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Paul Painter [a] , Chris Cleveland [a] & Mike Coleman [a]
[a] Polymer Science and Engineering Program Penn State University, University Park, PA, 16802

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An Infrared Spectroscopic Study of *p*-n-Alkoxybenzoic Acids

PAUL PAINTER*, CHRIS CLEVELAND and MIKE COLEMAN

Polymer Science and Engineering Program Penn State University
University Park, PA 16802

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The infrared spectra of various *p*-n-alkoxybenzoic acids are reported. The carbonyl stretching region of these materials is surprisingly sensitive to packing within the various crystal forms, a consequence of the sensitivity of these modes to hydrogen bonding and transition dipole coupling. The isotypic crystal form found in those acids with n>6 are characterized by a splitting in the carboxyl C=O stretching region, a consequence of interactions between the disordered arrangement of carboxyl groups from layer to layer. This splitting is not observed in those alkoxybenzoic acids where n<7. The infrared spectra also show that there is a solid state transformation from the crystalline state to conformationally disordered or "condis" crystals as intermediates between the crystalline and liquid crystalline forms.

Keywords: Order/Disorder; Carbonyl Splitting Stretching Vibrations; Crystallin/LC Forms

INTRODUCTION

Alkyl and alkoxybenzoic acids are intriguing molecules because they have liquid crystalline properties that are a result of their ability to form hydrogen bonded cyclic dimers (1). Moreover, the mesogenic properties of these materials also depends upon the alkyl chain length. In the *p*-n-alkoxybenzoic acids (AOBA's), for example, at atmospheric pressure the first two members of the series (methoxy and ethoxy, n = 1 and 2, respectively) are not mesogenic at all, a consequence of the close packing and high crystalline melting point of these molecules. The next five members of the series display nematic phases at ordinary pressures, while AOBA's with alkyl chains of length n = 8 to 13 display both smectic and nematic phases (1–4). In these nematogenic AOBA's there is a

* Corresponding Author.

delicate balance of packing energies and solid state polymorphism is also observed in many members of the series.

The relationship between the molecular organization and properties of these materials has been investigated systematically by Bryan et al. (2–4) using x-ray diffraction. These authors demonstrated that in the AOBA's with alkyl chain lengths of n = 7 to (at least) 18 a stable isotypic crystal form is obtained from certain polar solvents and the appearance of this structure in this series coincides with the ability to form smectic phases. A schematic view of the packing found in one of the layers of this crystal form is illustrated in figure 1 (for the decycloxybenzoic acid, 10-AOBA). There is an interdigitation of the alkyl chains, which are segregated from the aromatic/carboxylic acid parts of the hydrogen bonded dimers. Furthermore, as also pointed out by Bunning and Lydon in a separate x-ray diffraction study (5), there is an apparent disorder in the carboxyl groups as a result of the two possible arrangements of carboxylic acid dimers in the stacked layers, as illustrated in figure 2. These alternate arrangements of the bonds do not affect molecular conformation or crystal structure and appear randomly throughout the crystal. This will be important in terms of interpreting the spectroscopic results reported here and is a point we will return to later.

The arrangement of the dimers in one of the other crystal forms that has been observed is illustrated schematically in figure 3 for 6-AOBA. Comparing this structure to that shown in figure 1, it can be seen that the dimer conformations are similar in the two crystalline forms, but now the molecules have a more staggered arrangement of the aliphatic and aromatic/carboxylic acid parts of the molecules. In addition, the single and double carbon oxygen bonds are determined by x-ray diffraction to have their usual dimensions, meaning that the type of disorder illustrated in figure 2 is not found in this crystal structure.

Both of these crystal forms display solid/solid phase transformations; 6-AOBA has four while 10-AOBA has one, near 86°C, to a polymorph or polymorphs of unknown structure. Furthermore, Bryan et al. (4) noted that the relationship either form bears to the solid phases formed from the melt also remains unknown. We therefore thought that it would be interesting to see what information we could obtain from infrared spectroscopy. This technique is particularly suited to the study of hydrogen bonding and in certain systems also shows a sensitivity to weaker intermolecular interactions and hence modes of packing.

A number of spectroscopic studies of these materials have been reported previously (6–10). Most of these focused on changes observed at temperatures corresponding to the phase transitions. Azima et al. (6,7), for example, found intensity changes in various aromatic and aliphatic modes. Of more relevance to the work reported here, they noted that the carbonyl stretching mode of the hydrogen bonded dimer, observed at 1675 cm^{-1} in the smectic form of 8-AOBA, abruptly

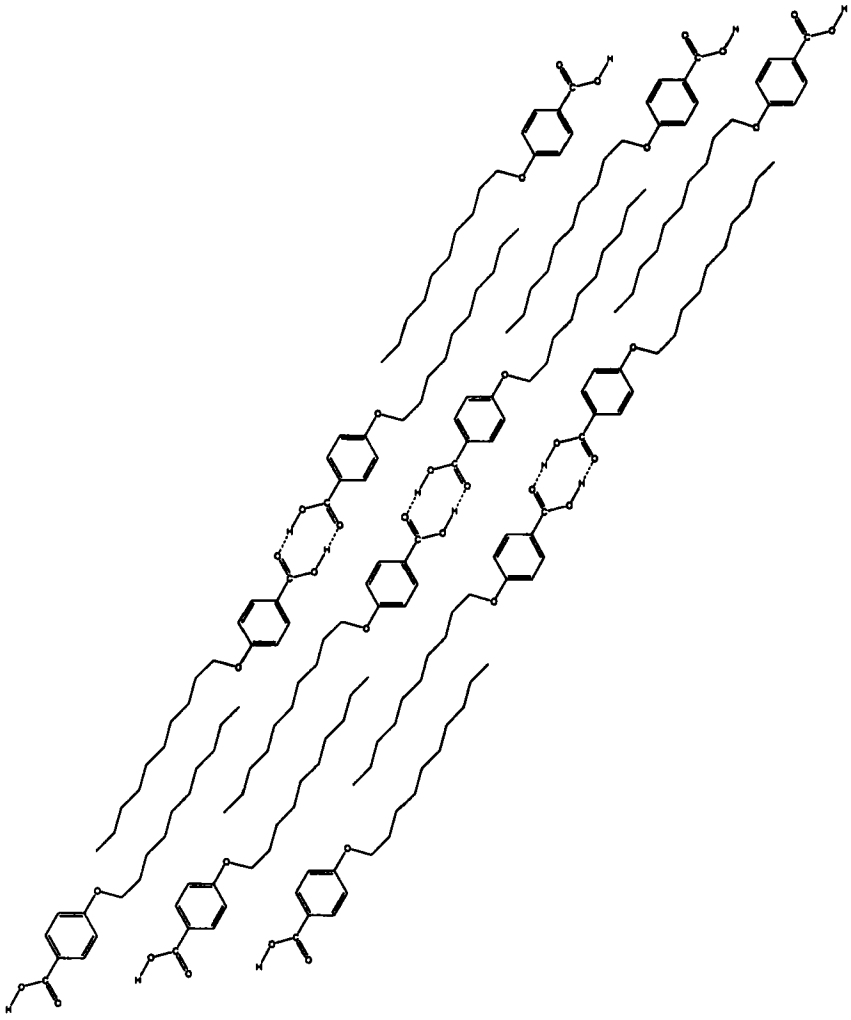

FIGURE 1 A schematic representation of the arrangement of hydrogen bonded dimers is one of the layers of the isotypic crystal form of 10-AOBA

shifts in frequency to 1680 cm^{-1} at the smectic-nematic transition and then gradually increases in wavenumber with temperature. They attributed the 1680 cm^{-1} band to an open dimer. In contrast, Privalko et al. (8) assigned a band near 1703 cm^{-1} to open dimers, while Krasnogolovets et al. (9) proposed that this band was due to open chain aggregates of the type found in crystalline acetic acid. In contrast, Kato et al. (10) stated that in the crystalline state of 4-hexyl benzoic acid only a dimer band near 1695 cm^{-1} is observed and a band due to "free" (non

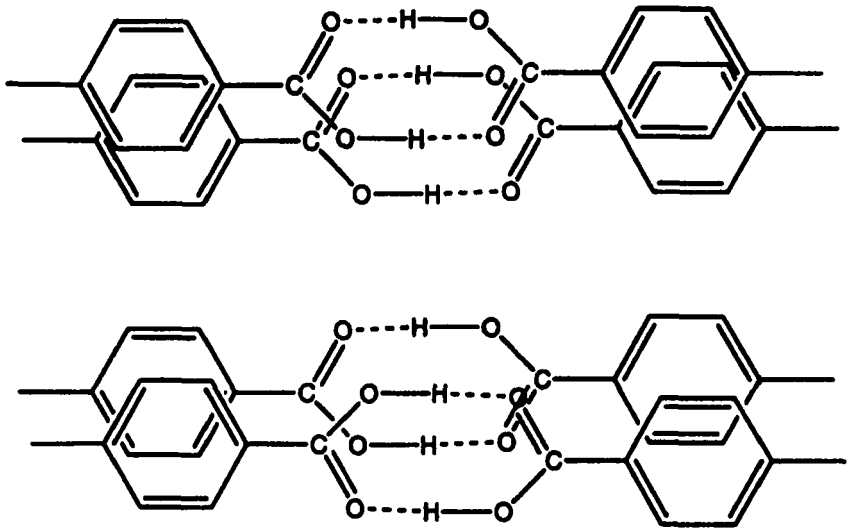

FIGURE 2 Two possible arrangements of the carboxylic acid dimers in adjacent stacked layers

hydrogen bonded) carbonyls appears at the crystalline/nematic transition. As the temperature is raised this band then shows an abrupt change in intensity at the nematic/isotropic transition.

