Molecular Crystals and Liquid Crystals

Far-Infrared Absorption in the Highly Ordered Smectic Phases of TBBA

S. Venugopalan [a] , J. R. Fernandes [a] & V. Surendranath [a]

[a] Raman Research Institute, Bangalore, 560006, India
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Far-Infrared Absorption in the Highly Ordered Smectic Phases of TBBA

S. VENUGOPALAN, J. R. FERNANDES and V. SURENDRANATH

Raman Research Institute, Bangalore 560006, India

The far-infrared absorption of terephthal-bis-butylaniline (TBBA) in the smectic H, VI, VII and crystalline phases has been studied in the range 30–650 cm^{-1}. Spectra of the former three phases closely resemble each other over the entire spectral range. On transforming to the crystalline phase several new modes appear, especially in the low frequency region. When compared to the Raman spectra of these phases, the present results show interesting differences which allow for further deductions in characterizing the mesophases considered here. The lineshape of bands in the range 460–510 cm^{-1} is seen to exhibit changes dependent upon the phase of the sample. A band centered at 476 $\pm$ 2 cm^{-1} exhibits a broadening in smectic H and VI phases as compared to phase VII. This has been attributed to the occurrence of intramolecular reorientations of the butyl chain segments in the former two phases. From a study of the half-widths (HWHM) of the band, the mean correlation time of these reorientations is estimated to be within the range of 1–2 psec.

I   INTRODUCTION

Among the many new smectic phases discovered recently,[1-6] the B and H phases are known to possess a high degree of local order correlating adjacent molecular layers. Both phases are characterized by a two dimensional hexagonal lattice within each layer. In the B phase the director is normal to the smectic planes, whereas in the H phase it is tilted. The nature of the intermolecular forces and the permissible degrees of freedom for the molecules in such mesophases, which exhibit almost quasicrystalline long range order, have been the subject of several experimental and theoretical studies.[3,7-9] In this regard, terephthal-bis-butylaniline (TBBA) whose molecular structure is shown in Figure 1, has been extensively studied using different techniques as it exhibits the smectic H phase[4] (previously referred to as smectic B by
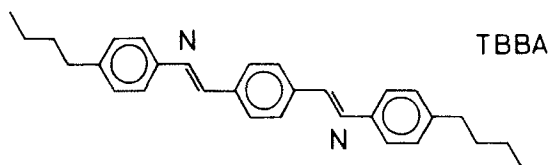
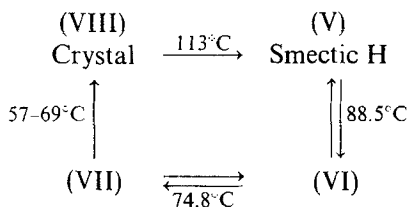FIGURE 1   Molecular structure of TBBA in the all-*trans* conformation.

some authors) in addition to three other stable liquid crystalline forms.[10] Calorimetric studies have shown[11] that two new monotropic metastable forms, labeled[3] VI and VII, appear when the smectic H phase is supercooled. Optical [10] and X-ray[1,3] studies have already provided interesting information on the structural characteristics of its different mesophases. In addition, Raman,[12-14] NMR[11,15] and quasielastic neutron scattering[16-18] techniques have also been employed in studies aimed at clarifying the nature of the molecular ordering in its smectic H and monotropic phases.

The far-infrared absorption in such highly ordered smectic phases has not been studied so far. In this paper we present the far-infrared absorption spectra of TBBA in its smectic H, VI and VII phases as well as the crystalline phase. The spectra of these phases are discussed in the light of their known structural and dynamical properties. The far-infrared spectra show interesting differences when compared to the low-frequency Raman spectra[13] and this leads to a further understanding of the nature of the mesophases. The lineshape of one of the bands is seen to exhibit distinct changes dependent upon the phase of the sample. The broadening of this band in the smectic H and VI phases is attributed to the occurrence of intramolecular reorientations of the butyl chains. The corresponding reorientational correlation times in both phases are estimated from a study of the half-widths of this band.

