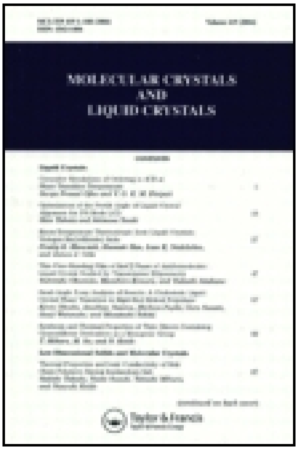

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FT-IR Studies of N-(p-Cyanobenzylidene)-p-Octyloxyaniline, 4′-Cyanobenzylidene-4-n-Hexyloxyaniline and 4′-n-Hexyloxybenlidene-4-Cyanoaniline

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FT-IR Studies of *N*-(*p*-Cyanobenzylidene)-*p*-Octyloxyaniline, 4′-Cyanobenzylidene-4-*n*-Hexyloxyaniline and 4′-*n*-Hexyloxybenlidene-4-Cyanoaniline

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The phase transitions of three related liquid crystals, *N*-(*p*-cyanobenzylidene)-*p*-octyloxyaniline (CBOOA), 4′-cyanobenzylidene-4-*n*-hexyloxyaniline (CBHA), and 4′-*n*-hexyloxybenlidene-4-cyanoaniline (HBAB) are studied by Fourier transform infrared spectrometry. The frequency, intensity and shape of the CN stretching band at 2200–2240 cm^{-1} are examined as a function of temperature. Shifts in the frequency and changes in the integrated band intensity are correlated with the different mesogenic states. Although a shift in frequency is noted only at the crystal to first mesogenic transition, distinct changes in the integrated band intensity are present at each of the phase transitions.

Keywords: n-(p-cyanobenzylidene)-p-octyloxyaniline, 4′-cyanobenzylidene-4-n-hexyloxyaniline, hexyloxybenlidene-4-cyanoaniline, FT-IR Band Shapes, liquid crystal transitions.

INTRODUCTION

For many years, infrared (IR) spectroscopy has been used to characterize the physical properties of mesogenic compounds such as their transition temperatures,[1,2] motional dynamics[3,4] and orientational parameters.[5,6] Many spectral features can undergo significant changes as a function of temperature.[7–9] Although most of the IR bands are sharp in the crystalline state, they may broaden, change intensity and shift in frequency between mesophases.[10,11]

Kardan and coworkers[12] have investigated the microstructures in carbonyl containing discotics and have found that the C═O stretching vibration in the 1700 cm^{-1} region is particularly sensitive to the compounds' phase transitions. At the crystal to mesophase transition, the band broadened, its intensity decreased and a shift in frequency from lower to higher wavenumbers was observed. A plot of the integrated intensities of the carbonyl band as a function of temperature was found to abruptly change at temperatures associated with the transitions from the crystal to mesophase and mesophase to isotropic liquid. Similarly, Yang and Walsman[9]

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have studied the individual properties of a series of alkanoate liquid crystal homologs, benzen-hexa-hexanoate (BH6), benzene-hexa-heptanoate (BH7), benzen-hexa-octanoate (BN8) and benzene-hexa-nananoate (BH9) as well as mixtures containing BH7 and BH8. Changes in the 1615 cm^{-1} infrared band, which was present in all of the BH_n compounds, were studied as a function of temperature. Both the shape and integrated intensity of the band were found to be sensitive to and correlated well with the independently determined phase transition temperatures.

In addition to carbonyl containing liquid crystals, many commercially important mesogenic materials contain a nitrile (CN) group. The CN stretching vibration, which occurs in the 2200–2300 cm^{-1} region, also has been used by several investigators to examine the orientational order[13,14] and phase transitions[15,16] of liquid crystals. Likewise, in the current study changes in the infrared spectrum have been used to characterize the thermotropic properties of three liquid crystalline compounds which contain a nitrile head group. The three compounds, which are all commercially available, were *n*-(*p*-cyanobenzylidene)-*p*-octyloxyaniline (CBOOA), 4′-cyanobenzylidene-4-*n*-hexyloxyaniline (CBHA), and 4′-*n*-hexyloxybenlidene-4-cyanoaniline (HBAB). The chemical structures for these mesogens are given in Figure 1. Two of the materials, CBOOA and CBHA, are homologs and the third compound, HBAB, has the same molecular formula as CBHA but has a reversed structure in terms of the imine linkage.

