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S. Venugopalan [a], J. R. Fernandes [a] & G. V. Vani [a]
[a] Raman Research Institute, Bangalore, 560006, India
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Far-Infrared and Raman Spectra of the Solid Phases of CBOOA

S. VENUGOPALAN, J. R. FERNANDES and G. V. VANI

Raman Research Institute, Bangalore 560006, India

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The far-infrared and the Raman spectra of crystalline CBOOA (*N-p*-cyanobenzilidene-*p-n*-octyloxyaniline) have been studied above 30 cm^{-1}. The temperature dependence of the far-infrared spectrum reveals the existence of a solid–solid transition at 65°C. The two solid modifications can be obtained, respectively, from solvent crystallization (Phase II) and solidification from the mesophase (Phase I). Differential scanning calorimetric results confirm that an endothermic change from Phase II to Phase I occurs at 65°C with an associated heat of transition of 2030 cal/mole. X-ray powder diffraction patterns establish that the structures of the two phases are different. Tentative vibrational assignments are made for the far-infrared and the Raman lines observed in the internal mode region. At frequencies below 120 cm^{-1}, both the far-infrared and the Raman spectra of Phase II exhibit distinct modes whereas, Phase I exhibits nearly quasicontinuous spectra. The possible implications of this result for the structure of Phase I and the formation of the mesophase are discussed.

I INTRODUCTION

The vibrational spectra of liquid crystalline materials have been useful in elucidating the structure of the different phases exhibited by them. Previous studies have shown that the spectra observed in the various phases can yield significant information regarding the nature of the order and intermolecular forces,[1–4] molecular conformations[5–6] as well as certain characteristics of the phase transitions.[7–9] While most of the studies so far have dealt with nematogenic materials, relatively fewer studies are available on the vibrational spectra of liquid crystals exhibiting the smectic phase as well.[10–12] Smectogenic materials are of particular interest in the light of current theories which indicate the possibility of a second order phase change in the case of smectic C—smectic A[13] and smectic A—nematic[14–16] transitions. In this connection, CBOOA (*N-p*-cyanobenzilidene-*p-n*-octyloxyaniline) whose molecular formula is shown in Figure 1, has attracted considerable attention recently because it undergoes the smectic A—nematic transition. Several

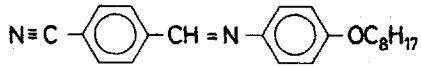

FIGURE 1 Molecular structure of CBOOA.

experimental studies have been carried out to determine the variation of its specific heat[17] (C_p), magnetic susceptibility,[17] light scattering [12,18] as well as elastic constants[19,20] in the vicinity of this transition, in order to ascertain the order of the transition. Thus, CBOOA offers an interesting case for the study of vibrational spectra in its different phases and such information should prove helpful in correlating their structural characteristics.

With this aim, we have undertaken a spectroscopic study of CBOOA. The results of our study on liquid crystalline CBOOA will be published separately. The purpose of this paper is to present the results of a far-infrared and Raman study of its solid phase. The spectra indicate the existence of a solid–solid transition in CBOOA and we present differential scanning calorimetric (DSC) results as well as X-ray powder diffraction data in evidence of this structural transition. Preliminary X-ray studies carried out recently[21] show that the point group symmetry of the stable room temperature phase is C_{2h}. On this basis, the factor group analysis of the external modes observed in this phase is considered. In the region of the internal modes, vibrational assignments are suggested for many of the spectral lines. Finally, we discuss the possible relevance of the observed solid–solid transition to the occurrence of the mesophase itself.

II EXPERIMENTAL

CBOOA obtained from Eastman Kodak Co.[22] was recrystallized in *n*-heptane or methanol and then outgassed in vacuum. The transition temperatures were determined using a hot stage microscope to within ± 0.2°C and they are as follows: solid-smectic A (73°C), smectic A—nematic (82.5°C) and nematic-isotropic (106.9°C). Further recrystallization did not significantly improve the nematic-isotropic transition temperature.

The far-infrared spectra were obtained[9] using the Polytec FIR 30 interferometer. The interferograms were not apodized and they were Fourier transformed in real time using a Nova 1200 on-line computer. The spectral range in this study was 30–240 cm^{-1} and it was covered using two different beam splitters. One has a usable transmission range of 20–160 cm^{-1}, while the other has a range of 50–450 cm^{-1}. Spectra in the two ranges were obtained with resolutions of 2.5 and 3 cm^{-1} respectively. The polycrystalline samples, about 50 μ in thickness, were contained between two wedged quartz windows. Samples were prepared either with the sieved powder of solvent crystallized material or by slowly cooling down a bubble free film of

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the isotropic liquid. A variable temperature cell was used for heating the samples. The temperature measurements were accurate to $\pm 1°C$, with the fluctuations being within 0.5°C. Other details related to the sample preparation and the experimental procedure have been described elsewhere.[9]

Raman spectra were obtained using a Spex 1401 double monochromator in conjunction with a cooled photomultiplier tube and photon counting electronics. The spectra were excited by a He-Cd laser with ~ 10 mw of output power at 4416 Å. Samples were contained in glass capillary tubes and the right angle scattering geometry was used. Finely powdered CBOOA crystallized from *n*-heptane as well as that solidified from the mesophase were used as samples. Even after about 3 hours of irradiation by the laser beam, the spectra showed no observable changes due to any possible photodecomposition of the samples. The spectral resolution was $\sim 5\ cm^{-1}$.

