of molecular aggregates in biological systems as well as on the nature of interactions of such additives with living systems. Insight into the nature of these interactions could be useful in attempting to rationalize reported results that show BHT to be a potent inactivator of mammalian and bacterial viruses. While the current views of membrane morphology are constantly shifting, such a study in conjunction with the results of this work should provide useful information to advance our understanding of the role of such molecules in transfer through lipid membranes.

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Registry No. POE (23), 9002-92-0; BHMP, 88-26-6; BHT, 128-37-0; BHA, 121-00-6.

Supplementary Material Available: Tables of density and volume data for BHT, BHMP, and BHA in aqueous micellar solution of POE(23) at 25, 35, and 45 °C (10 pages). Ordering information is given on any current masthead page.

Infrared Spectroscopic Characterization of Ultrathin Films of Disklike Molecules on Metallic Substrates

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Infrared spectra obtained for two families of disklike liquid crystalline molecules deposited on metallic surfaces have been extremely useful in the elucidation of the relative orientation of various structural subunits. The "cores" were found to lie flat on the external surface. However, the polyethylene branches or arms extending from the central ring lie on the external surface with the skeletal plane perpendicular to the surface. The relative orientations change significantly during phase transitions.

Introduction

Among liquid crystalline compounds, one of the most fascinating families is that consisting of disklike molecules or macromolecules. In the past several years a considerable effort has been under way to characterize the structural differences of the various phases found in these compounds.[1-8] Several phases have been identified, including crystalline, columnar, nematic, and isotropic. We have been working with the structures associated with benzene-hexa-*n*-alkanoates, shown schematically in Figure 1, with the number of methylene units plus methyl units ranging from 5 to 7 (n = 5, 6, and 7 denoted as BH6, BH7, and BH8, respectively). In our earlier study we primarily used vibrational spectroscopy to characterize the conformational changes associated with the methylene sequences and the ester group in the individual phases observed.[9] In that study we found strong evidence to suggest that the polyethylene chains are straight with fully planar zigzag conformation only for the BH8 molecule. Changes in the Raman spectra suggested that the conformation of the methylene sequences may disorder at temperatures above room temperature but well below the crystalline-nematic transition. Furthermore, we observed two specific conformations associated with the ester groups. The relative amount of the two varied significantly as a function of temperature with discrete changes occurring only at each phase transition.

In the present study we continue the characterization of conformation changes in this series of molecules, except that we use quite a different geometry to gain structural information complementary and supplementary to the previous analyses. Extremely thin samples (20-80 Å, or roughly 3-14 molecular layers) were cast on gold surfaces, and reflectance infrared spectra were obtained for these samples. The boundary conditions are such that only incident electromagnetic radiation with polarization in the plane of scattering has significant energy at the immediate surface.[10] In contrast, the electromagnetic waves with the polarization perpendicular to the scattering plane has a node at the surface and is not absorbed by the thin sample film.[10] Therefore, as a result of having such boundary conditions at the metallic surface, vibrations with components of the transition moments perpendicular to the metallic surface are expected to appear with enhanced intensity while those having transition moments nearly parallel to the surface are expected to appear weakly or not at all. Having such a unique macroscopic frame of reference, we expect these reflection experiments to yield information on structures and their changes which would otherwise be impossible to obtain. One should be cautious however, that, due to interaction of the molecules with the metal surface, the observations of these thin films may not be representative of the bulk structures. However, in our case, the phase transitions we observed by vibrational spectroscopy correspond well to optical and thermal observations on bulk samples.

Because of the well-defined macroscopic frame of reference associated with the reflectance technique, the present study is especially suitable for determining the orientation of these liquid crystalline molecules on substrates. This becomes particularly important for elucidating the orientation of ester groups, central benzene rings, and polymethylene chains with respect to each other and also with respect to the substrate plane. However, due to a lack of suitable infrared active vibrations, it has been difficult to determine the orientation of the benzene rings in BH6, BH7, and BH8 with respect to external surfaces. Therefore, another series of samples, tetrakis(octanoyloxy)-*p*-benzoquinone, which contains carbonyl (C=O) groups as part of the central planar "core", has

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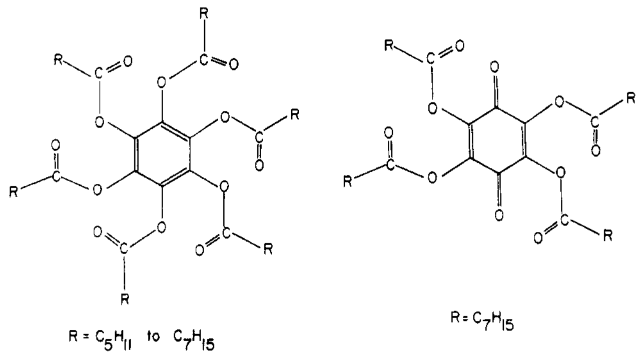

Figure 1. Schematic drawings of benzene–hexa-*n*-alkanoates (left) and tetra-*n*-octanoate (right).

