Raman Spectral Evidence for Conformational Changes in the Liquid-Crystal Homologous Series of the Alkoxyazoxybenzenes

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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.

Previous laser Raman studies of nematic liquid crystals have shown that various phases of these compounds give rise to different spectra.[1-3] However, it has not yet been possible to extract intramolecular structural information bearing on liquid-crystal phase transitions. In this Letter, evidence is presented which strongly suggests that spectral changes in certain bands of the alkoxyazoxybenzenes can be attributed to changes in the number of conformations of the molecules among the various phases. In addition, the Raman spectrum of a thermotropic smectic phase has been observed; this has not previously been reported to the best of our knowledge. These spectroscopic studies are of particular interest because the size and shape of the molecules are of critical importance in determining the nature of mesomorphic phases.

The alkoxyazoxybenzene (AAB) series is a well-studied class of liquid-crystalline materials because it is possible to vary the length-to-breadth ratio of the molecule merely by changing the length of the alkyl side chain.[4-6] Raman spectra of four members of the AAB homologous series (C_1,C_2,C_5,C_6)[7] have been reported,[2b] but few bands could be observed for the higher members (C_5 and C_6) in the fluid phases in the spectral region below 900 cm^{-1}. Of the various members of this series, diheptyloxyazoxybenzene (C_7) is especially interesting because it has three fluid phases (smectic, nematic, and isotropic).

We have obtained in the present work detailed Raman spectra of molecules in the AAB homologous series from 25 to 900 cm^{-1} for the first time. Changes in the spectra of these materials are observed in all phases. By a study of this series, as a function of chain length, 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 of the alkoxy tail. The temperature dependence of this band has also been determined in one member of the series.

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-diam capillary tubes. The laser beam was focused in the central region of the tube to 50 μm diam, 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,[8] carried out in subdued light, provided material 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. In addition, the transition temperatures of the C_4–C_7 compounds were found to be in good agreement with the calorimetric results of Arnold.[6] 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 differential scanning calorimetry.

Spectra for C_7 are shown in Fig. 1. The solid phase contains a large number of bands in the

