

Dynamics of phase transitions in a liquid crystalline compound (TBDA) probed by Raman spectroscopy

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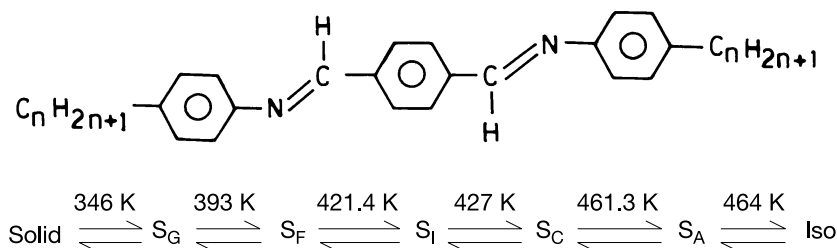
Abstract. The precise value of linewidths obtained after correcting for the slitwidth effect for five Raman bands associated with the core of a liquid crystalline compound, terephthal-bis-decyl aniline (TBDA), have been studied in the temperature range of 12–472 K. The variation of the linewidth with temperature confirms two already reported phase transitions at 346 and 427 K. However, the phase transition at 427 K is not purely first order as reported earlier, but of mixed order in nature. From the measured linewidths of the $\nu_{\phi-N}$ and $\nu_{C=N}$ modes below room temperature, the estimated activation energy for rotation along the $\phi-N$ bond closely matches with the S_I-S_C phase transition temperature suggesting that the rotation about the $\phi-N$ bond is closely linked with this transition.

1. Introduction

Raman spectroscopy is an important tool to investigate different types of phase transition owing to the fact that the changes in physical properties at molecular level are reflected in the measurable parameters of certain characteristic Raman modes. A fairly good volume of literature is available where the Raman technique has been applied to investigate the phase transitions in liquid crystalline materials [1–6]. In almost all such studies, much attention has been paid to analysing the major changes in the Raman spectra in going from one phase to another. However, some characteristic modes of the system may have sufficient information about the different inter/intra-molecular forces [7, 8] and the dynamics of phase transition can be investigated by studying the changes in linewidth as a function of temperature.

TBDA is a Schiff base liquid crystalline compound. Using different thermal characterization techniques (DSC, DTA/TGA, HSTM), it has been reported that TBDA undergoes a crystalline solid to smectic G (S_G) transition at 346 K (melting point), and smectic A (S_A) to isotropic liquid phase at 464 K (clearing point). In between the solid and isotropic liquid phases it goes through different liquid crystalline phases, known as smectic mesophases [9–11]. The molecular structure and the transition temperatures of TBDA are shown in scheme 1.

In one of our earlier studies [12] we have shown the utility of the variation of integrated intensity and peak position of some characteristic Raman modes to understand the molecular dynamics at a particular transition. In that study, a rotation around the $\phi-N$ (ϕ refers to the benzene ring) bond was suggested at 427 K, which corresponds to the reported S_I-S_C transition [13, 14]. The rotation around the $\phi-N$ bond will considerably affect the adjacent C=N bond also. In view of the fact that the TBDA molecule might be rotating around



Scheme 1.

the ϕ -N bond at the S_I - S_C transition, an analysis of temperature-dependent linewidth of the ϕ -N and C=N modes may provide crucial information. The present study has been undertaken to explore further details and to understand the dynamics of phase transition in TBDA at this transition by analysing primarily the variation of precise linewidth of the ϕ -N and C=N stretching modes as a function of temperature. However, variation of linewidth of three additional modes of benzene rings, which are also expected to be influenced slightly by rotation has also been studied.

2. Experimental details

TBDA was synthesized by the standard procedure [13, 14] and recrystallized from an absolute ethanol-benzene mixture repeatedly until the observed transition temperatures were found to be constant. The Raman spectra were obtained at different temperatures from 12 to 472 K in the 1100–1220 and 1520–1675 cm^{-1} regions on a Spex Ramalog 1403 double monochromator equipped with an RCA-31034 photomultiplier tube and CCD detector using the 488.0 nm line of an Ar^+ -laser as an excitation source. A slit combination of 200–400–400–200 μm , a scanning increment of 0.1 cm^{-1} and an integration time of 1.0 s were found to be suitable to record spectra with good signal-to-noise ratio. To record high-temperature spectra, the sample was kept in a 0.5 mm capillary tube (sealed on both sides), and placed in a highly evacuated chamber of a home-made high-temperature cell. The temperature was continuously monitored and measured accurately within $\pm 0.2^\circ\text{C}$, keeping a copper-constantan thermocouple in close contact with the sample. Low-temperature Raman spectra were recorded using a closed-cycle helium cryocooler.