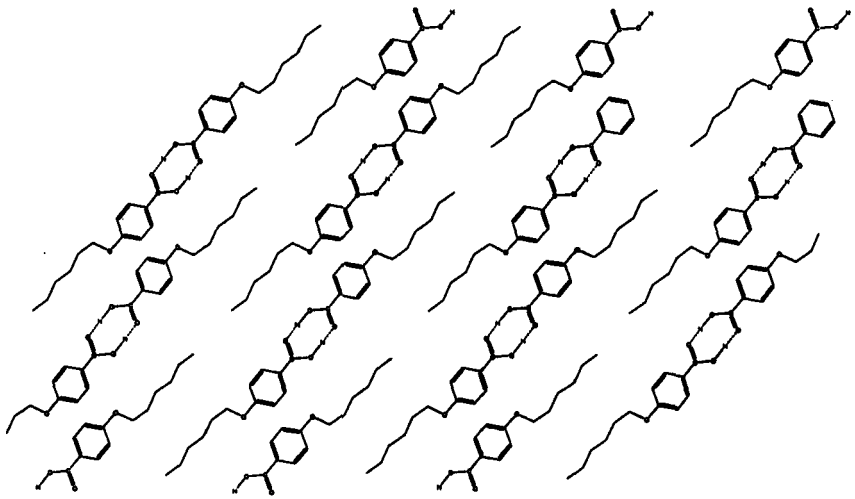

FIGURE 3 A schematic representation of the arrangement of the hydrogen bonded dimers in one of the layers of the crystal structure of 6-AOBA

In this study we will examine the carbonyl stretching region of the spectrum in more detail in order to resolve some of these differences in band assignments. We will also show that this region of the spectrum is much more complex than previously considered and very sensitive, not only to the degree of hydrogen bonding, but also local structure and packing. Furthermore, an examination of other regions of the spectrum indicates that the solid/solid phase transformation of 10 AOBA, and at least one of the transitions of 6 AOBA, involves a transition to a so-called "condis" crystal, as described by Wunderlich et al. (11).

EXPERIMENTAL

Tetrahydrofuran (THF), toluene, ethanol, potassium bromide (KBr) powder, 4-decyloxybenzoic acid (10-AOBA), 4-nonoxybenzoic acid (9-AOBA), and 4-hexoxybenzoic acid (6-AOBA) were purchased from Aldrich Chemical Company, Inc. KBr windows were purchased from Optovac. Both 10-AOBA and 6-AOBA were studied "as received" and also after recrystallization from ethanol and THF, respectively.

KBr pellet and powder samples were produced by first grinding the AOBA material with dry KBr powder (10–15 mg AOBA: 300 mg KBr powder) with a Wig-L-Bug grinder. The pellets were formed with a Graesby-Specac vacuum press. Thin films of the AOBA's were cast from THF at room temperature onto KBr windows. The samples were then placed in a vacuum oven held initially at a temperature 5°C above the highest thermal transition temperature and allowed to slowly recrystallize as the oven cooled over night. Spectra of AOBA solutions were recorded by using 0.1 mm pathlength KBr liquid calls purchased from Spectra Tech, Inc.

Infrared spectra were recorded on a Digilab FTS-45 Fourier Transform Infrared (FTIR) spectrometer using a minimum of 32 co-added scans at a resolution of 2 cm^{-1}. FTIR temperature studies were performed using a Harrick horizontal transmission cell equipped with a heating jacket that was mounted inside the sample chamber. The temperature was controlled by a Harrick digital process controller with an accuracy of ±0.1°C.

RESULTS AND DISCUSSION

Preliminary Considerations of the Spectra of 6-AOBA and 10-AOBA

In what follows we will show that the carbonyl stretching region of the infrared spectrum of the hydrogen bonded carboxylic acid groups of AOBA's is surpris-

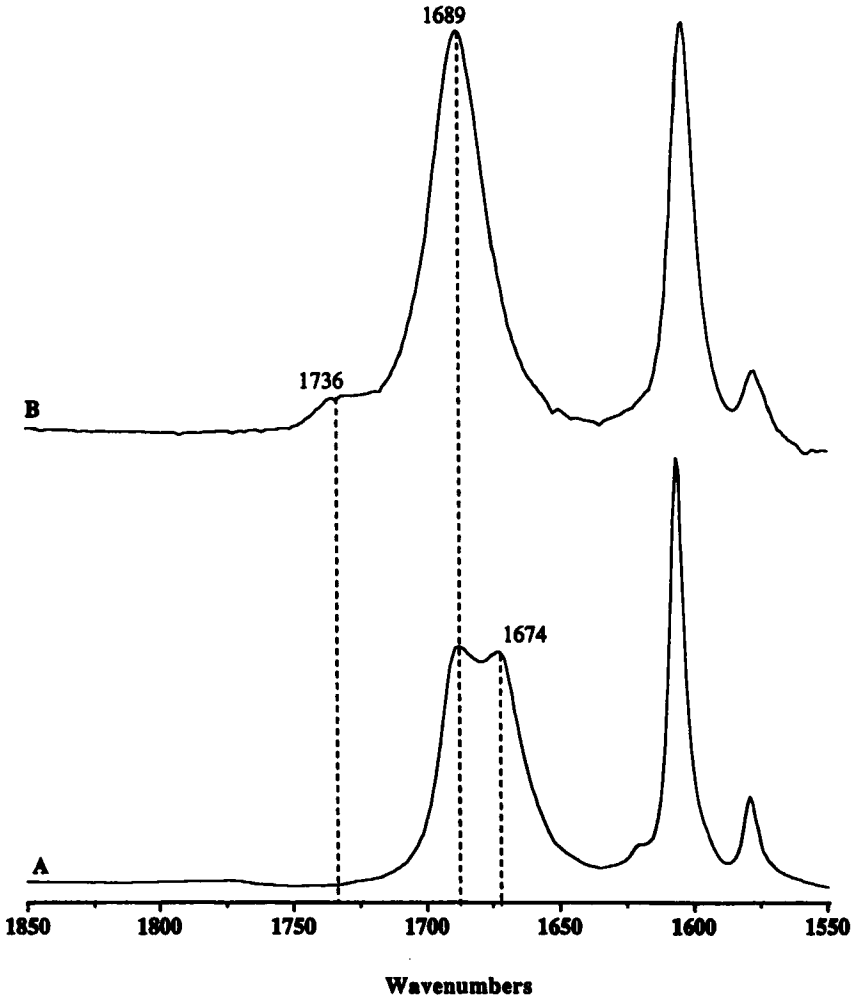

FIGURE 4 Infrared spectra of a KBr pellet of 10-AOBA A) at room temperature and B) at 150°C (in the carbonyl stretching region)

ingly complex, given what has been previously reported in the literature (6–10). To illustrate this, first consider the set of spectra of 10-AOBA and 6-AOBA shown in figures 4 and 5. Figure 4A shows the spectrum of 10-AOBA obtained by preparing the sample in the form of a KBr pellet. This spectrum is characteristic of what we observed in the "as-received" samples and is essentially identical to the spectrum obtained from samples recrystallized from ethanol, which gives the isotypic crystal form illustrated previously in figure 1 (3). There are clearly

two bands of almost equal intensity present in the spectrum, a feature not observed (or perhaps reported) previously, near 1689 and 1674 cm^{-1}, respectively. This apparent "doublet" is replaced by a single broad band near 1688 cm^{-1} upon heating to 150°C, as shown in figure 4B, where this material is in the isotropic state (a weak band due to "free" or non-hydrogen bonded carboxyl groups also appears near 1736 cm^{-1}).

