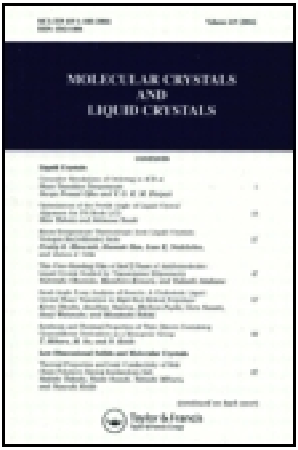

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Infrared Spectroscopic Study of Orientational Order and Phase Transformations in Liquid Crystalline CBOOA

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Infrared Spectroscopic Study of Orientational Order and Phase Transformations in Liquid Crystalline CBOOA

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An infrared study of the different phases of liquid crystalline CBOOA (*N*-*p*-cyanobenzilidene *p*-*n*-octyloxyaniline) has been made in the range 30–3100 cm^{-1}. From a study of the $—\text{C}{\equiv}\text{N}$ vibration in aligned samples, the absolute orientational order parameter, S, is determined in the smectic A and nematic phases. The variation of S is compared with the relative values determined earlier from diamagnetic anisotropy, NMR and birefringence studies. The far-infrared spectrum of the solid (Phase I) exhibits a mode whose intensity decreases gradually as the crystal–smectic A transition is approached. Also, a band observed at 296 cm^{-1} in the solid (Phase I) practically disappears in the fluid phases. These results are discussed in terms of possible pretransition effects and intramolecular changes characteristic of crystal-mesophase transitions. Dichroic effects are evident in the far-infrared absorption of the liquid crystalline phases and these are considered in relation to the influence of molecular structure on the absorption in this region.

I INTRODUCTION

Smectic liquid crystals have evoked considerable experimental and theoretical interest in recent years.[1,2] The identification of the different smectic forms as well as the nature of the molecular ordering and symmetry within all of these forms[2,3] are not yet fully understood. Furthermore, current theories on liquid crystals indicate the possibility of second order phase changes[4–6] at smectic C-smectic A (C–A) and smectic A-nematic (A–N) transitions. This has prompted many investigations on the physical properties of mesophases and their critical behaviour near these transitions.[7–9]

In this context, the liquid crystal CBOOA (*N*-*p*-cyanobenzilidene *p*-*n*-octyloxyaniline) has attracted considerable attention recently as it undergoes the A–N transition. Several experimental studies have been carried out to ascertain the variation of its elastic constants,[9–11] specific heat[12–14] as well as diamagnetic[14] and optical[15] anisotropies near this transition. The vibrational spectra of mesomorphic materials are often useful in gaining a better understanding of the molecular and the structural characteristics of their different phases. From an earlier study of the far-infrared and the Raman spectra of crystalline CBOOA, the occurrence of a solid–solid transition below the onset of the smectic A phase was demonstrated and the implications of this transition for the formation of the mesophase were considered.[16] The purpose of this paper is to present and discuss the results of a near and far-infrared spectroscopic study of liquid crystalline CBOOA in its different phases. The experimental results are discussed in relation to the orientational order obtaining in the mesophases, the influence of molecular structure on the far-infrared absorption of the fluid phases as well as certain features characterizing the crystal-smectic A transition.

II EXPERIMENTAL

CBOOA obtained from Eastman Kodak Co.[17] was recrystallized in *n*-heptane or methanol and outgassed in vacuum. The transition temperatures were measured using a hot stage microscope to within ±0.2°C and they are as follows: solid–smectic A (73°C); smectic A-nematic (A–N) (82.5°C); nematic–isotropic (N–I) (106.9°C). Further recrystallization did not significantly improve the N–I transition temperature. At room temperature, crystalline CBOOA can be obtained either in the stable or the metastable form; the two different forms[16] are prepared by solvent crystallization (Phase II) and solidification from the mesophase (Phase I), respectively. At 65°C, Phase II is known to transform[16] to Phase I, the latter being the only stable phase till the transition to the mesophase. In the present study, Phase II was investigated in the form of a thin layer of sieved powder or in a KBr pellet. Polycrystalline samples of Phase I were obtained by slow cooling and solidification of a bubble free film of the liquid crystal.

