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Raman, Infrared and Calorimetric Investigations of the Unstable Modifications Formed by Fast Cooling of the Mesophase

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Raman, Infrared and Calorimetric Investigations of the Unstable Modifications Formed by Fast Cooling of the Mesophase

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The metastable phases obtained by abrupt cooling of the mesophase are investigated by means of IR and Raman spectroscopy and by differential scanning calorimetry.

INTRODUCTION

As far back as 1933 Bernal and Crowfoot[1] pointed out that the number of investigations dealing with the solid phase of liquid crystals is surprisingly low in comparison with the number of the papers dedicated to the mesophase itself. Now, fifty years later, this statement retains much of its validity. In fact, among more than several thousand papers on mesomorphic materials only a few—hardly 15–20, study the solid phase. Robinder and Poirier[2] have shown that in addition to *p*-azoxyanisole (PAA), which is stable at room temperature, two more monotropic crystalline phases exist. In 1972 Neff[3] by means of differential thermal analysis established another crystal phase of 4-ethoxy-4-*n*-heptanoilazoxybenzene with melting temperature higher than the temperature of the ordinary phase, obtained by crystallization from ethanol solution. The glassy state of a liquid crystal was first identified for cholesteryl hydrogen phthalate[4]. Later, between 1973 and 1975 the formation of metastable phases by supercooling of the mesophase has been reported by a number of workers using X-ray diffraction, optical microscopy, molecular spectroscopy and thermal conductivity[5–9].

IR and FIR spectra of one stable and one unstable modifications of MBBA were recorded by Janik[10]. Differences between the spectra of these two modifications are greatest in the lattice vibration region, i.e. between 20 and 100 cm^{-1}. Schnur[11] by Raman spectroscopy has found two modifications in PAA—one obtained by slow crystallization of the nematic melt by itself and the other—monotropic phase II—produced by cooling. These two phases have different low frequency spectra in the 20–100 cm^{-1} region but essentially the same higher frequency spectra. Calorimetric measurements by Barral[12] demonstrated also stable and unstable solid modifications in *p*-ethoxybenzylidene, *p,n*-butylaniline (EBBA). Thermal investigations of quenched MBBA upon heating have been reported by Mayer *et al.*[13], Petrie[14] and Lydon[15]. Ogorodnik[16] has observed three unstable modifications of EBBA and has found that their melting temperatures are several degrees lower in comparison with that of the stable solid state. Le Brumant[17] using Raman spectroscopy has identified two unstable modifications in rapidly frozen MBBA. Solid state polymorphism of *p*-azoxyanisole has been studied by different experimental methods by Bata.[18] The good agreement between differential scanning calorimetry, polarizing microscopy, far IR spectroscopy and neutron diffraction results permitted three solid modifications to be identified.

Recently we published[19] the Raman spectra in the region 10–1650 cm^{-1} of two unstable modifications—one of which glasslike obtained by fast cooling of the nematic phase of EBBA and a stable solid phase reached by slow crystallization of the nematic melt by itself. Later we used vibrational spectroscopy and calorimetry in order to identify the metastable phase formed by fast freezing from the nematic phase of 4-nitrophenyl 4-*n*-octyloxybenzoate (NPOOB)[20].

The purpose of the present paper is to collect all our Raman, IR and calorimetric measurements of the metastable phases formed by some Schiff base liquid crystals and to clarify the structure of these phases.

EXPERIMENTAL PART

Raman spectra in the region 10–2000 cm^{-1} were taken with a conventional Raman system consisting of cw Ar laser, SPEX 1401 double monochromator, photon counting detection and either multichannel storage or strip chart recording. 5154 Å laser light was used for all measurements. The spectra were taken with 2.5 cm^{-1} band pass. The samples were placed in a good thermal contact with the cold finger of a variable temperature optical cryostat. The temperature, monitored with a Cu-constantan thermocouple, was stable within ± 0.5°K.

IR absorption spectra in the region 650–4000 cm^{-1} were recorded by UR-20 spectrophotometer (Carl-Zeiss Jena, DDR) provided with a variable temperature cell VLT-2 and automatic temperature controller TEM-IC (RIIC).

A Dupont 990 differential scanning calorimeter was employed to detect the phase transitions. It was calibrated with water, mercury, indium and tin. The sample weights used for these experiments varied from 15 to 25 mg and particular care was taken to ensure that the sample was not exposed to moisture or oxygen.

