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Raman Spectra of the Liquid Crystal Homologous Series of the Alkoxyazoxybenzenes†

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Abstract—A study of the Raman spectra of the alkoxyazoxybenzenes has revealed new bands which change markedly in all phases. Evidence is presented that indicates the existence of different alkoxy tail conformations between all observed phases. A tentative assignment of a band associated with an accordion mode is made. The possible effects of these results on mesophase stability are discussed.

1. Introduction

The nature of the forces that determine the order and molecular structure of liquid crystals is a topic of current interest. Several approaches, including vibrational spectroscopy, have been used as probes of these forces. The study of the vibrational, infrared and Raman spectra of liquid crystal materials provides an attractive approach for the elucidation of the molecular structure in the various phases exhibited by these materials.(1–9)

Although previous investigations have indicated the potential of this method, the fact that these compounds are large complex molecules leads to a fairly complicated spectrum, which is not easily interpreted. Some tentative band assignments have been made by Maier and Englert(6) by infrared spectroscopic examination of the alkoxyazoxybenzene homologous series. However, such an approach is not always successful in dealing with the subtle molecular changes which can occur as a function of phase in these and other large organic compounds.

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In dealing with the study of liquid crystals, we have chosen to study this same homologous series in which *n*-alkoxy tails of various lengths are attached to a central aromatic structure. This feature provides a simple mechanism for studying the effect of chain length on the vibrational spectra. Since the transition temperatures of these compounds vary as a function of chain length, it might be possible to correlate the thermodynamic properties of these materials with some features observed in these vibrational spectra.

We have attempted to utilize the group frequencies of the *n*-alkanes as a probe of the molecular structure of the *p*-alkoxyazoxybenzenes, hoping to take advantage of the knowledge gained from a simpler and well-studied system. The vibrational spectra of the *n*-alkanes have been investigated both theoretically and experimentally by a number of individuals.(10,12) While the spectrum of the *n*-alkanes does contain many lines, there is one normal vibration termed the " accordion " mode which shows a simple monotonic relation as a function of chain length. Further, this mode changes drastically between the crystal and liquid phases of the *n*-alkanes. This behavior has been interpreted in terms of changes in the number and kind of molecular conformations that exist as a function of phase. Consequently, the possible discovery of a corresponding mode in the *p*-alkoxyazoxybenzenes might be a very useful probe of molecular structure in the various phases of these liquid crystalline materials.

We have obtained in the present work detailed Raman spectra of molecules in the AAB homologous series from 25–1600 cm^{-1}. Changes in the spectra of these materials are observed in all phases. By a study of this series, as a function of chain length, circumstantial evidence is found indicating that one of the bands observed to decrease as a function of phase is probably associated with a particular longitudinal mode (accordion band) of the alkoxy tail. The temperature dependence of this band has also been determined in one member of the series.

2. Experimental

The experimental arrangement consisted of a Spex double monochrometer with an ITT FW 130 cooled photomultiplier tube and a photon counting system. The spectra were enhanced by the use of zero suppression and scale expansion techniques. The excitation source was a He–Ne laser providing 30 mW of 6328 Å radiation at the sample. The samples were contained in 1 mm diameter capillary tubes. The laser beam was focused in the central region of the tube to a 50 μ diameter, and 90° scattering from this central region was then sampled in order to minimize surface orientation effects. The temperature was continuously monitored and was accurate to within 0.5 °C. Fluctuations were less than 0.3 °C.

Observations of the weak bands studied in this experiment were severely handicapped by the presence of fluorescence resulting from photo and thermal decomposition of the sample. This was especially severe at higher temperatures. It was found that the purification and oxidation techniques of Dewar and Goldberg,(11) carried out in subdued light, provided materials that initially had almost no fluorescence. The purity of material prepared in this manner was in excess of 99.9%, determined by differential scanning calorimetry (dsc). The transition temperatures observed upon heating were in excellent agreement with the results of Arnold,(13) who has performed extensive thermodynamic studies on the alkoxyazoxybenzene homologous series. In order to minimize run times and thus avoid decomposition as much as possible at higher temperatures, a large spectral width of 10 cm^{-1} was used. In addition, in the isotropic phase, the spectra were obtained by running several samples in different, but overlapping spectral regions. The worst purity of a sample after such a run was completed, exhibiting extremely high fluorescence, was 99.2% by dsc.