Near infrared spectra were recorded in the range 2–15 μ using a Leitz double beam prism spectrograph[18] equipped with interchangeable NaCl and KBr prisms. For the slit program used in these measurements, the spectral resolution varied from 21 to 4 cm^{-1}, over a corresponding wavelength range of 2–15 μ. To facilitate accurate measurements of the half width of the absorption bands, an expanded wavelength scale was employed in the regions of interest. CBOOA samples were contained between a pair of

NaCl windows. Solid samples in Phase I were prepared without using any spacer between the windows. The resultant polycrystalline film, a few microns thick, was adequate to yield good, reproducible spectra. The liquid crystal and isotropic phases were studied using samples of ~20 μ thickness, a mylar spacer being used for this purpose. Liquid crystalline samples aligned in the homoeotropic configuration[19] were prepared by first rubbing the surfaces of the windows on chamois leather in a random manner. Nematic samples prepared after this surface treatment were uniaxial and they showed good extinction under crossed polarizers. Also, upon cooling to the smectic A phase, the homoeotropic alignment was still preserved with no apparent degradation whatsoever.

Far-infrared spectra in the range 30–700 cm^{-1} were obtained using the Polytec FIR-30 Fourier spectrometer.[20] The details related to the sample preparation and the experimental procedure have been described previously.[16,21] The spectral range 30–700 cm^{-1} was covered using three different beamsplitters. Sample cells with α-quartz windows were employed in the region 30–250 cm^{-1}, while diamond windows were used in the range 250–700 cm^{-1}. The effective sample apertures were 15 mm and 10 mm, respectively, in the two cases. The windows were sufficiently tapered to avoid unwanted interference fringe effects in the spectra. The spectral resolution was between 3–4 cm^{-1}. The optical transparency of the windows made it possible to monitor the phase transitions in the sample visually.

Polarization measurements in the range 30–250 cm^{-1} were carried out using a wire grid polarizer.[22] Hitherto, no polarization studies on oriented liquid crystals have been reported in the far-infrared region. The major difficulties encountered in this regard are the reduction in available energy with the use of a polarizer and the lack of adequate choice in window materials, which can facilitate the preparation of oriented samples at higher temperatures as well as permit a visual check of the alignment under a polarizing microscope. α-quartz windows are normally employed in the range below 250 cm^{-1} and here again the birefringence of the windows can pose added problems unless due precautions are taken. The α-quartz windows used in this study were cut with the two principal axes lying in the plane. They were rubbed parallel to the *c* axis and the nematic liquid crystal was allowed to flow between them along the direction of rubbing. The resultant sample was homogeneously[19] aligned parallel to the *c* axis. The degree of alignment in the nematic phase was not quite uniform over the entire sample. On cooling to the smectic A phase, the alignment deteriorated noticeably, although an overall tendency towards alignment along the original direction was still apparent.

As a result of reflection from the beamsplitter, the radiation from the interferometer is partially polarized with the vertical component of the electric vector being more intense. To exploit this feature and obtain spectra with better signal-to-noise ratio, vertically polarized radiation was used in all the measurements. The sample cell was rotated so that the direction of alignment of the sample and hence the *c* axis of the windows were all kept either parallel or perpendicular to the electric vector of the incident radiation. This procedure ensured that possible birefringence effects arising from the α-quartz windows were greatly minimized in our dichroic measurements. In a similar manner, the alignment of the sample could also be visually checked under a polarizing microscope, provided the incoming light was polarized along either of the two principal axes of the windows.

The sample cells were heated by a surrounding copper block whose temperature could be varied. Data were obtained nearly 15 min. after thermal equilibrium was reached. The temperature measurements were accurate to ± 1°C, with the fluctuations being within 0.5°C.

III EXPERIMENTAL RESULTS AND DISCUSSION

A Orientational order in CBOOA

The long range orientational ordering of molecules is an interesting and fundamental property of the liquid crystalline state. Hence the experimental study of orientational order in liquid crystals has been of particular interest and several methods have been used for this purpose.[23] We first consider briefly the method of determining the orientational order through infrared studies on aligned liquid crystals and then discuss the results obtained in the smectic A and nematic phases of CBOOA by this technique.

The orientational order parameter, S, is defined[19] as

$$S = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \qquad (1)$$

where, θ is the angle made by the long axis of any given molecule with the average direction of molecular alignment. The angular brackets denote averaging over all the molecules in the medium. In determining S from infrared studies, one needs a vibrational transition moment in the molecule, which makes a known angle α with the long axis of the molecule. Using a homogeneously aligned sample and polarized radiation, S can be evaluated from the two integrated absorption coefficients,[23,24] $I_{\parallel}$ and $I_{\perp}$; the subscripts $\parallel$ and $\perp$ denote, respectively, the cases where the incident radiation is polarized parallel and perpendicular to the direction of alignment of the sample. A simpler technique which avoids the need for polarized radiation utilizes homoeotropically aligned samples.[25] In this case, when the incident radiation propagates along the uniaxial direction of the sample, the choice of a specific direction of the electric vector becomes superfluous. An additional advantage is that aligned smectic A samples can be obtained more easily in the homoeotropic configuration. In contrast, it is necessary to cool the nematic phase in the presence of an external field,[19] in order to obtain a homogeneously aligned smectic A sample.

