the COO– group and have been studied in detail [22, 23]. The Raman bands due to those modes for *n*AHAPs showed similar temperature dependence; the temperature dependence of these bands is therefore not discussed here.

Figure 1 typically shows the Raman spectra of 7AHAP in crystalline solid (Cr) (room temperature) and nematic (N) (103°C) phases. Some of the bands

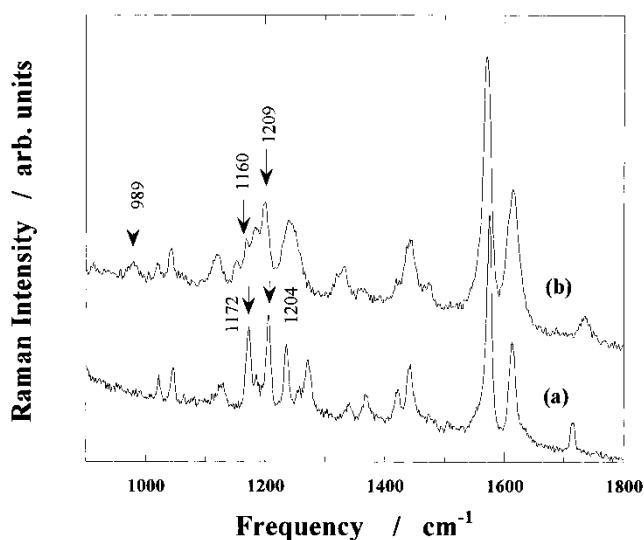


Figure 1. Raman spectra of 7AHAP: (a) solid (room temperature: 25°C), (b) nematic (103°C).

showed an abrupt change in intensity through the Cr–N phase transition.

The Raman band at 989 cm^{-1} in the N phase is not prominent but exhibits a considerable change through the phase transition Cr–N, as shown in figure 1. The band was not observed in the Cr phase but appeared clearly in the N phase. Figure 2 shows the intensity change and frequency shift of the band as a function of temperature. The weak band for 5AHAP increased in intensity and frequency through the Cr–N phase transition, similar to that of 7AHAP. In (6, 8)AHAPs, the corresponding band was very weak and the temperature dependence could not be clearly measured. The weak band of 4AHAP slightly decreased in the N phase. We have previously reported that the band at about 975 cm^{-1} shows a similar temperature dependence in the liquid crystalline benzene analogue with similar molecular structure to *n*AHAPs [1, 3]. Those compounds have an aniline ring in place of the aminopyridine ring of *n*AHAPs. The band around 975 cm^{-1} can be assigned to the CH in-plane deformation vibrational mode of the aniline rings [24–26]. It has been considered that the twist angle of the aniline ring, out of the C–N–C plane of the aniline compounds, changes through a phase transition [13]. That is, the change of the molecular conformation causes a change in steric interaction between the hydrogen of the Schiff's base and the hydrogen atoms of the aniline ring.

The *n*AHAP compounds have a core frame of HBA, as mentioned above. Sometimes HBAs show photochromism or thermochromism in the crystalline state. In the photochromic crystals, the salicylaldimino part of the molecule is planar, but the aniline ring lies 40°–50° out-of-plane, and the resulting structure is

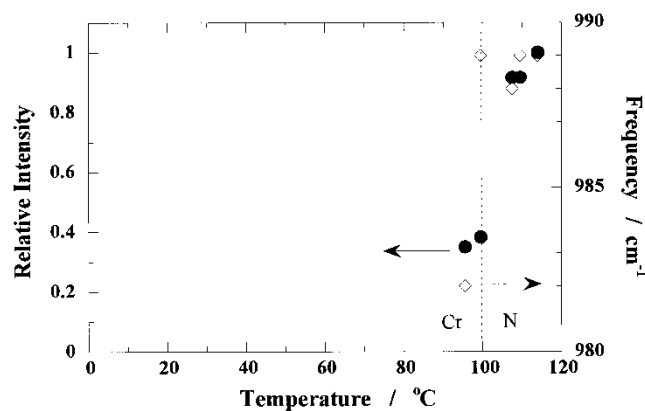


Figure 2. Temperature dependence of the intensity and frequency of the 989 cm^{-1} Raman band of 7AHAP. The band intensity is measured relative to the 1573 cm^{-1} band. ● intensity, ◇ frequency.

relatively open with no close face-to-face contacts between molecules [15, 16]. In the thermochromic crystals, the molecules are planar and pack face-to-face with short intermolecular contacts normal to the molecular planes [16]. Accordingly, photochromism and thermochromism were generally found to be mutually exclusive properties in the series of crystalline HBAs [15, 16]. Thus, the HBA part of molecule in non-photochromic *n*AHAP compounds is considered to adopt a planar conformation with respect to the other part of the molecule, and the HBA part in photochromic *n*AHAP compounds to adopt a non-planar conformation.