Since this study aims at analysing precise linewidth data, we also recorded plasma lines at the same slit setting as used for Raman spectra to eliminate the slit width effect. The slit function, $S = 2.62\text{ cm}^{-1}$, was calculated as the full width at half maximum (FWHM) of the plasma line recorded at 1576.60 cm^{-1} from the 488.0 nm line of an Ar^+ laser. In an ideal case, the plasma line should be very close to the position of the Raman band in question. To approach the bands under study as closely as possible, two more plasma lines at 1138.85 and 1172.50 cm^{-1} from the 488.0 nm line of an Ar^+ laser were recorded. The FWHMs of these two plasma lines were also found to be equal to 2.62 cm^{-1} . The spectra of TBDA recorded at different temperatures in the 1100–1220 and 1520–1675 cm^{-1} regions are given in figure 1.

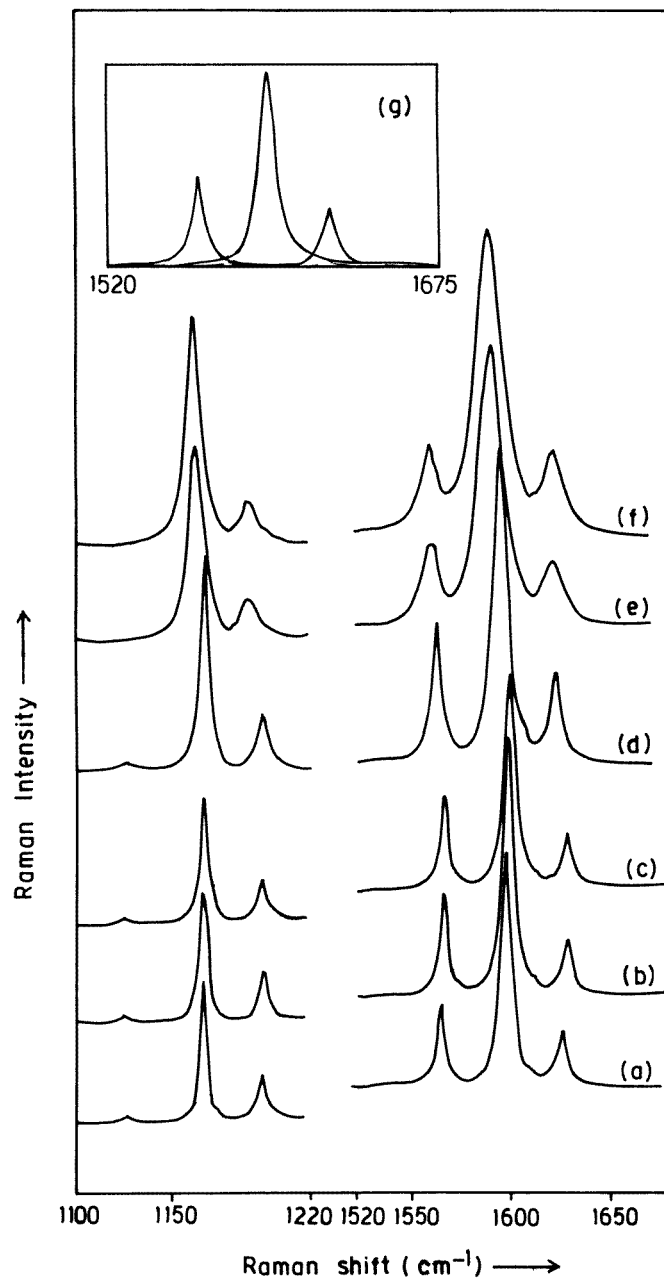


Figure 1. Raman spectra of TBDA in the 1100–1220 and 1520–1675 cm^{-1} regions at different temperatures: (a) 12 K; (b) 93.3 K; (c) 229 K; (d) 335 K; (e) 423 K; (f) 463 K; (g) deconvoluted spectra in the 1520–1675 cm^{-1} region at 335 K. The fitted and measured curves overlap in (g).

3. Deconvolution of Raman bands

It can be seen from figure 1 that the bands are overlapping in the wings. In order to obtain precise data on linewidth it is desirable to deconvolute the bands. This has been achieved

by fitting the spectral features in the 1100–1220 and 1520–1675 cm^{-1} regions with two and three Voigt profiles, respectively, and the linewidth for each band at every temperature was calculated from the spectra thus resolved. A representative deconvoluted spectrum at 335 K along with the recorded profile is given in figure 1 as inset. In general, the experimentally recorded Raman line profile at the usual resolution is always a combination of the true Raman line profile and the slit function [15]. Thus to draw any meaningful conclusion from the linewidth data, the true Raman linewidth (Γ) must be extracted from the experimentally observed linewidth $(\Delta\nu_{1/2})_R$. The FWHMs, $(\Delta\nu_{1/2})_R$, for all the three resolved bands after deconvolution were measured at different temperatures. The slit function, S , was measured as discussed in the experimental section. The parameter $X = S/(\Delta\nu_{1/2})_R$ was calculated for each case and the values of X were substituted into the following equation, suggested recently by Singh *et al* [16], to obtain the true Raman linewidth,

$$\Gamma = (\Delta\nu_{1/2})_R[0.998 + 0.020X - 1.16X^2 + 0.143X^3]. \quad (1)$$

The values of Γ thus calculated for all five Raman bands under study at different temperatures are plotted in figure 2.

