Polymorphism of the smectogen ethyl-p-azoxybenzoate: Far-infrared and Raman study

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The far-infrared spectra of the different phases of ethyl-p-azoxybenzoate have been studied in the 30–210 cm^{-1} range. Distinct differences are observed between the spectra of the two crystalline polymorphs that are stable above and below 102°C, solid I and solid II, respectively. The spectrum of solid I resembles that of the isotropic phase, while that of the smectic phase is highly broadened. These results are discussed in terms of the structure, molecular conformation, and packing obtaining in the different phases. In the region of the internal modes, the same Raman frequencies are observed in both polymorphs although relative intensity changes occur for several lines. From a comparison of the Raman line shapes corresponding to the N–O and N=N bond stretching vibrations in solid II and solid I, we conclude that in the latter case the reorientations of the azoxy group occur at a rate too slow to affect the vibrational relaxation of these modes.

I. INTRODUCTION

Thermotropic mesogens frequently exhibit polymorphic transitions in the solid phase.[1-5] Owing to the complex structure of mesogenic molecules, such transitions often involve not merely a change of crystal symmetry, but also molecular conformation. Thus, the possible relevance of these transitions to the formation and structure of the mesophase itself has evoked recent interest.[6] Infrared and Raman techniques, among others, have been used in the past to characterize these transitions in several mesogens.[7-14] However, in many of these cases, the lack of a detailed knowledge of the crystal structure of the different polymorphs has hampered a clearer understanding of the observed spectral changes. This is especially true of the low frequency spectra in the range below 200 cm^{-1}, where one often observes the most pronounced differences between the lattice modes of the various polymorphs.

In this paper, we report the results of a far-infrared (FIR) and Raman study of the smectogen ethyl-p-azoxybenzoate (EPAB). This investigation was motivated by the fact that, unlike the case with most other mesogens, detailed structural data are available[15-17] for this compound on its two crystalline polymorphs as also the smectic phase. EPAB exhibits the following phase transformations upon heating:

solid II $\xrightarrow{102\,°C}$ solid I $\xrightarrow{116\,°C}$ smectic A $\xrightarrow{124\,°C}$ isotropic phase;

here solid I and solid II denote the polymorphs stable, respectively, above and below 102°C. Amer and Shen have earlier reported the Raman spectra of EPAB in the 5–100 cm^{-1} range.[18] In the solid phase, they observed a single Raman mode at ~22 cm^{-1}, but did not report any differences between the spectra of solids I and II. In contrast, we have noticed marked changes between their FIR spectra in the 30–160 cm^{-1} range. In order to further understand these differences, we have studied the FIR absorption of the smectic A and isotropic phases as also the Raman spectra of solids I and II in the region of the internal modes. These results are discussed here in the light of the structural characteristics of the different phases of EPAB.

II. EXPERIMENTAL

EPAB obtained from Eastman Kodak Co. was used in the present experiments. The transition temperatures already mentioned were determined, to within an accuracy of 0.5°C, using a Perkin-Elmer differential scanning calorimeter (Model DSC-2). Polycrystalline samples of solid II and solid I were obtained, respectively, from solvent crystallization and solidification from the mesophase. Solid I supercools quite easily to room temperature where it exists as a metastable phase for several days[16] before slowly converting to solid II. This made it feasible to investigate the spectra of both polymorphs at room temperature. It is interesting to note that we have earlier observed a similar behavior in the higher temperature solid phase of CBOOA as well.[7]

The FIR absorption of solid II was studied by dispersing it in the form of fine powder in a polyethylene pellet. The spectra of solid I, smectic A and isotropic phases were obtained with a sample film, ~110 μ in thickness, contained between wedged crystal quartz windows. Other details of the FIR equipment and the experimental procedure have been described elsewhere.[19,20]

Raman spectra were excited by a He–Ne laser with ~90 mW of output power at 6328 Å. The polycrystalline samples were contained in glass capillary tubes and the right angle scattering geometry was used. The scattered radiation was dispersed by a Cary-81 double monochromator equipped with a modified external optics, and detected by a cooled RCA 8852 photomultiplier tube in conjunction with a photon counting system. Whenever required, an interference filter peaked at 6328 Å was inserted in the path of the incident radiation in order to suppress the plasma emission lines from the laser.