Since CBOOA has been used widely, its physical properties have been studied by a variety of techniques.[16–18] The compound is a dimorphic liquid crystal that has two mesophases (i.e., smectic A and nematic phases) between the crystal and isotropic liquid phases. Although all of its phase transitions, which occur at 72.5°C for the C—S_A, 83°C for the S_A—N, and 106.9°C for the N—I changes, can be detected by optical polarized microscopy, it is difficult to observe the S_A—N transition by differential scanning calorimetry (DSC).[14]

The remaining two compounds, CBHA and HBAB, are monomorphic liquid

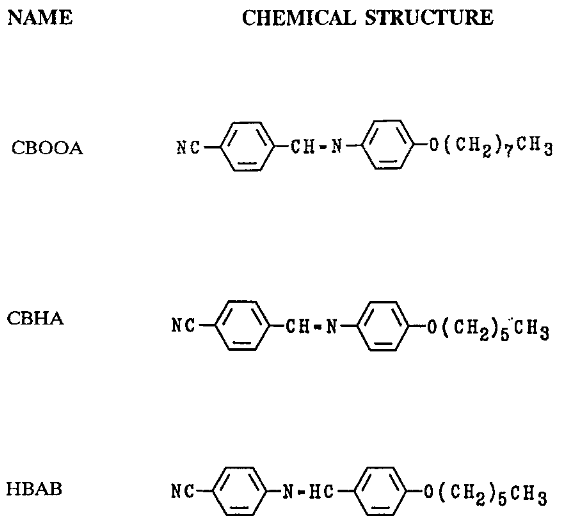

FIGURE 1 Chemical structures for the liquid crystalline compounds studied.

crystals, which do not exhibit smectic behavior but have only nematic states. The phase transitions in CBHA, which is used in electronic display devices,[19] occur respectively at 78°C (i.e., the C—N transition) and 107°C (i.e., the N—I transition). These same transitions are at 56°C and 102°C in HBAB which has been studied extensively by various experimental methods.[20-24]

EXPERIMENTAL SECTION

Materials

Two of the liquid crystals, CBHA and HBAB, were obtained from American Tokyo Kasei, Inc. (Portland, OR, USA) and the third material, CBOOA, was from the Eastman Kodak Company (Rochester, NY, USA). All of these compounds were used without further purification.

Infrared Spectrometric Measurements

The Fourier transform infrared (FT-IR) spectra were recorded in the absorption mode by using a Bomem (Quebec City, Quebec, Canada) Model DA-8 high-resolution FT-IR spectrometer equipped with an MCT detector. In order to obtain uniform sample loading, the solid liquid crystalline samples were placed between two KBr windows, preheated above their crystal to mesogenic phase transition

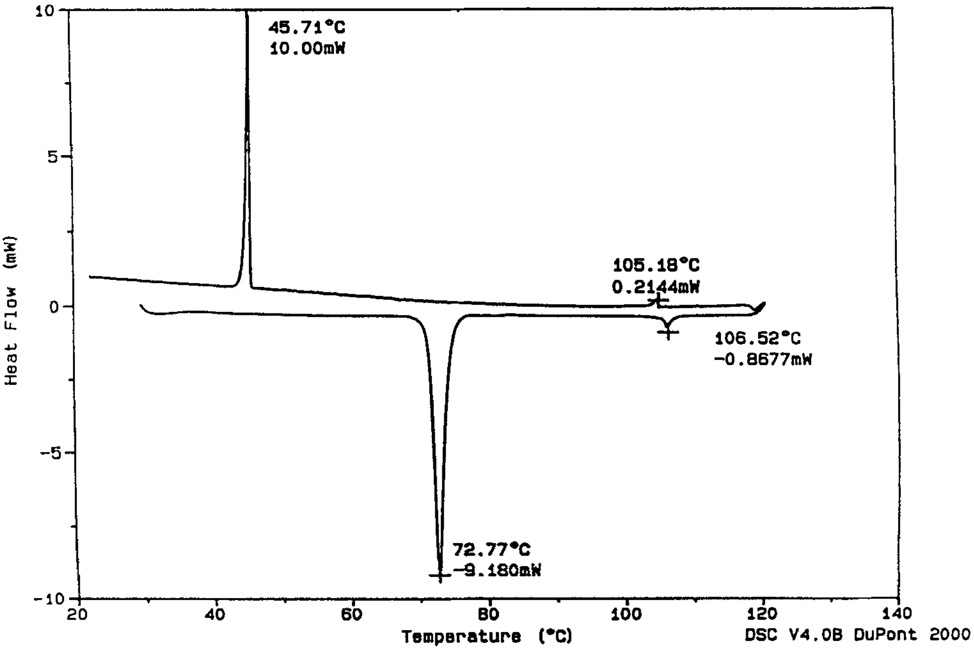

FIGURE 2 DSC thermogram of CBOOA. Conditions: heating curve, 10°C/min; cooling curve 5°C/min; nitrogen atmosphere.