II   EXPERIMENTAL

TBBA used in this study was synthesized following the procedure described earlier by Taylor *et al.*[10] The nematic–isotropic transition temperature was determined to be 235 ± 0.2°C using a hot stage microscope. From published data,[3,19] the temperature intervals where the two monotropic phases occur seem to show a variation. In order to clearly establish these intervals for the material used in this study, calorimetric measurements were carried out using a Perkin–Elmer differential scanning calorimeter (Model DSC-2). Except the crystal–smectic H transition which was observed during heating, the other transition temperatures indicated below were determined from the onset of the exotherms during cooling cycles. On this basis, to within ±0.5°C, the different transitions relevant to the present work can be

represented as follows:

$$\begin{array}{ccc}
\text{(VIII)} & & \text{(V)} \\
\text{Crystal} & \xrightarrow{113^\circ\text{C}} & \text{Smectic H} \\
\Big\uparrow \text{57--69}^\circ\text{C} & & \Big\updownarrow \text{88.5}^\circ\text{C} \\
\text{(VII)} & \xrightleftharpoons[74.8^\circ\text{C}]{} & \text{(VI)}
\end{array}$$

Monotropic phases VI and VII are metastable and their formation and stability can depend upon the thermal history of the sample.[18] Our DSC measurements indicate that the temperature at which phase VII solidifies can exhibit a considerable range as shown above. The thin sample films used in the infrared studies were seen to crystallize very often at 69°C. It was further noticed that when these samples were thermally cycled, crystallization could occur at even higher temperatures, either altogether bypassing phase VII or considerably shortening the temperature interval of its existence. In order to reliably obtain phases VI and VII, we therefore found it advantageous to start with a fresh sample in smectic H phase and slowly cool it down over a period of several hours to the required temperatures, thereby avoiding any thermal cycling.

Far-infrared spectra in the range 30–650 cm^{-1} were obtained using the Polytec FIR 30 Fourier spectrometer. The frequency region 30–250 cm^{-1} was studied using a sample cell fitted with α-quartz windows, whereas diamond windows were used in the range 100–650 cm^{-1}. All the spectra reported here were obtained using polydomain samples. Other details related to the sample preparation and the experimental procedure have been described elsewhere.[20,21]

For lineshape studies in the range 450–510 cm^{-1}, improved spectrophotometric accuracy was attained with the use of a Leitz double beam spectrograph in conjunction with a KBr prism and KBr sample cell windows. For each spectrum, two scans were averaged and the data digitized by hand. When compared to the measured linewidths, the spectral slitwidth of the Leitz spectrograph (2.5 cm^{-1}) was smaller by a factor of five or more. Hence the effects of instrumental broadening should be negligible in the present case and no further corrections were made to the data to account for the instrumental width.

III   RESULTS AND DISCUSSION

A   Far-infrared spectra

Figure 2 shows the far-infrared spectra of smectic H, VI, VII and crystalline phases in the range 30–220 cm^{-1}. The spectra of the first three phases look
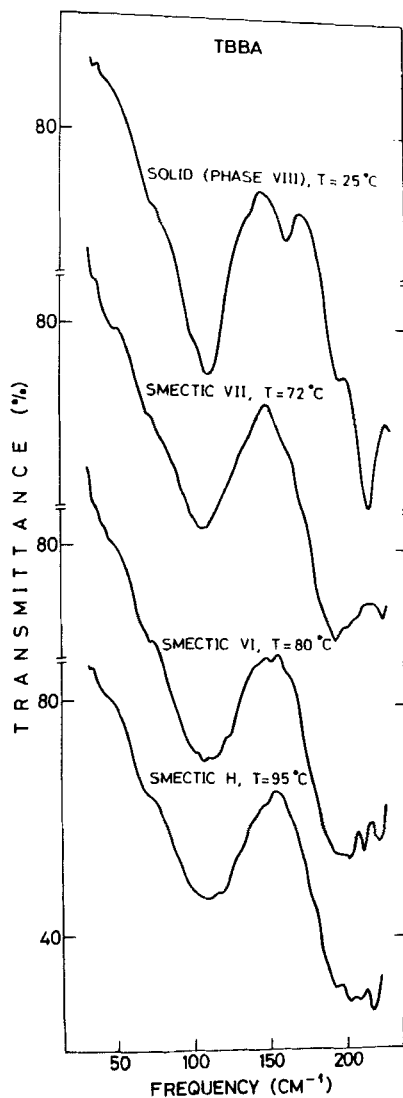
FIGURE 2   Far-infrared absorption spectra of TBBA in smectic H, VI, VII and solid phases in the range 30–220 cm^{-1}. The temperature corresponding to each phase is also shown.