III. RESULTS AND DISCUSSION

A. Molecular packing and conformation

Figure 1 shows the four possible rotational conformers of the EPAB molecule. The x-ray data of Krigbaum et al. show[15,16] that the molecules in solid II are all in the high energy cis–cis conformation. On the other

TABLE I. Crystallographic symmetry and the representation of the zone-center external optic modes in the two solid phases.

Solid phase	Space group	No. of molecules in the primitive cell	External optic modes	
			Infrared active	Raman active
II	C_i^1 ($P\bar{1}$)	2	$3A_u$	$6A_g$
I	C_{2h}^6 ($C2/c$)	4	$5A_u + 4B_u$	$6A_g + 6B_g$

FIG. 1. Four possible rotational conformers of the EPAB molecule. cis and trans denote the relative orientation of the ester C=O bond with respect to the central N–O bond.

hand, in solid I they are found to adopt the cis–trans and trans–cis conformations. There is evidence of disorder in solid I in the positions of the three atoms of the azoxy group, as they are found to occupy two sets of alternative sites.
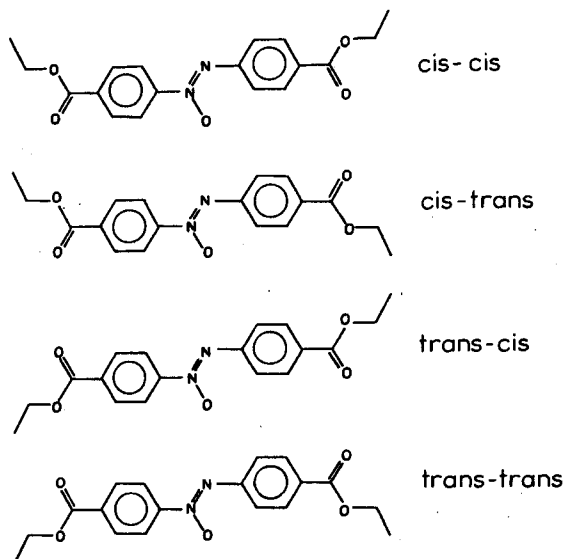
Although the x-ray data can yield only a time-averaged picture, it is reasonable to assume that the conformational disorder in solid I arises because of the reorientational jumps executed by the azoxy group between the two alternative positions. This picture is in accord with recent dielectric relaxation studies on the disordered solid phases [21-23] of several other liquid crystalline materials, all of which feature an absorption peak in the frequency range below 1 MHz. These peaks have been interpreted as arising from the intramolecular reorientations of specific polar groups in the disordered solid phases.

Table I summarizes the relevant crystal symmetries and the group theoretical representation of the zone-center external optic modes of solids II and I. As both polymorphs possess the inversion symmetry, no coincidences are expected between their infrared and Raman active modes except for any accidental degeneracies. The correlation of the molecular, site and factor group symmetry species is shown in Table II. We note that each intramolecular mode of the free molecule would give rise to two Davydov components in solid II. In the case of solid I, the number of Davydov components observable in the infrared and Raman spectra is doubled.

In the smectic phase, the x-ray data [17] are found to be consistent with the existence of centrosymmetric dimers, the centers of the two molecules being displaced along their long axes by ~ 6.3 Å. Such a molecular association would also lead to strong dipolar interactions between the ester and azoxy groups of adjacent molecules.

B. FIR spectra

The FIR spectra of the different phases of EPAB are shown in Figs. 2 and 3. Below 160 cm^{-1}, solid II exhibits a strong band centered at 80 cm^{-1} in addition to other weak features at 110, 131, and 145 cm^{-1}. Over the same range solid I exhibits a very broad absorption peak centered at 104 cm^{-1} and a weak shoulder at 150 cm^{-1}. The isotropic phase also shows a broad absorption band although it is less intense and its peak position is lower by ~10 cm^{-1} as compared to solid I. In all these cases, the higher frequency band at 180 ± 2 cm^{-1} is likely to originate from the intramolecular torsion of the CH$_3$ end groups.