3. Results

Spectra for the solid phases of the series are shown in Figs. 1a and b in the 25–1700 cm^{-1} spectral region. The spectra above 900 cm^{-1} are similar to that previously reported.(3,14)

Since we were interested in conformational changes associated with the alkoxy part of the molecule, the spectral region between 200–900 cm^{-1} was studied with great care.

The observation of the band at 80 cm^{-1} in the nematic and smectic phases in the higher homologues is similar to that previously

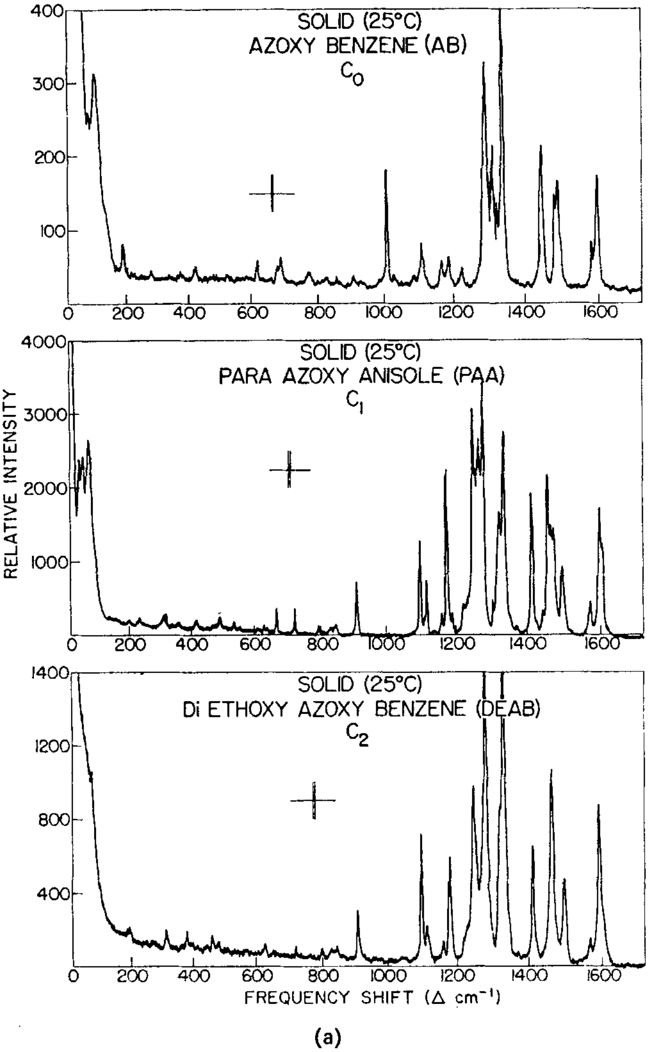
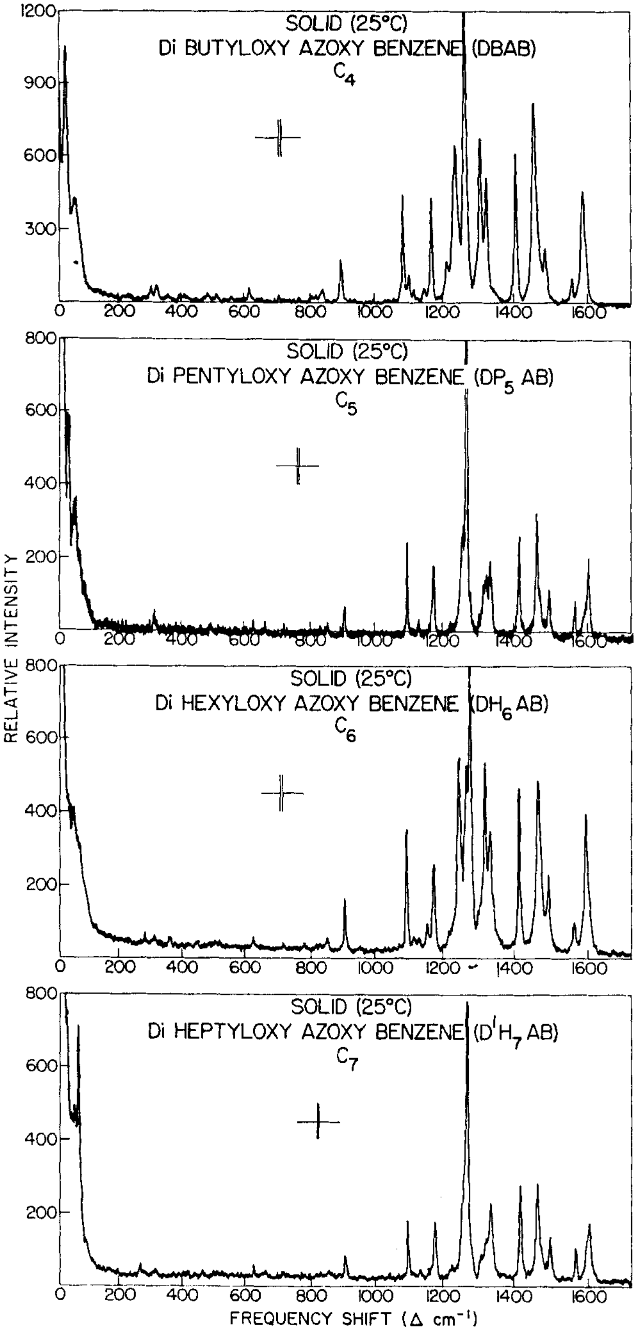


