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RAMAN SPECTRUM OF TEREPHTHAL-BIS-BUTYLANILINE IN THE LIQUID CRYSTALLINE STATES

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Raman spectra of the smectic H phase and two unidentified phases of terephthal-bis-butylaniline are studied in the 0-400cm^{-1} region. Observation of the Raman peaks due to lattice vibrations suggests that the latter two phases are closer to the crystalline solid phase rather than the smectic H phase.

TBBA (terephthal-bis-butylaniline) is known to exhibit several mesomorphic phases and has been studied using X-ray, optical, calorimetric and Raman scattering methods. Schnur et al. have reported that the lattice vibrations corresponding to cooperative intermolecular rotations are observed in the smectic H (S_H) phase of TBBA.$^{1)}$ On the other hand. calorimetric studies have shown that TBBA adopts monotropically two unidentified intermediate phases between the S_H phase and crystalline solid phase on cooling.$^{2)}$ With X-ray diffraction method, Doucet et al. have indicated that these phases have a molecular ordering closer to crystal than the S_H phase.$^{3)}$ Flick et al. have suggested from the observation of optical texture that these phases are smectic.$^{2)}$ It should be noted that the mesomorphic phases are present between the S_H and crystalline solid phases because the S_H phase has been thought to be a mesomorphic phase closest to crystal. A question is raised whether these two phases are smectic or crystalline solid. The exact nature of these intermediate phases has not as yet been clarified.

In this study, Raman spectra are reported on the S_H phase and two unidentified intermediate phases in TBBA. The various transitions of TBBA are shown here, according to the notation by Doucet et al;$^{3)}$

$$\begin{tikzcd}
\left(\begin{matrix}\mathrm{IX}\\ \mathrm{Cr}\end{matrix}\right) \arrow[r, leftrightarrow, "-42^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{VIII}\\ \mathrm{Cr}\end{matrix}\right) \arrow[r, "113^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{V}\\ S_H\end{matrix}\right) \arrow[r, leftrightarrow, "144^\circ\mathrm{C}"] \arrow[d, leftrightarrow, "87^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{IV}\\ S_C\end{matrix}\right) \arrow[r, leftrightarrow, "172^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{III}\\ S_A\end{matrix}\right) \arrow[r, leftrightarrow, "200^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{II}\\ \mathrm{N}\end{matrix}\right) \arrow[r, leftrightarrow, "236^\circ\mathrm{C}"] & \left(\begin{matrix}\mathrm{I}\\ \mathrm{L}\end{matrix}\right) \\
 & \mathrm{VII} \arrow[u, "63^\circ\mathrm{C}"] \arrow[r, leftrightarrow, "74^\circ\mathrm{C}"'] & \mathrm{VI} & & & &
\end{tikzcd}$$

where the transition temperatures are observed by differential scanning calorimetry except for that between the phases IX and VIII .

Experimentally, Raman spectra were observed on a JEOL Raman spectrophtometer

JRS-S1 with photon counting electronics and a Coherent Radiation CR-52 argon-ion laser. The exciting light was the 5145 Å line of the argon-ion laser. On occasion, the 6328 Å line of a He-Ne laser was employed to reduce the photochemical degradation of TBBA during measurement. TBBA was synthesized in our laboratory, and purified by successive recrystallization from hot ethanol. The sample was contained in a 1.5 mm diameter capillary tube. The temperature of the sample was controlled to within 0.1°C by a SCR controller of PID type.

Fig. 1 shows the Raman spectra of TBBA in the 0-30 cm^{-1} range in the crystalline solid VIII and S_H phase V on heating. The Raman peak at 19 cm^{-1} in the solid phase VIII is broadened with increasing temperature and disappears in the S_H phase. Schnur et al. have shown that this peak remains also in the S_H phase and interpreted that this peak results from the cogwheel-like mode corresponding to a relative rotation of the molecules about their long axes in the crystalline phase.[1)]