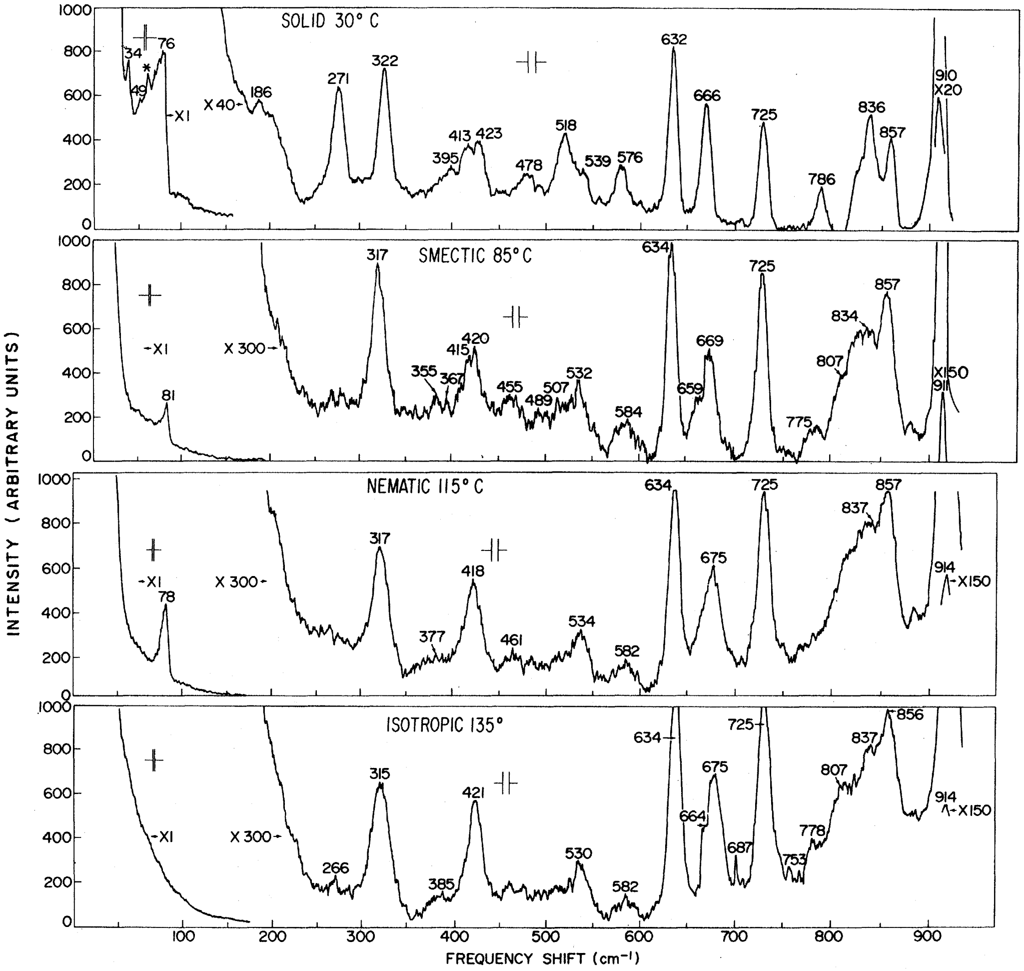

FIG. 1. Tracing of observed Raman spectra of diheptyloxyazoxybenzene (C_7) in observed phases. The phase and temperature are indicated on the spectra. The spectral slit widths were 1 cm^{-1} below 200 cm^{-1} and 10 cm^{-1} above 200 cm^{-1}. Intensity is given in arbitrary units relative to counts per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

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 7. 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. It should also be noted that the 200–900-cm^{-1} region contains many more bands for C_4–C_7 than does the corresponding spectral region for para-azoxyanisole (C_1). In addition, the Raman spectra for azoxybenzene (C_0) exhibited few bands. These results give further evidence that this spectral region contains information about the alkoxy tails in the AAB homologous series.

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 frequency of this "decreasing band" varied inversely with alkoxy chain length.

We were able to obtain the temperature dependence of the integrated intensity of this band in C_4. These data are presented in Fig. 2. Unfortunately, because of 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 quasidiscontinuous decrease in intensity from solid I to solid II (phase transitions were determined both optically and calorimetrically) and from solid II to the ne-

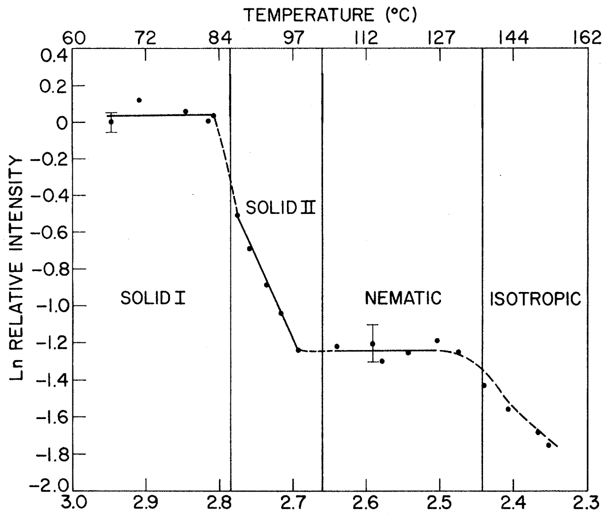

FIG. 2. Relative integrated intensity in logarithmic units of the accordion band in C_4 versus reciprocal temperature. The integrated intensity of the 340-cm^{-1} band was calculated relative to an adjacent band at 320 cm^{-1} which appeared to remain reasonably constant.

matic phase. Decomposition was rapid in the fluid phases; however, the intensity appears to be fairly constant in the nematic phase, while apparently decreasing in the isotropic phase.

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 accordionlike longitudinal mode in the alkanes (only Raman active). Schaufele and Shimanouchi[9] 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. Thus, strong 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.[11] 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. However, close quantitative agreement has not yet been achieved as a result of the increased complexity of the molecules being studied with respect to simple alkanes.

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 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.[12] 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.[9,11,12]

The results presented in this paper indicate that a similar situation exists 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. The increase in the number of allowed conformations would increase the entropy of the system, affecting the relative stabilities of each of the phases.

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,[9,12,13] it has been possible to identify the accordion mode in the alkoxyazoxybenzene series. From the temperature dependence of this mode, it is possible to deduce that several conformations exist in the fluid phase, 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.