Figure 1. Tracing the observed Raman spectra of solid phase at room temperature of (a) C_0–C_2; (b) C_4–C_7. The spectral slitwidth was 1 cm^{-1}.


SOLID (25°C)
Di BUTYLOXY AZOXY BENZENE (DBAB)
C_4
1200
900
600
300
SOLID (25°C)
Di PENTYLOXY AZOXY BENZENE (DP_5 AB)
C_5
800
600
400
200
SOLID (25°C)
Di HEXYLOXY AZOXY BENZENE (DH_6 AB)
C_6
800
600
400
200
SOLID (25°C)
Di HEPTYLOXY AZOXY BENZENE (D^IH_7 AB)
C_7
800
600
400
200
RELATIVE INTENSITY
0
200
400
600
800
1000
1200
1400
1600
FREQUENCY SHIFT (Δ cm^{-1})

(b)

observed(1,2,5) in *p*-azoxyanisole. It has been suggested(1) that this band is associated with intermolecular association in the solid and mesomorphic phases. If this is indeed the case, the observation of the greater intensity of this band in the higher homologues suggests that the length-to-breadth ratio of the molecules has an important effect on those lateral intermolecular associations.

Another apparent feature of the spectra is the odd-even effects in the 750–900 cm^{-1} region for (C_4–C_7). These spectra exhibit characteristics that vary both as a function of evenness or oddness and also as a function of phase. This seems to indicate that the end methyl groups of the alkoxy tail strongly interact with their environment. This is consistent with previously observed odd-even effects in thermodynamic measurements on this series.(13) It must be noted, however, that this " odd-even " effect is based on only four members of the series. More members must be investigated before the observation of alternate behavior in the Raman spectra can be definitively associated with the environment of the end groups of the alkoxy tails.

Spectra for C_7 are shown in Fig. 2. The solid phase contains a large number of bands in the 200–900 cm^{-1} region. The fluid phases also contain many bands in this region, although their overall intensity decreases by about a factor of seven. The specific differences observed between the various phases include changes in relative intensity of some bands, as well as the disappearance or emergence of others.

The band at 271 cm^{-1} in the solid phase of C_7 is of particular interest. It greatly decreases in the smectic phase, relative to the solid, and virtually disappears in the nematic and isotropic phases. Raman spectra of the phases of C_4–C_6 were also obtained. Each contained one band in this spectral region that decreased dramatically upon entering the mesomorphic phase from the solid. The solid spectra for these four compounds in the spectral region of 250–450 cm^{-1} are shown in Fig. 3. Raman spectra obtained in each observed phase for C_1, C_4 and C_6 are presented in Figs. 4, 5 and 6, respectively. Each shows a number of changes of relative intensity as a function of phase. C_1, however, does not contain a " disappearing band " in the spectral region of 200–500 cm^{-1}.