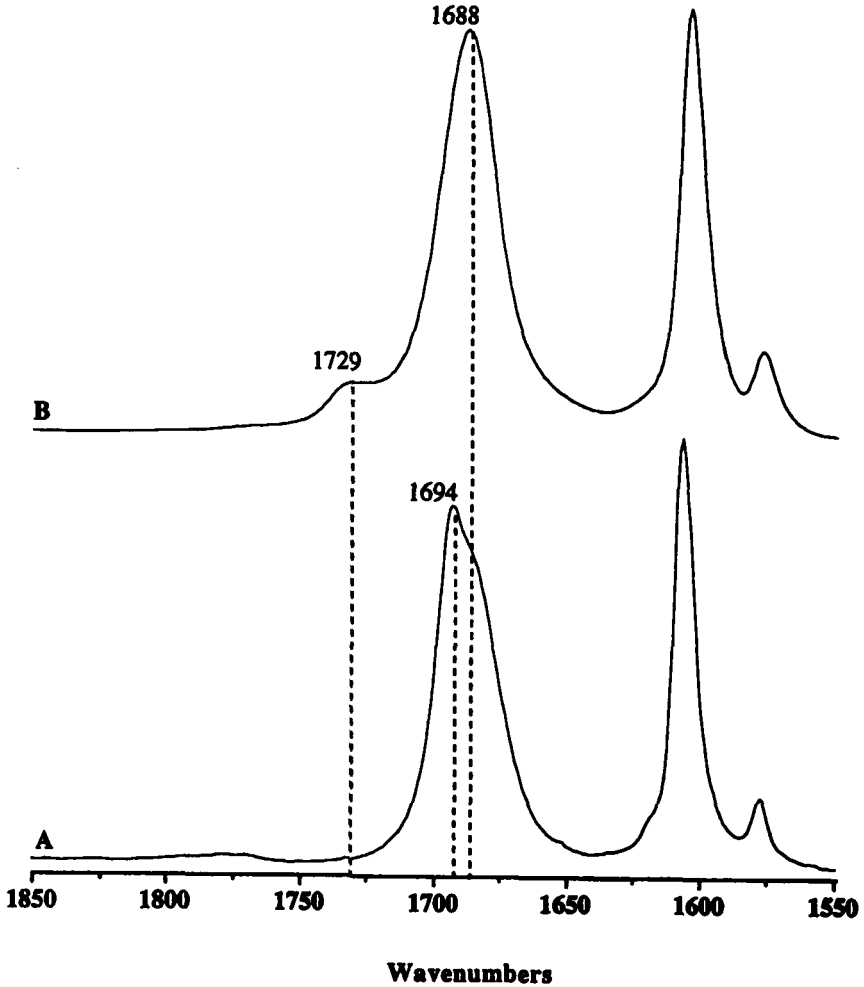

FIGURE 5 Infrared spectra of a KBr pellet of 6-AOBA A) at room temperature and B) at 150°C

The infrared spectrum of a KBr pellet of 6-AOBA, shown in figure 5A, also consists of two bands, but at higher frequencies, near 1694 and 1686 cm^{-1},

respectively. Note that the 1694 cm^{-1}band is more intense than the shoulder near 1686 cm^{-1}. These two bands are also replaced by a single broad band (figure 5B), again near 1688 cm^{-1}, in the isotropic state (plus the weak "free" band near 1730 cm^{-1}).

These observations immediately raise a number of questions. We would anticipate that the infrared spectrum of these materials would be dominated by the contributions from the centrosymmetric dimers, with the relatively weak intermolecular (i.e. inter-dimer) interactions having only minor effects. This is clearly not so and, intriguingly, the carbonyl bands due to the hydrogen bonded dimer in 10-AOBA are found at lower frequencies than in 6-AOBA, suggesting that the hydrogen bonds are much stronger in the former. The structures determined by x-ray diffraction, at least at first sight, give no reason to suspect this. Furthermore, why are there (apparently) two bands? It is well-known that there is strong transition dipole coupling between the carbonyl groups in each cyclic pair (12–14), resulting in a significant splitting of the symmetric and asymmetric carbonyl stretching modes. But, because of the center of symmetry, only one of these modes is infrared active (the other can be observed in the Raman spectrum). Are the "doublets" observed in the spectrum then due to inter-dimer interactions and are thus sensitive to crystal packing, or are we observing co-existing ordered phases, or even co-existing ordered and disordered phases, perhaps induced by the grinding with KBr and pressure necessary to produce KBr pellets?

We believe we can make sense of these observations, but given some of the confusing spectroscopic observations and proposed structures found in the literature it is useful to first clarify band assignments.

Infrared Spectroscopic Band Assignments in the Carbonyl Stretching Region of Carboxyl Acids

The types of structures found in carboxylic acids are illustrated in figure 6, together with known band assignments. A "free" carboxylic acid group, one that is not hydrogen bonded to any partner, would display a band in the range 1730–1740 cm^{-1}. Hydrogen bonding shifts the carbonyl stretching mode to lower frequencies, with the wavenumber shift being proportional to the strength of the hydrogen bond. In order to establish a "benchmark" we obtained the spectrum of 10-AOBA as a 1% (wt/vol) solution in toluene, as shown in figure 7, where a sharp band (13.8 cm^{-1}width at half-height) due to the cyclic dimer is observed at 1687 cm^{-1}, while the "free" band (which increases in intensity with dilution) is observed near 1730 cm^{-1}. As might be expected, this is very close in frequency to the band observed near 1688 cm^{-1} in the isotropic state. In between these modes the observed broad spectral envelope suggests there may be other weak

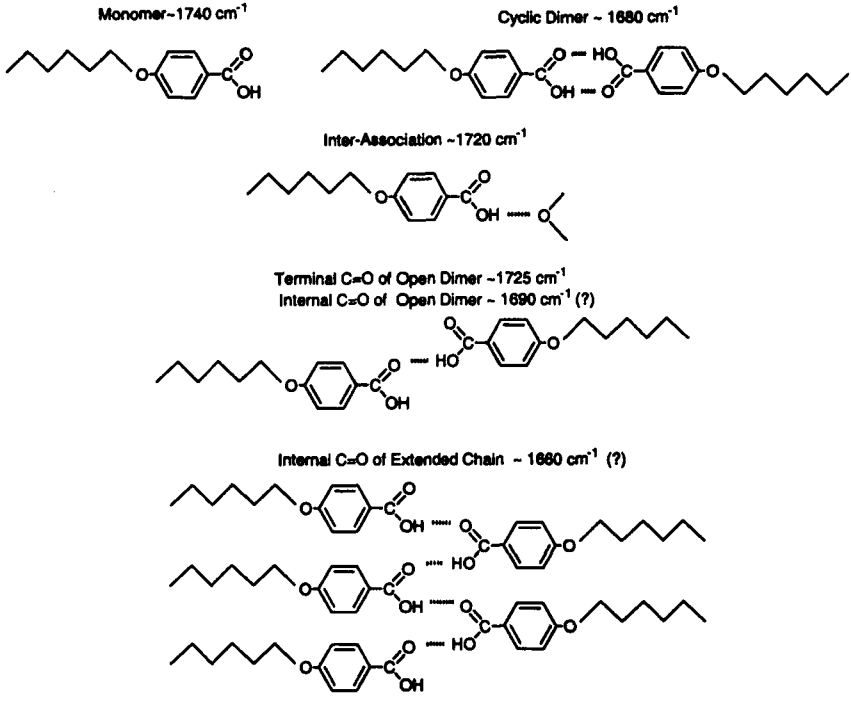

FIGURE 6 An illustration of the types of hydrogen bonded structures found in carboxylic acids

bands, and these would probably be due to open dimers. Hydrogen bonded structures are dynamic in solution or the melt, constantly breaking and reforming at the urgings of thermal motion. It is likely that random collisions between free acid groups would initially result in the formation of an open dimer, of the type illustrated in figure 6, but this would no doubt quickly convert to the cyclic dimer. Nevertheless, the time frame of vibrational motion is such that a few may be "caught" between the cyclic dimer and true free state, resulting in the observation of two bands between 1730 and 1687 cm^{-1}. One of these modes would be due to the end-group free carbonyl, which we know from our previous studies of hydrogen bonding in carboxylic acids (15,16), and from studies of blends of AOBA's with polyethers (17), appears near 1725 cm^{-1}. The hydrogen bonded carbonyl of the dimer would be at a lower frequency than this, perhaps coinciding with the band due to the cyclic dimer if the strength of the bond is the same, or at somewhat higher frequency if, as we suspect, the strength of this hydrogen bond is somewhat weaker than that found in the cyclic species.

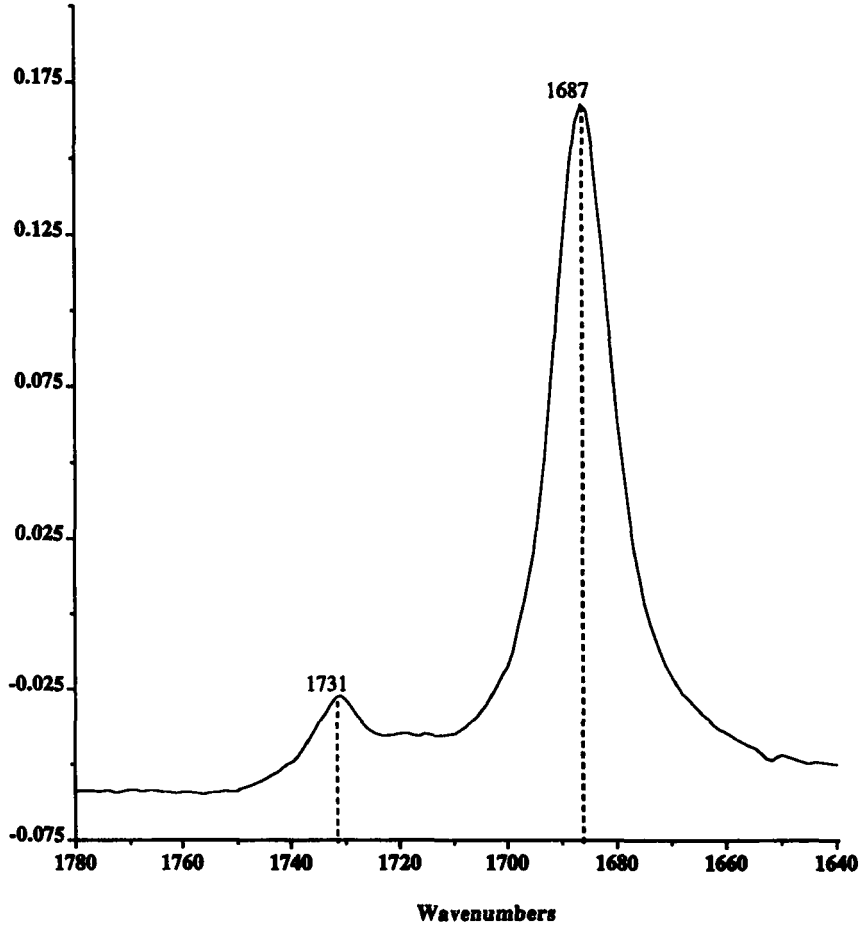

FIGURE 7 Infrared spectrum of 10-AOBA as a 1% solution in toluene (carbonyl stretching region)

