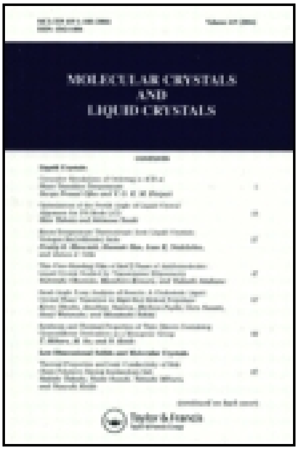

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RAMAN AND CALORIMETRIC EVIDENCES FOR THE EXISTENCE OF THREE SOLID MODIFICATIONS IN EBBA (°)

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The interest of spectral and calorimetric investigations on N-(p-ethoxybenzylidene)-p-butylaniline (EBBA) is closely related to actual strong interest for p-substituted Shiff bases as useful models for liquid crystalline states.

Various chemicals of this class exhibited an interesting strutural dependence on thermal history of the sample; for example, upon cooling of TBBA from smectic B phase a gradual change in Raman spectrum at liquid nitrogen temperature has been observed; furthermore, the low frequency vibrational dynamics at the crystal-smectic B transition seems to be influenced by thermal history 1); in MBBA, whose molecules are particularly near to our sample, Mayer et al. 2) by adiabatic calorimetry found that a metastable phase could be obtained simply by fast cooling of the liquid crystal phase. Above -3°C this form converts spontaneously, and exothermically, into the stable form. Sciensinska et al. 3) by I.R. measurements of MBBA in the region 80 - 400 cm^{-1}, found one stable and one metastable modifications both with well defined peaks in the whole region. The authors pointed out that the spectrum of stable solid differs from the unstable one in all the region investigated, but especially between 100 and 150 cm^{-1}. Schnur 4) also found two solid modifications in PAA - one obtained by slow crystallization of 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.

Barrall 5) by calorimetric measurements has also found stable and metastable modification of EBBA. No further efforts have been made in this direction and, to our knowledge, no more substances have been investigated.

EBBA was purified by successive recrystallization; the temperatures of ordinary phase transitions are: 37°C for solid into nematic and 80°C for clearing point.

Spectra were taken with a conventional Raman system, which is described in detail elsewhere 6). Calorimetric measurements were performed with a Dupont 9000 DSC equipment which was also used for thermal analysis.

Our calorimetric measurements and thermal analysis too showed that in addition to the usual stable solid phase obtained by crystallization of the sample by itself and named by us "solid I" other two interesting metastable solid modifications also exist. Fast cooling from the nematic phase with a rate of 5°C/min at least, produces a transition at about +14°C into a solid metastable phase called by us "solid II". At liquid nitrogen temperature, this phase is stable at least several days. At higher temperature the life of this phase becomes shorter, being 14 hours at -50°C and about 2 hours at -40°C. At -35°C this phase passes directly with a broad exothermic transition into another solid metastable phase. We called it "solid III"; this one also is stable at least several days if it is kept at liquid nitrogen temperature, while it requires some hours of room temperature storage for spontaneous conversion into the more stable "solid I" modification. Once obtained the solid I modification does not change any more. We can point out that the three solid modifications appear to pass one into the other by true first order processes, even if in the case of solid II into solid III into solid I the transition is so broad that the heat of transition is not detectable.

The scheme of the observed phase transition is shown in fig. 1.