We were able to obtain the temperature dependence of the

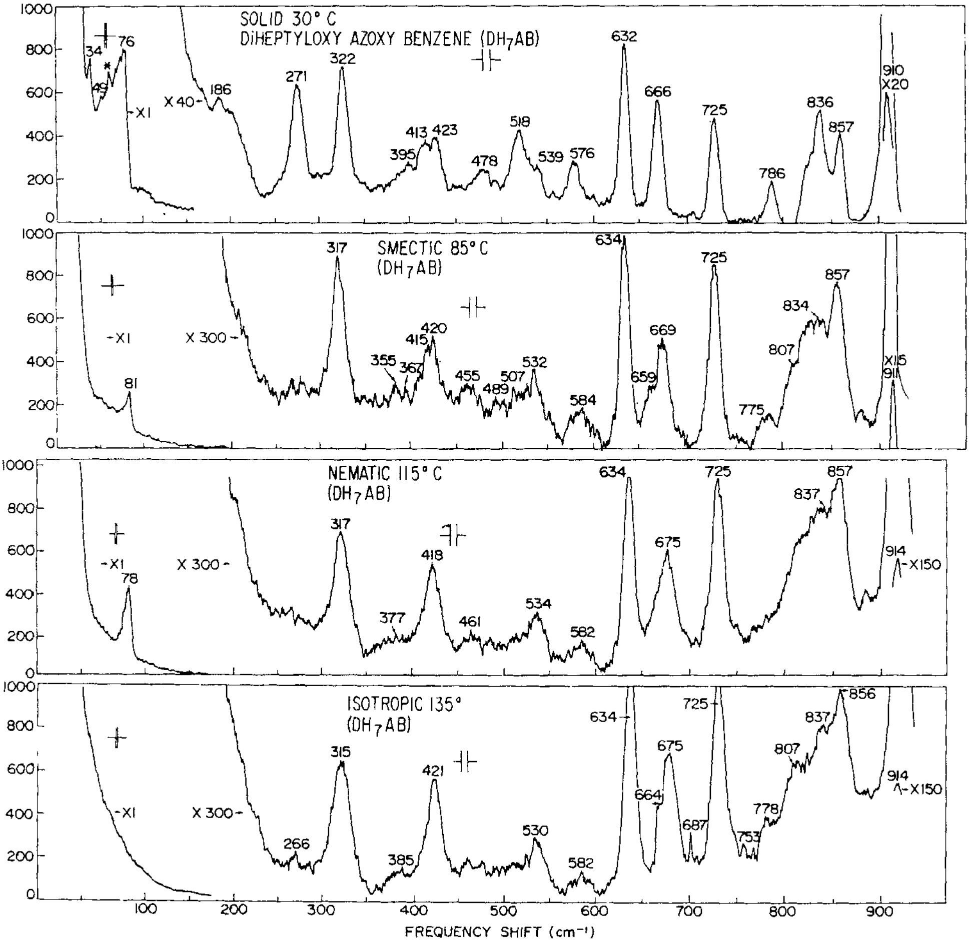


Figure 2. Tracing of observed Raman spectra of diheptyloxyazoxybenzene (C_7) in observed phases. The phase and temperature are indicated on the spectra. The spectral slitwidths were 1 cm^{-1} below 200 cm^{-1} and 10 cm^{-1} above 200 cm^{-1}. Intensity is given in arbitrary units relative to counts/second. The asterisk indicates regions of possible ghosts.