The following Schiff base liquid crystals were investigated: *p*-methoxybenzilidene *p,n*-butyaniline (MBBA), *p*-ethoxybenzylidene *p,n*-butylaniline (EBBA) and *p*-chlorbenzylidene *p,n*-pentylaniline (CBPA).

The chemicals were supplied by Eastman Kodak Ltd., (MBBA and EBBA) and by Thompson SCF (CBPA). Their purity was determined by checking the transition temperatures using both capillary melting point apparatus and DSC calorimeter. Particular attention was paid to the position of the nematic-isotropic transition temperature as this is very sensitive to impurities since it involves only very small enthalpy changes. Good agreement with the best literature values was found[21].

The temperature of phase transitions crystal-mesomorphic state-isotropic liquid are as follows:

MBBA: crystal $\xrightarrow{293°K}$ nematic $\xrightarrow{318°K}$ isotropic liquid
EBBA: crystal $\xrightarrow{309°K}$ nematic $\xrightarrow{350°K}$ isotropic liquid
CBPA: crystal $\xrightarrow{332°K}$ smectic B $\xrightarrow{353°K}$ smectic A $\xrightarrow{366°K}$ isotropic liquid.

RESULTS AND DISCUSSION

Our calorimetric measurements and thermal analysis showed that in addition to the usual stable solid modification obtained by slow crystallization of the sample by itself and named by us for all investigated chemicals "solid I", other metastable solid modifications also exist. Fast cooling from the nematic or smectic A phase at a rate of about 15°C/min. produced a transition into a solid metastable form which we shall call "solid II". The temperature T_g of the nematic-solid II phase transition is far below the

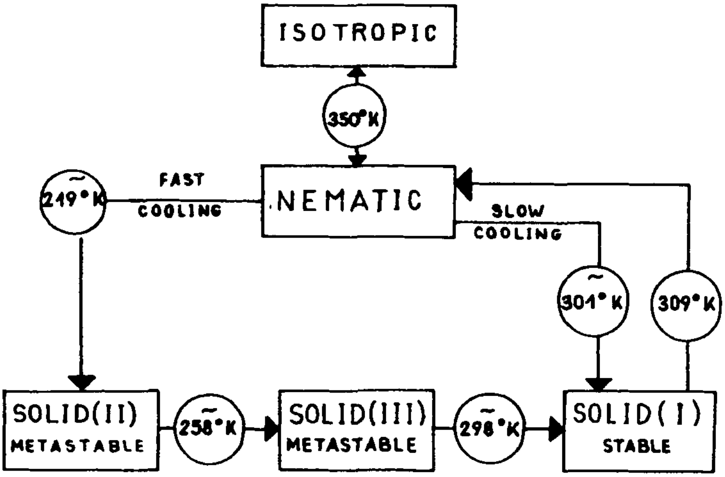

FIGURE 1 Scheme of the observed phase transition in EBBA.

temperature for the nematic-solid I transition being 206°K (MBBA), 217°K (EBBA) and 248°K (CBPA). At liquid nitrogen temperature solid II is stable at least for several days. At a higher temperature its life decreases and at about 253°K (258°K for EBBA, and 256°K for MBBA, 268°K for CBPA) passes directly with a broad exothermic transition into another solid metastable phase called by us "solid III". This is also stable at least several days if it is kept at liquid nitrogen temperature, while it requires only a few hours at room temperature storage for spontaneous conversion with liberation of heat the more stable solid I modification—the same obtained by slow crystallization from the melt. Once obtained this phase does not change anymore. The scheme for the observed phase transition in EBBA is shown on Figure 1. The same phase transitions are found for MBBA and CPBA, only the temperatures are a little bit different.

A cooling rate less than 5°C/min. will produce a very unstable mixture of solid II and solid I which soon passes in the stable solid modification solid I.