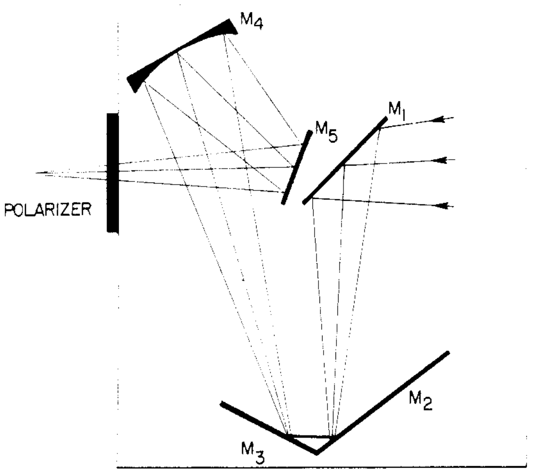

Figure 2. Schematic drawing of the external reflectance unit.

been prepared. Their structures have been compared to the molecules used in the previous study. The characterization of the new molecules and structural interpretations derived from the additional data obtained from the reflection experiment are presented in this paper.

Experimental Section

Tetrakis(octanoyloxy)-*p*-benzoquinone, denoted as QTE8, was synthesized in two steps from tetrahydroxy-*p*-benzoquinone[11] by a modified procedure of Verter.[12] Tetrahydroxy-*p*-benzoquinone (0.0087 mol) was refluxed with 10 equiv of acid chloride as the reaction vessel was swept with dry N_2. After 4 h, the excess acid chloride was removed under reduced pressure. The resulting brown-red solution was then cooled, and the residue titrated with cold ethanol (10–15 mL). The crude product was then purified by successive crystallizations from absolute alcohol to give pale yellow needles. The structure was confirmed by ^{1}H NMR spectroscopy at 300 MHz and also by elemental analysis. The density was found to be 1.0795 g/mL at 24 ± 1 °C by measuring in an aqueous sucrose solution containing sodium dodecyl sulfate.[13]

Chandrasekhar's original identification of QTE8 as a discotic[7,8] was subsequently withdrawn.[14] Our DSC and optical microscopy studies using highly purified samples show that this compound and its heptanoate ester analogue exhibit mesophases. Under crossed polars, the mesophase appears viscous and resembles a mosaic texture. The series of benzene–hexa-*n*-alkanoates is prepared as described earlier.[9] In the current study, BH8 is given the main emphasis.

The specular reflectance accessory used in this experiment was purchased from Harrick and is shown schematically in Figure 2. We have modified this accessory by replacing one of the reflecting surfaces by gold mirrors purchased from Edmund Scientific. The gold mirrors were cut into small sizes in order to fit the reflection accessory. After removal of the protective cover films from the gold surfaces, the mirrors were soaked in concentrated nitric acid for approximately 5 min to clean the surface, followed by washing with distilled water and rinsing with methanol. The mirrors were then kept in an evacuated oven overnight. The smoothness of the mirrors was checked by scanning electron microscopy, and the cleanliness was checked by X-ray photoelectron spectroscopy (XPS). Even though the critical angle needed to achieve maximum signal-to-noise ratio in infrared absorption experiments is 88° from normal,[10] we found, as have others,[15] that working in the range of 80–82° is experimentally preferable. Background scans taken with the accessory in place were stored for further use. Knowing the solution concentration (1.12×10^{-4} g/mL) and the density of the molecules (0.99 g/cm^3), thin sample films casted on the gold substrates with chloroform solution were calculated to be 100 Å. The thickness of these films was checked by XPS. These spectra were recorded on a Perkin-Elmer Physical Electronics 5106 spectrometer (Mg Kα source, 300 W). The pressure in the analysis chamber was 10^{-9}–10^{-8} Torr during data acquisition, and samples were analyzed at 25° from normal. The thickness obtained is 80 Å, consistent with the estimate made. It is also possible to calculate directly the reflectivity from thin-film-covered gold surfaces when the isotropic infrared spectrum and the optical constants of the gold are known. These calculations have been carried out for the samples used in the present study. The theoretical calculations and some of the results applicable to extremely thin films will be published shortly.