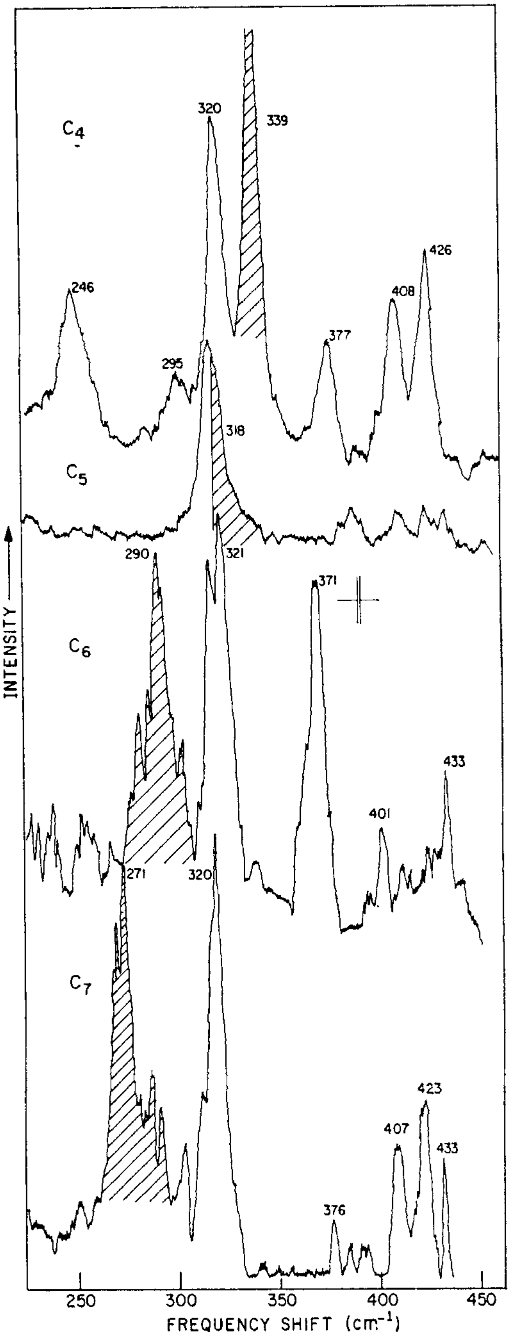


Figure 3. Tracing of observed Raman spectra of homologous series of alkoxyazoxybenzenes (C_4–C_7) in the solid phase. The spectral slitwidth was 1 cm^{-1}. The cross hatch denotes the accordion band.

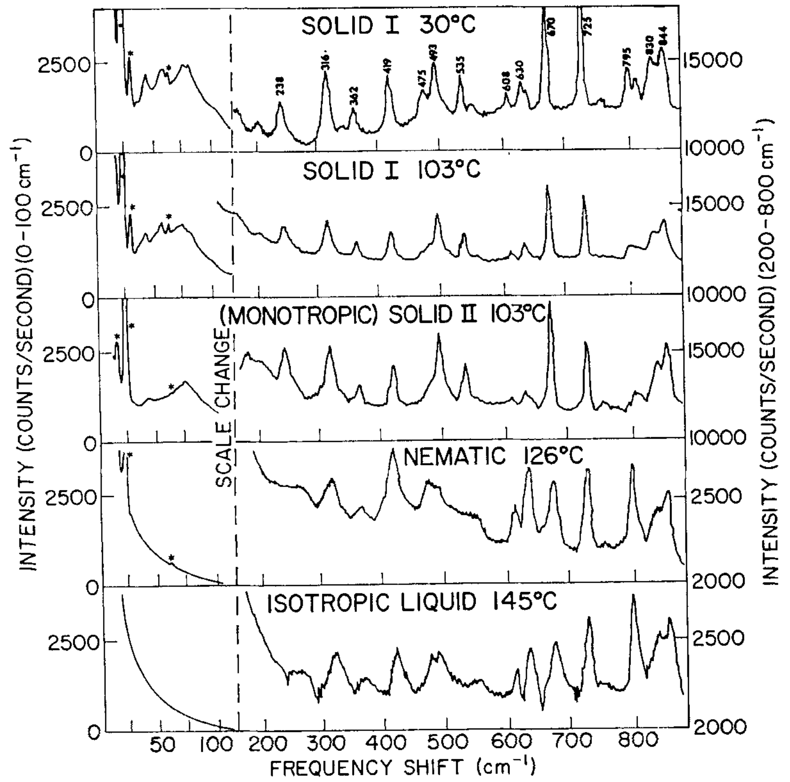


Figure 4. Tracing of observed Raman spectra of para-azoxyanisole (C_1) in observed phases. Experimental conditions were identical to those for Fig. 2.

integrated intensity of this disappearing band in C_4. These data are presented in Fig. 7. Unfortunately, due to severe decomposition problems, the temperature dependence of the disappearing bands in the other compounds could not be found with any great degree of certainty. The data presented for C_4 show a quasi-discontinuous decrease in intensity from solid I to solid II (phase transitions were determined both optically and calorimetrically) and from solid II to the nematic phase. The nematic to isotropic phase transition occurs at a higher temperature where decomposition was rapid and results uncertain. However, the intensity appears to be fairly constant in the nematic phase while apparently decreasing in the isotropic phase.