While the abrupt freezing from nematic or smectic A produces metastable phases, the quenching of smectic B does not give any. In our opinion this is due to the different structure of these three phases. The only structural restriction in the classical nematic liquid crystal is that the long axes of the molecules maintain a parallel or nearly parallel arrangement. The molecules are mobile in three dimensions and can rotate about the long axis. The freezing preserves this structure producing a metastable phase. Smectic A can be determined as an unstructured smectic liquid crystal. It has molecules arranged in mono-molecular layers with the long axes of the molecules perpendicular to the plane of the layers. Abrupt cooling of this mesophase

TABLE I

Enthalpy of phase transitions

	ΔH[kcal/mol]	ΔH[kcal/mol]
	solid II—solid III	solid III—solid I
MBBA	0.50 ± 0.07	0.100 ± 0.006
EBBA	0.67 ± 0.06	0.25 ± 0.01
CBPA	3.24 ± 0.25	0.15 ± 0.009

also keeps the existing disorder and forms an unstable modification. Smectic B, however, is different. This structured smectic liquid crystal has long range order in the arrangement of the molecules in the layers and forms a regular two dimensional lattice. The X-ray investigations indicate that smectic B is more ordered than smectic A and is close to the ordinary solid crystals. This is why fast cooling of this phase does not produce any metastable state.

The enthalpy ΔH of all phase transitions were calculated and the results are summarized in Table I.

As far as we know in the literature there are not any direct measurements of the enthalpy of various phase transitions in the solid phase of liquid crystals. However, there are data concerning only the enthalpy of the phase transitions metastable-nematic phase (ΔH metastable) and stable state-mesophase (ΔH stable) for MBBA, given by Janik[10] and Shinoda[22]. Although the absolute values of ΔH stable and ΔH metastable determined by these two authors differ, probably because of the impurity present, the residual enthalpy calculated from their data is close to ours—in our case we have two unstable modifications and the sum of $\Delta H_{\text{solid II}\to\text{solid III}}$ and $\Delta H_{\text{solid III}-\text{solid I}}$ for MBBA gives 0.60 kcal/mol which coincides with Janik's and Shinoda's results—0.783 kcal/mol and 0.767 kcal/mol respectively.

In Figures 2 and 3 we report the low frequency Raman spectra of the three phases of EBBA and CPBA (only for comparison also the nematic phase of EBBA). Striking differences among the solid phases are seen. The most ordered phase is solid I; in fact, low frequency peaks are narrow, sharp and scarcely split; the Rayleigh wing is also less intense than in the other two phases.

Solid III phase shows a much broader low frequency spectrum perturbed by a more intense Rayleigh wing, with a smaller number of peaks. This indicates that the partial disorder affects selection rules. It seems that hindered motions of the end chain are possible. In addition the low frequency spectrum looks not ònly perturbed but also structurally different—a fact which means that some modifications are present in the crystalline lattice.

The spectrum of solid II is closely related to the spectrum of the nematic phase—differences between them are practically limited to the low frequency

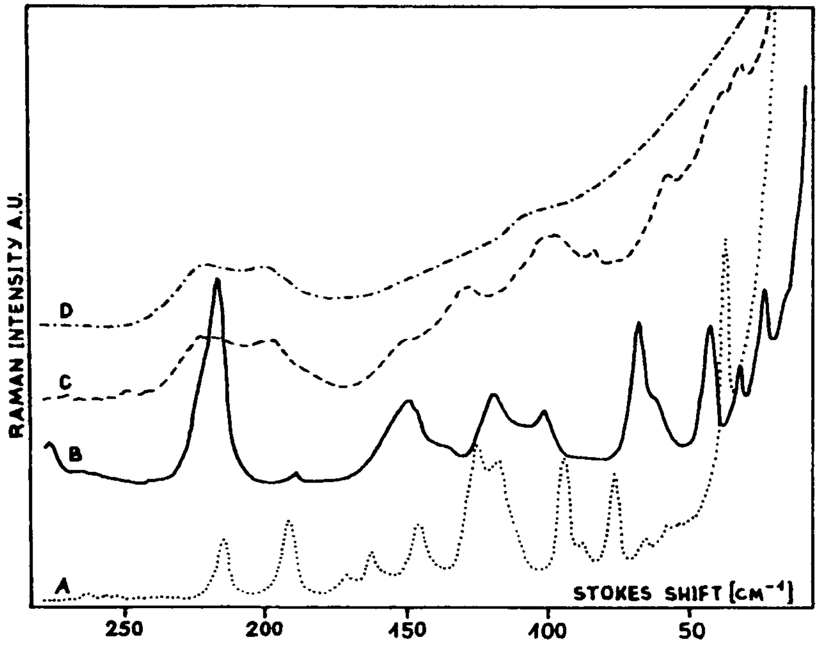

FIGURE 2 Low frequency Raman spectrum of EBBA: (A) solid I; (B) solid III; (C) solid II; (D) nematic phase; A, B, C at 90°K; D at 318°K.

