Dynamics of a low temperature phase transition in liquid crystal TB10A probed by Raman spectroscopy

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Dynamics of a low temperature phase transition in liquid crystal TB10A probed by Raman spectroscopy

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Raman spectra of TB10A were recorded in the regions, 925–1000 and 1140–1220 cm^{-1} from room temperature down to 20 K, during cooling and heating cycles. The subtle changes in the spectral features of the bands at ~ 975 and ~ 1195 cm^{-1} at 47 K were attributed to a hitherto unreported stable–metastable phase transition in TB10A. The dynamics of the new phase transition have been explained in terms of splitting of the non-planar mode at ~ 975 cm^{-1} owing to strong intermolecular interaction due to close molecular packing in the low temperature phase. The spectral anomaly of the 975 cm^{-1} band, in terms of variation of relative intensity with respect to temperature, also shows the hysterisis linked with the process of stable–metastable–stable modification in TB10A.

1. Introduction

Vibrational spectroscopy is a very effective and convenient method for investigating supercooled liquid crystal polymorphism, to study the solid state phases, the structural evolution and the associated conformational changes of the molecules. However, the Raman spectroscopic technique [1–5] has been mainly and widely used to establish a correlation between the liquid crystalline structures in different phases corresponding predominantly to external degrees of freedom. Though many temperature dependent Raman studies have been reported in the literature [6–10], there are very few Raman spectroscopic investigations on solid state polymorphism in supercooled liquid crystals [11–16] and most of them are confined to the lower frequency region [12, 13, 15, 16]. Various other techniques such as neutron diffractometry [17], X-ray diffractometry [18], and differential scanning calorimetry [19] have also been used to investigate phase transitions in supercooled liquid crystals. However,

in a recent study, Strela-Llopis and Pogorelov [20] asserted that structural and thermodynamic methods lead to contradictory results, whereas spectroscopic methods offer the possibility to resolve discrepancies and to monitor the influence of phase transitions on individual fragments of the investigated molecule.

Interestingly, in all previous studies [11–19], only nematogens have been used for the investigation of solid phase polymorphism in their supercooled state [11–16] and studies on supercooled smectogens are quite scarce. Here we have undertaken a low temperature Raman study, to an extent as low as 20 K, on a smectogen, TB10A (a higher homologue of TB$\bar{A}$A which exhibits only smectic phases) to understand its structural modifications at low temperatures. However, the basic interest of the low temperature spectral investigation on TB10A lies in the following two points. First, TB10A is an interesting compound due to its rich polymesomorphism and subtle properties and it is the only example of a non-ferroelectric liquid crystal that exhibits a weakly first order SmA–SmC transition [21]. Second, it is

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important to understand the low temperature dynamics of *p*-substituted Schiff's bases which are considered as useful models for many liquid crystalline systems.

2. Experimental details

TB10A was synthesized by a standard procedure [21, 22]. The structure of TB10A ($n = 10$) and its transition temperatures are given below.

Solid $\xleftrightarrow{346\,K}$ G $\xleftrightarrow{393\,K}$ SmF $\xleftrightarrow{421\,K}$ SmI $\xleftrightarrow{427.4\,K}$ SmC $\xleftrightarrow{463.2\,K}$ SmA $\xleftrightarrow{463\,K}$ I
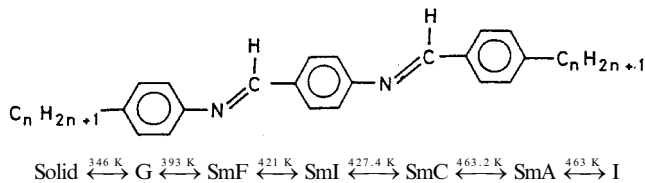
Raman spectra were recorded on a Spex-1403 double monochromator equipped with an RCA-31034 photo-multiplier tube. The 488.0 nm radiation from an Ar^+-laser was used and power at the sample site was kept as low as 25 mW. The other experimental conditions were the same as those explained in our recent studies. For the recording of the low temperature spectra, the samples were placed in good thermal contact with the cold finger of a variable temperature, closed cycle, helium cryocooler. The temperatures were monitored with a copper–constantan thermocouple with an accuracy of ± 0.5 K.