As the EPAB molecule carries a permanent dipole moment due to the central azoxy group, the Poley resonance [24,25] due to its librational motion about the long axis will contribute to the FIR absorption in the fluid phases. Furthermore, even in the isotropic phase, there would be a characteristic barrier which hinders the exchange between the different possible conformers of the molecule. At longer times, this conformational exchange will contribute to the overall dielectric relaxa-

TABLE II. Correlation of the molecular, site, and factor group symmetry species in the two solid phases.

Molecular group	Solid II			Solid I		
	Site group	Factor group	Activity	Site group	Factor group	Activity
C_1	C_1	C_i		C_1	C_{2h}	
A	A	A_u	Infrared	A	A_u	Infrared
					B_u	Infrared
		A_g	Raman		A_g	Raman
					B_g	Raman

tion process in the microwave region. As general theo-
retical considerations[26,27] and experimental observations
in other cases show,[28,29] the short-time behavior of such
a low frequency dipolar relaxation process should be
manifested as a torsional band in the FIR region. We
therefore attribute the broad band centered at 94 cm^{-1}
in the isotropic phase to the superposition of such a tor-
sional band and the Poley absorption. Recently, we
have shown that the FIR absorption spectra of the p-
azoxyanisole series of liquid crystals can also be under-
stood on this basis.[20]

Compared to both solid I and the isotropic phase, the
spectrum of the smectic phase appears highly broadened.
The extent of this broadening seems far too large to be
accounted for by any experimental artifact, such as the
effects arising from the scattering of radiation by the
polydomain liquid crystal sample. From the reproduci-
ble nature of this spectrum, we conclude that the broad-
ening arises due to the specific intermolecular interac-
tions obtaining in the smectic phase, i.e., the formation
of dimers and the resultant dipolar interactions between
the terminal and central polar groups of the two adjacent
molecules. The resultant changes in the shape of the
potential barrier which hinders the librational and low
frequency torsional modes may then cause the increased
broadening of these bands. The absence of such a broad-
ening in the isotropic phase is explained by the fact that
the concentration of such dimers would be negligible in
this phase. It is also seen that the molecular packing
in solids II and I is such that the ester and azoxy groups
of adjacent molecules are farther removed from each
other than in the smectic phase.

From Table I we note that three nondegenerate exter-
nal optic modes of A_u symmetry are expected in the FIR
spectrum of solid II. The observed spectrum contains
at least four distinct features below 160 cm^{-1}, indicating
that certain other low frequency, intramolecular defor-
mation or combination modes also occur in this region.
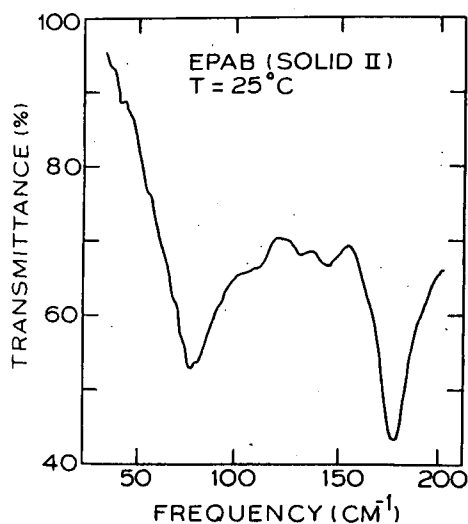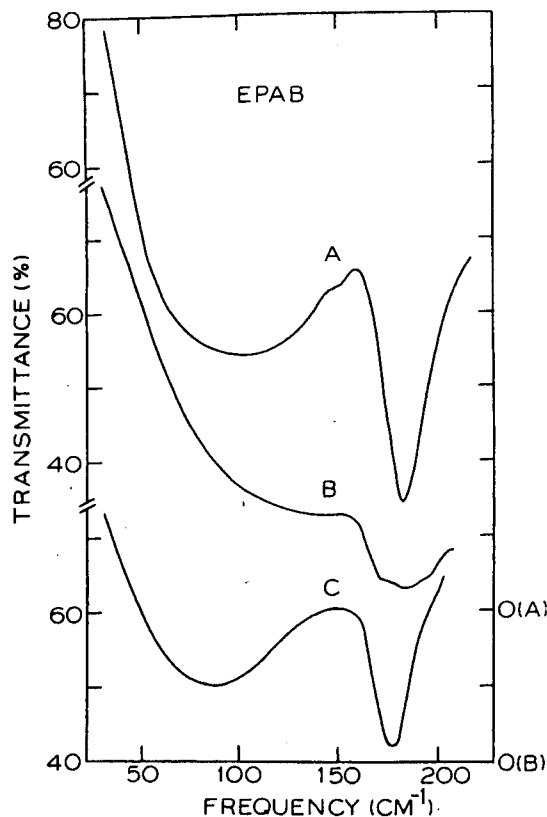The broad absorption band in solid I resembles that of