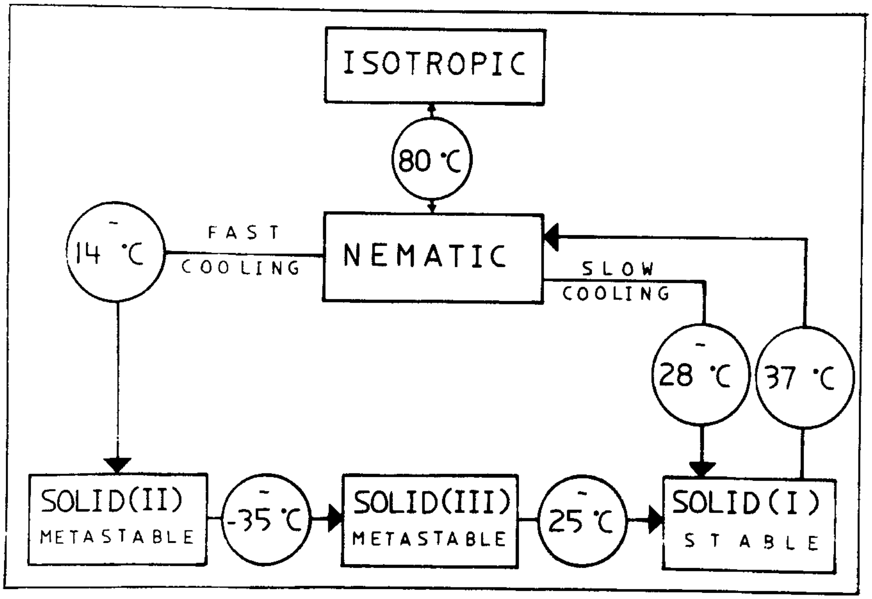

FIGURE 1 - Scheme of the observed phase transitions in EBBA.

Raman spectroscopy of the phases exhibited by EBBA provides a deeper insight of their microscopic constitution. The most meaningful region of the vibrational spectrum for a correct evaluation of the order parameters and of intermolecular forces is the low frequency region; it is clear in fact that a change in symmetry and/or in intermolecular coupling constants will directly affect this region, while alterations of less importance will take place at higher frequencies where modes are localized and therefore only indirectly sensitive to structural changes.

Looking at fig. 2 where we reported low frequency spectra of the three phases and (only for a comparison) of nematic phase, striking differences among the solid phases are seen. The most ordered phase appears to be solid I; in fact low frequency peaks are narrow, sharp and scarcely splitted; Raleigh wing, too, is less intense than in other two phases.

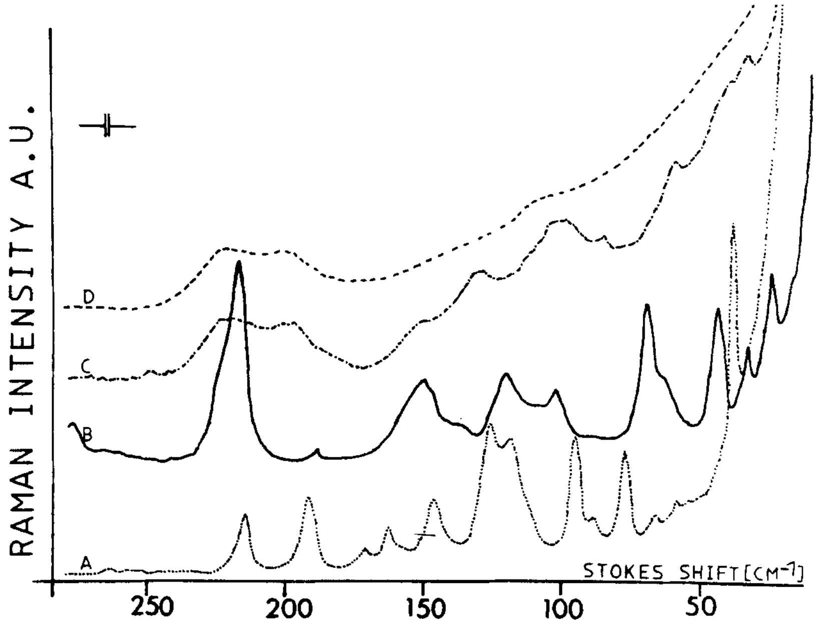

FIGURE 2 - Low frequency Raman spectra of A) Solid I, B) Solid III; C) Solid II; D) nematic phases of EBBA. A,B,C:-190°C; D:45°C.

Solid III, instead shows a much broader low frequency spectrum perturbed by a more intense Raleigh wing, with a smaller number of peaks. This indicates that partial disorder affects selection rules. It seems that hindered motions of the end chain are possible. In fact, differences in high frequency spectrum between solid III and solid I are mostly located at vibrations assigned to the end chain. In addition the low frequency spectrum looks not only perturbed, but also structurally different; a fact which should mean that some modification are present in the crystalline lattice.

Spectrum of solid II is closely related to the spectrum of nematic phase; differences between them are practically limited to low frequency region. It is important however to stress that solid II phase is distinct from the nematic 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 something like a superposition of weak bands is detectable; thus we could interpret solid II modification as a glassy one which is not much different from the nematic phase constitution and where however the coupling among molecules is stronger even though less definite.

