The Infrared and Raman Spectra of *p*-Azoxyanisole in the Crystalline, Nematic and Isotropic Liquid Phases

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The infrared and Raman spectra of *p*-azoxyanisole were measured in the crystalline, nematic, and isotropic liquid phases. In the internal vibrational region, abrupt changes in intensity were observed at the crystalline-nematic phase transition; however, no appreciable change was detected at the nematic-isotropic liquid phase transition. In the external vibrational region, some of the Raman lattice bands, which eventually vanish in the isotropic liquid phase, persist in the nematic phase, while some of the infrared lattice bands disappear and a new band appears as the crystalline-nematic phase transition point is reached and traversed. The assignments of the infrared and Raman bands which appear or disappear in the nematic phase are discussed.

The study of the infrared and Raman spectra of liquid crystal compounds provides an attractive approach for the elucidation of the forces that determine the order and molecular structure in the various phases exhibited by liquid crystal compounds. In spite of this, the number of investigations of infrared and Raman spectra with relation to this particular subject has been quite small.

The infrared spectra of a nematic liquid crystal compound, *p*-azoxyanisole (PAA), have been measured by Bulkin *et al.*[1,2] and by Gruger and Calvé.[3] Bulkin *et al.* reported the infrared spectra of the crystalline, nematic, and isotropic liquid phases in the 600—450 cm^{-1} and 200—50 cm^{-1} regions. They showed that the band at 509 cm^{-1} disappeared at the crystalline-nematic (c-n) phase transition,[1] and that the lattice bands below 150 cm^{-1} disappeared and a broad band emerged at about 100 cm^{-1} above the c-n phase transition temperature.[2] They also showed that the intensity of the disappearing bands began to decrease well below the transition temperature and suggested that there were pretransition effects.

The Raman spectra of PAA in the three phases have been measured by several investigators.[3-8] Amer *et al.*[4] measured the temperature dependence of the Raman bands in the 1300—1225 cm^{-1} and 100—30 cm^{-1} regions. They reported that the variation in the integrated intensity as well as in the bandwidth with the temperature has a characteristic quasi-discontinuity at the c-n phase transition. They also showed that the band at 75 cm^{-1} vanished completely, while the bands at 52 and 40 cm^{-1} persisted in the nematic phase. This result, however, does not agree with that obtained by Bulkin and Prochaska[5], who showed that the band at 52 cm^{-1} vanished while the bands at 70 and 45 cm^{-1} persisted in the nematic phase.

The purpose of this paper is to clarify the behavior of the Raman-active lattice modes of PAA in relation to the temperature variation and to explain the infrared and Raman bands, which change remarkably in intensity at the c-n phase transition.

Experimental

PAA purchased from Tokyo Kasei Kogyo Co., Ltd., was purified by recrystallization from methanol. The sample exhibited a nematic mesophase in the temperature range from 118 to 136 °C.

The infrared spectra were recorded with a Hitachi EPI-G3 spectrophotometer (4000—400 cm^{-1}) and a Hitachi FIS-3 spectrophotometer (400—30 cm^{-1}). The frequency accuracy is probably within ± 2 cm^{-1}. The spectra of the crystalline, nematic, and isotropic liquid phases were recorded as thin films sandwiched between KBr or silicon plates, depending on the frequency range. An electrically heated cell from Hitachi Co., Ltd., provided with an alumel-chromel thermocouple was used to measure the temperature variation.

The Raman spectra were obtained with a Shimadzu R-2D double monochromator equipped with a cooled photomultiplier (ITT FW 130) and a photon-counting system. The excitation source was an Ar^+ laser (Spectra Physics Model 165) operated at 514.5 nm. The output power at the laser-head was 80 mW for the crystalline phase, while it was 350 mW for the nematic and isotropic liquid phases. The frequencies were calibrated using emission lines from the laser and are believed accurate to ± 5 cm^{-1}. The spectral slitwidth was 1.2 cm^{-1} for the 1700—1000 cm^{-1} region, while it was 4.8 cm^{-1} for the 1000—100 cm^{-1} region. The sample cell was inserted in an electrically heated brass block and placed in a box packed with asbestos. The sample temperature was monitored constantly; the temperature fluctuations were less than 1 °C.