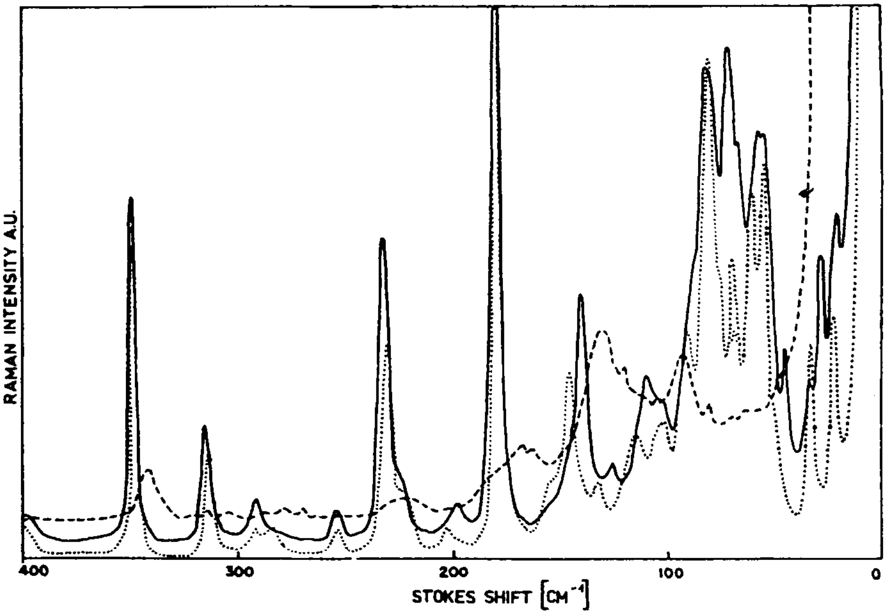

FIGURE 3 Low frequency Raman spectrum of CBPA at 90°K; dotted line–solid I, solid line-solid III, dashed line–solid II.