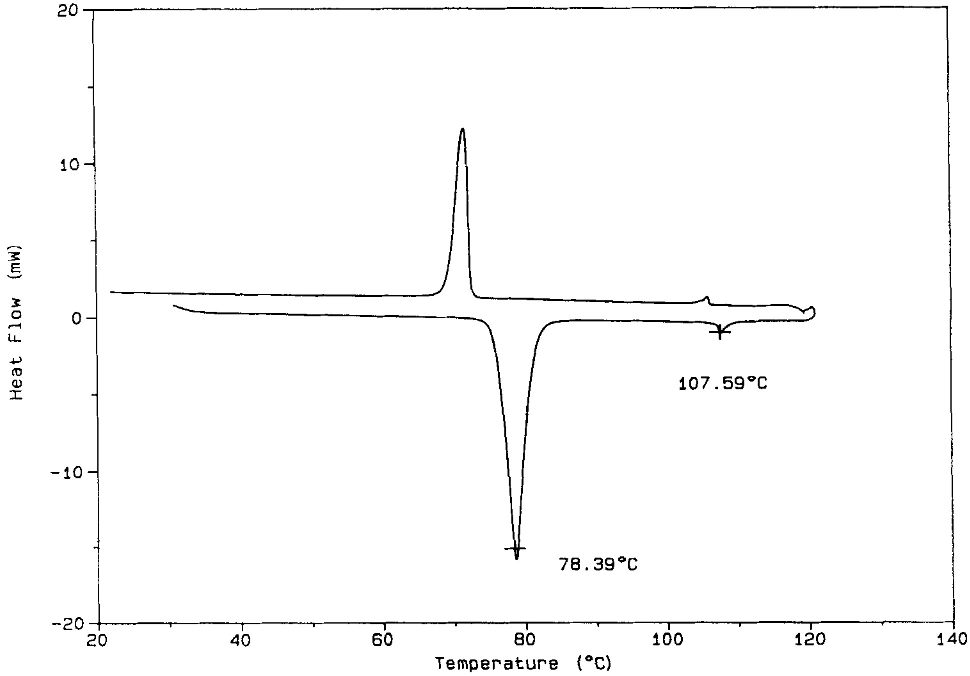

FIGURE 3 DSC thermogram of CBHA. Conditions: see Figure 2.

temperatures, and then cooled to room temperature before carrying out any of the spectral measurements. The temperature of the sample was controlled by using a Eurotherm Corporation (Reston, Virginia, USA) Model 808 hot-stage apparatus. The sample windows were masked to an aperture of approximately 2 mm using brass metal spacers to facilitate uniform heat transfer. Data were collected at a resolution of 0.5 cm^{-1} and transformed using a boxcar appodization. The baseline corrections and spectral manipulations were done using the instrument's software.

Differential Scanning Calorimetric and Optical Microscopic Measurements

The differential scanning calorimetric measurements were carried out with a TA (New Castle, DE, USA) Model 2910 DSC equipped with a controlled cooling Dewar using the TA Model 2000 PC-based controller. The heating and cooling curves were collected at rates of 10°C/min and 5°C/min, respectively, in a nitrogen atmosphere. The optical microscopy was carried out using a Leitz (McHenry, IL, USA) microscope equipped with a set of cross-polarizers and a Mettler Model FP52 hot-stage apparature.

RESULTS AND DISCUSSION

Differential Scanning Calorimetric (DSC) and Optical Microscopic (OM) Studies

The phase transition temperatures for the three liquid crystals initially were determined by both DSC and OM measurements. DSC scans for CBOOA, CBHA