DSC experiments were carried out using a Perkin–Elmer differential scanning calorimeter (Model DSC-1B). Samples crystallized from both methanol and *n*-heptane were used. About 5 mg of the sample was crimped in an aluminium sample pan with a cover and the sample chamber was continually flushed with nitrogen during the experiment. A heating rate of 4°C/min was employed and the data were obtained during heating. Both before and after a measurement, the transition temperatures of the sample were checked using the hot stage microscope. No differences were seen and thus it was ensured that there was no contamination of the sample due to the sample pan when the sample was thermally cycled between room temperature and the nematic-isotropic transition point.

The temperature calibration of the DSC instrument in the vicinity of the observed solid–solid transition was checked in two ways. As the peak corresponding to this transition occurs nearly 4° below that of the solid–smectic transition, the known value of the latter transition temperature served as a first check. In addition, the melting temperature of high purity azobenzene (trans), with a known melting point of 68.5°C, was also determined by DSC. In both cases, it was found that the correction to the DSC temperature readings in this region was $+4.5 \pm 0.2°C$.

X-ray powder diffraction photographs were taken using CuKα radiation and a standard Philips camera of radius 57.3 mm. Typically, exposures of about 10 hours were employed.

III EXPERIMENTAL RESULTS AND DISCUSSION

A Far-infrared spectra

We first discuss the far-infrared spectra of polycrystalline CBOOA at room temperature. Trace A of Figure 2 shows the spectrum of sieved powder

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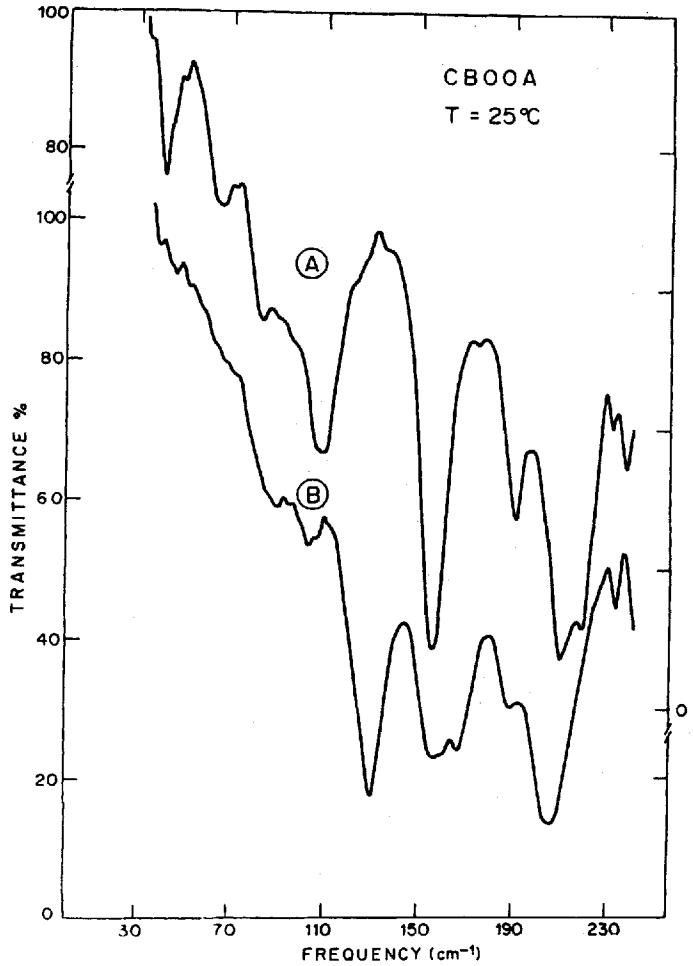

FIGURE 2 Far-infrared absorption spectra of polycrystalline CBOOA; $T = 25°C$.
A) Sample prepared from sieved powder of solvent crystallized CBOOA. The ordinate marks corresponding to this trace are indicated above the scale break on the right vertical axis.
B) Sample prepared by solidifying from the mesophase.

obtained from solvent-crystallized CBOOA. The spectrum was the same irrespective of whether *n*-heptane or methanol was used for crystallization. The spectrum in this case is characterized by distinct and strong absorption features down to the very low frequency region. Trace B shows the spectrum obtained when the sample was slowly cooled from the mesophase and allowed to solidify. Comparison of the two traces shows that the spectra are markedly different, especially in the region below 180 cm^{-1}. This region

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would include the external modes, translatory and rotatory, that would be characteristic of a complex molecular crystal. It is seen that the distinct lines present in trace A at frequencies below 120 cm^{-1} are either very weak or almost absent in trace B. In contrast, the strong lines at 128 cm^{-1} and 166 cm^{-1} present in trace B are not noticeable in trace A. Many similar differences are observed between the two spectra, in the case of weaker lines as well.