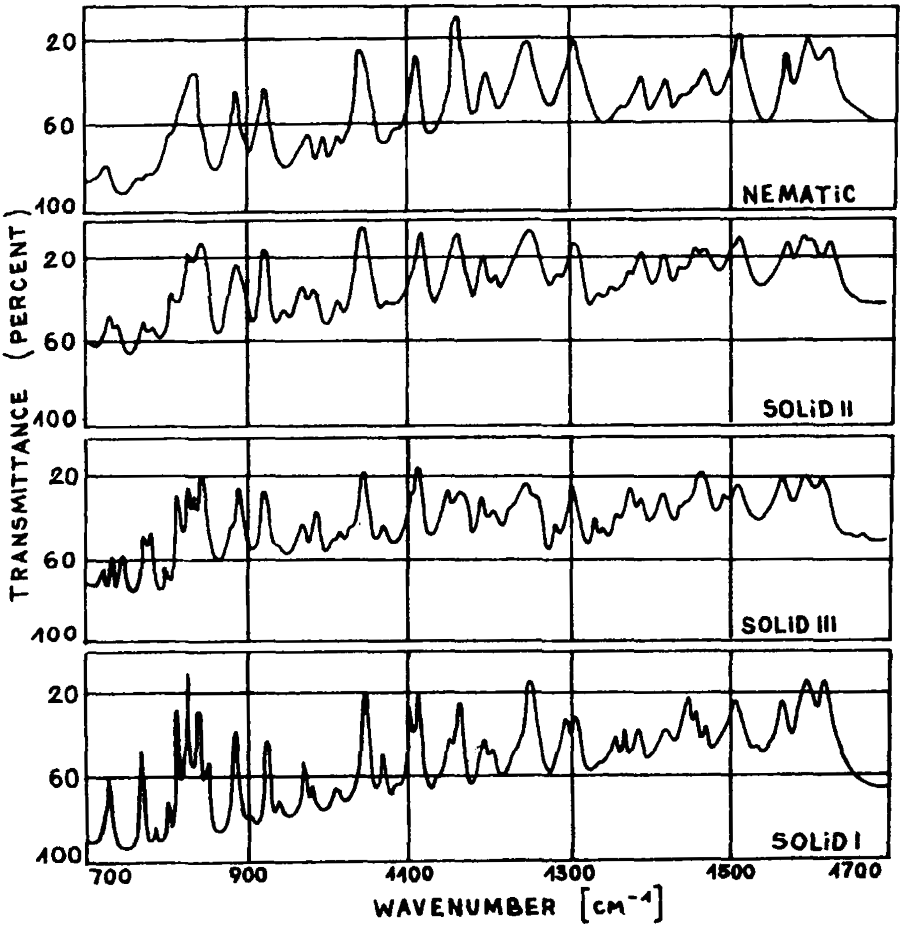

FIGURE 4 IR spectrum of EBBA; solid I, solid II and solid III at 90°K; nematic phase—at 318°K.

region—below 250 cm^{-1}. In fact, the overall IR spectra in the region 650–1650 cm^{-1} of solid II and nematic phases are very close (Figure 4). However, we must stress that solid II phase is distinct from the nematic one and is not simply an overcooled nematic phase because there is a measurable heat of transition from nematic into solid II. On the other hand in the low frequency region of solid II only a superposition of weak bands is detectable. The strong similarity existing between solid II and nematic is also outlined by similar frequencies half-widths and intensities of all IR and Raman bands from the spectra of these two phases with the exception a few bands at low frequency (below 250 cm^{-1}).

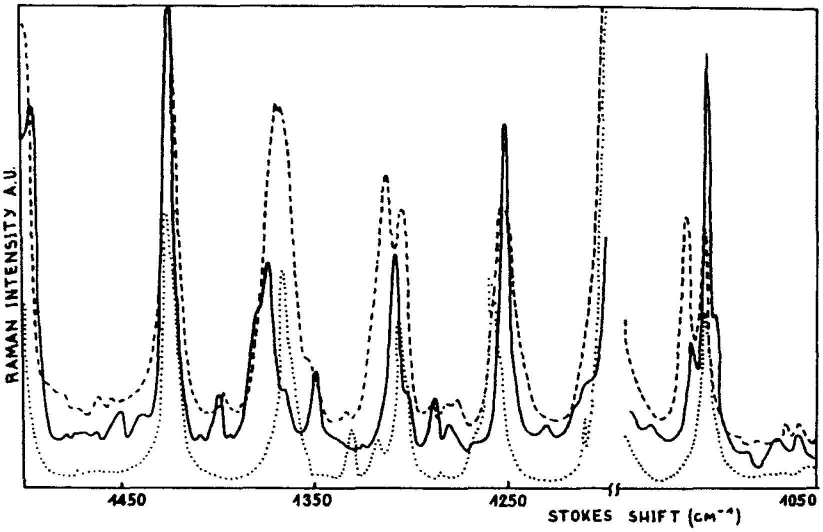

FIGURE 5 Raman spectrum of EBBA at 90°K; dotted line–solid I, solid line–solid III, dashed line–solid II.

Extra bands are observed in the spectra of solid II, solid III and even in the nematic phases. While in solid I the Raman bands corresponding to CH_2 twisting vibration in the region 1100–1300 cm^{-1} and twisting and rocking modes at 1460 and 720–750 cm^{-1} (IR active only) are single and narrow, in the other solid modifications they are split and broader. For example, the CH_2 twisting vibrations at 1100 and 1310 cm^{-1} from Raman spectrum of EBBA are split in solid II and solid III (Figure 5). The same results are obtained for all other investigated compounds. CH_2 rocking vibration at 725 cm^{-1} (active only in IR spectrum) is also a doublet in solid II and solid III, while in solid I is single and narrow (Figure 4). This is due to the additional rotational isomeric forms existing in the metastable states and indicating that the disorder in these phases is likely due to the presence of various conformers which are relatively rigid. This conclusion confirms other non-spectroscopic investigations. Andrew[23] recently connected the entropy excess of the metastable modification in relation to the stable one with a different rotational conformers of MBBA molecules. In particular he suggests that at the lower maximum of the anomaly (217°K) observed by Mayer[13], reorientational jumps of CH_3O groups about the long molecular axis start. The other maximum of the anomaly (212°K) is, according to Andrews[23] connected with an analogous increase of rotational conformations of the butyl chain. X-ray studies[24] of *p,n*-chlorobenzylidene *p*-chloraniline indicate that the metastable disorder is connected with a random orientation of $CH{=}N$ groups. Moreover, in the metastable modification the two benzene rings of the molecules are coplanar whereas in the stable modification one is tilted in relation to the other. Obviously more X-ray data are needed in order to clarify in detail the metastable solid phases.