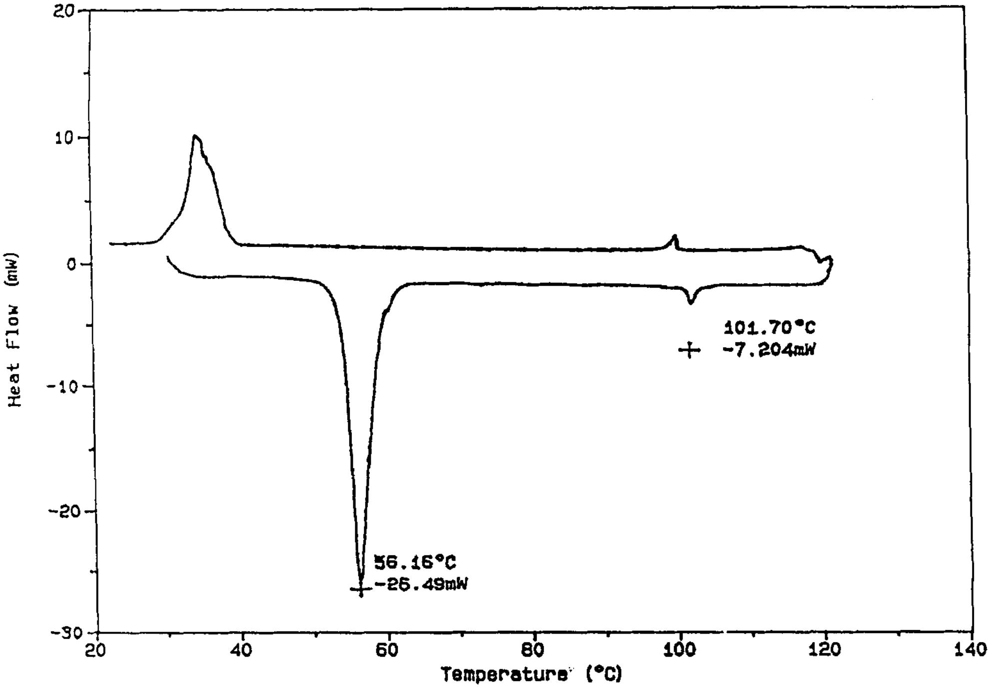

FIGURE 4 DSC thermogram of HBAB. Conditions: see Figure 2.

TABLE I

Transition temperatures for CBOOA, CBHA and HBAB measured by optical microscopy (OM), differential scanning calorimetry (DSC) and infrared spectrometry

Compound	Transition	DSC*	OM*	FT-IR*	Literature*
CBOOA	C - S_A	72.8	72.5	72.5	73.0 [13]
	S_A - N	-	83.0	83.0	83.0
	N - I	106.5	106.9	107.0	106.9
CBHA	C - N	78.4	78.0	77.5	78.0 [25]
	N - I	107.6	107.0	107.0	107.0
HBAB	C - N	56.2	55.8	54.5	56.5 [26]
	N - I	101.7	102.0	101.5	102.2

* All values in °C

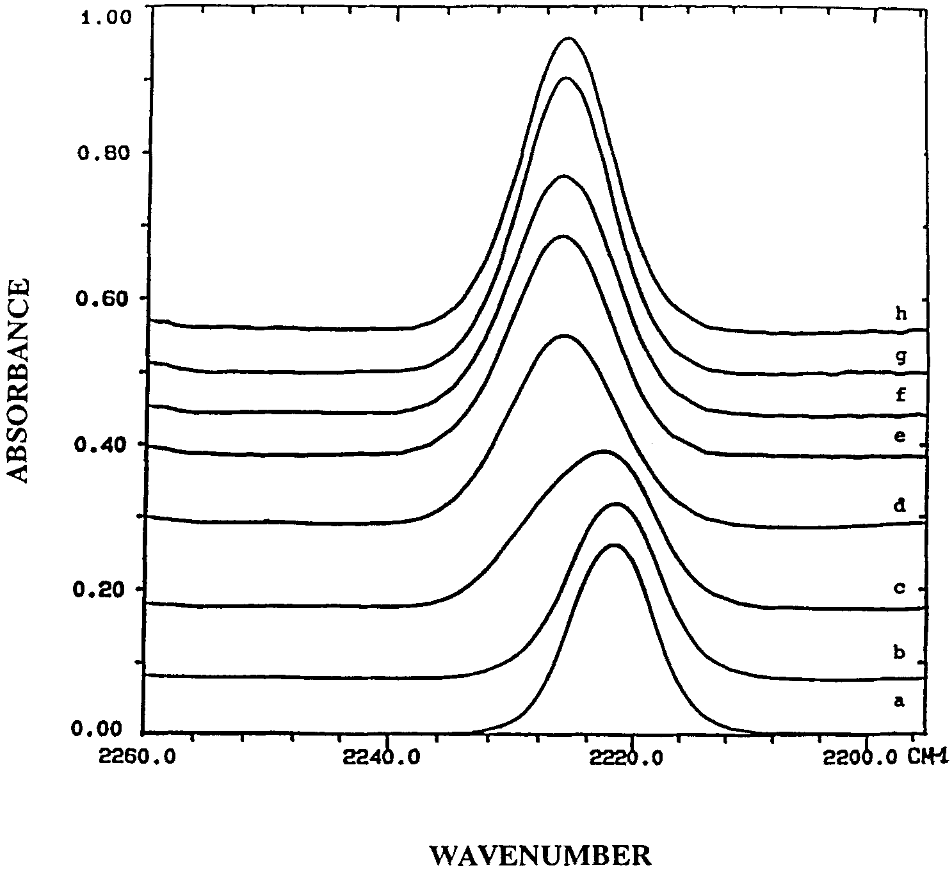

FIGURE 5 Nitrile stretching bands for CBOOA at selected temperatures. (a) 30°C, (b) 71°C [crystalline phase], (c) 72°C, (d) 72.2°C, (e) 72.5°C [smectic phase], (f) 83°C, (g) 107°C [nematic phase], (h) 110°C [isotropic phase].