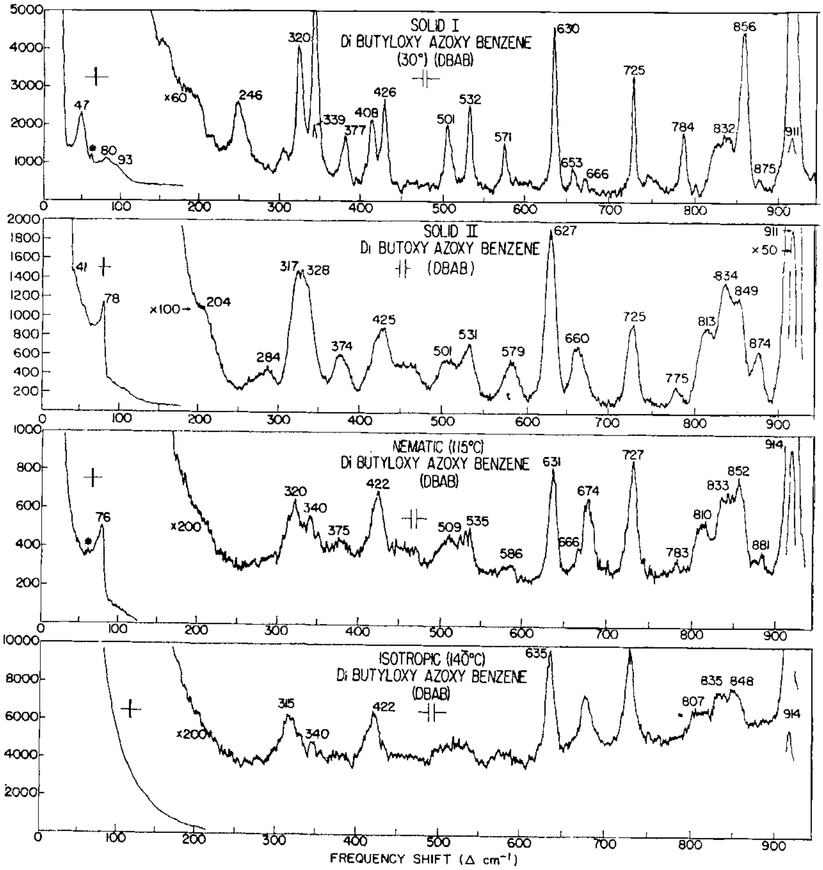


Figure 5. Tracing of observed Raman spectra of dibutyloxyazoxybenzene (C_4).

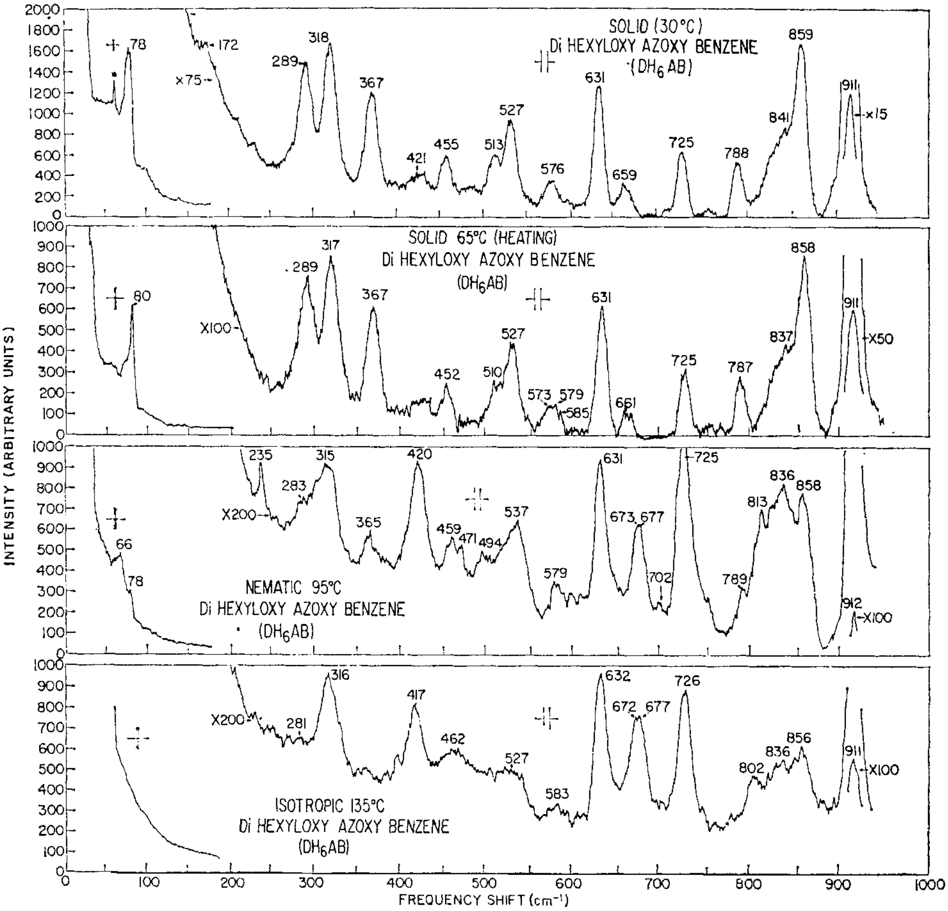


Figure 6. Tracing of observed Raman spectra of dihexyloxyazoxybenzene(C_6).