The half-widths δ of the bands in solid II and solid III at the same temperature (LNT) are much bigger than in solid I. For example δ of the bands at 1628 cm^{-1} (CH=N stretch), 1597 and 1575 cm^{-1} (S8 + S9 + S7 + CH=N stretch[24]) from Raman spectrum of EBBA are in solid II 11, 8 and 9 cm^{-1} respectively, 6, 5, 5 cm^{-1} in solid III and only 5, 3 and 4 cm^{-1} in solid I. The same result can be obtained for all other bands. The half-width of the Raman band 975 cm^{-1} (CH central wagging +S17 + S16 + S5[25]) changes from 10 to 4 cm^{-1} when EBBA passes from solid II into solid I via solid III, while in the same transitions δ of the band at 1165 cm^{-1} decreases two times at phase transition solid II—solid III (from 10 to 4.5 cm^{-1}) and reaches 3.5 cm^{-1} in slid I. Most drastic are the changes in the low frequency region where the band at about 220 cm^{-1} (EBBA) has a half-width of 24 cm^{-1} in solid II, 17 cm^{-1} in solid III while in solid I its value is only 9 cm^{-1}. Generally, all IR and Raman bands in solid II are twice as wide as in solid III and three-four times wider than in solid I. The half-widths of all vibrational bands in solid II are similar to those in the nematic phase.

During the phase transition solid II-solid III the spectrum changes drastically—the background decreases, the intensity of the bands increases, the half-width decreases, the splitting disappears. The phase transition solid III-solid I is connected with smaller changes in the spectrum. This is consistent with the smaller enthalpy changes at this phase transition.

What is the energy barrier U_a which the molecules have to overcome at the phase transition? It can be calculated using the changes in the normalized Raman intensity. Figures 6 and 7 give an example how this can be done for the phase transition solid II-solid III for CBPA. Let introduce the so-called "fractional change, β". This is the difference between the intensity of the last point before the beginning of the phase transition and that at the higher temperature where the intensity increases significantly. Plotting ln β vs. $1/T.10^3$ we can calculate U_a from the slope of the straight lines obtained (Figure 7). The results averaged on all bands investigated are given in Table II. The mean error is about 10% and is estimated from: (1) reproducibility of the slopes between runs; (2) estimated temperature uncertainty of ± 1°C; (3) estimated scattering intensity uncertainty of ±0.5% approximately.

As far as we know there are not many data in the literature concerning the activation energy of the phase transition metastable phase. Only Sorai[26] has estimated that U_a for the phase transition glass phase—stable solid state for different isomers of N(2-hydroxy 4-methoxybenzylidene) 4′-butylaniline (2,4-OH MBBA) is between 25.3 $kcal/mol^{-1}$ and 17.4 $kcal/mol^{-1}$. Having in mind the different structure of these compounds (two OH groups increase