and HBAB over the temperature range from 30°C to 120°C are shown, respectively, in Figures 2–4. The transitions temperatures for the three liquid crystals are summarized in Table I. The smectic to nematic phase transition for CBOOA was not detected by DSC as has been reported previously[14] and therefore each of the materials also were characterized by polarized OM measurements. The results from these measurements along with reported literature values for the phase transition temperatures also are summarized in Table I. The measured transition temperatures agreed with previously reported literature values as well as with those obtained by FT-IR as discussed below.

Infrared Studies

In carrying out the current study, IR spectra were acquired at 5°C intervals in the temperature range 30–110°C, however, near the phase transition temperature, the interval was reduced to 1°C and further reduced to 0.1°C at the phase transition temperature. Of particular interest were changes in the nitrile stretching vibration.

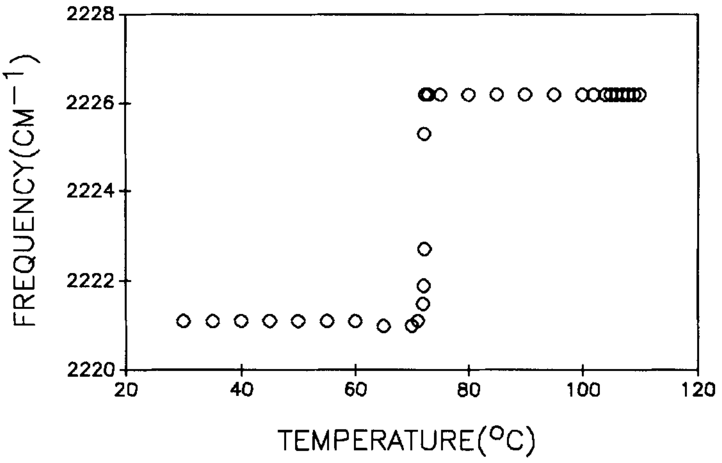

FIGURE 6 Changes in band frequency as a function of temperature for CBOOA.

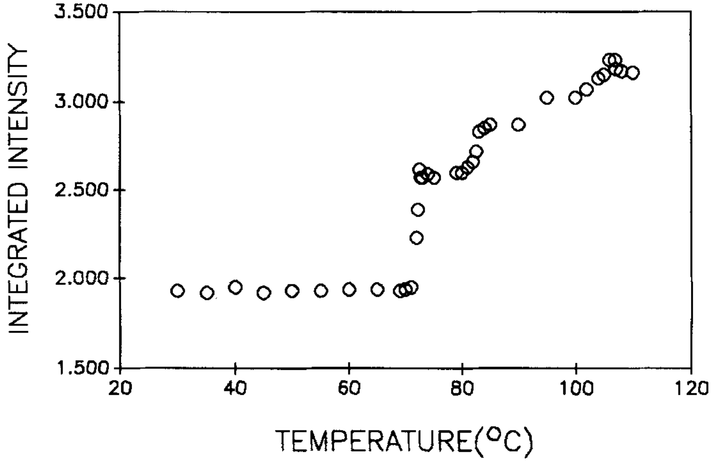

FIGURE 7 Changes in integrated intensity as a function of temperature for CBOOA.

The CN bands in all three samples were distinct and free from any overlap with neighboring bands.[13]

Shown in Figure 5 are representative infrared absorption spectra from the nitrile stretching region (2200–2240 cm^{-1}) for CBOOA. These spectra were obtained by a 4 point smoothing manipulation from the original spectra which were collected at a resolution of 0.5 cm^{-1}. Two trends can be observed in these data as the temperature was increased: 1) the nitrile stretching vibration shifted from lower to higher wavenumbers, and 2) the integrated band intensity increased. These changes occurred exactly at the crystal to smectic phase transition (Figure 5c, d). This is more apparent from the plot of frequency vs temperature shown in Figure 6. The central frequency of nitrile stretching band for CBOOA shifted 5 wavenumbers, from 2221 to 2226 cm^{-1}, at the crystal to smectic A phase transition. However,