Bands due to open dimers have been observed in solution studies of acetic acid (18,19), but are in our view misassigned. The vibrational mode due to the end-group of the open dimer was assigned to a band observed at a higher frequency than that of the free monomer species! Our studies of blends of acids with ethers (16,17), where the -OH group is bonded to the ether oxygen leaving a "free" carbonyl end-group, demonstrates that the end-group free carbonyl is always observed at a lower frequency than the free group of an isolated "monomer". This is not particularly important in terms of the rest of this study, but one other aspect of the spectrum of acetic acid is pertinent here. In the crystalline

state this molecule forms close-packed hydrogen bonded chains of the type illustrated at the bottom of figure 6. The hydrogen bonds in this structure are stronger (i.e. shorter) than in the open or cyclic dimer, presumably as a result of cooperative bonding effects, and therefore appears at a lower frequency, near 1648 cm^{-1} (20) as opposed to 1715 cm^{-1} for the cyclic species of acetic acid in solution (18). We noted in the introduction that Krasnagolovets et al. (9) reported that at temperatures just short of the solid-crystal/liquid crystal transition there is a transition to open chain aggregates. If so, one would presumably observe bands due to end groups between 1730 and 1685 cm^{-1}, and perhaps bands lower in frequency than 1685 cm^{-1}, if the open chain aggregates form stronger hydrogen bonds than those in the cyclic or open dimers (through reinforcing electrostatic cooperative effects), as in acetic acid. Indeed, we were initially tempted to assign the lower frequency mode of the 10-AOBA doublet (i.e. the 1674 cm^{-1} band) to such a structure, but there are various arguments that persuaded us that such long chain aggregates are not present in the AOBA's. The most convincing reasons have been summarized by Leiserowitz in his review of molecular packing in carboxylic acids (21). He called chain-like structures the catemer motif (or, more precisely, motifs) and essentially noted that there are various distortions that increase with the size of the substituent attached to the carboxylic acid group. Chain-like structures or catemers are thus observed in formic, acetic and β-tetrolic acid, but as the substituent gets larger, catemer structures become sterically unfavorable and much better packing is achieved with cyclic dimers.

Crystal Packing and the Infrared Spectra of AOBA's

This brings us back to the spectra of the KBr pellets of 6-AOBA and 10-AOBA shown in figures 4 and 5. Based on the arguments and assignments given in the preceding section we believe all of the bands observed at frequencies less than about 1700 cm^{-1} are due to cyclic dimers, but what accounts for their unusual sensitivity and the presence of multiple bands?

The first question we addressed was the effect of sample preparation. One obvious way to avoid the effects of grinding and pressure that are unavoidable in preparing KBr pellets is to prepare melt-crystallized samples as films on IR-transparent salt windows. Unfortunately, as we will show below, the spectra of films are even more complex. However, by simply grinding the crystals with KBr and obtaining the spectrum using diffuse reflectance, we did obtain results that clarified the situation. Figure 8 compares the carbonyl stretching region of the spectra of 6-AOBA, 9-AOBA and 10-AOBA. The spectrum of 9-AOBA has a very similar crystal structure to 10-AOBA (see figure 1) and we included it to show that an apparent doublet is observed in this region of the spectrum of other

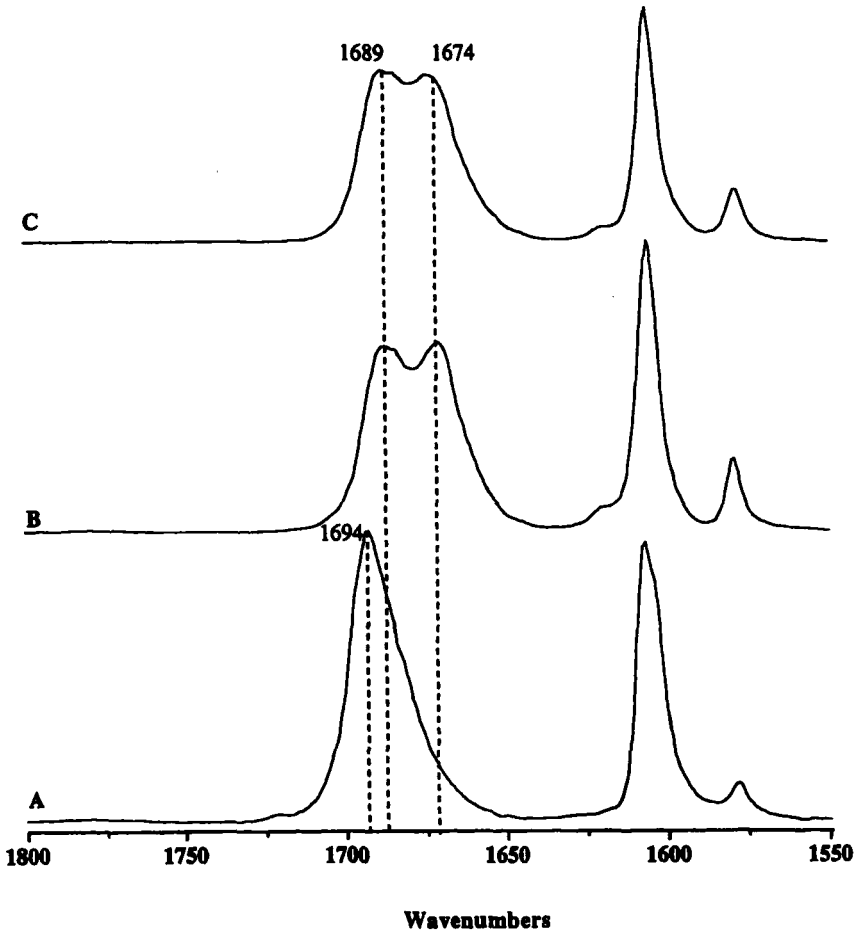

FIGURE 8 Diffuse reflectance infrared spectra of A) 6-AOBA, B) 9-AOBA and C) 10-AOBA in the carbonyl stretching region

samples and appears to be characteristic of the isotypic crystal form. The spectrum of 6-AOBA is very different to that observed in KBr pellets, however, displaying a single band near 1694 cm^{-1}, with now perhaps only a weak shoulder appearing near 1686 cm^{-1}. This certainly indicates that at least for this material, pressure results in the partial conversion of the original crystal form to a second ordered state. This is perhaps not surprising, given that 6-AOBA displays four solid phase transformations at temperatures below the crystalline/nematic transition.