Raman spectra were recorded at different temperatures while cooling the sample slowly at a rate of 1.5 K min^{-1}, from room temperature to 20 K. The sample temperature was then raised slowly from 20 K to room temperature at a rate of 2 K min^{-1} while recording the spectra at different temperatures in the 100–2000 cm^{-1} region. However, we concentrated our study in the 925–1000 and 1140–1220 cm^{-1} regions. The observed spectra in the 925–1000 cm^{-1} region during cooling and heating cycles are shown in figures 1 and 2, respectively, while the observed spectra in the 1140–1220 cm^{-1} region during cooling and heating cycles are shown in figures 3 and 4, respectively.

3. Low temperature Raman spectra and evidence of an S–M (Stable-Metastable) transition

The room temperature Raman spectrum in the 925–1000 cm^{-1} region was recorded separately, see spectrum (f) of figure 1; it exhibits a shoulder on the lower wavenumber side of the 975 cm^{-1} band. On lowering the temperature, the intensity of the shoulder gradually decreases and finally disappears at around 200 K. On further cooling, this shoulder again starts appearing below 135 K, shows up clearly at 93 K, and its intensity relative to the main band increases down to 47 K (see figure 1). At 47 K, the 975 cm^{-1} band is clearly resolved into two distinct bands at ~ 973 and ~ 978 cm^{-1}.
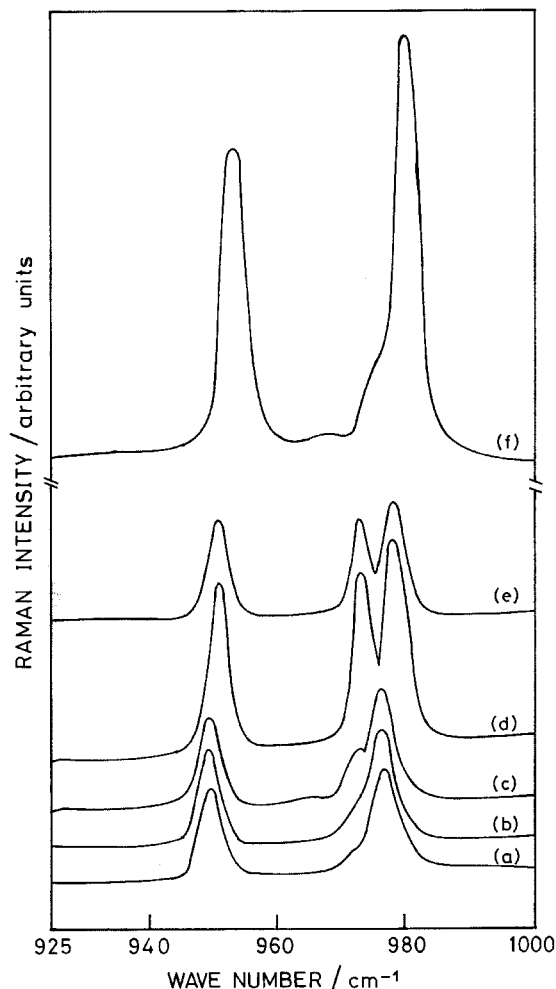

Figure 1. The observed Raman spectra of TB10A in the region 925–1000 cm^{-1} at different temperatures during a cooling cycle: (a) 229 K; (b) 135 K; (c) 93 K; (d) 47 K; (e) 20 K; (f) room temperature spectrum recorded separately.