Results

The molecular structure of PAA, $CH_3O\text{-}C_6H_4\text{-}N(O){=}N\text{-}C_6H_4\text{-}OCH_3$, has been determined by X-ray diffraction.[9] The –N=N– bond is twisted away from the planar *trans* form by 4.2°, and the angle between the normals of the two benzene rings is 22.6°. Hence, the molecule has no symmetry at all. The PAA crystal belongs to the monoclinic system, and the space group is $C_{2h}^5\text{-}P2_1/a$, with four molecules in a Bravais unit cell.

Intramolecular Mode The infrared spectra between 1800 and 400 cm^{-1} of PAA in the crystalline, nematic, and isotropic liquid phases are given in Fig. 1. The Raman spectra for the three phases are shown between 1700 and 100 cm^{-1} in Fig. 2. The Raman bands in the 1700—1000 cm^{-1} region are extremely intense compared with those in the lower-frequency range. The spectra in the 1700—1000 cm^{-1} region were recorded with the slit-width one fourth of that in the 1000—100 cm^{-1} region.

Neither the infrared nor the Raman spectra exhibit any significant change at the nematic-isotropic liquid (n-i) phase transition: the infrared and Raman spectra of the nematic phase are virtually the same as

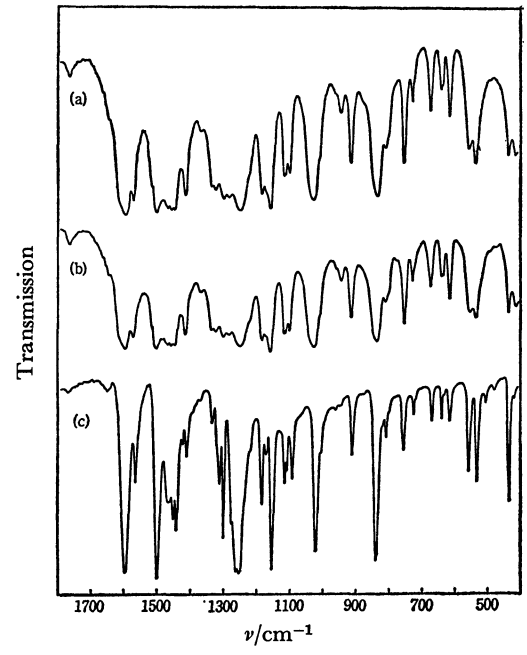

Fig. 1. Infrared spectra between 1800 and 400 cm^{-1} of PAA.
(a): isotropic liquid phase (at 140 °C). (b): nematic phase (at 125 °C). (c): crystalline phase (at 25 °C).

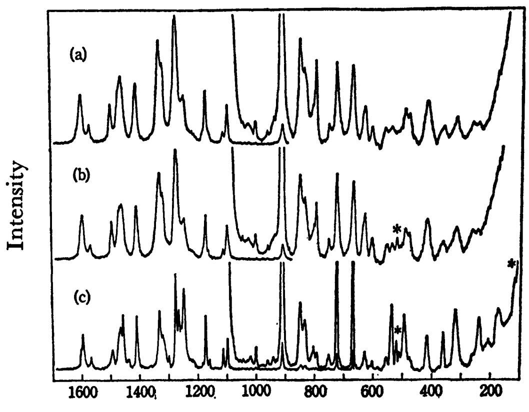

Fig. 2. Raman spectra between 1700 and 100 cm^{-1} of PAA. Spectral slit-width is 1.2 cm^{-1} for the 1700—1000 cm^{-1} region, while it is 4.8 cm^{-1} for the 1000—100 cm^{-1} region.
(a): isotropic liquid phase (at 140 °C). (b): nematic phase (at 125 °C). (c): crystalline phase (at 25 °C).
* denotes the emission lines from the Ar$^+$ laser.

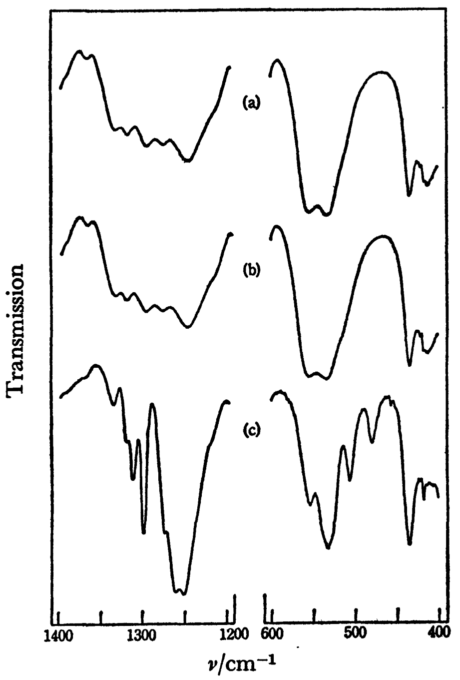

Fig. 3. Temperature dependence of the infrared bands at 1311, 509 and 482 cm^{-1}.
(a): isotropic liquid phase (at 140 °C). (b): nematic phase (at 125 °C). (c): crystalline phase (at 25 °C).