FIG. 3. Far-infrared absorption spectra of solid I and the
fluid phases. (A) solid I at 25 °C; (B) smectic phase at 116 °C;
(C) isotropic phase at 125 °C. The respective ordinate scale
zeroes corresponding to spectra A and B are indicated along
the right vertical axis.

the isotropic phase. The Poley absorption is an improb-
able cause of this broad feature as there is no evidence
to suggest that the molecules in solid I are free to re-
orient about their long axes. However, as in the iso-
tropic phase, the conformational disorder due to the
hindered reorientations of the polar azoxy group should
once again lead to a torsional band in this case in the
FIR region. In addition, there must be present the nine
external optic modes of representation $5A_u + 4B_u$. The
superposition of so many features within a relatively
narrow spectral region appears to be the most likely
explanation for the composite, unresolved absorption
profile observed in solid I.

C. Raman spectra

The detailed Raman spectra of EPAB in the internal
mode region have not been published so far.[18] The most
intense Raman lines of both polymorphs occur in the
range of 1000–1750 cm^{-1}. Figure 4 shows the spectrum
of solid II in this interval. As is seen from Table II, all
these Raman lines must be of A_g symmetry. The num-
ber of Raman active Davydov components should, in
principle, be doubled in solid I as now modes of both A_g
and B_g symmetry must be present. However, no new
lines were present in solid I over this spectral range
although there were clear changes in the relative inten-

FIG. 2. Far-infrared absorption spectrum of solid II at 25 °C.

sities of several lines. This indicates that the coupling between the four molecules in the primitive cell is rather weak. Consequently, the magnitude of the factor group splitting between the A_g and B_g modes is too small to be observed for all these intramolecular modes, unless one takes recourse to polarization studies on oriented single crystals of solid I.