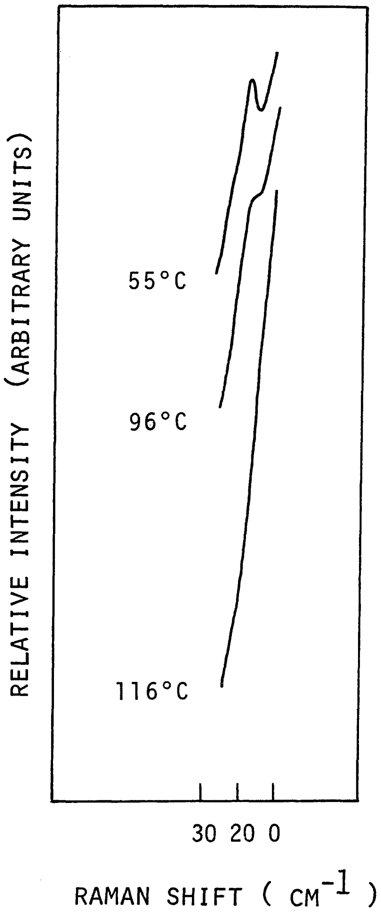

Fig. 1. Raman spectra of TBBA in the crystalline solid phase VIII (55°C and 96°C) and S_H phase V (116°C) on heating.

Two models have been proposed on the basis of X-ray diffraction patterns for the molecular arrangements of TBBA in the S_H phase, as shown in Fig. 2. One of the models (a) assumes a cooperative rotational motion of the molecules around their long axes.[3)] The intersections of the molecular axes with a plane perpendicular to their directions approximately form a hexagonal lattice. It is very similar to the structure of some of the plastic crystals.[4)]

In another model (b), the molecules are stationary in the S_H phase with all the molecular planes essentially parallel to the direction of tilt.[5)] In this model, the molecular axes are also arranged in a pseudo-hexagonal form within the smectic layers. Each model suggests the S_H phase of TBBA to adopt a highly ordered structure close to crystalline solids. One expects for both models the appearence of Raman peaks associated with intermolecular lattice vibrations.

Contrary to this expectation, our experimental results indicate that the S_H phase of TBBA gives no Raman peak due to the lattice vibrations in the low frequency region as seen in Fig. 3. TBBA in the solid phase VIII shows three intense Raman peaks at 19 cm^{-1}, 100 cm^{-1} and 150 cm^{-1} together with two weak ones at 80 cm^{-1} and

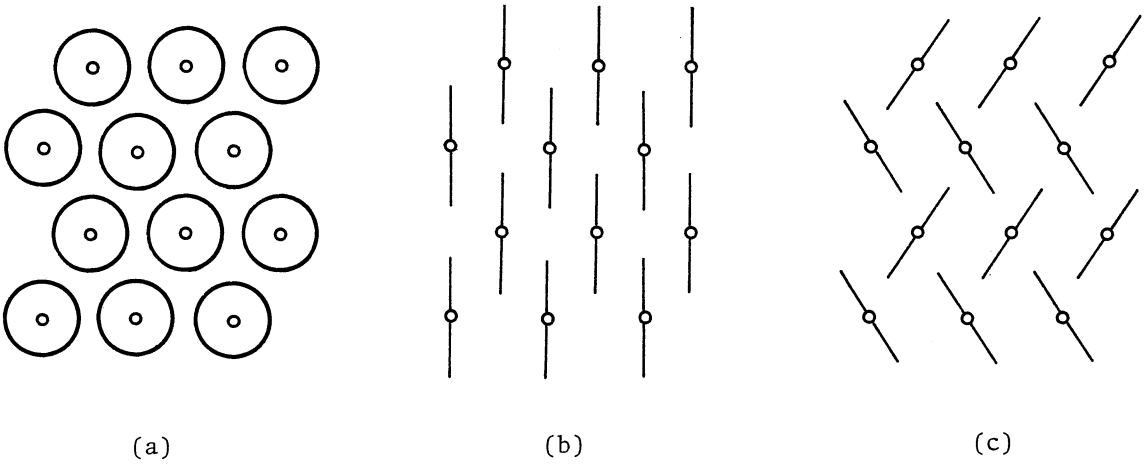
(a) (b) (c)

Fig. 2. Schematic representations of the structural models proposed for the smectic H (a and b) and VI (c) phases for molecular arrangement of TBBA. The structures (a) and (c) have been suggested by Doucet et al. and (b) by de Vries. The plane of the drawing is perpendicular to the long molecular axes. The small circles show the positions of the molecular axes. The larger circles in (a) show that the molecules are rotating. The lines in (b) and (c) show the average orientation of the molecular planes.

132 cm^{-1} at room temperature. These peaks are definitely ascribed to the lattice vibrations since most of them disappear in the isotropic liquid phase except for the 130 cm^{-1} Raman peak, which will be discussed later.