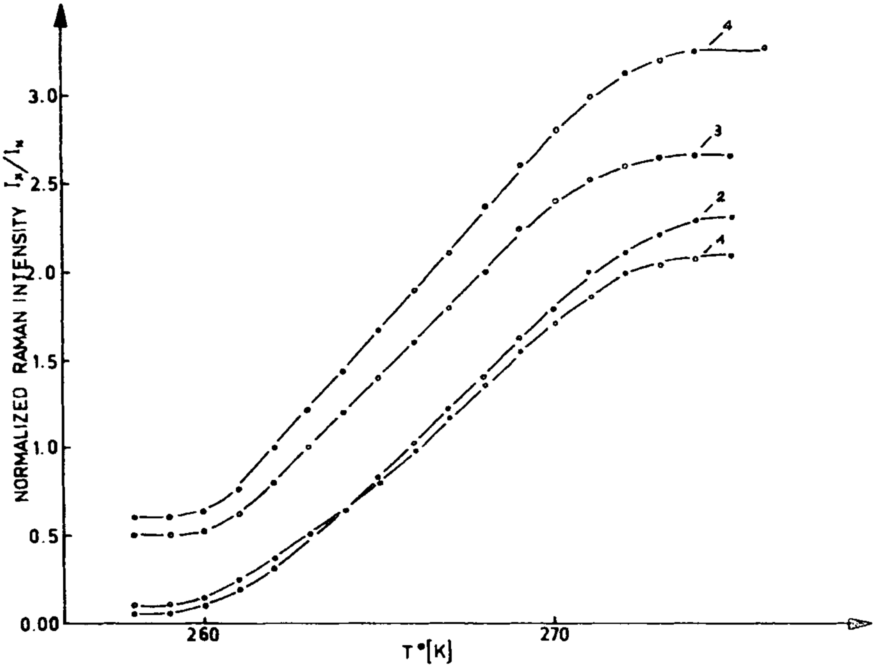

FIGURE 6 The normalized intensity of the bands; (1) 982 cm^{-1}; (2) 1194 cm^{-1}; (3) 1605 cm^{-1} and (4) 1626 cm^{-1} during the phase transition solid II-solid I of CBPA. The band at 1575 cm^{-1} is used for normalization.

the melting and clearing temperatures and stabilize the mesophase) we should say that the coincidence between our data and Sorai's is satisfactory.

All data obtained allow us to formulate some conclusions about the structure of the observed metastable phases. The solid II phase can be identified as a non-equilibrium glassy liquid crystal which is not much different from the nematic phase constitution with the coupling among the molecules stronger even though not definite. For the glassy crystals the configurational degrees of freedom frozen in at T_g would consist mainly of the conformational changes, the internal rotation and the overall molecular orientation, while in the ordinary glassy liquid an additional degree of freedom such as transitional modes, molecular reorientation around short axes would take part in the residual entropy too. In the case of glassy liquid crystal the degree of freedom frozen in at T_g will be reduced compared with those for the glassy liquid because of higher degree of orientational order has been established in the liquid crystalline state. However, the quenched degree of freedom will be greater than those for glassy crystals because there exists no positional order in the liquid crystalline state. Many evidences confirm this conclusion —the overall vibrational spectrum of solid II in its band position, integral