remarkably similar. All three of them exhibit two strong, broad absorption bands centered at 105 and 210 cm^{-1}, in addition to weak shoulders at about 50 and 70 cm^{-1}. The band at 105 cm^{-1} is slightly broader in smectic H and VI phases as compared to phase VII. On transforming to the crystalline phase, new modes appear at 161, 193 and 212 cm^{-1}. The shoulders observed at 98 and 138 cm^{-1} were also consistently reproducible. The position of the strong central band is shifted upwards and appears at $\sim$110 cm^{-1} in the crystalline phase.

While the bands occurring in the range 190–212 cm^{-1} are likely to arise from CH_3 torsional modes, the intense, broad absorption centred around 105 cm^{-1} closely resembles similar far-infrared bands observed in other liquid crystals[21-25] and polar liquids.[26,27] In these cases, the broad absorption bands were thought to arise from hindered rotatory modes of the molecules, reflecting their nearest neighbour intermolecular coupling. It has also been suggested[25] that these modes may originate from the librations of the C_6H_4 groups. Further work is needed before the broad absorption band observed in the present case can be assigned with certainty to either of these two origins.

When compared to the Raman spectra of TBBA in the same frequency range,[13] the far-infrared spectra shown here reveal interesting departures. Firstly, the Raman spectra of VII and crystalline phases were found to be completely identical. However, when one considers their far-infrared spectra, the spectrum of phase VII closely resembles that of smectic H rather than the crystal. Secondly, except for one mode at 19 cm^{-1}, the remaining Raman lines were found to persist in all four phases, but they disappeared in the smectic C phase. In contrast, we found that the far-infrared absorption in smectic C phase was also very similar to that in smectic H except for slight additional broadening. This indicates that different molecular interactions are observed in the Raman and far-infrared spectra of these mesophases. The X-ray results[3] of Doucet et al. show that in smectic H as also VI and VII phases, a local three-dimensional ordering of molecules prevails with a correlation length of five or more molecules across the layers. In contrast, the smectic C phase does not possess any positional order correlating molecules within a layer or in adjacent layers. Hence the disappearance of the low-frequency Raman lines in the smectic C phase, but not in the lower temperature phases, implies that these are intermolecular modes which are sensitive to longer-range order extending to several molecular lengths. By the same reasoning, from the similarity of the far-infrared spectra in all of these mesophases, including smectic C, it can be argued that these spectra arise primarily from short-range and intramolecular effects within a given layer as opposed to the relatively longer-range order manifested in the Raman spectra. This picture is also in accord with

the conclusion that emerges when one compares the low-frequency infra-red[21,22,25] and Raman spectra[28-30] of other liquid crystals as well.