These differences suggest the possible existence of two different polymorphic forms of crystalline CBOOA. Indeed, the DSC and X-ray powder diffraction results presented below provide direct confirmation of such a structural change. In the following discussion, the two different forms of CBOOA obtained by solvent crystallization and solidification from the mesophase, will be referred to as Phase II and Phase I respectively.

Figure 3 shows the temperature dependence of the spectrum of Phase II. It is seen that at 65°C, the spectrum changes abruptly and resembles a temperature broadened version of trace B in Figure 2. In other words, the far-infrared spectra reveal that Phase II transforms to Phase I at 65°C. However, it was noticed that Phase I can be supercooled to room temperature

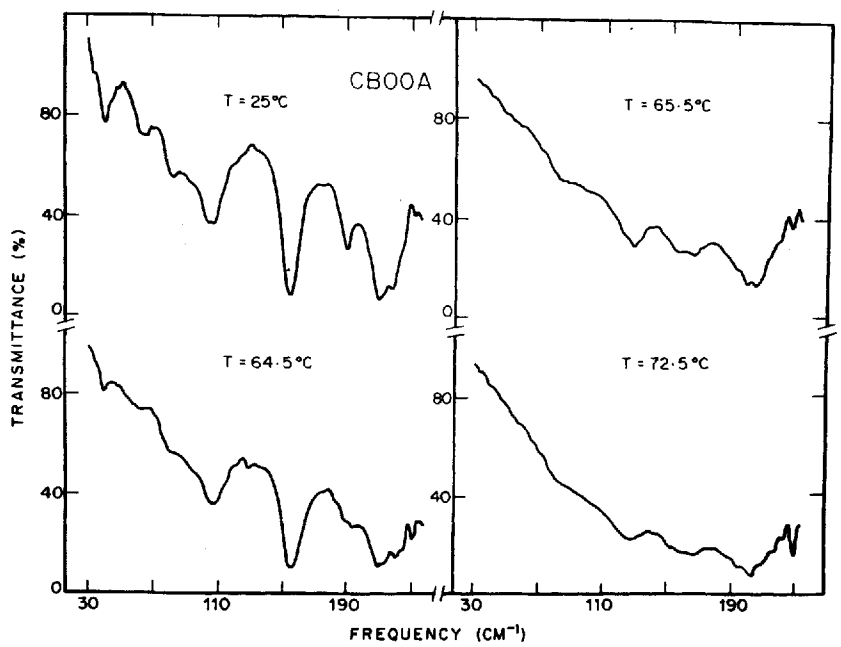

FIGURE 3. Temperature dependence of the absorption spectrum of CBOOA initially in Phase II. The sudden change in the spectral features at 65°C arises because of the transition to Phase I.

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and remain as a metastable phase for days together. This suggests that the energy barrier separating the two phases is high enough to hinder ready and spontaneous conversion to Phase II. Nevertheless, it was established from the spectra that when supercooled, Phase I does convert to Phase II over a period of several hours, if traces of the latter phase were present in the sample. This shows that Phase II is the thermodynamically stable form of CBOOA below 65°C, while Phase I is the stable form above 65°C till the transition to the smectic phase. While grinding the samples at room temperature, it was also noticed that Phase II could convert to Phase I or vice versa depending upon the energy imparted to the sample during grinding.[23] In the present investigation, these factors were kept in mind and appropriate precautions were taken while obtaining the spectral, thermodynamic and X-ray powder diffraction data on the two phases.

B Raman spectra

Figure 4 shows the Raman spectra of polycrystalline CBOOA at room temperature. Traces A and B correspond, respectively, to Phases II and I. In the case of Phase II, the sample was crystallized from *n*-heptane and then carefully powdered. The same sample was then melted and solidified for obtaining the spectrum of Phase I. On comparing the two spectra, we again note that marked differences occur below about 200 cm^{-1} and that in this region, the distinct low frequency modes present in Phase II are not noticeable in Phase I. At higher frequencies, however, the two spectra are nearly identical with regard to the observed modes. This is consistent with the expectation that when the crystal symmetry of a complex molecular crystal changes due to a polymorphic transition, the intermolecular modes would be affected to a much greater extent than the intramolecular modes. Indeed, the far-infrared spectra of the two phases of CBOOA also support this expectation.