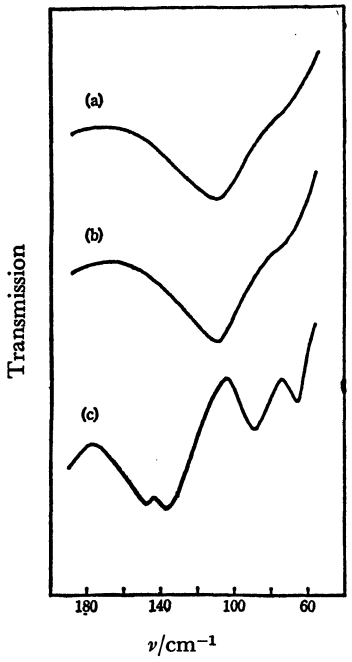

Fig. 4. Infrared spectra of PAA in the external vibrational region.
(a): isotropic liquid phase (at 140 °C). (b): nematic phase (at 125 °C). (c): crystalline phase (at 25 °C).

those of the isotropic liquid phase, except for slightly different band-widths due to the different temperatures. In sharp contrast to this, several of the spectral features change almost abruptly at the c-n phase transition: many infrared and Raman bands change in their relative intensities, some increasing while others decrease. Most of the bands become broadened in the nematic phase. Further, some of the infrared and Raman bands exhibit small frequency shifts.

Of particular interest is the fact that the infrared bands at 1311, 509, and 482 cm^{-1} in the crystalline phase disappear above the c-n phase transition temperature (Fig. 3). Bulkin *et al.*1) noticed that the infrared band at 509 cm^{-1} vanishes at the c-n phase transition; however, they failed to observe the disappearance of the bands at 1311 and 482 cm^{-1}.

Intermolecular Modes The infrared spectra between 180 and 60 cm^{-1} of PAA in the crystalline, nematic, and isotropic liquid phases are reproduced in Fig. 4. In the crystalline phase, four bands are observed at 150, 137, 89 and 67 cm^{-1}. In the nematic and isotropic liquid phases, some of the bands disappear, and, instead, an intense and broad band appears at about 108 cm^{-1}. This observation is in accord with that reported by Bulkin *et al.*[2])

The Raman spectra below 140 cm^{-1} for the three phases are shown in Fig. 5. Five bands are clearly seen at 94, 75, 56, 42 and 21 cm^{-1} in the crystalline phase. In the nematic phase, the 75 cm^{-1} band disappears and the bands at 56 and 42 cm^{-1} decrease in intensity. In the isotropic liquid phase, only the band at 94 cm^{-1} exists. The behavior of the band at 21 cm^{-1} is not clear because of the overlapping by the Rayleigh wing. This result agrees with that obtained by Amer *et al.*;[4,6]) however, it does not agree with those obtained by Bulkin *et al.*[5]) and Gruger and Calvé.[3]) Bulkin *et al.* claimed that it was the 56 cm^{-1} band that disappeared in the nematic phase. On the other hand, Gruger and Calvé reported that the three bands at 75, 56, and 42 cm^{-1} all existed in the nematic phase at 119 °C, but at 125 °C (still in the nematic phase) only the 42 cm^{-1} band remained. The conclusions differ from one to another because of the extreme difficulty of obtaining high-quality Raman spectra below 100 cm^{-1} of the nematic and isotropic liquid phases as a result of the sudden broadening of the Rayleigh wing at the c-n phase transition. We examined the temperature dependence of these three lattice bands with great care and obtained good reproducible spectra, thus confirming that the band at 75 cm^{-1} vanishes unambiguously, whereas the bands at 56 and 42 cm^{-1}, although they become very much weakened, still exist in the nematic phase.