Based on the Raman spectra,[13] a question arose as to whether phase VII should be considered a mesophase or a different modification of the crystal-line form. The present results show that the spectrum of phase VII is much closer to smectic H and VI phases than the crystal. Infrared spectra at fre-quencies above 200 cm^{-1}, discussed below, also reflect the same situation. Hence phase VII can be taken to represent a distinct liquid crystalline form. The microscopic texture observations of Flick et al.[19] are also in support of this idea.
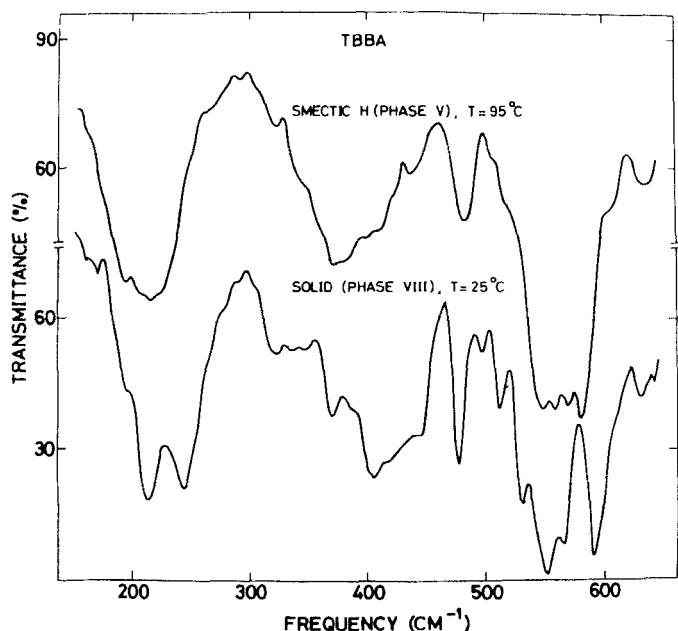

FIGURE 3   Far-infrared absorption spectra of TBBA in smectic H and solid phases in the range 150–650 cm^{-1}. The temperature corresponding to each phase is also indicated.

Figure 3 shows the spectra of smectic H and crystalline phases in the range 150–650 cm^{-1}. Again, spectra of smectic VI and VII phases were found to be almost identical to that of smectic H phase and hence they are not shown here. In this spectral region, one expects to see largely modes characteristic of the skeletal deformations of the butyl chains and the phenyl groups of the TBBA molecule. Compared to the smectic H phase, the spectrum of the crystalline phase shows additional structure in some regions, apart from intensity changes.

B   Molecular dynamics

It is well known that vibrational bandshapes can often yield considerable information on the dynamics of molecular reorientations.[31] Assuming that the vibrational and reorientational motions are uncoupled and that the intrinsic spectrum is Lorentzian[32] in both cases, the experimentally measured half-width Γ (half-width at half maximum) can be expressed as a sum[33]

$$\Gamma = \Gamma_V + \Gamma_R \qquad (1)$$

where, Γ_V and Γ_R are the respective half-widths of the vibrational and reorientational spectra. The above relation follows from the fact that the observed lineshape is given by the convolution of the vibrational and the reorientational spectra. If the latter two spectra are represented by Lorentzians, their convolution yields another Lorentzian whose half-width satisfies Eq. (1).

The mean reorientational correlation time τ_R is then given by

$$\tau_R = (2\pi c \Gamma_R)^{-1} \qquad (2)$$

where c is the velocity of light and Γ_R is expressed in units of cm^{-1}.

We have used the above approach in analyzing the observed spectra of TBBA. Some conclusions derived from earlier studies on the molecular dynamics of TBBA which are relevant to our discussion are summarized in Table I, together with available estimates of correlation times for each type of reorientational motion.

TABLE I

Some conclusions derived from earlier studies on the molecular dynamics of TBBA. Available estimates of correlation times (τ) for each type of reorientational motion are also given.

	Type of motion					
	Body reorientation around long axis		Reorientation of phenyl groups		Reorientation of butyl chain segments	
Phase	Allowed?	$\tau(10^{-12}$ sec)	Allowed?	$\tau(10^{-12}$ sec)	Allowed?	$\tau(10^{-12}$ sec)
S_H	Yes[a]	18[a]	Possibly yes[c]	$\gtrsim 10^c$	Yes[d]	$\ll 18^a$
VI	Most probably no[b]		Probably no[b]. If allowed,	$\tau \gtrsim 10^c$	Yes[d]	
VII	Most probably no[b]		Probably no[b]. If allowed,	$\tau \gtrsim 10^c$	No[d]	

[a] Ref. 16.
[b] Ref. 15.
[c] Ref. 34.
[d] Ref. 35.