However, the relative intensity of the new band does not change appreciably down to 20 K. The 1195 cm^{-1} band in the region 1140–1225 cm^{-1}, develops a shoulder towards the higher wavenumber side at 90 K (see figure 3) while cooling from its room temperature state, which was recorded separately, see spectrum (g) of figure 3. On further cooling, the shoulder becomes more distinct and partially resolved at 47 K and the relative intensity does not change appreciably down to 20 K. During the heating cycle, the intensity of the new band from the 975 cm^{-1} band (see figure 2) increases up to 226 K, assuming an even higher intensity than the main band above 132 K, and then starts decreasing on further rise in temperature above 226 K. However, no such anomaly was observed for the partially resolved shoulder of the 1195 cm^{-1} band, and the aforesaid nature of the 1195 cm^{-1} band persists up to room temperature without any appreciable change (see figure 4). On the basis
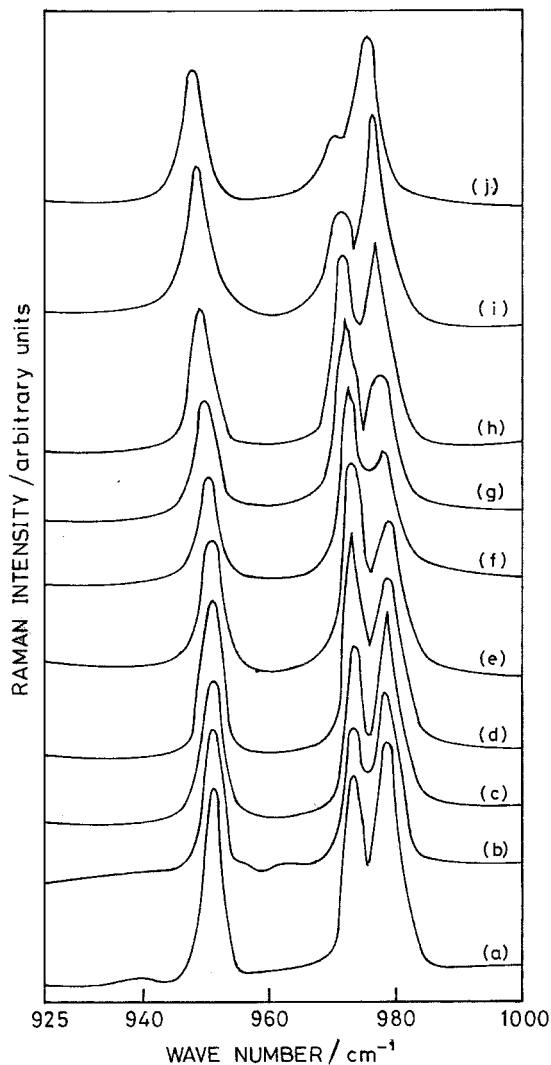
Figure 2. The observed Raman spectra of TB10A in the region 925–1000 cm⁻¹ at different temperatures during a heating cycle: (a) 67 K; (b) 87.5 K; (c) 112 K; (d) 132 K; (e) 162.5 K; (f) 205 K; (g) 226 K; (h) 257 K; (i) room temperature; (j) room temperature after 60 h.

Figure 3. The observed Raman spectra of TB10A in the region 1140–1220 cm⁻¹ at different temperatures during a cooling cycle: (a) 229 K; (b) 210 K; (c) 135 K; (d) 93 K; (e) 47 K; (f) 20 K; (g) room temperature spectrum recorded separately.

of Raman depolarization data, IR data [23], and previous studies [24] on similar compounds, the bands at 975 and 1195 cm⁻¹ may be ascribed to aromatic C–H central wagging ($\nu_{17} + \nu_{16} + \nu_5$) and ϕ-N bending modes, respectively. Such types of assignment, in turn, help us in a qualitative discussion of the spectral anomaly at the S–M transition.