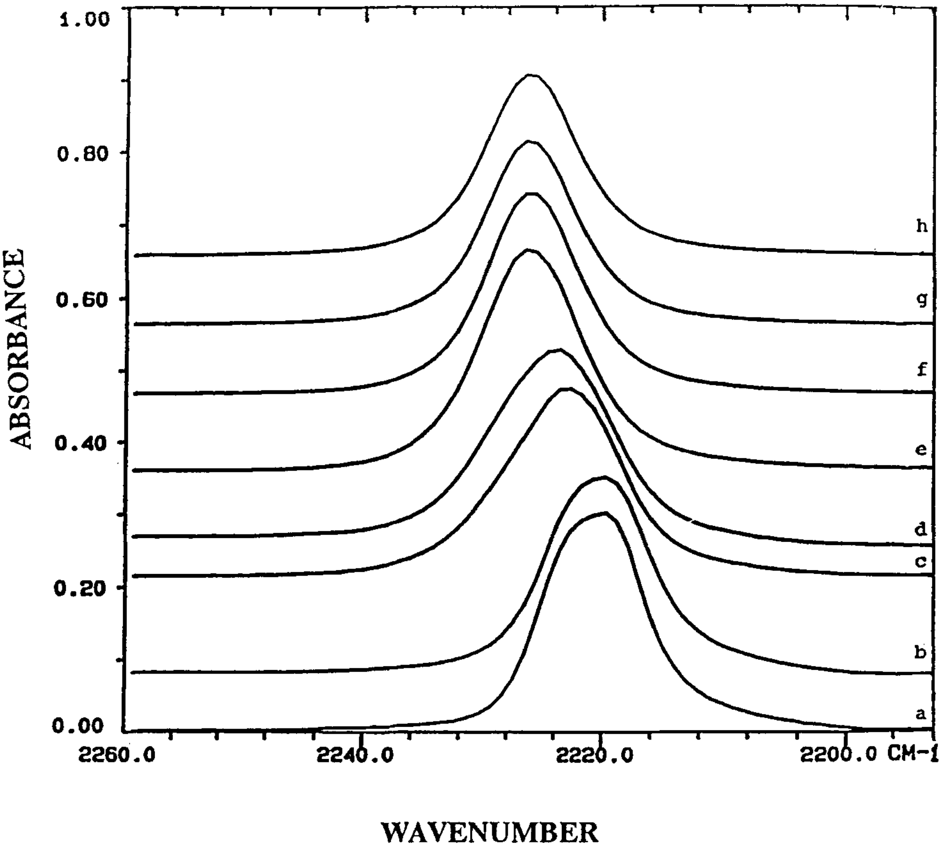

FIGURE 8 Nitrile stretching bands for CBHA at selected temperatures. (a) 35°C, (b) 72°C [crystal phase], (c) 75°C, (d) 76°C, (e) 77°C, (f) 105°C, (g) 107°C [nematic phase], (h) 110°C [isotropic].

these data also indicate that the frequency of the nitrile stretching vibration was not sensitive to either the smectic to nematic or nematic to isotropic changes.

In addition to the above trends, the shape and intensity of the nitrile band also changed at the C—S_A transition. In the crystal phase (Figure 5a, b), the bands were sharp and their intensity remained constant with temperature, however, between the crystal and smectic A phase (Figure 5b–d) the band broadened and its intensity increased. Similarly, between the smectic A and nematic phases (Figure 5d–f) as well as between the nematic and isotropic phases (Figure 5g–h) the intensity again increased. These changes are readily apparent in Figure 7 which shows a plot of integrated band intensity vs temperature. The observed changes from the smectic A to the nematic phase is especially significant since this transition is difficult to observe by DSC.[14] Thus, FT-IR provides a sensitive way of characterizing such transitions.

The advantage of using integrated band intensity to characterize the phase transitions in liquid crystals also can be demonstrated from the spectral data for the other two liquid crystals, CBHA and HBAB. Shown in Figures 8 and 9 are representative infrared absorption spectra from the nitrile stretching band for CBHA