The NMR results of Deloche et al.[15] are consistent with the interpretation that body reorientations of the molecules around the long axis are frozen in phase VI. As the outer two phenyl rings were selectively deuterated in their experiment, it follows that the phenyl rings are also probably stationary in phase VI. Lugomer[34] reported correlation times of $\sim 8 \times 10^{-12}$ sec. for reorientations of the phenyl groups in the smectic C phase of diheptyloxy-azoxybenzene. Even assuming that such reorientations are permitted in both the smectic H and VI phases of TBBA, the corresponding correlation times would be expected to be larger than the above value because of the quasi-crystalline molecular ordering that prevails in both of these phases. The estimate in Table I for the correlation times associated with reorientations of the phenyl groups is based on the above considerations.

The correlation time for butyl chain reorientations in smectic H and VI phases has not yet been determined. For the solid phase, Volino et al.[36] deduced the result that the last methylene and the methyl groups—the butyl chain extremities—rotate with a correlation time of $\sim 8 \times 10^{-12}$ sec. at 104°C. It can therefore be expected that in the mesophases the τ values corresponding to chain reorientations would be considerably smaller than this value.

The Γ_R values estimated in this study are, as will be seen below, in the range 3.5–4.6 cm^{-1} with an uncertainty of ± 1 cm^{-1}. From Table I and Eq. (2) it follows that reorientations of the entire molecule as also those of the phenyl groups alone are expected to have characteristic Γ_R values well within 1 cm^{-1}. Within the above mentioned uncertainty, it is not possible for us to measure such small changes in the half-widths. However, if the correlation times for the butyl chain reorientations in the mesophases are sufficiently small, the corresponding values of Γ_R can be determined from our spectra through the study of a mode which can be assigned to deformations of the butyl chain.

With this motivation, lineshape studies were carried out on the modes observed in the range 450–510 cm^{-1}. A $\angle$C—C—C bending mode of the butyl chain[37] as well as an out-of-plane deformation of the phenyl groups may contribute to the absorption in the vicinity of this region. The absorbance of the solid phase in this region is shown in Figure 4. One observes two distinct peaks centred at 476 and 494 cm^{-1}. The absorbance in the mesophases is shown in Figure 5. The asymmetry on the low frequency side of all three spectra clearly indicates the presence of a weaker mode in addition to the strong peak centred at ~ 484 cm^{-1}. It appears that the mode seen in the solid phase at 494 cm^{-1} has undergone a frequency shift and is seen in the mesophases at ~ 484 cm^{-1}. The relative intensity of the mode at 476 cm^{-1} shows a dramatic increase in the solid phase when compared to the meso-phases. This behaviour is strikingly similar to what has been observed in
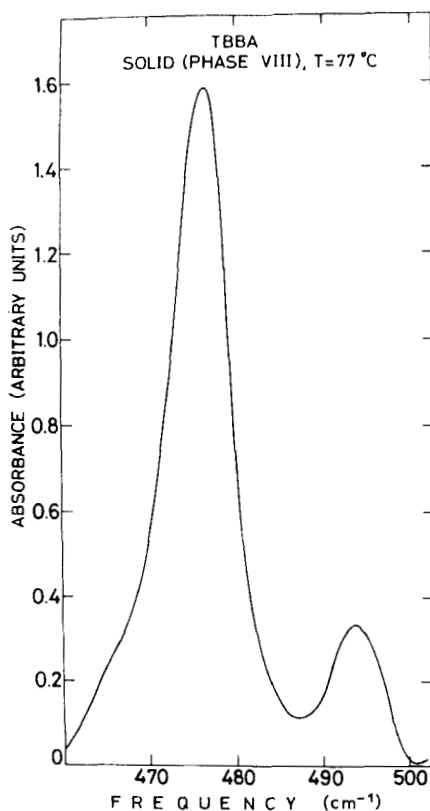
FIGURE 4   Absorbance of the solid phase of TBBA (T = 77°C) in the spectral interval 460–500 cm^{-1}

several other cases as a result of conformational changes in alkyl chains at solid–fluid phase transitions.[24,38,39] Hence the mode at 476 cm^{-1} is assigned to a deformation of the butyl chain. The decrease in the intensity of this mode in the mesophases further suggests that, as compared to the solid phase, the butyl chains exhibit substantial "melting" in the mesophases.