4. Discussion

Figure 2 gives the variation of linewidth (corrected for slit effect) with temperature for five Raman bands (1165, 1195, 1563, 1594 and 1625 cm^{-1}). It is evident from the figure that all the bands show a sudden change in linewidth at 346 K (solid– S_G). It is further noticed that the 1195 cm^{-1} ($\nu_{\phi-N}$) and 1625 cm^{-1} ($\phi_{C=N}$) bands show a similar variation in linewidth whereas the two benzene ring modes, $\nu_{8a'}$ (1563 cm^{-1}) and ν_{8a} (1594 cm^{-1}), produce insignificant change in linewidth at the S_I – S_C transition. However, the change is more pronounced for the ν_{9a} (1165 cm^{-1}) mode at this transition.

In order to understand the origin of these changes in linewidth, it is necessary to look carefully at the structure of the TBDA molecule, which nevertheless plays a major role in phase transitions at different temperatures. As is evident from the structure, the TBDA molecule may be considered as consisting of two distinct parts: the three staggered benzene rings connected by Schiff bases form one part called the core, while the other part consists of the long alkyl chains ($\text{C}_{10}\text{H}_{21}$) attached to both sides of the core. It is important to note here that all the Raman bands under study which show changes in linewidths at the solid– S_G and S_I – S_C transitions are associated with the core, indicating that the core no longer remains rigid during these transitions.

To understand the dynamics of the first transition, i.e., solid– S_G , we consider the packing structure in the S_G phase. The S_G phase of TBDA has a pseudo-hexagonal packing with a local herringbone structure [9]. Even though translational freedom between the molecules is almost nil in this phase [9], the lateral gap between each of the pseudo-hexagonally packed clusters [10] may facilitate long alkyl chains vibrating more freely, thereby producing strain on the core, especially on the peripheral benzene rings and the ϕ –N and C=N bonds. This would make their individual frequencies slightly different and thus would broaden the Raman bands. A sudden increase in linewidth observed in the present study and a similar trend observed in the peak position and integrated intensity in our earlier study [12] for all the Raman bands at the solid– S_G transition confirms the first-order character of this transition.

At the S_I – S_C transition [14], the hexagonally close packed structure of the S_I phase transforms into a two-dimensional (2D) liquid-like structure in the S_C phase. Being a 2D liquid, the S_C phase has only short-range correlation between the molecular positions within the layer over a certain distance (known as a cluster) [9, 10]. Because of the fluid character,