When a homoeotropically oriented sample is used, the "dichroic" ratio, R, can be defined as the ratio of the integrated absorption of the band in the liquid crystal to that in the isotropic phase. Then, it is relatively straightforward to show that

$$R = 1 - S(1 - \tfrac{3}{2}\sin^2\alpha) \tag{2}$$

and hence,

$$S = \frac{1 - R}{1 - \frac{3}{2}\sin^2\alpha}\,. \tag{3}$$

The integrated absorption of the band, corrected for the effects of finite spectral slit width, was estimated following Ramsay's procedure.[26]

Saupe and Maier have pointed out[23] that the evaluation of orientational order parameter from dichroic studies must include appropriate corrections for the anisotropy in the refractive indices and the polarizability of the liquid crystalline medium. They show that when a homogeneously aligned sample is used, the resultant corrections to the order parameter can amount[23] to as much as 10%. In contrast, when a homoeotropically aligned sample is used, we estimate that the necessary correction is well within 2%. This is mainly because the difference between the ordinary and extraordinary refractive indices of the liquid crystal is generally greater than that between the ordinary index of the liquid crystal and the index of the isotropic phase. It is the latter two quantities that are of interest when a homoeotropically aligned sample is used, as in the present case. As the desired correction is less than our experimental uncertainties, it is not included in our determination of S. Thus, within the experimental accuracy, the present study leads to the *absolute* values of S in the liquid crystalline phases of CBOOA, whereas the earlier studies[14,15,27] yielded only the *relative* values of S.

The infrared absorption band used in our study of the orientational order is the localized, —C≡N stretching mode arising from the nitrile group at one end of the CBOOA molecule. This is a distinct and strong vibrational band, almost free from any overlap with neighbouring lines and having its transition moment nearly parallel to the long axis of the molecule. The molecular structure of CBOOA is shown in Figure 1. Owing to the lack of any specific knowledge concerning the statistical distribution of the different possible conformations of the octyl tail in the mesophases, we take the long axis of the CBOOA molecule as the line passing through the centres of the

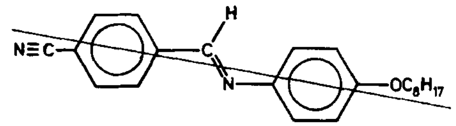

FIGURE 1 Molecular structure of CBOOA. The long axis of the molecule is taken to be the line joining the centres of the two benzene rings.

two benzene rings. On this basis, the angle α between the transition moment of the —C≡N stretching mode and the long axis of the molecule[28] is estimated to be ~10°. Using a homoeotropically aligned sample and unpolarized radiation in conjunction with the experimental geometry mentioned above, the absorption strength of this band was studied as a function of temperature. Figure 2 shows the typical results obtained. As the temperature is increased, the degree of ordering of the molecules is expected to decrease. In view of the near parallelism of the —C≡N transition moment with the long axis of the molecule, the absorption strength should hence increase with increasing temperature and this is consistent with the observed behaviour. At the transition to the isotropic phase, the absorption strength showed a discontinuous increase corresponding to a discontinuous change in the molecular ordering at the nematic-isotropic transition.

From the corrected integrated absorption strengths[26] and Eq. (3), the variation of S was determined as a function of temperature and these results

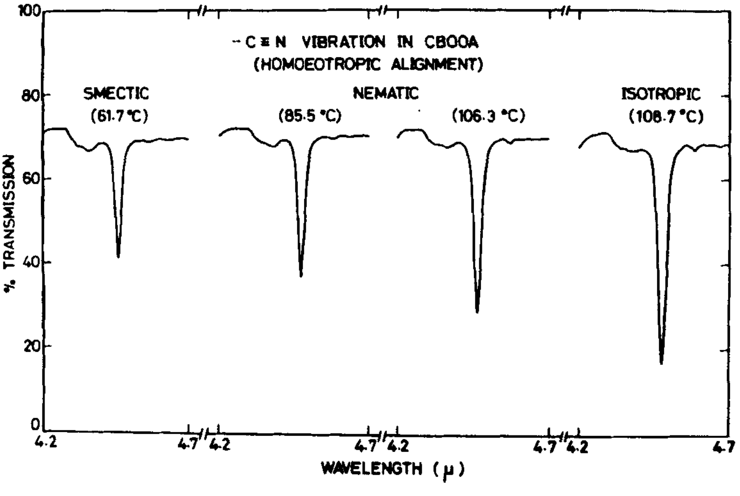

FIGURE 2 Absorption strength of the —C≡N stretching mode of CBOOA in the smectic A, nematic and isotropic phases. Below 73°C, the smectic A phase is supercooled. The liquid crystalline samples were homoeotropically aligned. The sample temperature corresponding to each trace is also shown.