The absorbance values in the mesophases were calculated from the transmission spectra after correcting the apparent baselines for errors arising due to overlap between the wings of adjacent bands. The resultant data, shown in Figure 5, were fitted on an IBM 360 computer to the sum of two Lorentzian components using the least squares method. For both components, our computing procedure treats the peak height, the half-width and the peak position as adjustable parameters and determines the optimal values of these six parameters in relation to all the data points in each spectrum. All three spectra could be satisfactorily fitted to a sum of two
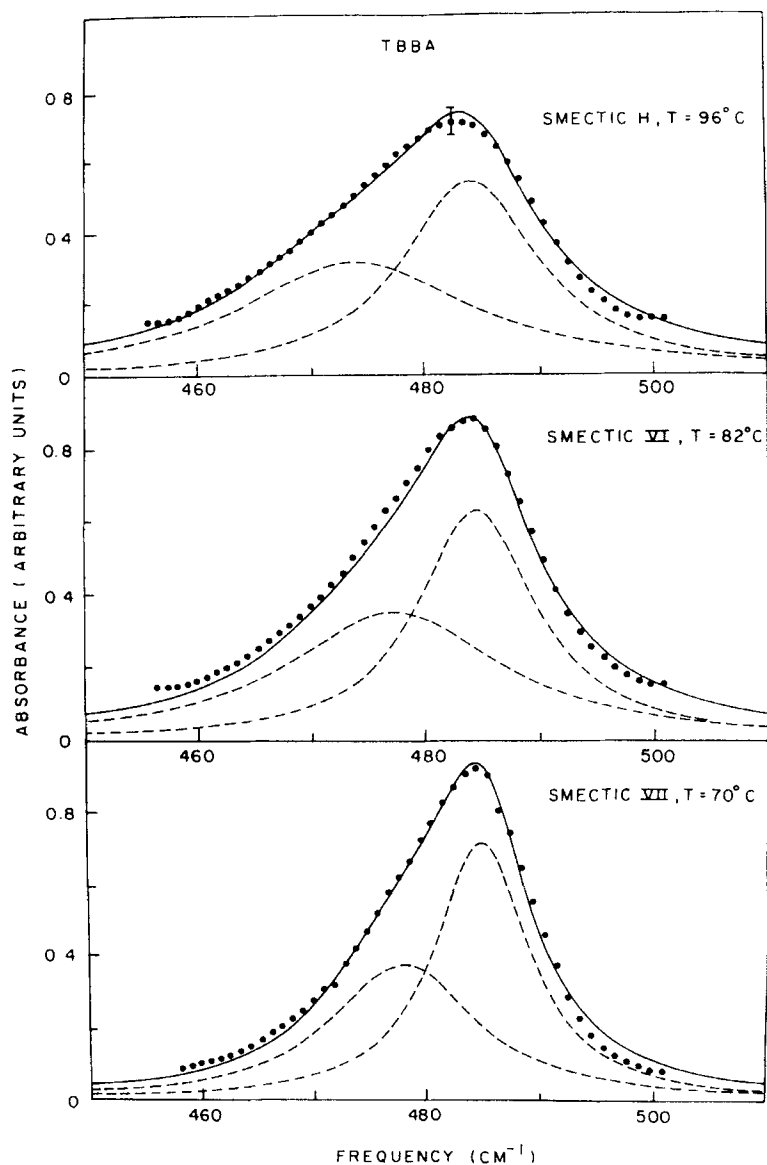
FIGURE 5   Absorbance of smectic H, VI and VII phases of TBBA in the range 460–500 cm^{-1}. The temperature corresponding to each phase is indicated. Dots denote the absorbance values and the typical uncertainty associated with these data is shown on the top trace. For each set of data, the broken curves denote the least squares fitted Lorentzian components and the solid curve represents the sum of the intensities of the two Lorentzian components.