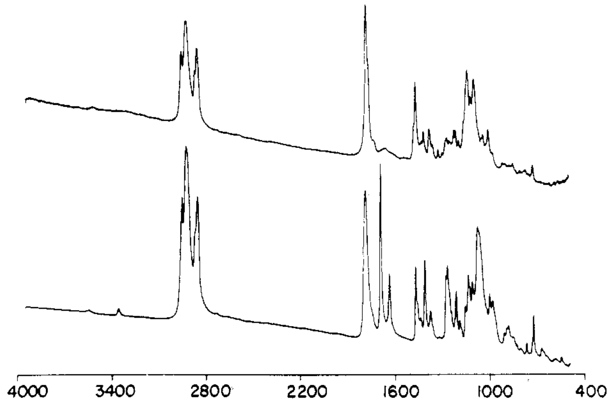

Figure 3. Infrared spectra (400–4000 cm^{-1}) of BH8 (top) and QTE8 (bottom) obtained by the transmission technique.

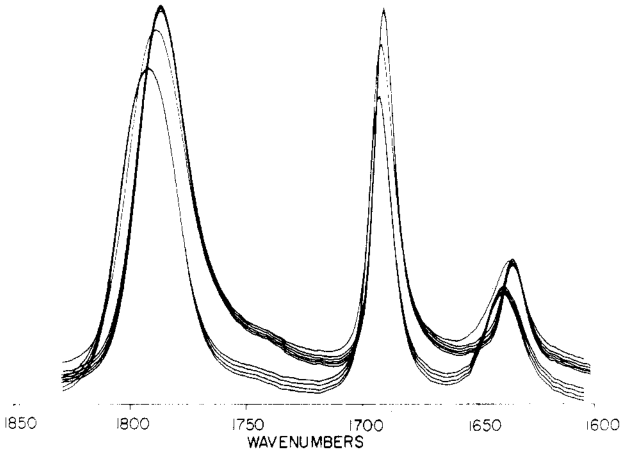

Figure 4. Infrared data (1600–1900 cm^{-1}) of QTE8 as a function of temperature.

Spectra were obtained with an International Business Machine Model 32 Fourier transform infrared spectrometer. For trans-

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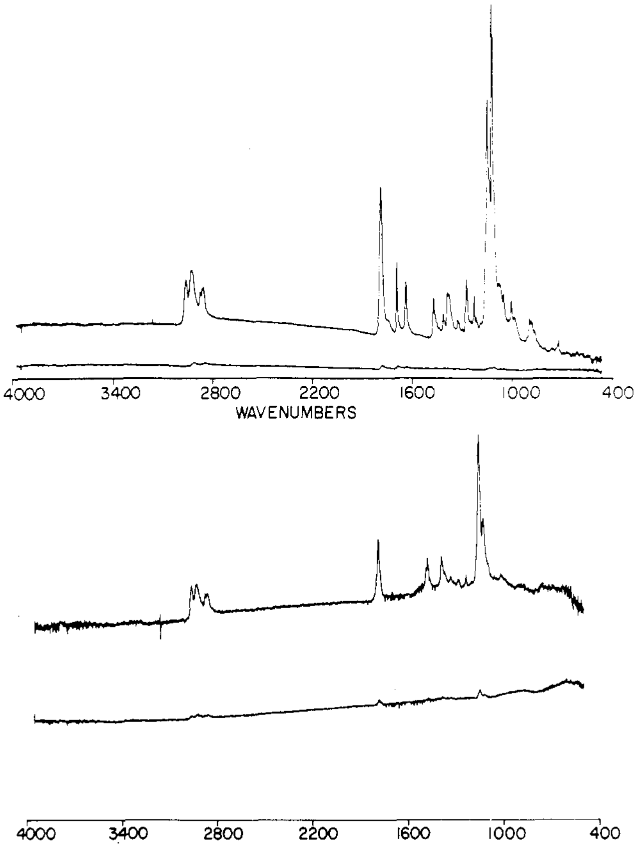

Figure 5. Infared spectra (400–4000 cm^{-1}) obtained by the reflectance technique for QTE8 (top) and BH8 (bottom): top, perpendicular polarization; bottom, parallel polarization.