The use of polycrystalline samples for Raman studies leads to a large amount of stray light, thereby precluding the observation of very low frequency modes. Hence, we attempted to grow single crystals of CBOOA from a solution in *n*-heptane and obtained thin platelets with the typical dimensions $0.5 \times 1.5 \times 2$ mm. However, the crystals contained many flaws and hence cutting, polishing and orienting them proved difficult. Consequently, we have used an unoriented single crystallite in Phase II and obtained its Raman spectrum in the 30–150 cm^{-1} range. Trace A of Figure 5 shows that additional low frequency modes are observed in this case as compared to Figure 4. In order to obtain a corresponding spectrum of a single crystal of Phase I, the crystal was first heated to 66°C. However, it became opaque and polycrystalline in this process. This could arise from

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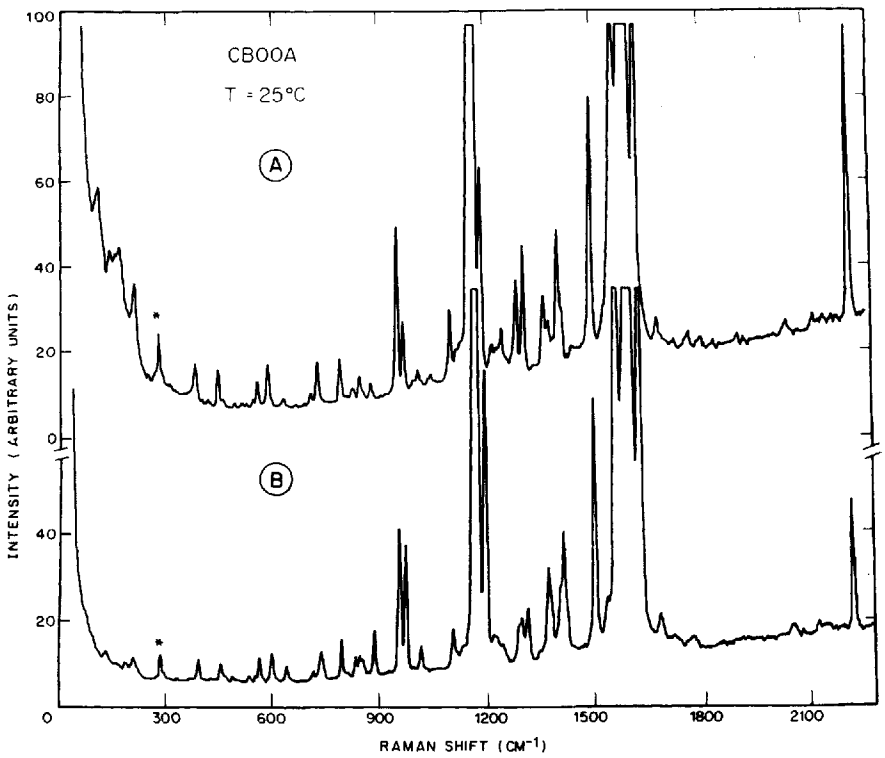

FIGURE 4. Raman spectra of polycrystalline CBOOA; $T = 25°C$. The spectral feature denoted by an asterisk is likely to be due to a plasma line from the laser.
A) Sample crystallized from *n*-heptane.
B) Sample solidified from the mesophase.

strains in the crystal or a disruptive volume change attending the transformation to Phase I. Nevertheless, the sample, now in Phase I, yielded a low frequency spectrum in the same range under a comparable stray light level and this is shown in Trace B. It is clear that again the low frequency modes are extremely weak in Phase I.

It is of interest to consider the vibrational spectra of the two phases, ı relation to the crystal symmetry of both phases. Detailed structural data re not available at this time for either phase. However, preliminary X-ray tudies on single crystals grown from *n*-heptane, indicate[21] that the crystal ıtructure of Phase II belongs to the space group $C_{2h}^5(P2_1/a)$. The primitive ınit cell possesses the point group symmetry C_{2h} with four molecules of ⊃BOOA situated at sites having C_1 symmetry. The coupling between the our molecules in the unit cell would lead to 24 zone-center external or ıattice modes. A factor group analysis using the method of coupling[24]

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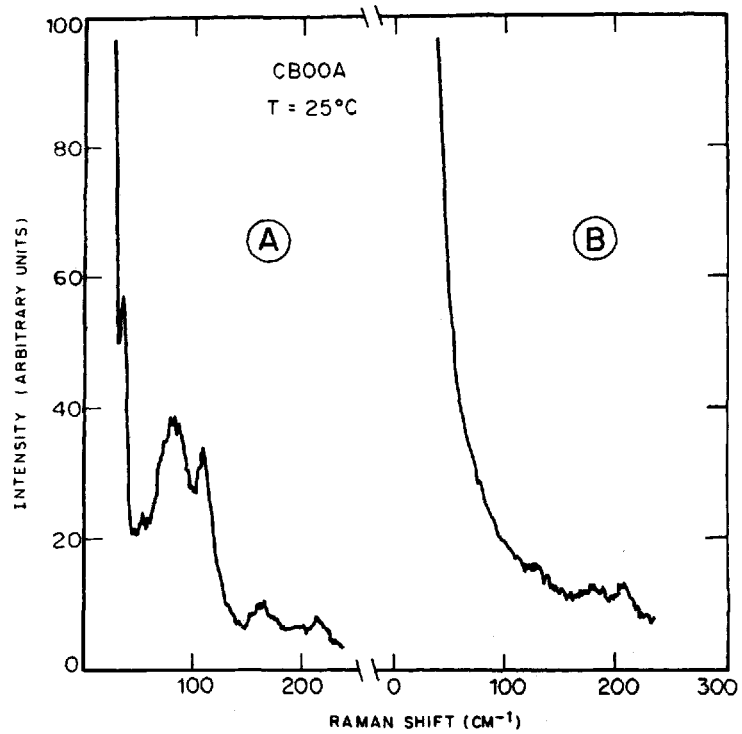