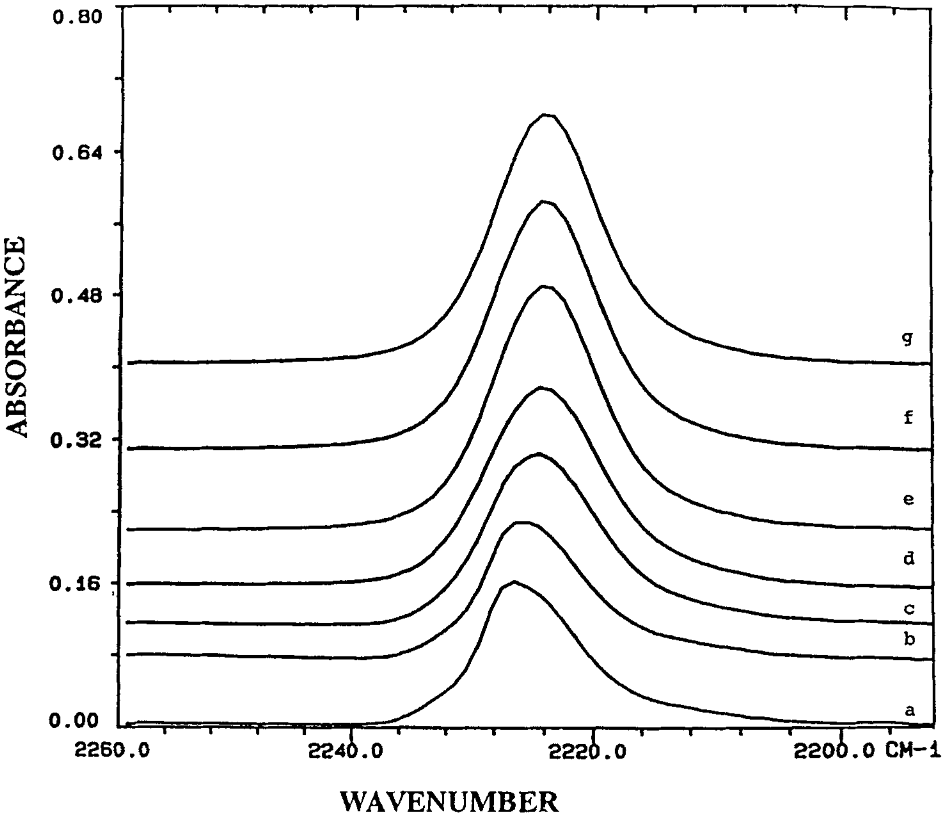

FIGURE 9 Nitrile stretching bands for HBAB at selected temperatures. (a) 30°C, (b) 50°C, (c) 53°C [crystal phase], (d) 56°C, (e) 100°C, (f) 102°C [nematic phase], (g) 105°C [isotropic phase].

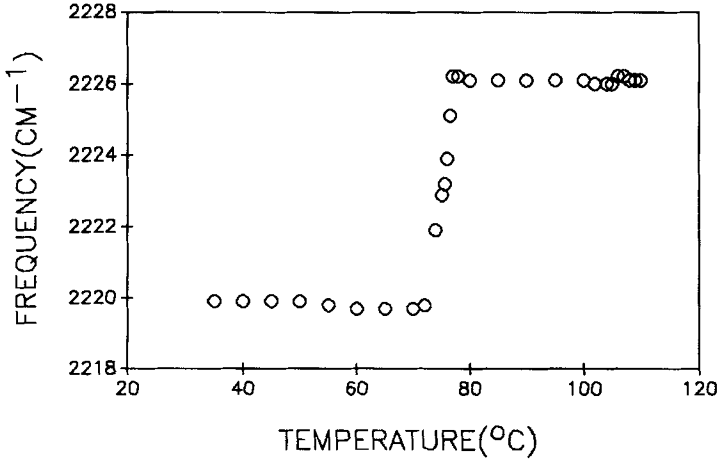

FIGURE 10 Changes in band frequency as a function of temperature for CBHA.

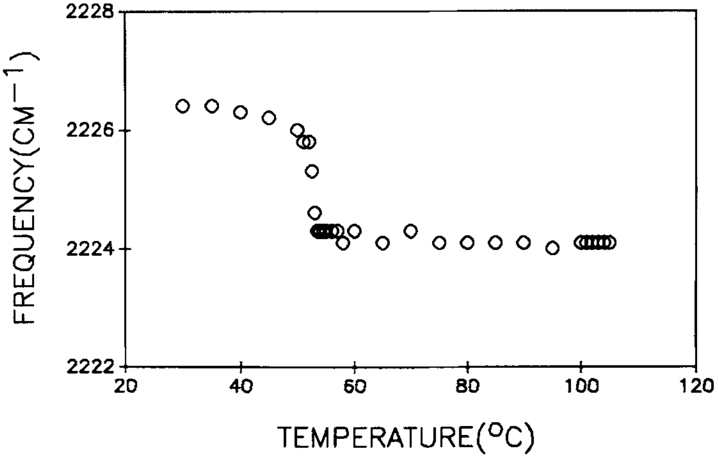

FIGURE 11 Changes in band frequency as a function of temperature for HBAB.