mission spectra, the sample was placed in a heating cell built in our laboratory and spectra were obtained at temperatures ranging from 20 to 100 °C. All spectra were taken at 2-cm^{-1} spectral resolution with a room-temperature DTGS detector. A total of 500 scans was necessary to achieve acceptable signal-to-noise ratio in transmission experiments. The infrared spectra of QTE8 and BH8 are shown in Figure 3. The infrared data obtained by the transmission technique as a function of temperature are shown in Figure 4. Generally, 1000 scans were signal averaged to obtain an acceptable signal-to-noise ratio in the reflection mode. We have also modified the reflectance accessory so higher temperature measurements can be obtained as well. The temperature can be set confidently at ±0.2 °C in order for us to obtain spectra from mesophases stable over only 1 or 2 °C ranges. A Perkin-Elmer wire grid polarizer was used to obtain incident radiation with polarization oriented parallel to the plane of scattering; i.e., perpendicular to the metallic substrate plane. As expected, only the incident radiation with polarization parallel to the scattering plane is absorbed by this sample. These reflectance spectra of the two polarizations are shown in Figure 5. The temperature dependence of the reflection spectra with perpendicular polarization is shown in Figures 6 and 7. Raman spectra were obtained for the benzene-*n*-alkonates in the powder form. The Raman instrument used has been described previously.[9] The spectrum obtained for BH8 is shown in Figure 8. Since QTE8 is off-white in color, the considerable fluorescence present makes the Raman data difficult, if not impossible, to obtain.

We have developed a considerable number of algorithms for the IBM 9000 computer associated with the Fourier transform infrared spectrometer in order to analyze spectroscopic data. To obtain a more quantitative measure of the contributions of overlapping components, a band deconvolution routine using nonlinear regression algorithms was carried out. This program has been described previously.[9,16]

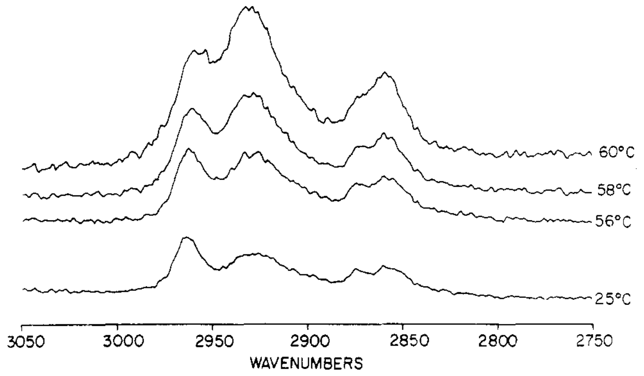

Figure 6. Infrared reflection spectra of the CH stretching region of QTE8 at various temperatures.

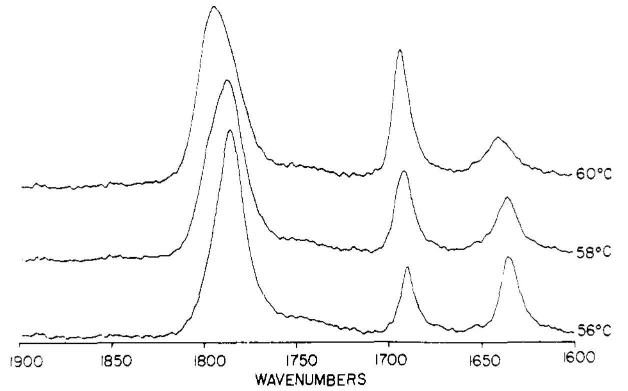

Figure 7. Infrared reflection spectra of the C=O stretching region of QTE8 at various temperatures.

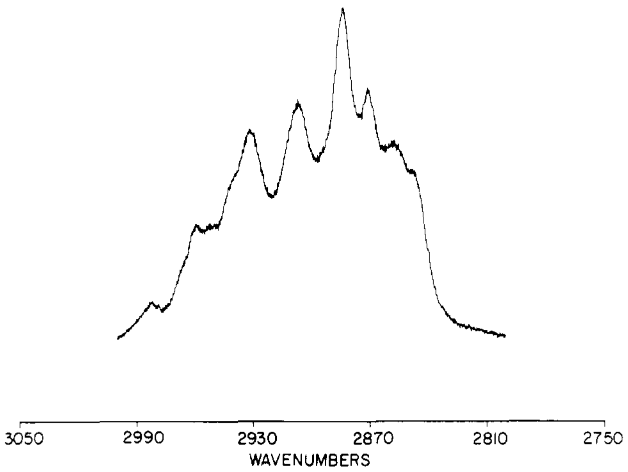

Figure 8. Raman spectrum (3050–2750 cm^{-1}) of BH8. Transmission spectrum was obtained at room temperature (25 °C).

Results and Discussion

The model which is generally accepted for disklike liquid crystalline molecules is based on a columnar hexagonal array in which the "cores" are stacked, most likely, aperiodically atop one another with the branches extended from the core.[1-8] However, it should be stated that the structures of BH*n*'s have been characterized to a much greater extent than has QTE8. Although scattering techniques are useful in the determination of long-range order, details of the microstructures and their changes have yet to be obtained. Elucidation of the microstructures of these disklike molecules and their changes as a function of temperature on external surfaces are the major goals of the present study. The straightness of the arms, the relative orientation of the polymethylene skeletal plane to the ester group, and the central core are the major questions to be answered for each phase.