FIGURE 5 Low frequency Raman spectra of crystalline CBOOA at 25°C.
A) The sample in this case is a single crystal grown from a solution of CBOOA in *n*-heptan.
B) Spectrum obtained when the sample corresponding to trace A was heated to 66°C and then cooled to room temperature. The resultant sample, however, was not a single crystal.

shows that all of them are non-degenerate modes and their representatio is given by $6A_g + 6B_g + 6A_u + 6B_u$. Among these, the three acoustic mode belong to $A_u + 2B_u$ and the representation of the external optical modes i given by $6A_g + 6B_g + 5A_u + 4B_u$. Modes of A_u and B_u symmetry a infrared active and Raman inactive while those of A_g and B_g symmetry ar Raman active and infrared inactive. However, accidental degeneracies ma occur between the Raman and infrared active modes. If suitable single crysta become available, it would be of interest to carry out polarization studi and determine the symmetries of the observed low frequency modes both phases.

As noted earlier, the Raman spectra of the two phases show no mark differences in the internal mode region. In this region, the vibrations of t CBOOA molecule would include those modes which are characteris of the distinct molecular units comprising CBOOA. The free CBO

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molecule possesses the point group symmetry C_1 and hence all of its internal modes would be infrared as well as Raman active. In the crystalline state, the coupling between the different CBOOA molecules in the unit cell can, in principle, cause each of these internal modes to split further into infrared and Raman active modes. Considering the frequencies of the vibrational modes observed in this study, we have made an attempt to correlate many of them with the characteristic vibrations of the different molecular units constituting CBOOA.

The study of intramolecular vibrational modes can often serve as a useful probe of changes in molecular conformations in the various phases of mesogens. This possibility is especially interesting in relation to the flexible end chains, as they can have a considerable influence on the anisotropic interactions between the molecules.[25] From a study of the Raman spectra of akoxyazoxybenzenes, Schnur has suggested[6] the existence of longitudinal, "accordion" vibrations of their alkoxy tail parts. As compared to the solid phase, the intensity of the bands assigned to the accordion mode was seen to decrease markedly upon entering the mesophase. This was interpreted to signify that the allowed conformations of the alkoxy tails differ significantly between the various phases. As the CBOOA molecule possesses a long octyloxy tail, a similar accordion mode may be observable in the present case also. Considering the molecular symmetry of CBOOA, the mode can exhibit infrared activity. On the basis of previous results obtained in alkoxyazoxybenzenes, it is expected that in CBOOA, such a mode should occur in the frequency range between 250–300 cm^{-1}. With this consideration as well as in the context of our study of liquid crystalline CBOOA,[26] we have extended the frequency range of our far-infrared study using diamond windows. The results indicate that in Phase I there is a distinct mode at 296 cm^{-1} which shows significant changes at the Phase II–Phase I transition. At the transition to the smectic A phase as well as in the other two fluid phases, this mode virtually disappears. This behaviour is in agreement with that already observed in alkoxyazoxybenzenes[6] and hence this mode is tentatively identified as the longitudinal, accordion mode belonging to the octyloxy tail. We plan to obtain further confirmation of this result from a study of other members of the homologous series, *N-p*-cyanobenzilidene *p-n*-alkoxyaniline. Details related to these results will be presented elsewhere as a part of our study on liquid crystalline CBOOA.[26]

Tables I and II list, respectively, the observed far-infrared and Raman frequencies in both phases of CBOOA. Possible correlations with characteristic group vibrations of the CBOOA molecule are also suggested in several cases. As indicated in the tables, there is some overlap between the frequency regions of the various possible modes. In addition, designations such as rocking and twisting modes are only approximate as considerable

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TABLE I

Far-infrared absorption frequencies (in cm^{-1}) of the two phases of CBOOA at 25°C, in the range 30–220 cm^{-1} and their proposed assignments.[a] The frequencies are accurate to ± 1 cm^{-1}

Phase II	Phase I		Proposed assignment
33 (sh)			Lattice modes
40	45 (vw)		
49 (sh)			
64	70 (sh)		
82	84 (sh)	Libration C_6H_4; $\tau(CH_2CH_2)$	
	88		
94 (sh)	93 (sh)		
	98		
	101		
107			
122 (sh)	128		
136 (sh)			
154	157		
	166		
190	187	$\tau(CH_3)$	
208	204		
217	219 (sh)		

[a] Note: sh = shoulder, vw = very weak
$\tau(CH_2CH_2)$ and $\tau(CH_3)$ denote; respectively, the twisting modes associated with the polymethylene chain and the methyl group

coupling between these motions can occur in a complex molecule. For these reasons, complications can arise in the assignments of some of the modes. Nevertheless, when the present spectra are compared with those of other liquid crystalline materials[1,3,27] as well as organic compounds that contain structural groups similar to those comprising CBOOA, a tentative correlation of several of the observed modes with characteristic group vibrations can be made. The present assignments have been proposed on this basis.