Through the Raman spectroscopic study of *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]methylanilines [AHMs] analogous to the *n*AHAPs, it was found that in photochromic compounds the band ascribed to the CH in-plane deformation vibration showed considerable intensity [3]; it decreased abruptly at the Cr–N phase transition. On the other hand, the corresponding band showed weak intensity or was unobservable in the other members that were non-photochromic. The band increased in intensity and frequency in higher temperature phases. The different temperature dependence of the CH in-plane deformational vibration mode has been explained by the different temperature dependence of the molecular conformation. In the non-planar conformation (photochromic), the band is strong in intensity and of high frequency because of a weak steric interaction due to the long distance between the hydrogen of the Schiff's base and the hydrogen of the aniline ring. On the other hand, the band in the planar conformation is weak in intensity and of low frequency because of steric hindrance due to the short distance between the hydrogen of the Schiff's base and the hydrogen of the aniline ring. In the photochromic group with non-planar conformation in the solid, the twist angle between the aniline ring and Schiff's base is reasonably considered to decrease during the Cr–N phase transition; hence the intensity and the frequency of the band decrease in the N phase. In the non-photochromic group with planar conformation in the solid, the twist angle is considered to increase; and the intensity and the frequency of the band increase in the N phase. Thus, the variable behavior of the temperature dependence of the band is explained by the different internal twist in the aniline ring in relation to the rest of the molecule.

In *n*AHAPs, the band around 990 cm^{-1} can be assigned to the CH in-plane deformation vibrational mode of the pyridyl ring because the Raman spectrum does not greatly differ from that of the benzene analogue, as mentioned above. The compound 7AHAP is non-photochromic and the band ascribed

to the CH in-plane vibration is not clearly observed in the solid. Accordingly, in the Cr phase of 7AHAP, the twist angle of the pyridyl ring with respect to the rest part of the molecule may be small. The angle presumably increases through the phase transition Cr–N. It is considered that in the Cr phase the band ascribed to the CH in-plane deformational vibration is not seen because of steric hindrance due to the short distance between the hydrogen of the Schiff's base and the hydrogen of the pyridyl ring. In the N phase, the band appears because of a weak steric interaction due to the long distance between the hydrogen of the Schiff's base and the hydrogen of the pyridyl ring. The compound 4AHAP is considered to have the non-planar conformation in the solid because of the photochromic one. The twist angle between the pyridyl ring and the Schiff's base is presumably decreased during the Cr–N phase transition; hence the intensity of the band decreases in the N phase.

The prominent 1172 cm^{-1} band at room temperature decreases through the Cr–N phase transition. Figure 3 shows the intensity change and frequency shift of this band. The corresponding band of the other members exhibited similar temperature behaviour to that of 7AHAP. This band is assigned to the C(ring)–O(alkoxy) stretching vibration [11]. The alkoxy chain part of the molecule is considered to assume higher degrees of orientational and vibrational freedom on melting, as mentioned above. This can affect the force constant of the C–O stretching mode; thus, the 1172 cm^{-1} band may decrease in intensity and frequency in the N phase.

The band at 1204 cm^{-1} slightly decreased in intensity and increased in frequency through the Cr–N phase transition, as shown in figure 4. The band has been assigned to the C(ring)–N (Schiff's base) stretching

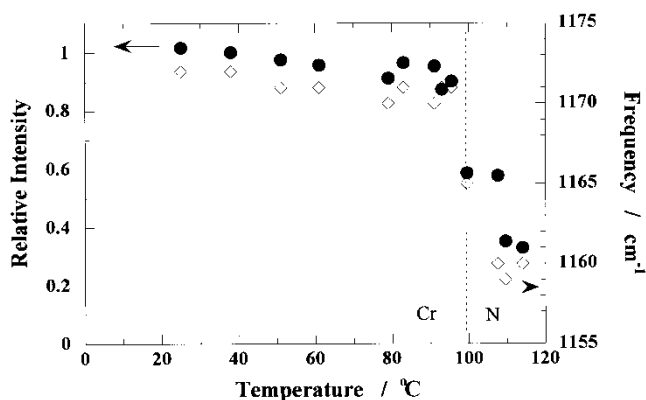


Figure 3. Temperature dependence of the intensity and frequency of the 1172 cm^{-1} Raman band of 7AHAP: ● intensity, ◇ frequency.