Our discussion will first center on the structure of these disklike molecules on the metallic surface, and then the characterization

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of the changes as the temperature is raised will be discussed. In our previous study, we interpreted spectroscopic data for BH6, -7, and -8 to show that the branches possessed an all-trans conformation only for BH8 in the crystalline state. A considerable amount of our analysis is based on comparisons between our present observations and the enormous number of analyses available for *n*-alkanes.

The task of analyzing the conformations of these molecules on external surfaces is made easier by analyzing well-assigned vibrations which are localized in nature with well-defined transition moments. Various localized vibrations such as CH_2 rocking, bending, and stretching are examples. The frequency of individual vibrations is characteristic of chain conformations and packings associated with highly ordered *n*-alkanes.[9]

The Raman spectrum of BH8 in the crystalline state shows a strong resemblance to that of *n*-alkanes with fully extended trans conformations, suggesting that the polymethylene chains of BH8 are in trans conformation in the crystalline state. The number of small peaks in the 2800–3200-cm^{-1} region is associated with the overtone progression of CH_2 bending modes that have borrowed a considerable intensity from the CH_2 stretching fundamental. Their frequencies are virtually identical with the components observed for the equivalent normal paraffins in the solid state.[9] Although Raman data are not available for the QTE8 molecule, all interpretable infrared spectroscopic features, such as the frequencies found for the asymmetric and symmetric CH_2 stretching vibrations, suggest that in the crystalline state the polymethylene chains are straight for both QTE8 and BH8 molecules on external surfaces.

The infrared spectra of BH8 and QTE8 are shown in Figures 3, 5, and 6. Two bands near the 2964-cm^{-1} region and one at 2873 cm^{-1} can be assigned to the CH_3 asymmetric and symmetric stretching vibrations, respectively.[16] The bands at 2928 and 2858 cm^{-1} are assigned to the methylene asymmetric and symmetric stretching vibrations, respectively.[17] If the polymethylene chains are indeed fully trans in conformation, the corresponding methylene stretching vibrations are expected near 2920 and 2855 cm^{-1} as we observed. This qualitative agreement supports the conclusion derived from the Raman analyses that the BH8 and QTE8 molecules have essentially straight extended chains in contrast to other molecules in the BH*n* family with shorter methylene sequences.

From the comparison of the spectra shown in Figures 3, 5 and 6, it is quite evident that substantial intensity differences exist between the spectra obtained by transmission and reflection techniques and that these differences are useful for structural characterization. The symmetric methyl stretching has a transition moment parallel to the terminal C–C bond and in the skeletal plane, while the transition moment of the asymmetric methylene stretching is perpendicular to the polymethylene chain. Therefore, the relative intensity of the methyl and methylene stretching vibrations gives valuable information on the orientation of methylene sequences on a metallic surface. External reflection spectroscopy was applied to measure the orientation of methylene chains in lauric acid on oxidized surfaces of iron mirrors[18] and cadmium arachidate on silver.[18,19] In those cases, the intensity of the methylene stretching vibration was much weaker than that of symmetric methyl stretching vibration in the reflection spectrum. On the basis of these results, it was concluded that the methylene chain axis was perpendicular to the metallic surface for these molecules.[19,20]

However, in our case, a different geometry is likely to exist. The arms associated with these disklike molecules are likely to be straight, extending away from the central ring. Physically, it is unlikely that the arms can have perpendicular orientation to an external surface. In order to obtain more detailed information on the side chain orientation, the overlapping bands in the CH stretching region were resolved by the least-squares curve-fitting procedure described earlier. Relative intensities of individual components were calculated by dividing the intensity of each band of the reflection spectrum by that of the corresponding band of the transmission spectrum in the isotropic state. These are shown in Figure 9 as a function of temperature. The relative intensity of each band decreases with decreasing temperature from 60 to 56 °C, the interval in which the isotropic–liquid crystal and liquid crystal–crystal phase transitions take place. The average of the relative intensity of the symmetric and asymmetric methylene stretchings is higher than the relative intensity of methyl symmetric stretching vibration throughout the temperature range studied, suggesting that the methylene chains tend to favor the orientation parallel to the metal surface.