C Differential scanning calorimetry

As discussed earlier, the thermal characteristics of the two phases as well as the metastable nature of Phase I below 65°C, could be inferred from the far-infrared spectra. DSC measurements were undertaken in order to obtain direct evidence of the solid–solid transition and also determine the latent heat of this transition.

Figure 6 shows the typical DSC results. In trace 1, the sample used was recrystallized from *n*-heptane. We note that there is a distinct endothermic peak at 68.8°C in addition to the peak at 73°C. The latter peak represents

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TABLE II

Raman shifts (in cm^{-1}) of the two phases of CBOOA at 25°C, in the range 30–2300 cm^{-1} and their proposed assignments.[a] The Raman shifts are accurate to $\pm 3\ cm^{-1}$.

Phase II	Phase I	Proposed assignment				
34						
70 (sh)	64 (sh)					
80	86 (sh)					
106	96 (sh)	Libration C_6H_4;		Lattice		
	124 (sh)	$\tau(CH_2CH_2)$		modes		
138	130					
160	175					
165	182 (vw)					
203		$\tau(CH_3)$				
212	205					
378	360 (vw)	Libration CHN				
	389					
	422 (vw)					
445	454					
490 (vw)	486 (vw)					
512 (vw)		C_6H_4—C≡N				
527 (vw)	532 (vw)	interaction				
543 (vw)	552 (vw)					
555	562					
585	596					
628	636	Γ				
703	713 (vw)					
724	734	$\rho(CH_2)$				
788	792	ω				
806 (vw)						
824	830 (vw)	γ	$\rho(CH_2)$			
842	842 (vw)					
	852 (sh)					
873	883	$\rho(CH_3)$				
948	955	γ				
965	972					
1007 (vw)	1015	δ		ω_C		
1043 (vw)						
1100	1106	δ				
1131 (sh)	1133 (vw)	$\tau(CH_2)$				
1163	1166	ω_C δ				
1189	1195					
1220 (vw)	1219 (vw)	$\gamma(CH_2)$			$\tau(CH_2)$	
1234 (vw)						
1249	1243 (vw)	C—O—C stretch				$\gamma(CH_2)$
1287	1286	ω				
1307	1294					
	1310					
	1344 (sh)					
1364	1370	$\delta(CH_3)$				
1376 (vw)						
1402	1404 (sh)					
1412 (sh)	1411					

(Continued)

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TABLE II (*continued*)

Phase II	Phase I	Proposed assignment
	1418	
1444 (vw)		$\delta(CH_2)$
1495	1498	ω; $\delta(CH_3)$
1532 (sh)	1536	
1557	1560	
1587	1591	ω; C=N stretch
1621	1622	
1678	1680	
1724 (vw)	1718 (vw)	γ overtones?
1767	1769 (vw)	
1800 (vw)		
2046 (vw)	2050 (vw)	
2115 (vw)	2122 (vw)	
2225	2218	C≡N stretch

[a] Note: The note under Table I is applicable here also. In the case of the other symbols describing the proposed assignments, we follow here the notations given in Table 3 of Ref. 1.

the solid–smectic transition and is shown truncated in all the four traces. The peak centered at 68.8°C provides direct evidence of a transformation occurring in the solid phase. To within 10%, the corresponding energy of transition is estimated to be 2030 cal/mole. Trace 2 shows the DSC curve obtained after resolidifying the sample and cooling it to room temperature. The peak at 68.8°C is absent now and this confirms that when solidified from the mesophase one obtains Phase I, which becomes supercooled and exists below the transition temperature as a metastable form. Traces 3 and 4 are, respectively, the analogues of traces 1 and 2 except that the starting sample had been crystallized from methanol. We note that the solid–solid transition peak is distorted on the low temperature side due to the presence of additional structure. We feel that one of the possible contributing factors could be the presence of methanol in the crystal as solvent of crystallization. Then, upon heating, it would disappear from the crystal at ~65°C, giving rise to the additional structure. This point could be checked further by cooling the sample below the freezing point of methanol and observing the peak corresponding to the "melting" of methanol at −94°C. We were unable to perform this check as the DSC instrument was limited by its temperature range.