Of particular interest is the structure of TBBA in the S_H phase. There have been a number of studies on this subject. One of the arguments has been focused on whether the molecules are rotating or stationary as well as on whether the rotational motion, if any, is collective or diffusive. Schnur et al. have observed the 19 cm^{-1} Raman peak in the S_H phase and assigned it to a collective rotational motion of the molecules around their long axes,1) as described before. In this study, no such a Raman peak was observed on the S_H phase of TBBA, as is evident from Figs. 1 and 3. This suggests strongly that the rotational motion in the S_H phase is not collective but diffusive in nature. A recent study of Hervet et al. using high-resolution quasielastic neutron scattering has revealed the presence of rapid and isotropic rotation of the molecules about their long axes for the S_H phase of TBBA,6) which is consistent with the structural model proposed by Doucet et al. as mentioned above, except that the molecules undergo a cooperative rotational motion. For the S_H phase of TBBA, this idea explains the disappearence of the Raman peaks owing to the lattice vibrations which have been observed in the 0-150 cm^{-1} frequency range on the phase VI and subsequent low temperature phases. Therefore, it can be concluded that the TBBA molecules undergo noncooperative motions of rotation and translation in the S_H phase.

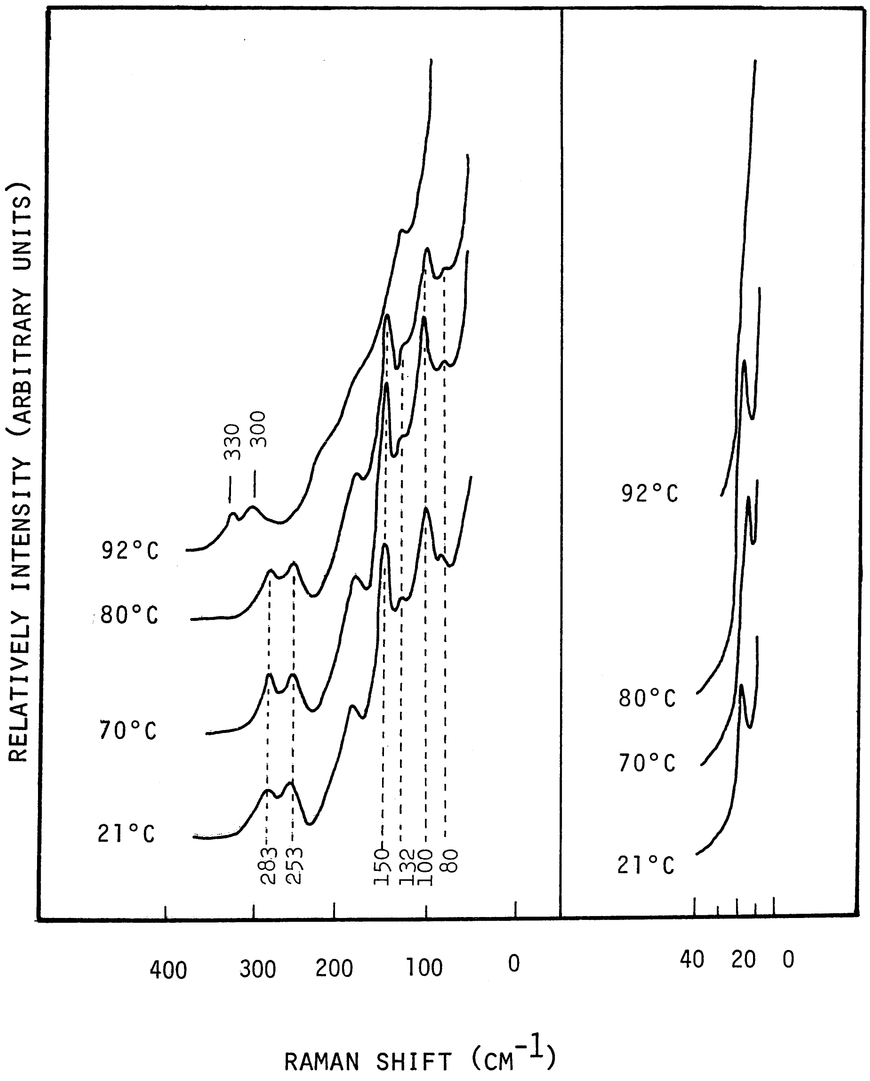

Fig. 3. Raman spectra of TBBA in the S_H phase V (92°C), phase VI (80°C), phase VII (70°C) and crystalline solid phase VIII (21°C) on cooling.