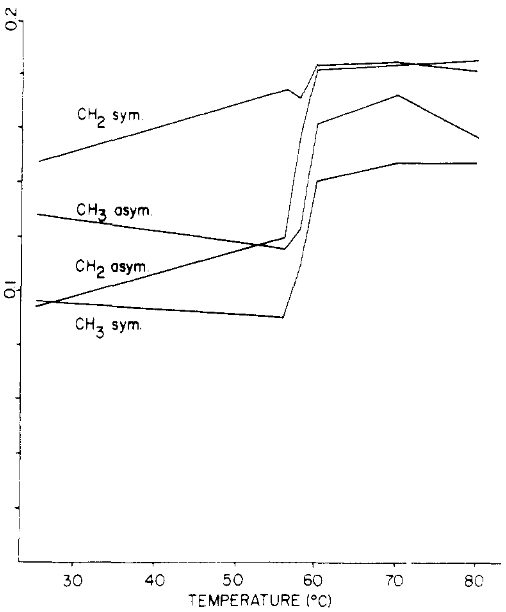

Figure 9. Relative intensity of the C–H stretching vibrations in the reflection spectrum to those in the transmission spectrum of the isotropic melt as a function of temperature for QTE8.

The most striking feature of the reflection spectrum in the C–H stretching region is the change in the relative intensity of symmetric and asymmetric methylene stretching vibrations. As shown in Figures 6 and 9, the intensity of the asymmetric methylene stretching decreased relative to that of the symmetric methylene stretching with decreasing temperature. From single-crystal studies of *n*-alkanes we expect the symmetric methylene stretching at 2850 cm^{-1} and the asymmetric methylene stretching at 2920 cm^{-1} to have transition moments in and out of the skeleton plane, respectively.[21-23] The differences in the relative intensity of these two vibrations suggest that the plane containing the planar zigzag backbone is perpendicular to the external surface in the crystalline state.

Our conclusion regarding the perpendicular orientation of the skeletal plane on the external metallic surface can be supported by the intensity and positions of the methyl group vibrations observed. Usually three vibrations are assignable to the CH_3 groups. The symmetric vibration is observed at 2873 cm^{-1}. Two asymmetric CH_3 stretching vibrations should be observed near 2963 and 2953 cm^{-1}. Based on polarization studies of *n*-alkanes, the effective transition moment associated with the higher frequency component is parallel to the skeletal plane and that of the lower frequency component is perpendicular to the skeletal plane.[21-23] We see a strong band at 2961 cm^{-1} in BH8 and at 2964 cm^{-1} in QTE8 in the reflection spectra. However, a strong

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band is observed approximately 10 cm^{-1} lower in the transmission spectrum obtained for each molecule. This difference cannot be attributed to the optical effects associated with thin films.[24] Instead, we assigned the two bands to the two asymmetric stretchings associated with the methyl vibrations. Considering that only the vibrations with transition moments perpendicular to the metallic plane can be observed by the reflection technique, we would reach the same conclusion, that the skeletal plane is indeed perpendicular to the metallic surface as suggested earlier.

It is also important to interpret the orientation of the core and the ester group relative to the metallic surface. For BH8, no infrared active vibrations containing well-defined transition moments in the plane of the benzene ring can be found. However, vibrational analysis has been carried out for the tetraacetate analogue of QTE8.[23] The band at 1690 cm^{-1} is associated with the C=O attached to the aromatic ring (the quinone carbonyl) with the transition moment in the plane containing the core ring.[25] On the other hand, the C=O stretching vibration found near 1780 cm^{-1} for both molecules is assigned to the ester group. The direction of the ester group is suggested to be at an angle with respect to the central core.[26] The infrared spectra obtained support the hypothesis that these disklike molecules sit on the external surface just like a chip on a table. As can be seen in Figure 5, the intensity associated with the quinone C=O stretching vibration is extremely weak relative to the ester C=O stretching. Its integral intensity is only 15% of the 1786-cm^{-1} band. This is to be compared to the significantly larger ratio measured by the transmission technique for thick films. The nonzero intensity of the 1690-cm^{-1} component may be due to surface imperfection or the existence of ring distortion.[27] The significant difference between the intensity of the two vibrations in the reflection spectra suggests that, if these two factors exist, their effects cannot be very large. From the interpretation of the QTE8 data, and the strong evidence for a common orientation of side chains parallel to the interface, we speculate that the core of BH8 molecule also lies flat on the metallic surface, although we have no direct evidence to support such a conclusion.

The structural aspects of QTE8 and BH8 may differ in steric interactions between the arms attached to the core. Even though the phase transitions found by optical and thermal measurements are quite similar in characteristics for QTE8 and BH8, few, if any, previous studies have been carried out to analyze the structures associated with these thermal transitions. In our previous study of BH6, BH7, and BH8 molecules the possibility arose that two distinct conformations may exist for the ester group. This conclusion was based on a band deconvolution technique applied to the C=O stretching vibrations in the 1700-cm^{-1} region. Even though the polymethylene bands do not exhibit any significant differences between the discotic and isotropic phases, we found that the vibrations associated with the ester group are extremely sensitive indicators of the phase transitions observed by thermal measurements. We found two conformations as predicted from the theoretical conformational analysis.[24] The relative population of the individual conformations is strongly dependent on temperature. Although it was not possible to prove at that time, our analysis in conjunction with theoretical conformational calculations suggests that the orientation of the ester group in each conformation may be different. In order to interpret the microstructural changes associated with QTE8 molecules on an external metallic surface, it is important to establish that such microstructural changes in conformation actually occur for both molecules.