There are many hypotheses and suggestions regarding S–M transitions and solid modifications in similar compounds available in the literature [11, 25, 26]. Andrews [25] put forward a hypothesis that the main distinction between stable and metastable states is manifested in different structures of butyl chains and the position of methoxy groups with reference to benzene rings. Later Arendt *et al.* [11] suggested that the rotation of aromatic
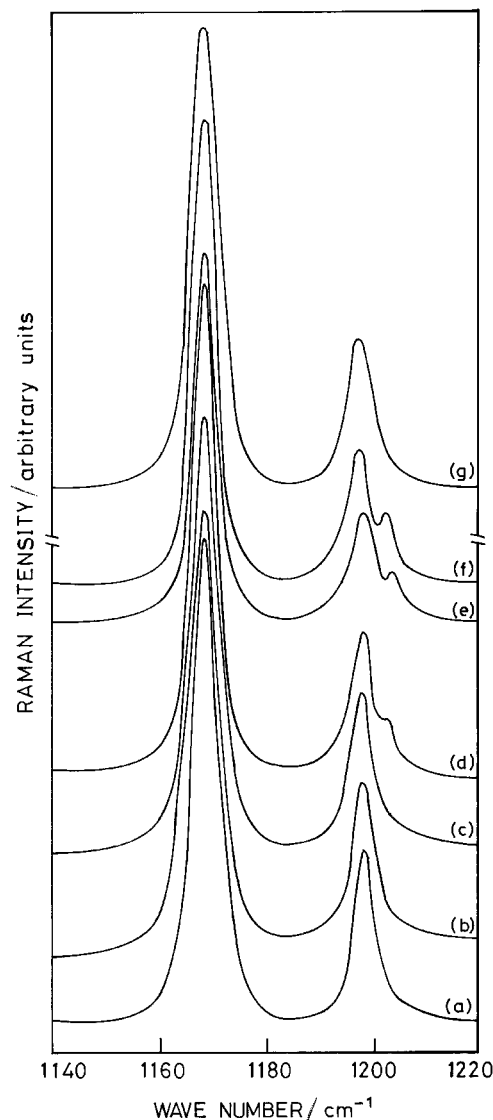
rings around the C(H)=N bond also leads to a metastable modification. However, an important suggestion regarding this was made by Bernstein and Schmidt [26] from their X-ray investigations on *p*-chlorobenzylidene-*p'*-chloroaniline, a Schiff's base. According to them, the metastable disorder is associated with a random orientation of the –C(H)=N– groups which, in turn, suggests that the stable modification is associated with a tilted configuration of benzene rings, whereas the metastable modification is associated with a planar configuration of benzene rings of the *p*-chlorobenzylidene-*p'*-chloroaniline molecule. This suggestion in particular is important for the present discussion, because it demonstrates the role
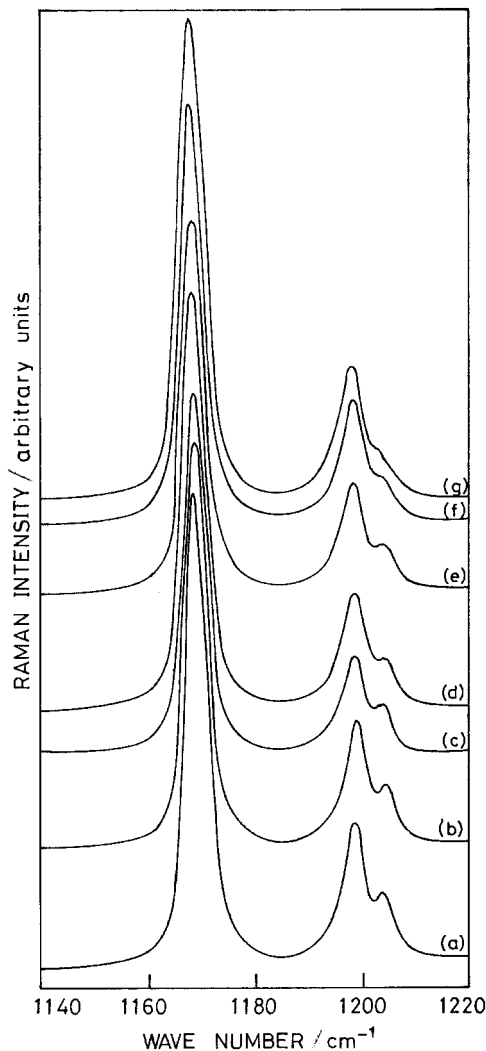
Figure 4. The observed Raman spectra of TB10A in the region 1140–1220 cm⁻¹ at different temperatures during a heating cycle: (a) 67 K; (b) 87.5; (c) 112 K; (d) 132 K; (e) 162.5 K; (f) 205 K; (g) 226 K; (h) 257 K; (i) room temperature; (j) room temperature after 60 h.

of intra–inter-molecular orientation in relation to the phenomenon of metastable modifications. Moreover, the above suggestions were recently strongly corroborated by Pogorelov and Strela-Llopis [14] in a low temperature Raman study on MBBA.