The modes at 1330 and 1460 cm^{-1} can be assigned, respectively, to the N–O and N=N bond stretching vibrations.[30] In view of the observed disorder in the positions of the atoms of the azoxy group[16] in solid I, we have compared the respective lineshapes of these two modes in both solid phases. These measurements were performed using a spectral resolution of 1.2 cm^{-1}, which is 7–10 times smaller than the FWHM (full width at half maximum intensity) of the lines in question. Hence the effects of instrumental broadening on the observed line shapes should be negligible. No measurable broadening was seen in solid I for the mode at 1330 cm^{-1}, although it should be noted that the shoulder at 1320 cm^{-1} interferes with the task of estimating the intrinsic width of the N–O stretching mode in both solid phases. The FWHM of the N=N stretching mode increases by ~ 4 cm^{-1} on going from solid II to solid I, as is shown in Fig. 5. The relative intensity of the band at 1485 cm^{-1} also increases in solid I, as compared to solid II. If the broadening of the line at 1460 cm^{-1} were to originate from the reorientations of the azoxy group in solid I, they would have to occur on a rather fast time scale, with a correlation time in the range of 2–3 psec. This however seems unlikely as no such broadening was seen for the N–O stretching mode. Also, as noted earlier, the typical reorientation rates of intramolecular polar groups in the disordered solid phases of other mesogens are found to be well below 1 MHz. One therefore expects that the reorientations of the azoxy groups in solid I should also occur on a similar, slow time scale. If so, this motion would appear frozen so far as the infrared and Raman spectra of solid I are concerned. We are thus led to attribute the broadening of the band at
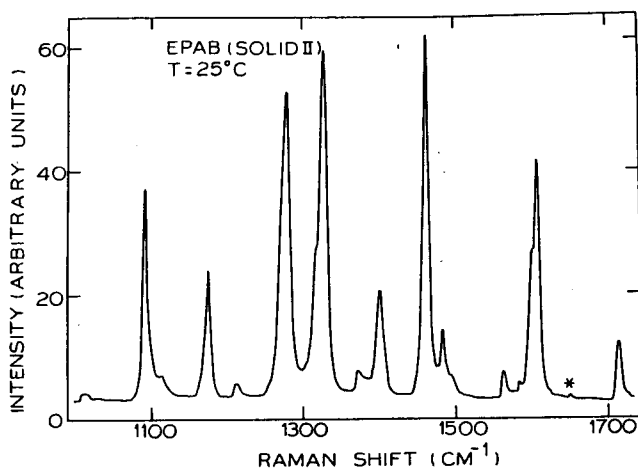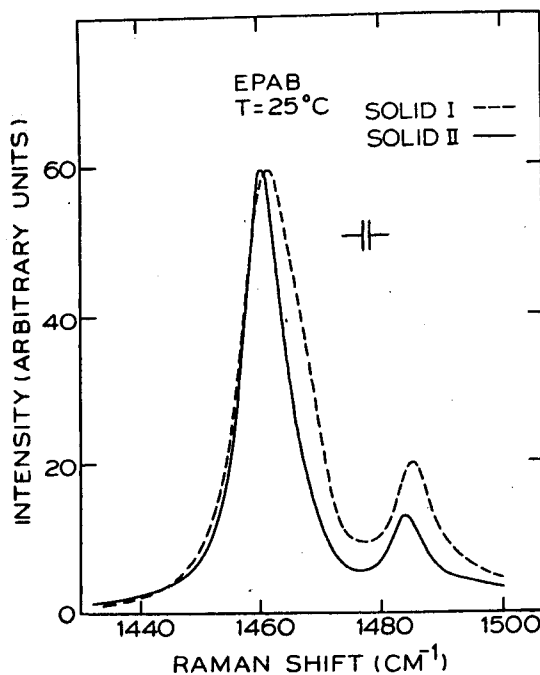

FIG. 5. Raman line shapes of the band at 1460 cm^{-1} in solids II and I; T = 25 °C. In order to facilitate a direct comparison of the line shapes, the observed spectrum of solid I has been numerically scaled up by a factor of 1.5 so as to normalize the peak intensity of this band in both phases. The spectral slit width employed is also indicated.

1460 cm^{-1} to an unresolved Davydov component of the N=N stretching mode in solid I. This is also supported by the fact that the line shape is quite symmetric in solid II, but exhibits an asymmetry on the higher frequency side in the case of solid I.

IV. CONCLUSIONS

The present study shows that the spectral changes which accompany the phase transitions in liquid crystalline substances are better understood when they can be correlated with the structural characteristics of the different phases. As expected, the signatures of the two solid modifications of EPAB are found to be distinctly different in the FIR region. Although the spectrum of solid I has a superficial resemblance to that of the isotropic phase, evidently the factors contributing to the broad band absorption can not be entirely identical in the two cases. The FIR spectrum of the isotropic phase would be dominated by the Poley absorption and the torsional band associated with the *cis–trans* isomerism of the molecules. The latter feature should be present in solid I also in view of the conformational disorder obtaining in this phase. In addition, the infrared-active external optic modes must contribute to the FIR absorption of solid I.

The Raman line corresponding to the N–O bond stretching mode shows no significant broadening between solids II and I. Based on this and the evidence from the dielectric dispersion studies of other mesogens, we conclude that the reorientations of the azoxy groups in

FIG. 4. Raman spectrum of solid II in the 1000–1730 cm^{-1} range; T = 25 °C. The asterisk denotes a possible plasma emission line from the laser.

solid I should be far too slow to influence the line shapes of the N–O and N=N bond stretching modes. Hence the broadening of the latter mode in solid I is attributed to the presence of an unresolved Davydov component on the higher frequency side of the main peak.

ACKNOWLEDGMENTS

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