As can be seen in Figure 4, the ester group frequencies in QTE8 are sensitive to changes in temperature. The transition temperatures associated with the crystalline–liquid crystalline and the liquid crystalline–isotropic phase transitions have already been established by optical and thermal measurements. The C=O stretching vibration is observed at 1756 cm^{-1} in the crystalline state. This band shifts discontinuously to 1788 cm^{-1} in the liquid crystalline phase followed by a further shift to 1792 cm^{-1} in the isotropic phase. These changes are analogous to the differences observed for the BH8 molecule. Repeating the deconvolution procedure we carried out earlier for the BHn molecules, two bands with fixed positions at 1786 and 1792 cm^{-1} also gave the best fit to the series of spectra obtained as a function of temperature. Each component is described by four parameters: position, half-width, intensity, and g, where g is the relative contribution of the Gaussian contribution in a Cauchy function.[9] A representative band and the deconvoluted peaks are shown in Figure 10. The integral intensity of the two components found at each of the phase transition temperatures is shown in Figure 11. Even though the range of the intermediate discotic or liquid crystalline phase in QTE8 is much narrower than the corresponding range found for the BH8 molecule, it is clear that the relative amount of the two components can vary substantially and reversibly as a function of temperature. This behavior is identical with that found for the BH8 molecule. Generally speaking, all of the spectroscopic evidence shows that the phase transitions associated with the two molecules are quite similar in all aspects. Figure 12 shows the relative intensity of the C=O stretching vibrations and CH stretching region calculated by dividing the band intensity in the reflection spectrum by that in the transmission spectrum in the isotropic state. The intensity of the ester C=O stretching does not change significantly with temperature, while the intensity of the ring C=O stretching increases sharply with increasing temperature in the region corresponding to the phase transitions. The orientational order of the core quinone ring increases significantly

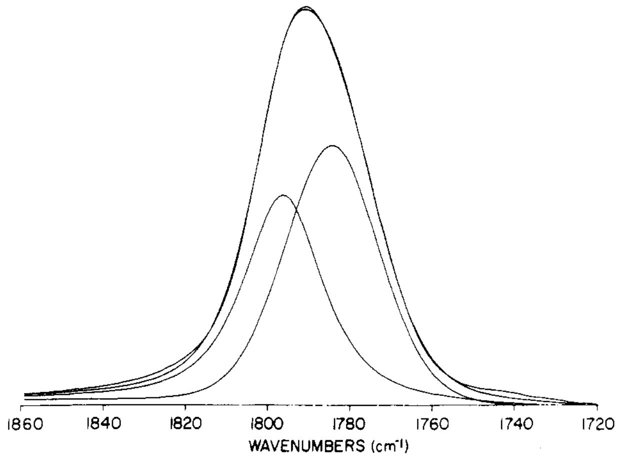

Figure 10. Data and the deconvoluted peaks for QTE8 in the infrared spectra of the C=O stretching region.

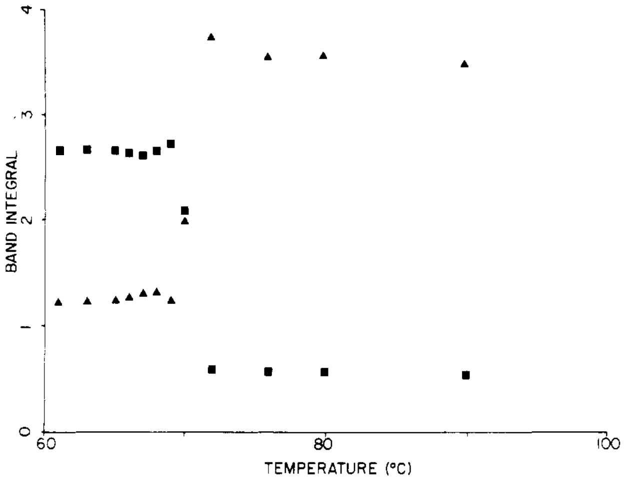

Figure 11. Integral intensity of the two components in the C=O stretching region as a function of temperature (■, 1792 cm^{-1}; ▲, 1786 cm^{-1}).