As shown above, TB10A consists of a staggered or zig-zag core connected by Schiff's base linkages and long saturated aliphatic chains ($n = 10$) on both sides of the core. From the structure of TB10A, it is difficult to predict whether the three benzene rings are in a particular plane or tilted with respect to each other. At room temperature, in the solid state, there is still enough room for orientational motion to take place about the C=N bond, and as a result, the possibility of tilted configurations of the benzene rings cannot be ruled

out. When the temperature decreases and the sample enters a very low temperature state, all the orientational motions cease, and hence the benzene rings have no other choice than to acquire a planar configuration in accordance with a close packed arrangement. This results in a metastable state which involves a planar mutual configuration of the benzene rings as suggested by Bernstein and Schmidt [26]. However, this planar configuration of the benzene rings leads to a decrease in intermolecular spacing resulting in a splitting of the associated Raman modes [27]. The band at $\sim 975 \, \text{cm}^{-1}$, which is largely due to the cumulative effect of certain out-of-plane ring modes ($v_{17} + v_{16} + v_5$) [24], is likely to be affected more than the in-plane modes [27]. The band at $\sim 975 \, \text{cm}^{-1}$, therefore, splits into two distinct peaks at ~ 973 and $978 \, \text{cm}^{-1}$ in the metastable state. However, according to figure 1, the splitting process of the $975 \, \text{cm}^{-1}$ band did not occur suddenly; rather it started at $\sim 93 \, \text{K}$ and was complete at $\sim 47 \, \text{K}$ which indicates that the metastable modification is formed by a second order transition process. Because of close molecular packing, strong intermolecular interactions between different Schiff's base linkages, (–CH=N–), which play a vital role in the S–M modification due to their random orientation [11], and subsequent planar modification of the benzene rings [26], possibly results in partial splitting of the $v_{\phi-N}$ mode at $\sim 1195 \, \text{cm}^{-1}$. Evidence of shorter inter-planar spacing and close molecular packing in metastable phases has also been reported for some nematogenic compounds [17, 28].

After the cooling process was over, the TB10A sample was heated slowly at a rate of $2 \, \text{K min}^{-1}$ up to room temperature. The resulting spectra in the 900–1025 and 1140–1220 cm⁻¹ region are reproduced in figures 2 and 4, respectively. An important observation that can be made from both figures is that the splitting of the bands at ~ 975 and $\sim 1195 \, \text{cm}^{-1}$ during cooling (started at $\sim 90 \, \text{K}$, completed at $\sim 45 \, \text{K}$) do not follow identical temperature paths during heating. The splitting which appeared at $\sim 90 \, \text{K}$ during the cooling cycle, persisted up to room temperature for both bands. Furthermore, the splitting was still observed after 60 h—see spectra (j) and (g) of figure 2 and 4, respectively—on monitoring the Raman spectra after every 10 h. It was only after 84 h that the spectral features of the ~ 975 and $\sim 1195 \, \text{cm}^{-1}$ bands attained their original room temperature features.

4. Molecular dynamics at the S–M transition

The above observation was, however, not quite unexpected in view of previous studies on nematogens. Scienscinska *et al.* [16] made such an observation in their low temperature IR study on MBBA where the sample having an S–M transition at 275 K needed several hours to regain its stable state after it had been

cooled to a temperature of 200 K. Later Arendt *et al.* [11] in their low temperature Raman study on MBBA cooled the sample to 78 K, far below its S–M transition at 275 K, and observed that the stable state was attained after several days. These two studies reveal that the lower the temperature to which a sample is cooled below room temperature, the greater are the restrictions imposed upon various molecular motions such as rotation, reorientation, etc., resulting in longer relaxation times for regaining the stable state.