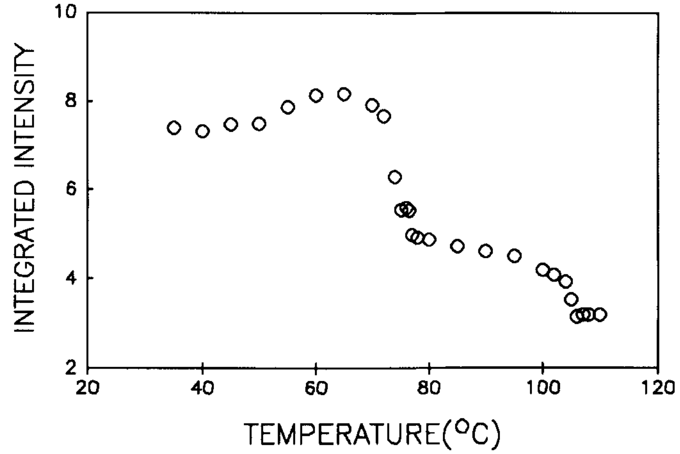

FIGURE 12 Changes in integrated intensity as a function of temperature for CBHA.

and HBAB. As in the case of CBOOA, the original spectra have been smoothed by a factor of 4. Although, the bands were slightly asymmetrical in the crystal phase they were symmetrical in both the nematic and isotropic phases. Again as the temperature was increased, the nitrile stretching band shifted in frequency at the crystal to mesophase transition (i.e., C—N). The shift for CBHA, which is a homolog of CBOOA, also was from lower to higher wavenumber, 2220 to 2226 cm^{-1}, however, for HBAB the shift was from higher to lower frequency, 2226 to 2224 cm^{-1}. As in the case of CBOOA, there were no obvious shifts at the nematic to isotropic phase transitions for either liquid crystal.

The changes in the nitrile stretching band frequency as a function of temperature for CBHA and HBAB are shown in Figures 10 and 11, respectively. As in the case of CBOOA, in order to observe both phase transitions in CBHA and HBAB, plots of integrated intensity as a function of temperature were constructed (Figure 12

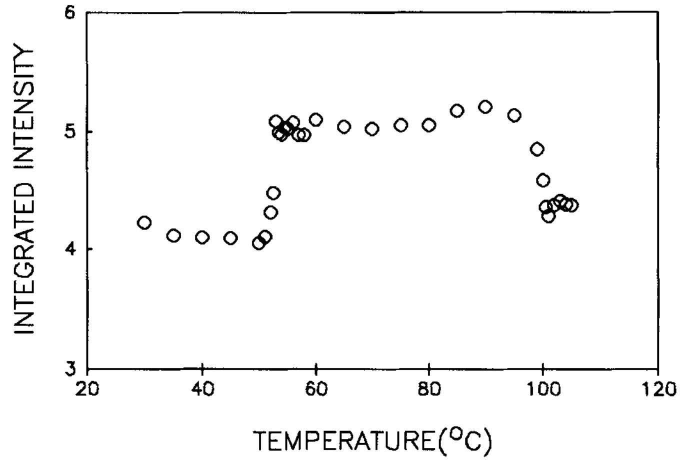

FIGURE 13 Changes in integrated intensity as a function of temperature for HBAB.

and Figure 13). The integrated intensity for CBHA (Figure 12) decreased abruptly at the crystal to nematic phase transition, and again at the nematic to isotropic liquid phase transition. In the case of HBAB, the integrated intensity (Figure 13) increased abruptly at the crystal to nematic phase transition, and then decreased at the nematic to isotropic liquid phases transition. Both phase transitions for CBHA and HBAB are readily apparent from the infrared method. However, as can be seen from the DSC scan for the nematic to isotropic, the transition is small. The purpose of the current research has been to study the influence of the mesogenic state on infrared properties of three liquid crystal compounds. The frequency shifts and integrated intensity of nitrile stretching bands of CBOOA, CBHA and HBAB have been measured as a function of temperature. In two of the samples, CBOOA and CBHA, shifts of 5–6 wavenumbers from lower to higher frequency were noted at the crystal to first mesogenic transition, however, in HBAB the shift was considerable smaller, (i.e., 2 wavenumbers and was from higher to lower frequency. These trends presumably reflect differences in packing and alignment in the crystal and mesogenic state for CBOOA and CBHA compared to HBAB. Additionally, the observed changes in the integrated band intensities presumably arise from texture differences in the mesogenic phases.

CONCLUSIONS

Further studies are in progress in order to correlate the observed infrared features with crystal and texture data. Additionally, vibrational rotational correlation function calculations are in progress in an effort to examine microscopic time fluctuations in these materials.

Acknowledgment

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