The solid–solid transition temperature as determined from the peak in trace 1 is 68.8°C. However, as seen from Figure 1, the far-infrared spectra indicate that the transition sets in at ~65°C. This apparent discrepancy is reconciled by noting that in trace 1 of Figure 6, the onset of the transition occurs at ~65°C and the peak merely denotes the temperature at which

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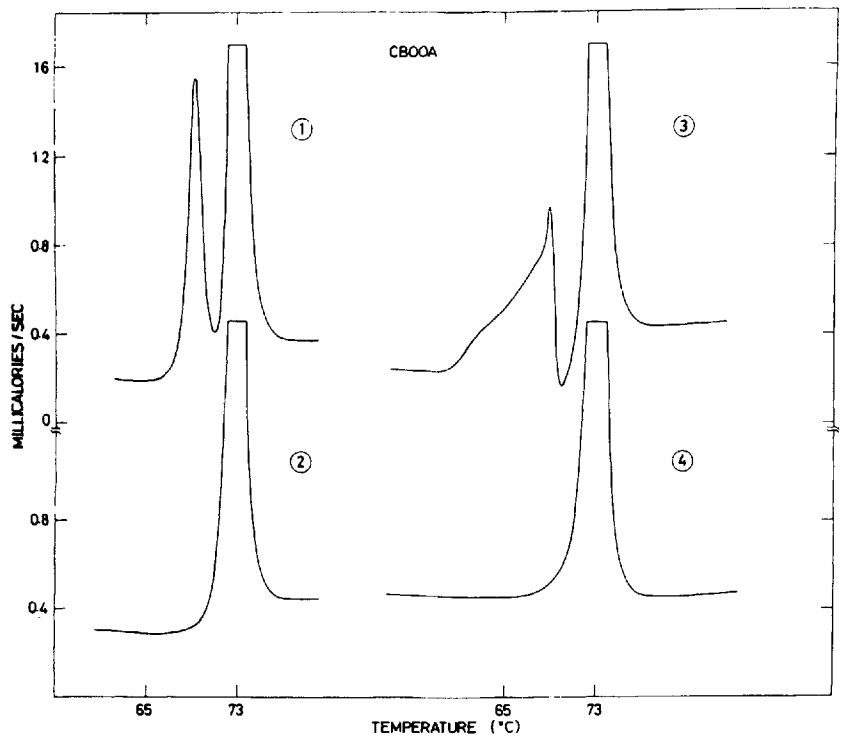

FIGURE 6 Differential scanning calorimetric (DSC) data of CBOOA in the vicinity of the solid-smectic transition.
1) Sample crystallized from *n*-heptane.
2) DSC curve obtained when the sample corresponding to trace 1 was taken to the isotropic phase, then solidified and cooled down to room temperature.
3) Sample crystallized from methanol.
4) DSC curve obtained when the sample corresponding to trace 3 was taken to the isotropic phase, then solidified and cooled down to room temperature.

energy is being absorbed at the maximum pace. Thus, if a sample in Phase II is maintained at ~65°C for a sufficient length of time, as was the case during far-infrared measurements, it would absorb energy and change over to Phase I.

It is of interest to note here that Cladis[20] and Hardouin *et al.*,[17] respectively, have earlier reported differential thermal analysis as well as specific heat measurements on CBOOA. However, no evidence for the solid–solid transition was reported in either study. Presumably, this is because in both cases the starting sample may have been solidified from the mesophase and thus existed in Phase I to begin with.

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D X-ray diffraction data

X-ray powder photographs of both phases were obtained at room temperature. As Phase I is metastable at room temperature and grinding may cause interconversion between the two phases, it is necessary to unambiguously ascertain the phase of the sample, in order to avoid discrepancies or apparent anomalies in the X-ray data. Hence, we observed the following precautions. In the case of Phase II, the sample crystallized from *n*-heptane was carefully powdered imparting minimal force. Then it was allowed to stand for about 30 hours to facilitate complete conversion to Phase II, before the X-ray exposure was commenced. The phase of the sample was also confirmed by its far-infrared spectrum in the region below 150 cm^{-1}. In the case of Phase I, the exposure was commenced immediately after careful grinding. Simultaneously, using a portion of the sample, the far-infrared spectrum was recorded at different time intervals. It was thus ensured that for the duration of the X-ray exposure, the sample indeed did remain in Phase I without undergoing any appreciable conversion to Phase II.

Figure 7 shows the respective densitometer traces of the powder photographs of the two phases. In the case of Phase I, the powder photograph revealed streaks of additional darkening near the equatorial plane, for the three diffraction maxima lying within the angular range 16–20°. Hence the densitometer trace also shows a corresponding enhancement in the peak intensities of these three diffraction maxima. It is not clear at this time whether the additional streaks of darkening represent a genuine effect or they arise due to some artifact of the experimental conditions. Nevertheless, it can be seen that the two traces in Figure 7 exhibit marked differences with regard to the diffraction maxima observed in each case. This shows that the two phases clearly differ in their crystal structure.

IV CONCLUSIONS

From a study of the vibrational spectra of CBOOA we have demonstrated that it possesses two distinct solid phases. In particular, we note that it was possible to elucidate their stability regions as well as their thermal behaviour through the study of their far-infrared spectra alone. Both the DSC and the X-ray results indicate that the two phases differ markedly in their structure and molecular packing and this fact is also evident from their low frequency infrared and Raman spectra.