As regards our results on TB10A, for which the S–M transition point is at ∼ 47 K, when the sample was cooled down to 20 K, two plausible explanations can be offered for the effects. In the first, in accordance with the earlier studies [11, 16] and what has been said above, the cooling of the sample to 20 K could in itself result in a longer relaxation time. TB10A, having long aliphatic terminal chains offers extensive steric hindrance in a typical close packed structure at extremely low temperatures leading to a shallow potential well (in terms of molecular energy) for molecular reorientation, thereby causing a slow relaxation towards regaining the stable state. In the second explanation, since the cooling is done to 20 K below the already low transition temperature of 47 K, the system probably does not have an opportunity to develop enough hysterisis towards regaining the stable state. Moreover, both these explanations are reflected in the splitting of the 975 cm^{-1} band in terms of the variation of the relative intensity ratios (RIR) with respect to temperature. The relative intensity ratios of the two split bands at ∼ 973 cm^{-1} (main band) and 978 cm^{-1} (new band) at different temperatures during the cooling and heating cycles have been calculated and are presented in the table. At some temperatures where the 975 cm^{-1} band was not split the relative intensity of the main band was taken as it is and the value was

chosen to be slightly higher (6) than the highest RIR value (5.7) for the sake of showing the data graphically, in a convenient way. The data given in the table are represented in figure 5. A close look at figure 5 reveals the hysterisis linked with the molecular motions, especially the out-of-plane benzene ring modes [24], towards regaining their status in the stable state. This, in turn, reveals the sensitivity of the 975 cm^{-1} band [29] in the identification of the nature of stable–metastable–stable transition in TB10A.
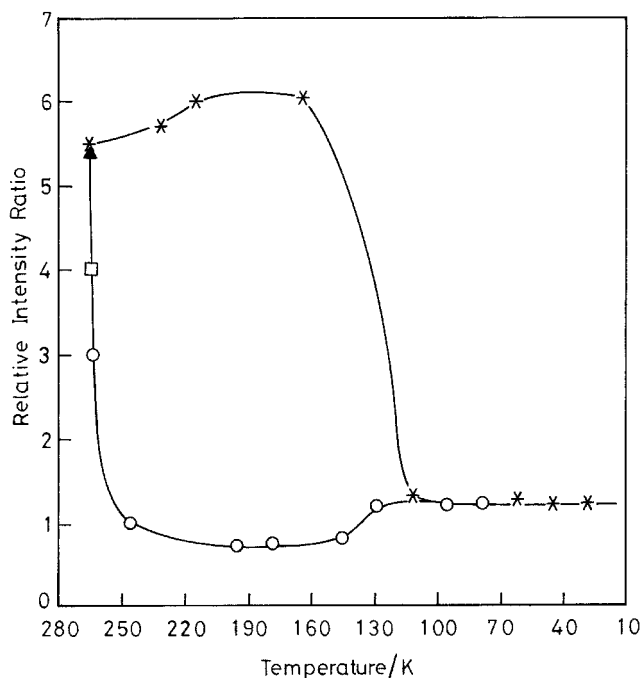

Figure 5. Variation of relative intensity ratio with respect to peak position: (○) heating cycle, (∗) cooling cycle, (□) after 60 hrs, (▲) after 84 hrs.

Table Relative intensity ratios of the ∼ 973 and 978 cm^{-1} bands at different temperatures. I_1 = Relative intensity of the original band (∼ 975 cm^{-1}); I_2 = relative intensity of the new band (∼ 978 cm^{-1}).

Cooling cycle		Heating cycle	
Temperatures/K	Rel. intensity ratio (I_1/I_2)	Temperatures/K	Rel. intensity ratio (I_1/I_2)
273	5.5	67	1.174
229	5.7	88	1.175
210	6.0[a]	112	1.174
135	6.0[a]	132	0.8
112	2.0	162	0.75
93	1.27	205	0.73
60	1.25	226	0.70
47	1.175	257	1.01
20	1.174	273	2.5
		273 (after 60 h)	4.0
		273 (after 84 h)	5.4

5. Conclusion

In conclusion, this low temperature Raman study has provided evidence for the attainment of a metastable state resulting from the change in configuration of the benzene rings due to rapid orientation of the –C(H)=N– groups. It also gives clear evidence of a hysterisis linked with the metastable to stable transformation in TB10A, a molecule having long alkyl terminal chains. Nevertheless, this discussion also shows the sensitivity of the $975\,cm^{-1}$ band in relation to the stable–metastable–stable transition in TB10A and the identification of its nature.

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