A confirmation for the order classification we propose arises from three other facts:

i) Extra bands are observed in the spectra of solid II, solid III and even in nematic phase. While in solid I the bands assigned to CH_2 and CH_3 rocking at 730 and 890 cm^{-1}, CH_2 twisting vibration at 1100 and at 1310 cm^{-1} are single and narrow, in other solid modifications they are splitted and broader. This is due to the additional rotational isomeric forms existing in these two solid modifications and indicates that the disorder of two metastable phases is likely due to the motions of the ends of EBBA molecules, namely to restrict rotations of $O\ C_2\ H_5$ group about the ring to oxygen bonds and to acquisition of disorder in butyl tail. Andrews 7) in his theoretical explanation of the results in 2) reached the same conclusions. In fact many molecules, some of them not even possessing liquid crystalline phase, with end alkyl or alkoxy tails have similar behaviour, i.e. di-(p-methoxyphenil)-trans-cyclohexane-1,4-dicarboxylate 7), p-azoxyanisole 4,8), n-pentyl 9) and n-heptyl 10) quaternary ammonium salts.

ii) In the higher frequency region, frequencies that can be assigned to stretch vibrations decrease when we pass from solid II into solid I via solid III; in the same order the frequencies of bending vibrations increase. For example, the band at 1628 cm^{-1} (CH=N stretch vibration 11)) is shifted by 1 cm^{-1} towards lower frequencies at every phase transition solid II - solid III - solid I. The changes are even bigger for other stretch vibrations. The band assigned to benzene ring -N bend vibration increases from 1170 cm^{-1} in solid II to 1175 cm^{-1} in solid I. The frequency of aromatic CH bend vibration at 1201 cm^{-1} solid I is shifted six wavenumbers down in solid III and by another 10 cm^{-1} to lower frequencies in solid II. This is a well known fact in the spectroscopy of condensed phases [12] which means that intermolecular forces become stronger and stronger when the sample is passing from solid II via solid III into solid I. The strong similarity between solid II and nematic phase is outlined by similar frequencies of all bands with the exeption a few at low frequency (below 250 cm^{-1}).

iii) If we compare the haldfwidths we will see that at the same temperature (LNT) there is the same classification for the structural order. For example the halfwidths of the bands 1628 (CH=N stretch), 1597 and 1575 cm^{-1} (S8 + S9 + S7+ C=N stretch [11]) are in solid II 11, 8, 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 could be obtained for all other bands. For example the half width of the band 975 cm^{-1} (CH central wagging +S17+S16+S5 [11] changes from 10 to 4 to 3 cm^{-1} when EBBA passes from solid II into solid I via solid III, while in the same transitions 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 solid I. The most drastic are the changes in the low frequency region, where the band at about 220 cm^{-1} has a halfwidth of 24 cm^{-1} in solid II, 17 cm^{-1} in solid III while in solid I its value is only 9 cm^{-1}. Practically we could say that all bands in solid II are two times wider than in solid III and three times wider than in solid I. The halfwidth of all bands in solid II phases at the highest possible temperatures (-40°C) are similar to those in nematic phase at 38°C.

In any condensed phase there are basically three main broadening mechanisms: dissipation losses of vibrational energy into thermal by exchange and electrical interactions of the particles, intermolecular forces and rotational brownian motion[13]. The first mechanism leads to a small broadening (less than 1 cm^{-1}) almost independent from the temperature and can be neglected [14]. The changes in the intermolecular forces with the temperature result in small linear increase in the half width, while the third mechanism related it is to jump activation energy leads to an exponential increase. The halfwidth in ascending order solid I - solid III - solid II indicates that the molecular jump freedom is mostly restricted in stable solid I while in solid III and especially in solid II molecular freedom is much larger. The similarity of the band halfwidth in solid II and in nematic phase indiçates that the activation energy which the molecules have to overcome in their jumps in solid II is nearly equal to that of the nematic phase, even though temperatures are different. This means that solid II modification is close to nematic phase in its structure and molecular freedom.

Conclusion

The Raman spectra in the region 10 - 1650 cm^{-1} and calorimetric measurements of solid EBBA demonstrate great differences among three solid modifications, two of which are metastable. Solid I (stable) is obtained by crystallization by itself from the nematic phase or by conversion from solid III (second metastable form) after some hours at room temperature; solid II (first metastable form, glassy form) by abrupt cooling of liquid crystal phase and solid III by solid II at -35°C.

The measurements of the frequency and halfwidth indicate that intermolecular forces change in ascending order solid II, solid III, solid I while the molecular jump freedom decreases in the same order.

Preliminary Raman work and calorimetric results show that the same solid modifications exist in a sample very similar to EBBA- N-(p-propoxybenzylidene)p-pentylaniline (PBPA).

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References and footnote

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