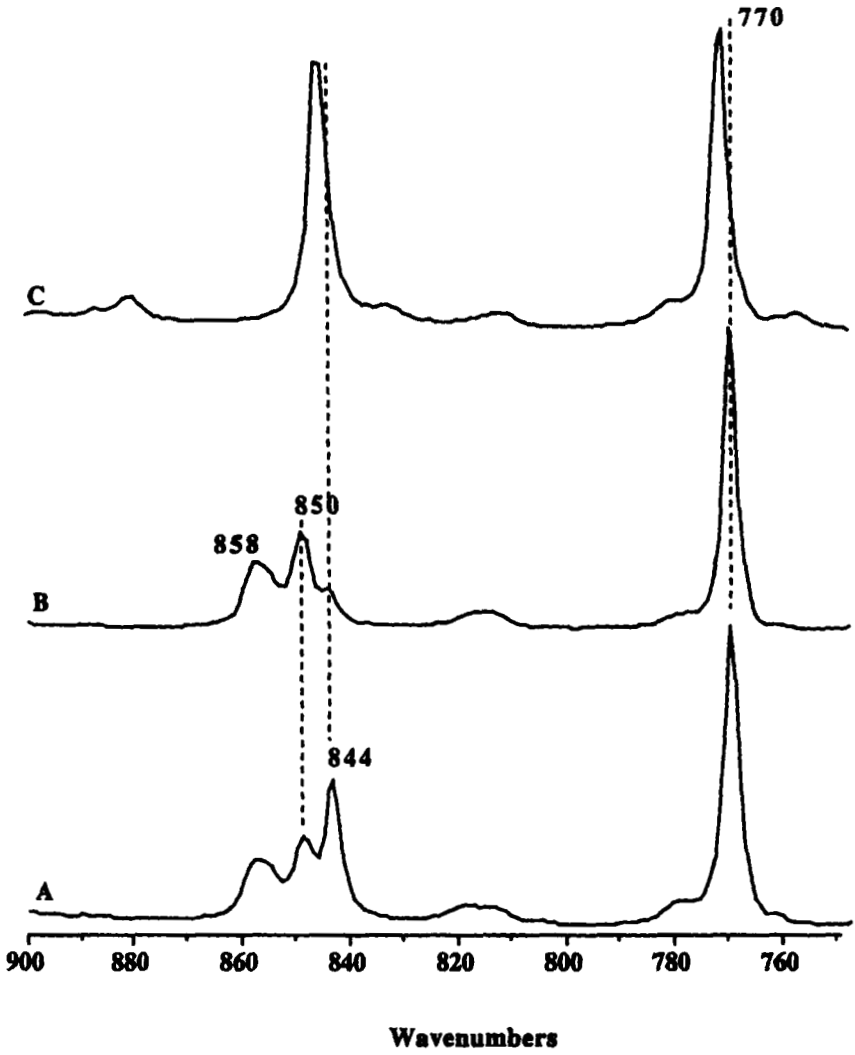

FIGURE 9 Infrared spectra in the aromatic (CH out-of-plane bending region of the spectrum of A) 6-AOBA prepared as a KBr pellet, B) 6-AOBA in diffuse reflectance, and C) 10-AOBA in diffuse reflectance

This interpretation is supported by an examination of the out-of-plane aromatic CH bending region of the spectrum between 900 and 760 cm^{-1}, shown in figure 9. The bottom two plots (A and B) compare the diffuse reflectance and KBr pellet spectra of 6-AOBA, and it can be seen that the modes near 850 cm^{-1}

are very sensitive to structure. Both spectra display three bands, near 858, 850 and 844 cm^{-1}, but the bands near 850 and 844 cm^{-1} vary in relative intensity. Even more dramatic changes are observed as the temperature is raised, as we will discuss below, but clearly the pressure involved in making a KBr pellet increases the intensity of the band near 844 cm^{-1} relative to that at 850 cm^{-1}, corresponding to an increase in the 1686 cm^{-1} band relative to the 1674 cm^{-1} band in the carbonyl stretching region. This presence of multiple peaks that vary in tandem with those in the carbonyl stretching region indicates that the doublet in 6-AOBA is caused by co-existing phases, as opposed to interactions between carbonyl groups within a given crystal structure.

This is probably not the case in 9 and 10-AOBA, however. Here only a single, relatively sharp band near 845 cm^{-1} is observed in the out-of-plane bending region and this is also more intense than the equivalent mode in 6-AOBA. This intensity difference is probably symmetry related, as the crystal structure of 6-AOBA determined by Bryan et al (4) belongs to the space group P21/c ($\equiv C_{2h}$) while that of 10-AOBA belongs to $P\bar{1}$ ($\equiv C_i$) (3,5). The important point is that this region of the spectrum of 9 and 10-AOBA indicates the presence of just one phase. Note also that although the mode near 770 cm^{-1} is apparently not as sensitive to the symmetry of packing as that near 850 cm^{-1}, in that only one band appears in the spectrum of 6-AOBA near 770 cm^{-1}, in the spectra of 9 and 10 AOBA this mode is shifted to slightly higher wavenumbers, indicating a difference in local environment.

This leaves the origin of the apparent doublet in the carbonyl stretching region of 9 and 10-AOBA, together with its shift to lower frequency relative to the isolated dimers observed in dilute solutions of toluene and the band observed in 6-AOBA, as an interesting problem. We believe the answer is related to the intimate details of the packing of the dimers in the crystal.

If the crystal structure of 10-AOBA illustrated in figure 1 is examined carefully it can be seen that the aromatic acid parts of the molecule are segregated from the aliphatic parts of the chain in such a fashion that the aromatic CH groups juxtapose the carbonyl groups on adjacent molecules in the same layer, allowing the formation of weak hydrogen bonds between these CH groups and the second lone-pair electrons of the carbonyl oxygen (i.e. those not involved in hydrogen bonding to the carboxyl OH group), as illustrated in figure 10. Such arrangements have been observed in a number of benzoic acid structures, as discussed by Leiserowitz (21), and would be expected to result in a shift of the carbonyl stretching mode of the hydrogen bonded dimer to a lower frequency than observed for the structure found in the crystal form of 6-AOBA, illustrated in figure 3, where the aromatic rings and carboxylic acid pairs are offset from one another. Leiserowitz (21) also noted that benzoic acids which have an alignment

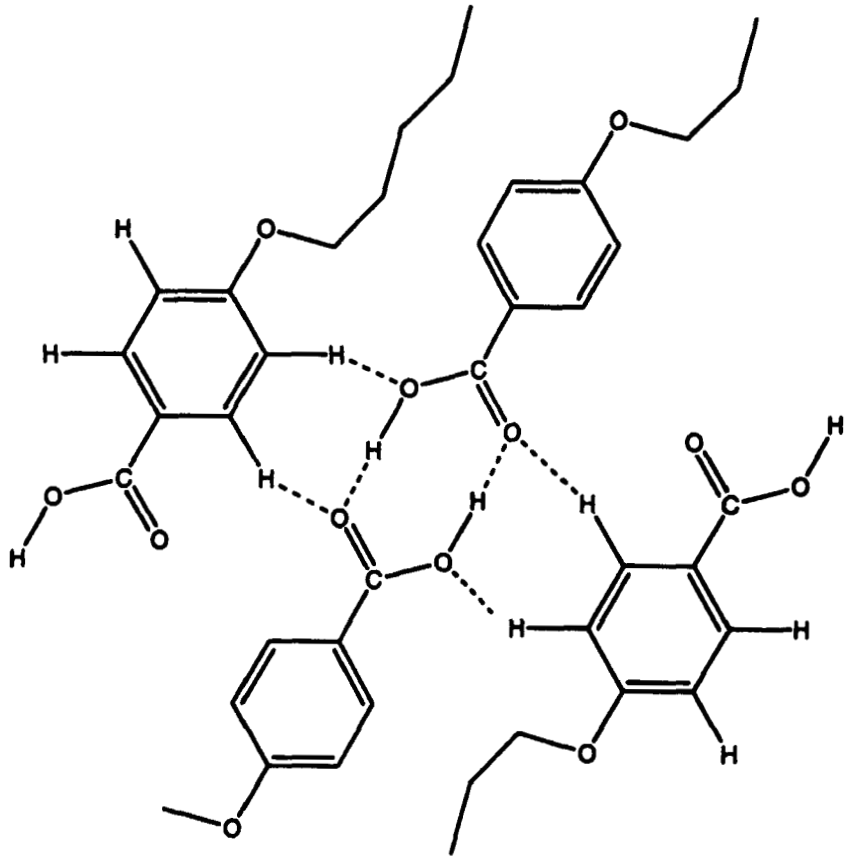

FIGURE 10 Juxtaposition of the aromatic **CH groups and hydrogen bonded** cyclic dimers in adjacent dimers in the 10-AOBA crystal structure

between groups of the type shown in figure 10 tend to show disorder between the arrangement of the carboxyl groups in adjacent layers, as illustrated earlier in figure 2, and we believe this accounts for the "splitting" of the carbonyl modes observed in the spectra of 9 and 10-AOBA. The crystal structure of the 6-AOBA discussed here does not display this disorder.

As we mentioned earlier, the carbonyl groups of carboxylic acids interact strongly through transition dipole coupling (12–14), but because of symmetry considerations only a single infrared band is predicted to be active. Carbonyl groups within a layer (e.g. adjacent dimers in the plane of figure 1) could interact in this manner, but the distance between acid pairs is of the order of 8Å. As the