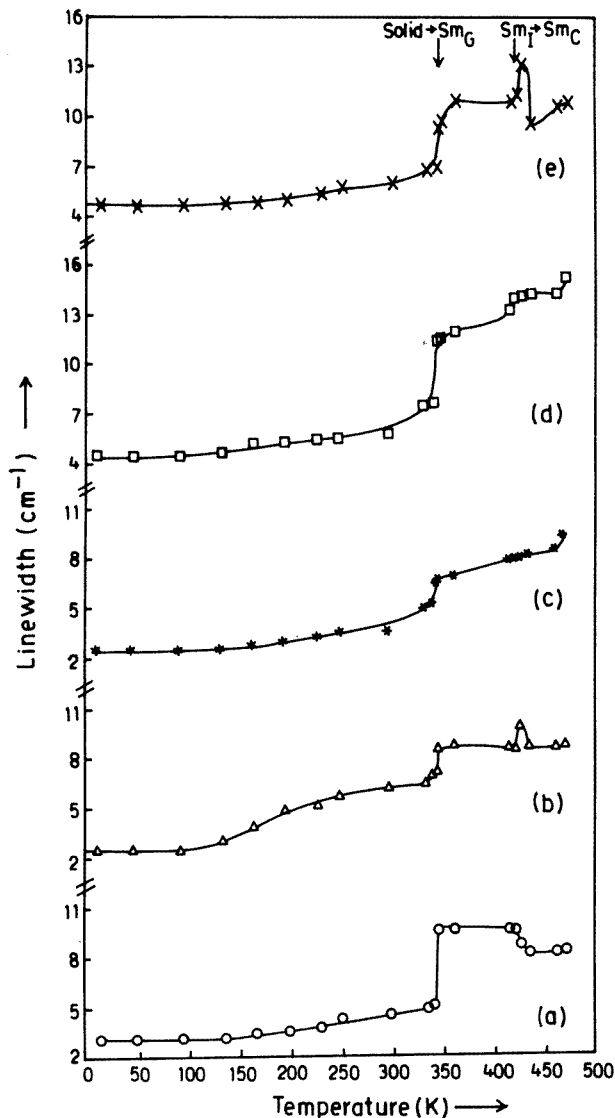


Figure 2. Variation of linewidth of five Raman bands with temperature: (a) 1165 cm^{-1} ; (b) 1195 cm^{-1} ; (c) 1563 cm^{-1} ; (d) 1594 cm^{-1} ; (e) 1625 cm^{-1} bands.

the distance between the centres of the clusters is not related to the local lattice spacing, neither are the intermolecular directions correlated. Taking these aspects into consideration, there is a strong possibility of an intramolecular rotation along a flexible single bond (ϕ -N). In an earlier study we have interpreted this as core disorder [12], where the peripheral benzene rings of the core rotate slightly around a flexible single bond (ϕ -N) at the S_I - S_C transition. If we consider a simple picture of the Raman linewidth as a cumulative effect of linewidths originating mainly from the temperature-independent vibrational dephasing and temperature-dependent orientational motions, the activation energy for the reorientational motion around the ϕ -N bond can be obtained from the estimated contribution of the

orientational motion (Γ_r) to the Raman linewidth using the standard relation [17–20]

$$\Gamma_r = A e^{-U/RT} \quad (2)$$

where A is a constant related to the entropy of the system and U is the activation energy at temperature T . From the slope of $\ln \Gamma_r$ against $1/T$, we obtain $U = 0.859 \text{ kcal mol}^{-1}$. When the activation energy $U \cong RT$ at temperature T , the system is expected to have sufficient energy to rotate almost freely around the ϕ -N bond. The calculated temperature of 431.9 K corresponding to the activation energy of 0.859 kcal mol⁻¹ for rotation around the ϕ -N bond closely matches the S_I - S_C transition temperature of 427 K. This provides clear evidence that the S_I - S_C transition is intimately linked with rotation around the ϕ -N bond.

Unlike the solid- S_C transition, the S_I - S_C transition is not purely first order; rather it involves certain second-order characteristics. This is evident from the observed unusual fluctuations in the linewidth associated with the $\nu_{\phi-N}$ and $\nu_{C=N}$ modes at the S_I - S_C transition (figure 2). These two modes show a sudden increase followed by a sudden decrease in a small temperature interval, resembling a peak, on the increasing trend of linewidth. This observation is interesting because it suggests the nature of this transition. The S_I - S_C transition as reported earlier [14] was not a purely first-order type and the hidden second-order characteristics were not observed clearly. From our experimental results, the linewidth increases suddenly near this transition, attains a peak value in the middle and then decreases on completion of the transition. If we consider that only the orientational contribution to Raman linewidth is affected by the temperature then, as a result of induced fluidity, the rotation around the ϕ -N bond increases from the beginning to the middle of the transition and then decreases suddenly at the end of the transition in order to attain a stable configuration in the S_C phase. This sort of behaviour of linewidth can be rationalized by assuming that the S_I - S_C transition involves certain second-order characteristics in its so-called impure first-order transition property, as its completion requires a larger temperature interval before attaining the next phase (S_C), in comparison to a purely first-order one. In other words, we can say that the first-order transitions, which are generally distinguished by sudden changes in most of the physical quantities near phase transition, are not always purely first order, but may sometimes be of mixed order in nature. The ν_{9a} benzene ring mode at 1165 cm⁻¹ also shows a gradual decrease in linewidth with temperature (figure 2) at this transition, providing additional support for the view that this transition is not of purely first-order type.

5. Conclusions

The main results of the present study can be summarized as follows. The study of variation of linewidth with temperature serves a threefold purpose. Firstly, it shows clearly the phase transitions at 346 and 427 K. Secondly, the S_I - S_C transition is not purely first order but mixed order in nature as it involves certain second-order characteristics. Thirdly, from the observed low-temperature linewidth of the bands associated with the $\nu_{\phi-N}$ and $\nu_{C=N}$ modes, the activation energy for orientation around the ϕ -N bond is calculated as $\sim 0.859 \text{ kcal mol}^{-1}$, which corresponds to a transition temperature of 431.9 K for the S_I - S_C transition and is very close to the actual transition temperature of 427 K. This provides clear evidence that the rotation of peripheral benzene rings around the ϕ -N bond is closely linked with the S_I - S_C transition.

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