On cooling the S_H phase, TBBA exhibits monotropically two phases VI and VII before reaching the crystalline solid phase VIII. These phases have been considered to be smectic on the basis of an X-ray diffraction study because of the presence of a layer structure and the absence of long-range three-dimensional order.[3] The smectic nature of these phases has been also suggested by optical microscopic studies.[2] However, Raman spectra of these phases show several Raman peaks owing to lattice vibrations characteristic of a long-order crystalline state. There is no remarkable difference in the Raman spectra among the phases VI, VII and VIII, except for a decrease in the intensity of quasielastic scattering with decreasing temperature. Therefore, the phases VI and VII seem to have a highly ordered molecular structure, to a large extent, closer to the crystalline phase VIII rather than the S_H phase, as far as the lattice vibrations are concerned. Doucet et al. have proposed for the phase VI a structural model with a herringbone-type arrangement of the molecules in one layer, and suggested the freezing of the rotational motion of the TBBA molecules around their long axes on cooling the S_H phase down to the phase VI, as shown in Fig. 2(c).3) This implies that the molecule occupies a special lattice point with a definite orientation. The apperarence of the lattice vibrations in the Raman spectrum as shown in Fig. 3 supports this model for the phase VI.

As mentioned above, TBBA shows a great similarity in the Raman spectra among the phases VI, VII and VIII. However, the exact structures of these phases have not as yet been reported in literatures. No attempts have been made to elucidate the structural parameters of the phases VII and VIII of interest, except for the work by Doucet et al. They have indexed the X-ray diffraction peaks of TBBA in the phases V to VIII on the basis of a monoclinic lattice and found that the phase VII presents a great difference from the phase VI. The c-value in the phase VII is double the corresponding value in the phase VI which has a c-value nearly equal to the molecular length. These differences, which were found in X-ray diffraction study, have not been apparently observed in the present Raman study. The small enthalpy change associated with the VI-VII transition suggests no remarkable difference in the structure and ordering of the molecules between the phases VI and VII.2) This is consistent with the Raman spectral change of TBBA with those phase transitions.

Fig. 3 includes also Raman peaks due to the intramolecular vibrations of TBBA in addition to the lattice vibrations. Two Raman peaks 253 cm^{-1} and 283 cm^{-1} in the phases VI and VII can be assigned to the deformation vibration of the butyl group in TBBA, normally called "longitudinal accordion vibration", and on heating to the S_H phase shift to higher frequencies, 300 cm^{-1} and 330 cm^{-1}, respectively. The frequency of accordion vibration is inversely proportional to the length of the alkyl chains or to the number of carbon atoms in the chains.7) The increase in the accordion vibrational frequency indicates that on going to higher temperature phases the butyl group takes several different conformations including the gauche-form in addition to the extended trans-form which is considered to be the most stable form in crystalline solids. Futhermore, this doublet decreases successively its intensity with increasing its peak width on heating the S_H phase to the nematic and isotropic phases. The appearance of this doublet in the phases VI and VII with the same frequency as in the phase VIII indicates that there is no significant difference in the butyl group conformations among those phases. This is consistent with the results obtained from the lattice vibration mentioned above.

The S_H phase as well as the higher temperature phases show a broad peak at 130 cm^{-1} which is incidentally very close to the 132 cm^{-1} weak peak observed in the phase VI and lower temperature phases. The exact origin of this peak is not certain at this time, but it is believed to be associated with the torsional motion of the butyl group with respect to the phenyl group in TBBA.8)

The present work on the Raman spectrum of TBBA has been performed to elucidate the nature of two monotropic intermediate phases appearing between the S_H phase and crystalline solid phase on cooling. Although the appearance of the lattice modes indicates that those intermediate phases are almost solid-like in nature, it would be difficult to derive definite conclusions about the classification of these phases into some of the smectic and crystalline solid modifications from the Raman spectrum alone. However, it can be said that the phases VI and VII are closer to the crystalline solid phase VIII rather than the S_H phase V, with respect to the molecular alignment and ordering, and possess an ordered region sufficient to yield the Raman peaks due to the lattice modes. A further Raman experiment is in progress on the phases VI and VII.

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