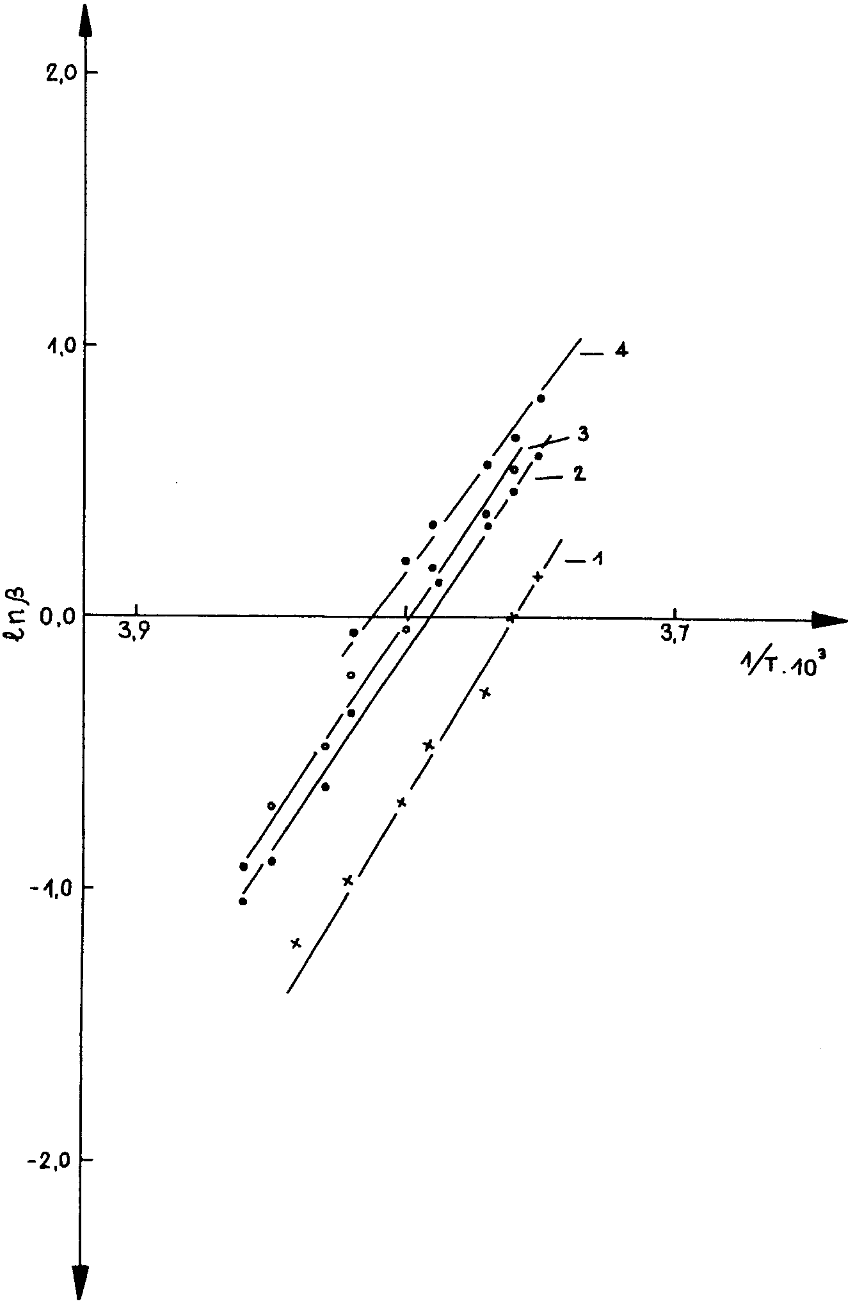

FIGURE 7 The dependence of ln β vs. $1/T.10^3$ for the bands; (1) 982 cm^{-1}; (2) 1194 cm^{-1}; (3) 1605 cm^{-1}; (4) 1626 cm^{-1}.

TABLE II

Energy barrier at the phase transition

	U_a[kcal/mol]	U_a[kcal/mol]
	solid II—solid III	solid III—solid I
MBBA	10	3
EBBA	11	3
CBPA	31	3

intensity, half-widths and especially low frequency region is very close to that of the nematic. The X-ray diffraction pattern of MBBA glassy liquid crystal is within the experimental error, the same as that of room temperature nematic[15]. Even visually it can be demonstrated that MBBA, EBBA and CBPA form a glassy state by fast cooling of the nematic or smectic A phase. If a microscopic slide carrying a drop of MBBA is plunged into a bath of liquid nitrogen, held there for a few seconds and then withdrawn for inspection it can be seen that the material has a clearly glassy appearance. If it is allowed to warm to room temperature at 256 K it rapidly becomes white and opaque as the phase transition occurs. It is important, however, to stress that solid II phase is distinct from nematic and is not simply an overcooled nematic phase because there is a measurable heat of transition from nematic into solid II.

The solid III phase is a metastable crystalline solid—the same observed by Mayer[13] and Petrie[14] for MBBA. Only one of our chemicals, CBPA has a smectic *B* phase but the overall Raman and IR spectrum of solid III in its band position, half-widths and intensities of the bands is very close to that of the smectic *B*. The overall profile of the diffraction pattern of solid III phase of MBBA is also similar to that of a smectic *B* phase. In fact, it contains one sharp outer reflection and one sharp inner reflection with a weak second order reflection[15]. Obviously, more chemicals possessing different smectic phases and forming metastable modifications have to be investigated in order to clarify in detail the structure of solid III phase.

CONCLUSION

The Raman spectra in the region 10–1650 cm^{-1}, IR absorption spectra between 650 and 4000 cm^{-1} and calorimetric measurements of quenched MBBA, EBBA and CBPA demonstrate the great differences among their solid modifications, two of which are metastable. Solid I (stable one) can be reached either by crystallization from the nematic phase by itself or by conversion of solid III (second metastable form) after some hours of room temperature storage. Solid II (the first metastable modification) formed by abrupt freezing of the nematic or smectic A phase is defined as a glassy liquid crystal while solid III can be identified as a monotropic smectic modification.

The enthalpy and the activation energy for all phase transitions in the solid state are calculated and the results are compared with those available in the literature for similar compounds.

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