Lorentzian components, one centred at 476 ± 2 cm^{-1} and the other at 484 ± 2 cm^{-1}.

In order to determine the reorientational broadening associated with the mode at ~ 476 cm^{-1}, one must first estimate the value of Γ_V in each mesophase. Usually Γ_V is taken to be the half-width in the solid phase[33] where all reorientational motions are assumed to be frozen. In the present case, the vibrational half-width of the mode in question may be sensitive to conformational changes in the butyl chain at the solid–mesophase transition. Any direct comparison between the half-width in the solid phase and that in the mesophases can then lead to substantial errors in the estimates of Γ_R. As all available evidence[3,15,35] indicates that body as well as chain reorientations are frozen in phase VII, we have taken the computed half-width of the mode in phase VII as the intrinsic vibrational half-width characteristic of all three mesophases. Implicit here are the assumptions that Γ_V shows no appreciable change within the short temperature interval of interest and that the statistical weights of the chain conformations do not change significantly between these three phases.

TABLE II

Half-widths and mean reorientational correlation times deduced from the absorption band centred at 476 ± 2 cm^{-1}. For the smectic H and VI phases, Γ_R is given by the difference between their respective values of Γ and the corresponding value in phase VII. $\tau_R = (2\pi c \Gamma_R)^{-1}$

Smectic phase	T (°C)	Γ (cm^{-1})	Γ_R (cm^{-1})	τ_R (10^{-12} sec)
VII	70	7.8	—	—
VI	82	11.3	3.5 ± 1.0	1.6 ± 0.5
H	96	12.4	4.6 ± 1.0	1.2 ± 0.3

The Γ_R and τ_R values corresponding to smectic H and VI phases were estimated on this basis by comparing the half-widths in both of these phases with that in phase VII. These data are given in Table II. As discussed earlier, the present values of τ_R refer, most probably, to the mean correlation time for reorientations of the butyl chain segments in smectic H and VI phases. The values of Γ_R are found to be comparable in both of these phases. This is in accord with spin-lattice relaxation[35] measurements which show that these reorientations are not yet quenched in phase VI, although they freeze out in phase VII.

From Figure 5, the half-width of the mode centred at 484 cm^{-1} is found to be, within ± 1 cm^{-1}, unchanged in all three phases. It is likely that this mode originates from a skeletal out-of-plane deformation of the phenyl

groups in the molecule. If so, the lack of a measurable reorientational broadening for this mode in our experiments is not too surprising as only the reorientations of the entire molecule or those of the phenyl groups can affect the width of this mode. As noted already, both mechanisms are expected to have typical correlation times which are too large to be measured within our accuracy.

IV CONCLUSIONS

The present study shows that smectic H, VI and VII phases all possess closely similar infrared spectra which are yet different from the spectra of the solid phase. On this basis, phase VII can be considered to represent a distinct liquid crystalline form rather than a modification of the crystalline phase. The infrared absorption of these mesophases is seen to be primarily influenced by intramolecular and short-range effects within a given molecular layer rather than by interactions sensitive to longer-range correlations within a layer or between adjacent layers.

From a study of the linewidths of a band at 476 ± 2 cm^{-1} in smectic H, VI and VII phases, we have estimated the mean correlation times for intramolecular reorientations in smectic H and VI phases. These reorientations are most probably of the butyl chain segments in the TBBA molecule. The values of Γ_R are found to be comparable in both smectic H and VI phases. This is in agreement with spin-lattice relaxation measurements which show that these reorientations persist in phase VI, but freeze out in phase VII.

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32. By Lorentzian we mean here a spectral distribution of the form

$$I(v) = \frac{A}{[(v - v_0)^2 + \Gamma^2]}$$

where v_0 is the frequency of the band centre, Γ is the half-width at half maximum and A is a constant.
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