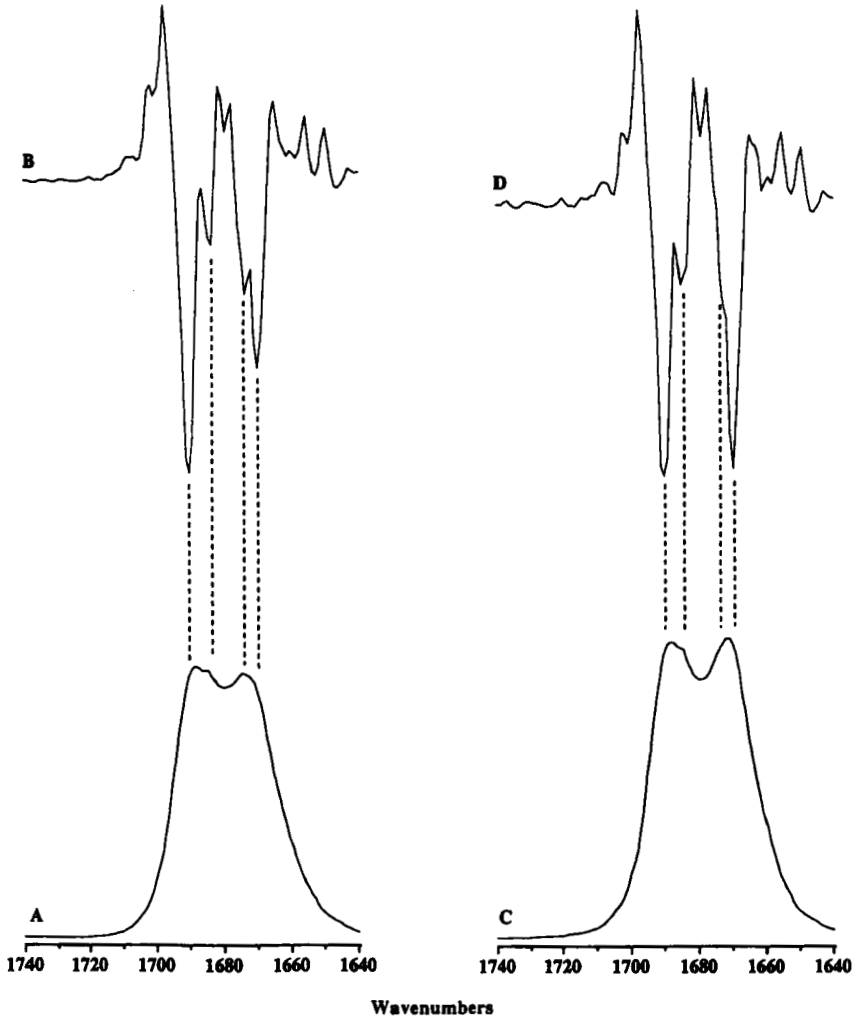

FIGURE 11 Diffuse reflectance spectra of (left) 10-AOBA and (right) 9-AOBA and their respective second derivatives

transition dipole coupling interaction strength varies inversely with the cube of the separation (12–14), even if symmetry consideration permitted a splitting it would probably be relatively small. In the "stacking direction" of the layers (i.e. in the direction perpendicular to the plane of figure 1), the distance between superimposed carboxylic acid groups is only half this, of the order of 4Å, so this interaction should be appreciable. However, each group in adjacent layers

belongs to a different unit cell and the selection rules for translational symmetry are such that only in-phase vibrations of these adjacent groups should be observed, again giving a single infrared active mode. *However, for 9 and 10-AOBO (and other AOBA's that crystallize in this isotypic crystal form) this symmetry relationship between adjacent carboxylic acid groups is lost in the random arrangement of the groups.* We should then see a superposition of splitting due to the two possible arrangements shown in figure 2. There would actually be two sets of splittings, each corresponding to one of the arrangements shown in this figure, (assuming interactions are only significant between adjacent layers). If each of these doublets is separated or split by approximately the same amount, then we would only observe two bands, each of these being a superposition of two others. Moreover, if each of the overlapping bands were at slightly different frequencies, the "composite" band would be broader than that found in the dilute solution spectrum (figure 7) and what we normally expect in a highly crystalline material. This appears to be what we observe. In addition, although we do not wish to push this observation too far, because of the effects of noise and errors, there is evidence for the presence of four overlapping peaks in the diffuse reflectance spectra, as shown in figure 11, which displays both the spectra of 9-AOBA and 10-AOBA and their respective second derivatives.

The Effect of Temperature on the Infrared Spectra

As the temperature is raised the 10-AOBA and 6-AOBA crystal structures studied here undergo the following transitions (3–5):

10-AOBA

$$K_{II} \xrightarrow{85^{\circ}C} K_{I} \xrightarrow{97^{\circ}C} S_{c} \xrightarrow{125^{\circ}C} N \xrightarrow{143^{\circ}C} I$$

6-AOBA

$$K_{V} \xrightarrow{58^{\circ}C} K_{IV} \xrightarrow{71^{\circ}C} K_{III} \xrightarrow{87^{\circ}C} K_{II} \xrightarrow{99^{\circ}C} K_{I} \xrightarrow{101^{\circ}C} N \xrightarrow{145^{\circ}C} I$$

where K represents a crystalline solid state structure, S and N are the smectic and nematic liquid crystalline phases, respectively, and I the isotropic state.

The carbonyl stretching region of the infrared spectrum of a KBr pellet of 10-AOBA, recorded as a function of temperature, is shown in figure 12. It can be seen that at 94°C, where the K_{II} solid state phase has been converted to the K_{I} phase, the apparent "doublet" has been replaced by a broad band envelope,

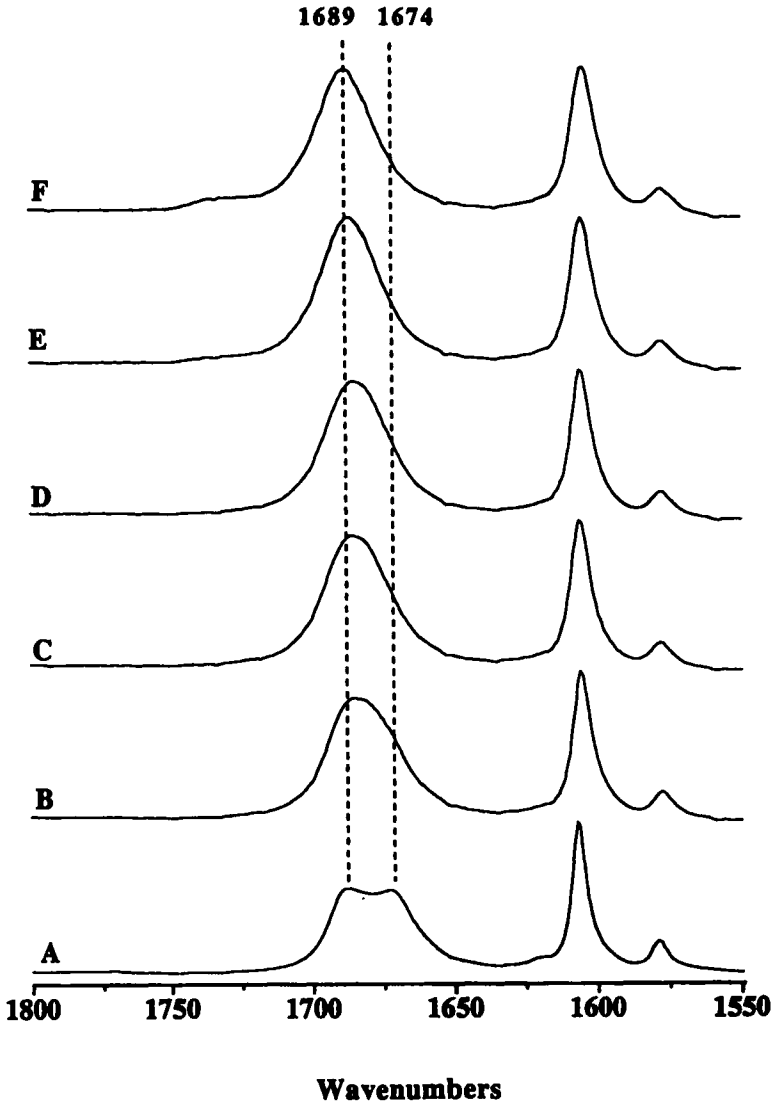

FIGURE 12 The carbonyl stretching region of the infrared spectrum of a KBr pellet of 10-AOBA at A) 25°C, B) 94°C, C) 105°C, D) 110°C, E) 135°C, F) 150°C

which also appears to consist of overlapping bands centered at a somewhat higher frequency than the mid-point of the low temperature "doublet". As the temperature is raised the band envelope shifts to slightly higher frequencies and becomes less broad in the nematic and isotropic states-a result of the disappear-

ance of the lower frequency band in the composite observed at intermediate temperatures. Also, as the isotropic state is reached a broad, weak band envelope between 1710 and 1740 cm^{-1} appears, the result of overlapping monomer and perhaps open dimer carbonyl bands.