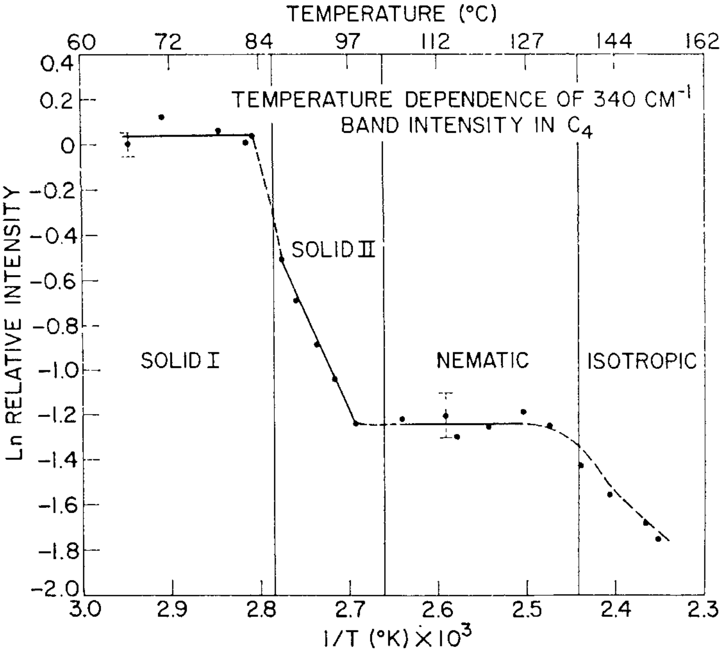


Figure 7. The relative integrated intensity of logarithmic units of the accordion band in C_4 versus reciprocal temperature. The integrated intensity of the 340 cm^{-1} band was calculated relative to the adjacent 320 cm^{-1} band which appeared to remain reasonably constant.

4. Discussion

The observation of a dramatic decrease in intensity of a band in the AAB series upon entering the fluid state is similar to the decrease observed for the band associated with the accordion-like longitudinal mode in the alkanes (only Raman active). Schaufele and Shimanouchi(12) established through spectroscopic study and analysis the existence of this vibrational mode. The mode is characteristic of the chain backbone, and its frequency is inversely proportional to the length of the polymethylene chain. It had been previously found(10) that low frequency (below 600 cm^{-1}) vibrations of the polymethylene solids could be fitted to a first order approximation for the fundamental longitudinal frequency of a linear chain of identical harmonic oscillators. The frequency of the " decreasing bands " in the AAB series also exhibit this inverse frequency relationship. Additional information is provided by the observation of the proposed accordion band at 100 °K in the solid and also in the isotropic phase at 440 °K. This removes the possibility that the band might be associated with difference bands or with a combination band of the lattice modes.

Circumstantial evidence that these bands are associated with accordion modes of the alkoxy tails is provided by the dramatic decrease in intensity of these bands, and the inverse frequency shift with carbon number.[12] It has been possible to use a simple model of an accordion with one fixed end to predict qualitatively the observed frequency versus chain length relationship, similar to that done for alkanes. The results are shown in Fig. 8. However, close quantitative agreement has not yet been achieved due to the increased complexity of the molecules being studied with respect to simple alkanes.