Previous studies on mesogens have shown that monotropic solid phases can be obtained in some cases by cooling the liquid crystalline phase. The low frequency vibrational spectra of the monotropic solid phases have been

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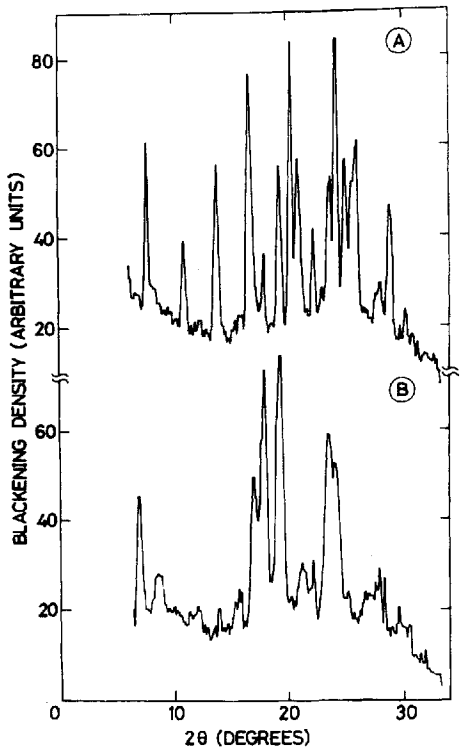

FIGURE 7 Densitometer traces of X-ray powder diffraction photographs of CBOOA in the two phases; $T = 25°C$. (A) and (B) here have the same connotation as in the caption of Figure 4.

studied in the cases of *p*-azoxyanisole[5] (PAA) and *p*-methoxybenzilidene *p'*-butylaniline[27] (MBBA). In both these cases, the spectra of the monotropic phases show certain differences when compared to their respective stable phases, especially at frequencies below 150 cm^{-1}. This behaviour is in general agreement with that reported here for the two phases of CBOOA. The spectral changes indicate that in all these cases the molecular ordering within the crystal is different between the stable and metastable phases. In spite of this broad similarity, the observed thermodynamic behaviour of CBOOA is distinctly different from that seen in the cases of PAA[28] or MBBA.[29] In the latter two cases, either the stable phase or the metastable monotropic phases can fuse and directly transform to the mesophase. However, this is not the case in CBOOA. In this case, even if one starts with the stable solid, Phase II, the formation of the mesophase always proceeds via the transition to Phase I. In other words, Phase II becomes thermodynamically unstable prior to the occurrence of the smectic A phase.

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Furthermore, as Phase I can also be formed while approaching the smectic A phase from below, it cannot be regarded as a monotropic form.

It thus appears reasonable to regard the transition from Phase II to Phase I as a pre-transition effect. Pre-transition phenomena exhibited by the solid phases of mesogens and their relevance to the formation and structure of the mesophase itself have evoked recent interest. For example, Wendorff *et al.*[30] have carried out an X-ray study of cholesteryl esters and find that slightly below their melting point, the order in directions normal to the long axes of the molecules decreases markedly. They interpret this as an anticipation of the transition to the mesophase which, of course, exhibits complete disorder in directions normal to the long axes of the molecules. Also, from an infrared study of *p*-azoxyanisole and its higher homologs, Bulkin *et al.*[7] noted that as the crystal-nematic transition is approached, several infrared bands disappear gradually. They attribute this phenomenon to the creation of lattice defects due to the movement of the molecules from lattice to interstitial sites. The existence of a "soft solid" region below the crystal-nematic transition has also been suggested in the cases of *p*-azoxyanisole[31,32] and *p*-methoxybenzilidene *p'*-butylaniline.[27]

The transition in CBOOA from Phase II to Phase I occurs just below the onset of the smectic A phase. It is thus of interest to consider whether this solid–solid transition represents an anticipation of the transition to the smectic A phase. If so, the structure of Phase I would reflect a corresponding lowering of crystalline order. From the infrared and Raman spectra, we note that certain low frequency modes are considerably broadened or attenuated in Phase I as compared to Phase II. This would imply that the corresponding degrees of freedom associated with the molecules are well coupled in Phase II, whereas in Phase I they tend to become more free and diffusive, thereby reducing the crystalline order as well. The additional degrees of freedom thus activated may relate to the entire molecule or they could be intramolecular in character. The latter case is of importance considering the presence of the relatively flexible octyloxy tail in the CBOOA molecule and the role played by conformational changes in the alkyl chains near many phase transitions.[6,33] As suggested by Andrews,[34] the latent heat associated with the transition from Phase II to Phase I can arise, in part, if one assumes the onset of a "melting" disorder of the octyloxy tail. However, any calculation of the latent heat of the transition on this basis must take account of the fact that the newly accessible conformations of the octyloxy tail would be limited by the coupling of the tail with the phenyl ring. In addition, further disorder associated with the orientation of the CH=N groups and the phenyl rings may also exist.[35] These considerations as well as the low frequency spectra reported here suggest that the structure of Phase I can be expected to be more disordered than that of Phase II. The large endothermic

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