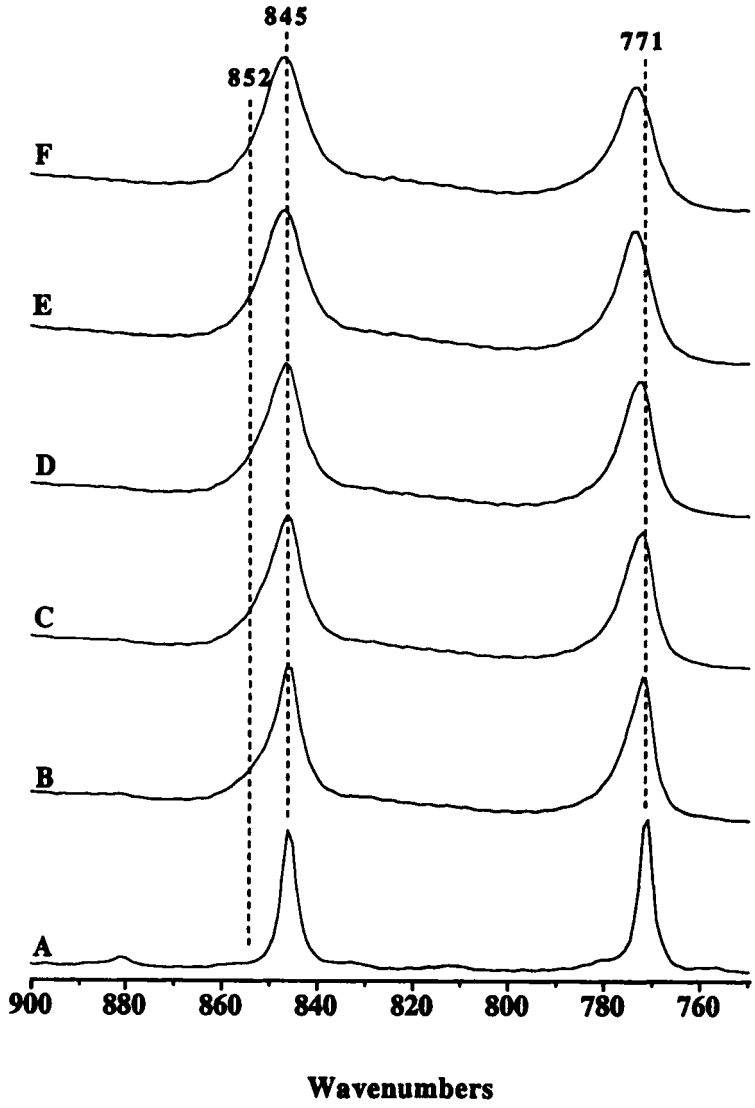

FIGURE 13 The aromatic CH out-of-phase bending region of the spectrum of a KBr pellet of 10-AOBA at A) 25°C, B) 94°C, C) 105°C, D) 110°C, E) 135°C, F) 150°C

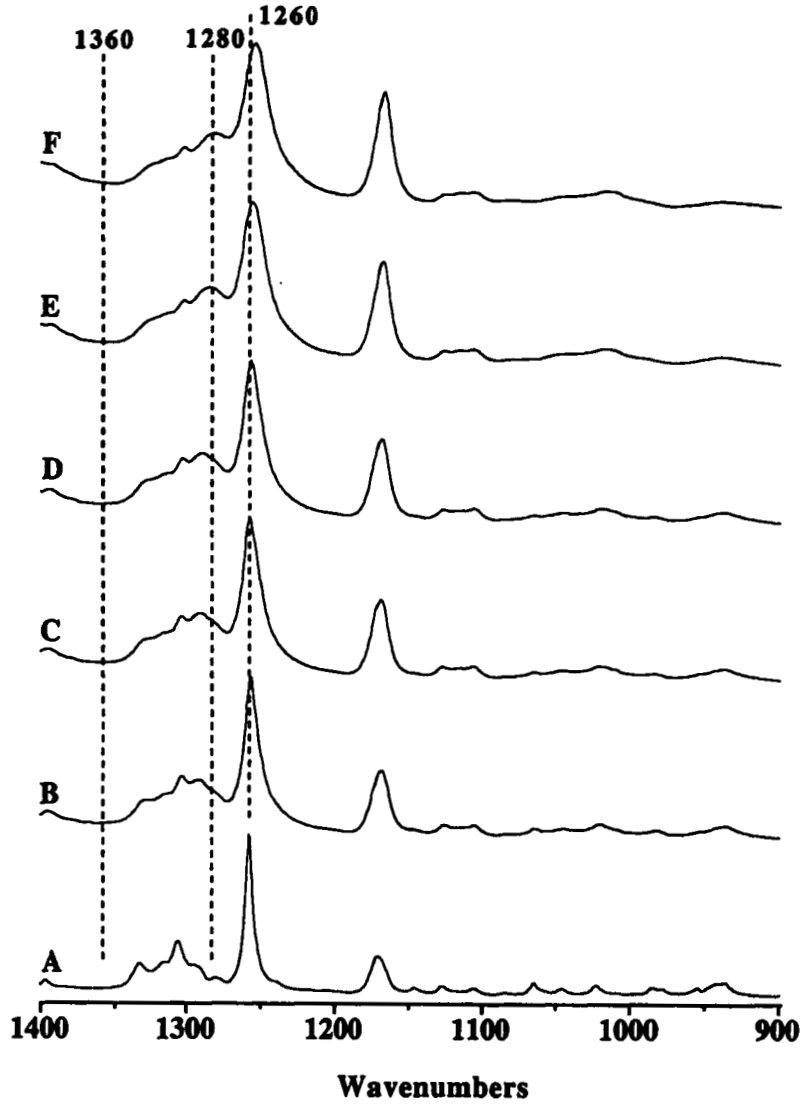

FIGURE 14 The 1400 cm^{-1} – 900 cm^{-1}region of the spectrum of a KBr pellet of 10-AOBA at A) 25°C, B) 94°C, C) 105°C, D) 110°C, E) 135°C, F) 150°C

These results tell us that the K_{II} crystal form is less ordered than the K_I structure, with at least a partial breakup of the aromatic CH/carbonyl oxygen interactions and a further (perhaps lateral) disordering of the arrangements of the stacked acid groups. This interpretation is supported by the changes in other regions of the spectrum. The out-of-plane aromatic CH bending modes also

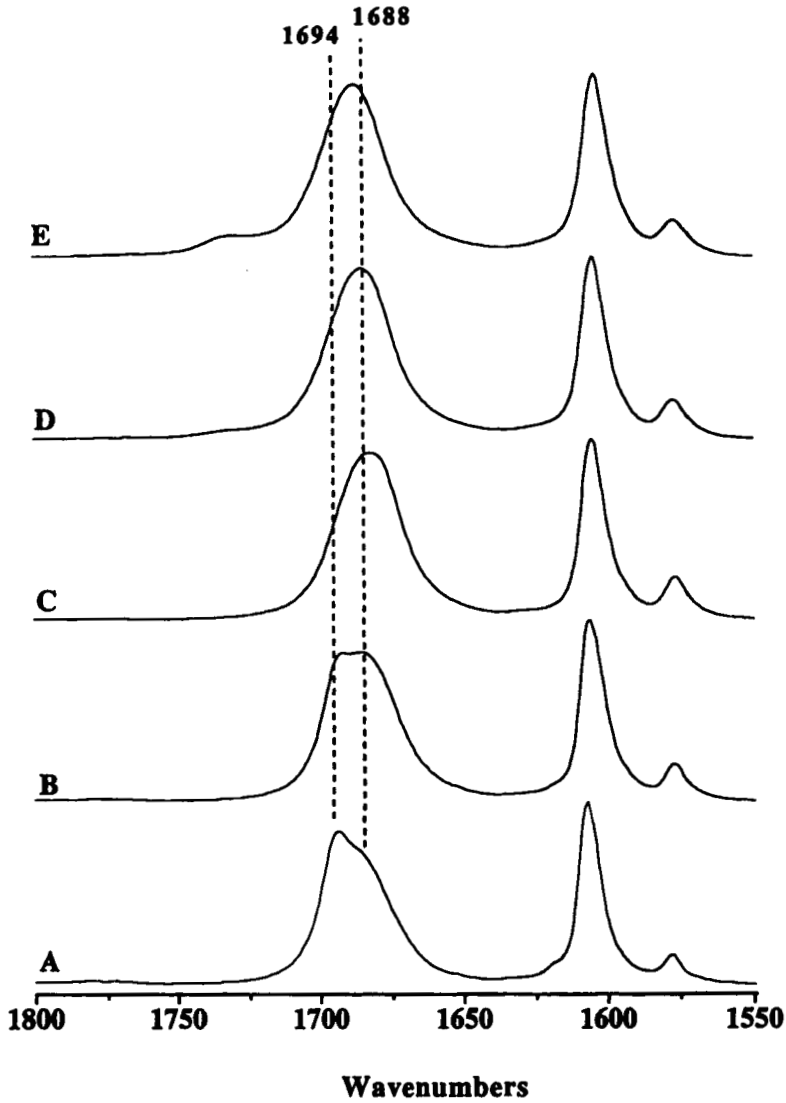

FIGURE 15 The carbonyl stretching region of the infrared spectrum of a KBr pellet of 6-AOBA at A) 25°C, B) 60°C, C) 85°C, D) 125°C, E) 155°C

broaden and shift with temperature, as shown in figure 13, with a shoulder appearing on the side of the 845 cm^{-1} mode. Bands due to CH_2 wagging modes between 1360 and 1280 cm^{-1} and the (predominately) aromatic C-O ether stretching mode near 1260 cm^{-1} also broaden, shift and change in relative intensity, as shown in figure 14, indicating conformational changes and disordering in

the alkoxy chains. These observations strongly indicate that the K_{II} form is a "conformationally disordered" or "condis" crystal, as suggested by Wunderlich et al. (11), and in these materials appears to be an intermediate state between the crystalline and liquid crystalline forms.