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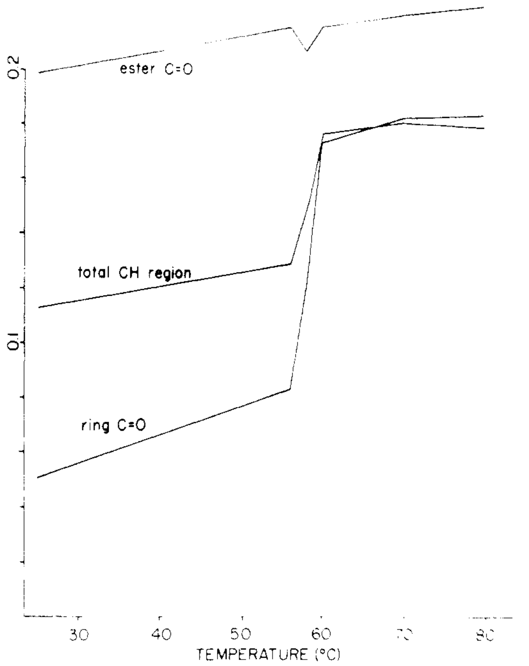

Figure 12. Relative intensity of the C═O stretching vibration and CH stretching region in the reflection spectrum to those in the transmission spectrum of the isotropic melt as a function of temperature.

with decreasing temperature in the phase transition region. The relative intensity of the ester C═O stretching vibration is still significantly higher than that of the ring C═O stretching vibration even in the isotropic state, suggesting that the core ring even in this state may still be oriented parallel to the external metallic surface.

The Raman spectra associated with these molecules changed quite substantially as a function of temperature, particularly for the 2800–3200-cm^{-1} region, even well below the crystal–liquid crystal transition. On the basis of that analysis, we were tempted to conclude that the chains were disordered even in the liquid crystalline phase.[9] However, the results obtained from the reflection technique suggest a modification is needed. The changes in both the methyl and methylene bands occur discontinuously as a function of temperature. The shift in the frequency of the methyl asymmetric stretching vibration from 2964 to 2958 cm^{-1} occurred during the discotic–isotropic phase transition and was interpreted as the disordering of the terminal methyl group. The asymmetric methylene stretching band did increase in relative intensity with increasing temperature, and the substantial increase took place during the discotic–isotropic phase transition. These results suggest that the disordering process proceeds even above the crystal–liquid crystal transition and the degree of chain disorder is less than the Raman data would indicate. It is also possible some of the spectroscopic differences observed arise from changes in intermolecular interactions. However, a quantitative analysis is really impossible at this time.

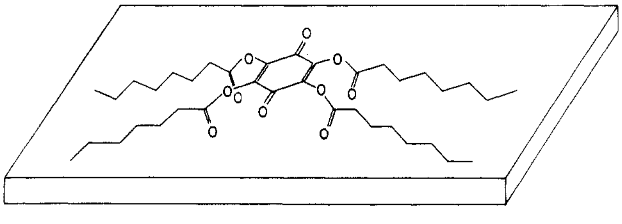

Figure 13. Schematic drawing of QTE8 molecule on a metallic surface.

Conclusion

We have shown that the reflection technique is a powerful one to assess the relative orientation of molecules on external metallic surfaces. Because of the unique boundary conditions associated with the conducting surface, the presence of only one polarization defines a workable macroscopic surface on which to attach the molecules. In this experiment, we determined the relative orientation of a simple molecule, a disklike molecule which can form a liquid crystalline discotic phase. From the infrared spectra obtained, we conclude that the conformation of the molecule on the surface is as shown schematically in Figure 13. The polymethylene arms have very specific orientations with the plane containing the skeletal backbone perpendicular to the metallic surface and the chain axis parallel to the metallic surface. The disklike core is situated flat on the surface. The ester group is oriented perpendicular to the plane of the external surface, consistent with conformational analysis of a similar class of molecules. We measured with microstructure of these disklike molecules in each of the three phases observed. The data obtained suggest that the plane of the core does not deviate significantly from the plane of the external surface in either crystalline or discotic phases. The vibrations associated with the polymethylene sequences also exhibit large discontinuous changes at temperatures associated with each description. The spectroscopic characteristics indicate the polymethylenes are largely disordered, particularly in the isotropic phase.

We feel that reflectance spectroscopy is a useful technique for structural characterization. However, it would be overly speculative to suggest our observations for these ultrathin films can be generalized to the transitions observed for the bulk. The structural changes we observed for BH8 or QTE8 on the metallic surface do occur at temperatures close to but lower than the transition temperatures measured for the bulk. Of course, we cannot rule out the specific interactions between the molecules and the metallic surface. Even with these reservations, the reflection technique still has significant utility as a characterization tool.

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