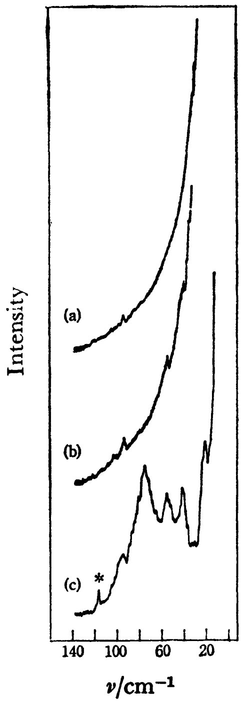

Fig. 5. Raman spectra of PAA in the external vibrational region.
(a): isotropic liquid phase (at 140 °C). (b): nematic phase (at 125 °C). (c): crystalline phase (at 25 °C). * denotes the emission line from the Ar$^+$ laser.

Discussion

A nematic mesophase may be characterized by the tendency of all molecules to align themselves parallel to a preferred axis in space, although they are not fixed in position. Such a tendency, however, may still be present in the isotropic liquid phase, though among much smaller groups of molecules.[17])

McLoughlin *et al.*[10]) concluded, from the volume changes at the c-n and n-i phase transitions, that there is, usually, no room for PAA molecules to rotate freely about their own long axes, in either the nematic or isotropic liquid phase. This suggests that the rotational motion about the long axis of a PAA molecule is hindered by neighboring molecules and becomes a librational oscillation even in the nematic and isotropic liquid phases; the frequency of the oscillation, however, is possibly different from that of the corresponding librational mode in the crystalline phase as a result of the different intermolecular force field.

The appearance of an intense and broad infrared band at 108 cm^{-1} at the c-n phase transition might be well explained if one could assume that this band originates from the librational oscillation about the molecular long axis, and further, that the short-range order is responsible for the librational oscillation appearing in the infrared spectra. It has been known that the polar molecules in the liquid state exhibit a broad and intense absorption in the far-infrared region (mostly below 100 cm^{-1});[11–13]) this absorption band can be explained as due to the librational oscillation of each polar molecule within the cage formed by its neighbors.[14,15]) Thus, it seems reasonable to assume that the infrared band at 108 cm^{-1} of PAA has the same origin as the absorption of polar molecules. Evans *et al.*[16]) explained a strong band centered near 130 cm^{-1} of a liquid crystal compound, *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA), in its nematic and isotropic liquid phases as being due to this type of absorption.

On the other hand, the disappearance of the Raman band at 75 cm^{-1} at the c-n phase transition may be interpreted on the assumption that this band is due to the Raman-active librational mode about the long axis, but the long-range order is essential to the appearance of the librational oscillation in the Raman spectra.

We have seen that the Raman bands at 56 cm^{-1} and 42 cm^{-1} persist in the nematic phase, although they vanish in the isotropic liquid phase. Thus, these bands can be assigned either to the librational modes about the molecular short axes or to the translational modes along the axes; along these axes, the long-range order still exists in the nematic phase. The Raman band at 94 cm^{-1} must be an internal mode because this band is seen in the isotropic liquid phase; besides, it does not exhibit any appreciable frequency shift through the phase transitions.

In the internal vibrational region, the infrared bands at 1311, 509, and 482 cm^{-1} vanish above the c-n phase transition point. These bands may be assigned to combination modes between the librational mode about the molecular long axis and intramolecular modes; in the nematic phase, the librational mode disappears and, hence, its combination modes. It is difficult to explain these bands, except for the band at 1311 cm^{-1}, in terms of the crystal-field splitting, because they are far from any adjacent bands. The following combinations are, though, considered probable; 1247 (R)+67 (IR)=1314, 437 (IR)+75 (R)=512, and 418 (R)+67 (IR)=485.

In a nematic liquid crystal compound, *N*-anisyliden-*p*-aminophenyl acetate (APAPA), the infrared and Raman bands arising from rotational isomers which exist in the nematic and isotropic liquid phases were identified, and the energy difference between the isomers was estimated.[18] Therefore, it seems highly probable that more than one molecular conformation around the C–OCH_3 bonds are present for PAA in the nematic and isotropic liquid phases. The remarkable intensity changes at the c-n phase transition might be caused by the changes not only in the molecular orientation but also in the conformation.

Bulkin *et al.*[1,5] reported that there are pretransition effects at the c-n phase transition. It is true that the peak heights and band-widths of the infrared and Raman bands start to change well below the transition temperature, but this is what one would expect from the temperature variation in the spectra of any compounds, regardless of the phase transition. we found that the appearance or disappearance of the infrared and Raman bands took place almost abruptly at the transition temperature.

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