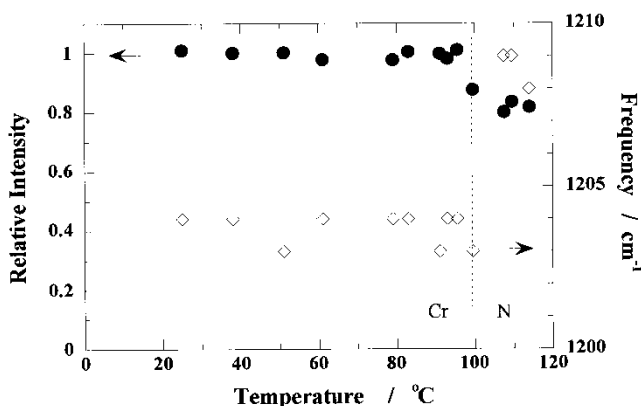


Figure 4. Temperature dependence of the intensity and frequency of the 1204 cm^{-1} Raman band of 7AHAP: ● intensity, ◇ frequency.

vibrational mode [11, 25, 26]. In the other n AHAPs, the temperature dependence of the corresponding band was similar to that of 7AHAP. The temperature dependence of the C–N bond stretching vibrational mode can be explained by the change of the twist angle, in analogy with the CH in-plane deformation vibration. Such a rotation around the C–N bond would result in an increasing of degree of structural disorder of the molecule; accordingly, the band decreases in intensity. It has been reported in the study of *N*-benzylideneaniline, whose aromatic frame is similar to n AHAP, that the increase in non-coplanarity of the aniline ring provides for effective participation of the nitrogen lone pair [26]. This participation results in the shift of the C–N band to a higher frequency. However, the change in frequency was not significant, as shown in figure 4. Thus, the C–N stretching mode is considered to be less sensitive to change of molecular conformation than the CH in-plane deformational mode.

The change of molecular conformation described above may be expected to affect the other vibrational modes related to the core. The band at 1613 cm^{-1} slightly increases in intensity as 7AHAP undergoes the phase transition. The band has been assigned to the coupling mode of the C–N stretching and the vibrational mode of the ring [27]. Accordingly, the influence of the change of molecular conformation can be considered to be small and the change in intensity is not significant. The Raman band at 1439 cm^{-1} for 7AHAP has been assigned to the in-plane ring vibration [22]. Hence, hardly any change of the band was observed through the phase transition.

3.3. Photochromism

The compounds (4, 6, 8)AHAP exhibited weak photochromism in the crystalline solid phase; these

Table 2. Rate constants of n AHAP compounds.

n	k_1/s^{-1}	k_2/s^{-1}
4	6.8×10^{-4}	4.4×10^{-5}
6	4.8×10^{-3}	6.9×10^{-5}
8	5.6×10^{-4}	3.3×10^{-5}

are yellow or pale yellow when freshly prepared. At room temperature the colour of the homologues exhibiting photochromism deepened to orange under UV irradiation. Kinetic analysis of the thermal fading of the species coloured by UV irradiation exhibited a good fit to a double-exponential equation, consisting of a two-stage transient decay (rate constants k_1 and k_2) [28]. The rate constants for each homologue are shown in table 2. The rate constants for 4AHAP and 8AHAP were almost equivalent to those observed with photochromic HBA [28]. The rates for 6AHAP were faster than those of HBA. It must be stated that there is no definite correlation between photochromism and the length of the terminal alkoxy chain.

N-Salicylidene-3-aminopyridines are not photochromic in the solid state [18], as described above; the chromophore of the compounds studied is *N*-salicylidene-3-aminopyridine. However, (4, 6, 8) AHAPs exhibited photochromism. This may be a change of molecular conformation for the chromophore in n AHAPs. The occurrence of photochromism depends on various factors: molecular structure, molecular packing, molecular conformation, etc. [15]. A more detailed understanding of the photochromic behaviour of n AHAPs is at present not available.

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