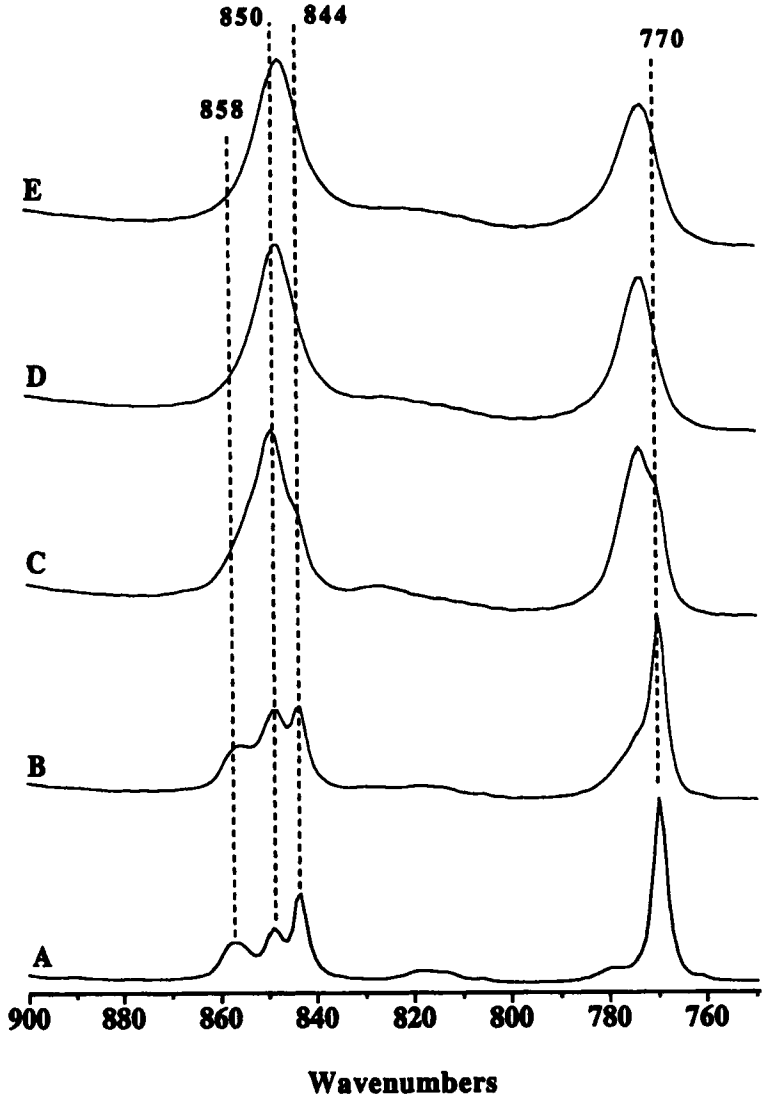

FIGURE 16 The aromatic CH out-of-plane bending region of the spectrum of a KBr pellet of 6-AOBA at A) 25°C, B) 60°C, C) 85°C, D) 125°C, E) 155°C

The changes observed in the carbonyl stretching region of the spectrum of the KBr pellet of 6-AOBA as a function of temperature are shown in figure 15. There are two bands, one near 1694 cm^{-1} assigned above to the crystal form obtained from ethanol solution, and the other, the lower frequency band near 1686 cm^{-1}, assigned to the presence of a coexisting second crystalline phase induced by the pressure used to make KBr pellets. At 60°C, just above the $K_V \rightarrow K_{IV}$ transition, the 1684 cm^{-1} band dominates, but a weak should near 1694 cm^{-1} is still discernable, indicating that there are still co-existing structures. At higher temperatures we simply observe a broad envelope, presumably due to the effect of interactions between cyclic dimers in a broad range of environments.

The out-of-plane aromatic modes near 850 cm^{-1} and 770 cm^{-1} display similar trends (figure 16). The most clear cut transition is $K_V \rightarrow K_{IV}$, where a band near 848 cm^{-1} increases significantly in intensity relative to that near 845 cm^{-1} and a band near 774 cm^{-1} increases relative to that at 771 cm^{-1}. At higher temperatures only broad bands that shift gradually in frequency are observed. This suggests that there are two well-organized crystal structures in 6-AOBA, a stable form obtained from solution which can at least partly be converted by pressure and temperature ($K_V \rightarrow K_{IV}$,) to a second structure. The remaining solid-state structures appear to be various forms of "condis crystals", again an intermediate state between the crystal and liquid crystal forms.

The Spectra of 10-AOBA and 6-AOBA Samples Crystallized from the Melt

Finally, both 10-AOBA and 6-AOBA were recrystallized from the melt, and the spectra in the carbonyl stretching region at 25°C are illustrated in figure 17. It is immediately obvious that these spectra are broader and more complex than those obtained using the KBr pellets and diffuse reflectance (figures 4, 5, and 8). The spectra appear to be composed of a number of overlapping bands, characteristic of the various crystalline and liquid crystalline forms obtained in the spectra of the KBr pellets studied as a function of temperature.

CONCLUSIONS

The infrared spectra of the *p*-n-alkoxybenzoic acids are sensitive to the modes of packing found in the crystalline state. The isotypic crystal form characteristic of the alkoxybenzoic acids where n>6 have a disorder in the arrangement of the stacked layers of carboxylic acid dimers that leads to a splitting of the carboxyl

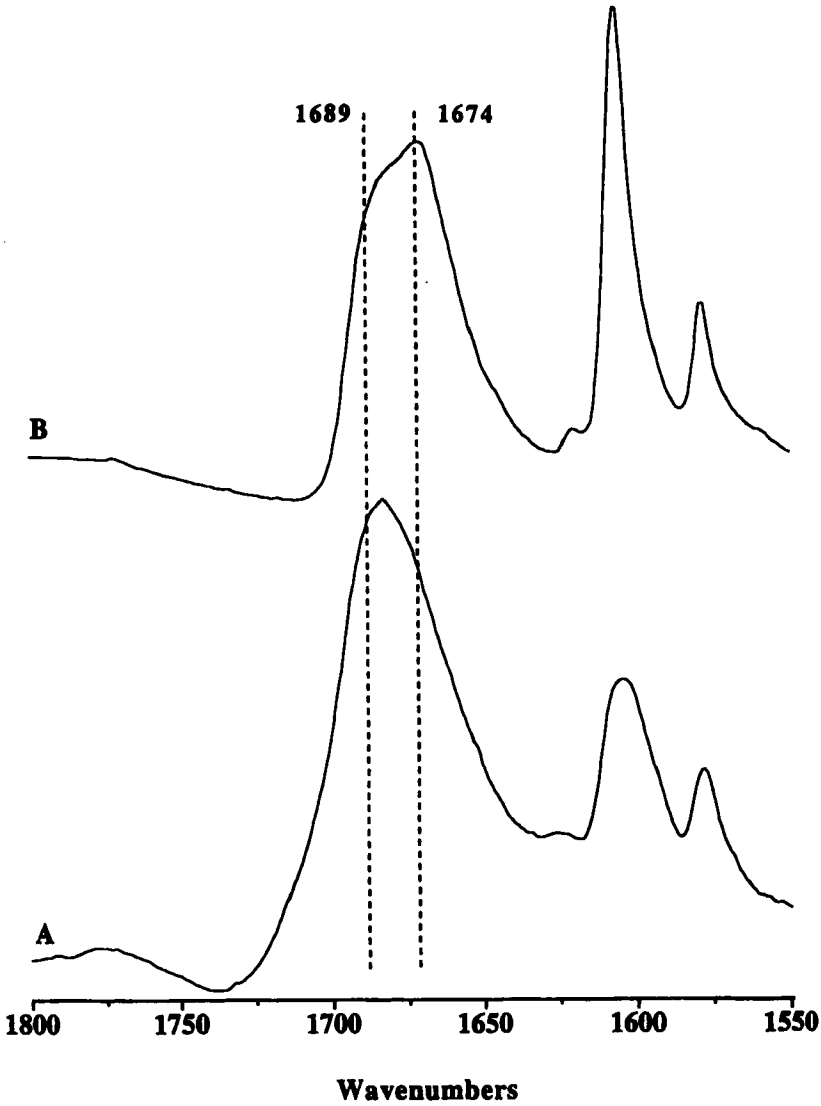

FIGURE 17 FTIR spectra of melt crystallized films of A) 6-AOBA and B) 10-AOBA in the carbonyl stretching region

stretching mode, a result of transition dipole coupling. Furthermore, within the layer there is the type of close contact between aromatic CH groups and one of the lone pairs on the carboxyl oxygen on adjacent dimers that is characteristic of

hydrogen bonding and results in a shift of the C=O stretching mode to lower frequencies than the band observed in those alkoxybenzoic acids with n<7.

The infrared spectra are also sensitive to polymorphism. For the 10-alkoxybenzoic acid the single solid state transition observed near 85°C in previous studies involves the transformation from the isotypic crystal form to a conformationally disordered or "condis" crystal. This appears to be the intermediate state between the crystalline and liquid crystalline forms. There are apparently two stable crystal forms in 6-alkoxybenzoic acid which co-exist at temperatures above the first solid state transition temperature (58°C). The three higher temperature transitions appear to involve transformations to "condis" crystals, again as intermediates between the crystalline and liquid crystalline states.

Acknowledgements

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