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[1] B. J. Bulkin and F. T. Prochaska, J. Chem. Phys. 54, 635 (1971).

[2a] N. M. Amer, Y. R. Shen, and H. Rosen, Phys. Rev. Lett. 27, 718 (1970).

[2b] N. M. Amer and Y. R. Shen, J. Chem. Phys. 56, 2654 (1972).

[3] W. J. Borer, S. S. Mitra, and C. W. Brown, Phys. Rev. Lett. 27, 379 (1971).

[4] W. Maier and G. Englert, Z. Phys. Chem. (Frankfurt am Main) 19, 168 (1959).

[5] B. Bulkin, D. Grumbaum, and A. Santoro, J. Chem. Phys. 51, 1602 (1969).

[6] H. Arnold, Z. Phys. Chem. (Leipzig) 226, 146 (1964).

[7] C_n denotes the number of carbons in the tail of the alkoxyazoxybenzene molecule; thus, C_4 represents dipentyloxyazoxybenzene.

[8] M. Dewar and R. Goldberg, Tetrahedron Lett. 24, 2717 (1966).

[9] R. F. Schaufele and T. Shimanouchi, J. Chem. Phys. 47, 3609 (1967).

[10] S. Mizushima and T. Shimanouchi, J. Amer. Chem. Soc. 71, 1320 (1949).

[11] The observation of the proposed accordion band at 100°K in the solid and also in the isotropic phase at 440°K removes the possibility that the band is associated with difference bands or with a combination band of the lattice modes.

[12] R. F. Schaufele, J. Chem. Phys. 49, 4168 (1968).

[13] R. G. Snyder and J. H. Schachtschneider, Spectrochim. Acta 19, 117 (1963).

Nuclear-Magnetic-Resonance Study of the Formation and Structure of an Adsorbed ^{3}He Monolayer*

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Nuclear magnetic relaxation times have been measured for fractional monolayer coverages of ^{3}He adsorbed on Vycor glass. Above $\frac{1}{3}$ monolayer the spin-lattice relaxation time decreases sharply, and the spin-spin relaxation time increases, indicating a considerable change in the configuration and mobility of the atoms. Above $\frac{1}{2}$ monolayer the atoms probably condense into a two-dimensional solid, with exchange tunneling of characteristic frequency considerably larger than that in bulk solid ^{3}He.

For several years there has been speculation concerning the nature of an adsorbed monolayer of helium atoms, with special interest as to whether the state of this layer is like a liquid, a solid, or a collection of atoms isolated by the potentials of the adsorbent sites.[1] Although the monolayer density corresponds to that of a high-pressure solid, the observed temperature dependences of the specific heat[1,2] ($C \propto T^2$) and nuclear magnetic susceptibility[3] ($\chi \propto T^{-1}$) are consistent with either solid or liquidlike behavior. Much more definitive conclusions can be drawn from measurements of the nuclear spin-lattice (T_1) and spin-spin (T_2) relaxation times, from which it is possible to calculate both the correlation time τ_c, which is related to mobility, and the second moment of the NMR line M_2, which depends on the spatial arrangement of the atoms. We have now carried out these measurements using a substrate of Vycor porous glass, and we find that the configuration of the atoms is strongly dependent on the fractional coverage θ, in particular indicating a solid arrangement for values of θ higher than about $\frac{1}{2}$.

A continuous-wave magnetic resonance technique was used at resonant frequency $\omega_0/2\pi = 6.24$ MHz. T_1 was determined by saturating the signal and observing the time constant of the recovery when the saturation condition was removed. Two methods were used for measuring T_2, depending on the width of the resonance line which was quite broad (about $\frac{2}{3}$ G) at the lowest coverages, but became progressively narrower as the coverage increased. The resonances at one monolayer and higher coverages all had the same linewidth (~0.16 G) which was, therefore, taken to be due to the inhomogeneity of the applied magnetic field. Thus for each broad line T_2 was taken as the reciprocal of the difference between the observed width of the line at half-height and the width due to the magnet inhomogeneity. For the complete monolayer, T_2 was obtained from measurements of T_1 and the saturation factor Z. We assumed that the latter would be given by[4]

$$Z = 1/(1 + \gamma^2 H_1^2 T_1 T_2), \tag{1}$$