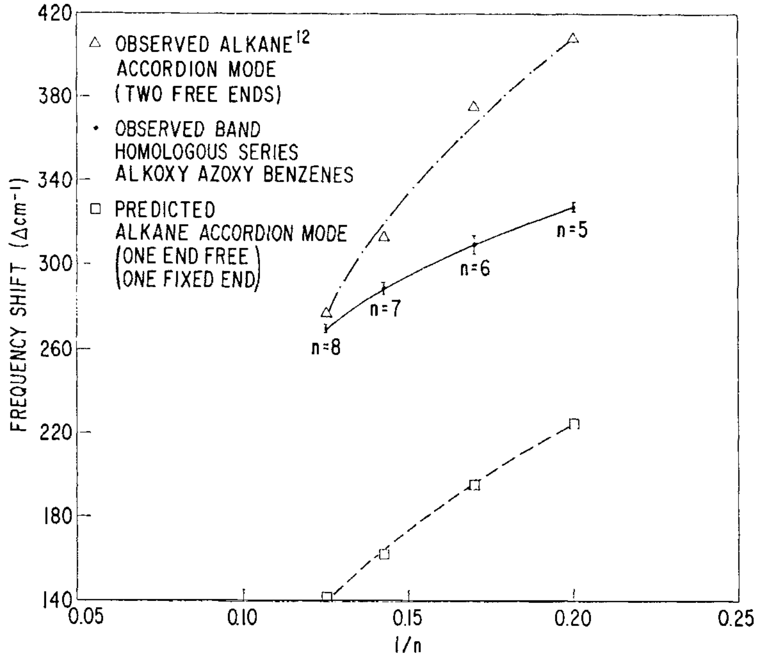


Figure 8. Predicted and observed frequency versus chain length relationship for alkanes, alkoxyazoxyhomologous series (AAB), and hypothetical alkane chain with one end fixed. In the AAB series the oxygen was treated as if it were a carbon that participates in the accordion motion. Therefore *n* equals the number of carbons in the alkoxy tail plus one (for the oxygen).

For alkane solids, the frequency of the accordion mode approached zero for infinite length chains, while in the isotropic liquid a limiting frequency has been observed. These observations have led to the proposal of chain shortening in alkane fluids. The data obtained for the liquid crystal case are more ambiguous and a limiting frequency has not yet been observed. This is not surprising considering the small number of samples studied. Therefore, the nature of the differing conformations produced in the phases cannot be ascertained with any certainty from the data presented here. (It would be necessary to look at C_{30}–C_{100}, for instance, which is a highly difficult experimental task.)

5. Conclusion

The existence of the accordion mode in the alkane series and its behavior have implications pertaining to the role of conformational changes in solid–fluid phase transitions. For the alkane solids, one or at the most two, strong bands have been observed in the solid phase. This has been interpreted to signify the existence of one or two dominant conformations.(16) For alkane solids, this band is associated with the single, fully extended, trans-conformation. New bands observed in the alkane isotropic phase have been correlated with kinks in the alkane chain, producing many gauche conformers, resulting in chain shortening.(10,12,16) The evidence for chain shortening is based on the observation of a finite limiting frequency for the accordion mode in the isotropic phase in long chain alkanes.

The results presented in this paper seem to indicate that a similar situation may exist in the AAB series. The data suggest the existence of one or perhaps two predominant conformations in the solid phase, while many different conformations are allowed in the fluid phases. The temperature dependence of the accordion mode in C_4 indicates decreasing populations of the dominant conformations in the higher temperature phases. This implies that greater numbers of conformations are allowed as order decreases in the fluid phases. These conformational changes would produce changes of length in the molecule. The increase in the number of allowed conformations would increase the entropy of the system. These interpretations are consistent with the gas liquid chromatographic (glc) results of Chow and Martire.(17) Their glc investigation provided experimental evidence for increasing entropy in C_6, which was explained in terms of conformational changes.

In conclusion, the Raman spectra of the alkoxyazoxybenzene series has been studied as a function of chain length and temperature. By comparison with the previously reported studies on the alkane series,(10,12,16) a tentative circumstantial assignment of an " accordion mode " in the alkoxyazoxybenzene series has been made. From the temperature dependence of this mode, it is possible to deduce that several conformations exist in the fluid phases, while only one or two seem to be present in the solid phase. The intensity of this mode appears to change as a function of the particular fluid phase (smectic, nematic and isotropic), indicating differing types and populations of conformations in all observed phases. Raman spectroscopy is proving to be an exceptionally valuable tool in the study of the intramolecular structure of mesomorphic materials.

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14. Except for the fact that we did not observe a band at 1142 cm^{-1} as reported by Amer and Shen. This band was seen in samples that were recrystallized several times, but not oxidized by the Dewar and Goldberg technique. The band was completely removed after this oxidation procedure, suggesting that it probably is associated with an "azo" impurity.
15. C_n denotes the number of carbons in the tail of the alkoxyazoxybenzene molecule; thus, C_5 represents dipentyloxyazoxybenzene.
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