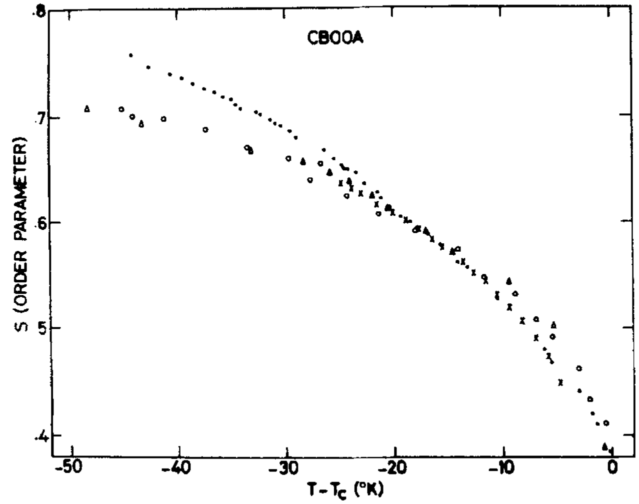

FIGURE 3 Variation of S in the smectic A and nematic phases of CBOOA. Open circles denote the values determined in this study. The variation of S determined from three other studies is also shown after each set of data is normalized to the present data at $T - T_c = -19$ K; T_c corresponds to the respective N–I transition temperature in each case. The open triangles are from diamagnetic anisotropy data (Reference 14); filled circles, NMR results (Reference 27); crosses, birefringence results (Reference 15).

are shown in Figure 3. It can be seen that the values of S determined in this study at the A–N and N–I transitions, are, respectively, 0.62 and 0.41; these are closed to the typical values found near these transitions.[5,29] The S values are estimated to be accurate to within the experimental scatter, which is less than 5%.

Three earlier studies have been carried out to determine the variation of orientational order in CBOOA.[14,15,27] From a study of its birefringence in the nematic phase, Huang *et al.* reported[15] that their results did not agree with the NMR data[27] or the diamagnetic anisotropy results.[14] The discrepancy was reported to be substantial especially at temperatures close to the N–I transition. In view of this, it is of interest to compare the present values of S with the earlier results. Figure 3 shows these data normalized to ours at a relative temperature of $T - T_c = 19$°K; here T_c denotes the respective N–I transition temperature for each set of data. The relative temperature chosen here for normalizing the different sets of data corresponds to the lowest common point on the temperature scale, where all the four sets of data relate to the nematic phase. It is seen that in the nematic phase, the agreement between the different sets of data is reasonably satisfactory, the deviations being within the typical limits normally encountered while comparing the values obtained by different methods. The substantial differences noticed by Huang *et al.* are attributable to the fact that these authors compared the different sets of data on a temperature scale referred to the A–N transition temperature. This tends to produce considerable discrepancies, especially at higher temperatures, because the different samples are characterized by slightly different N–I transition temperatures, presumably due to different amount of impurities in them. Nevertheless, as McColl[30] has shown, the presence of small amounts of impurities in a nematic phase does not normally affect the value of the orientational order parameter at the N–I transition. It is thus clear that a proper comparison of the orientational order in the nematic phase must be based on a temperature scale referred to the N–I transition temperature, although one can, in principle, choose to normalize the different sets of data at any given temperature within the nematic range.

In the smectic A phase, the present results agree closely with the diamagnetic anisotropy data.[14] However, the NMR experiments[27] show a much steeper increase in S at lower temperatures, than either of these two sets of data. The magnetic fields used in both the NMR and the diamagnetic anisotropy measurements are comparable, being nearly 28 and 21.0 kilogauss, respectively. This indicates that the apparently higher orientational order obtained from the NMR measurements is not entirely accounted for by the orienting effects of the magnetic field. Optically, our samples were seen to maintain good homoeotropic alignment in the smectic A phase also. Thus, the origin of the observed differences in the smectic A phase between the NMR results on the one hand and the present results as well as the diamagnetic anisotropy data on the other, remains to be clarified.

The diamagnetic anisotropy results do not depend upon any specific assumptions regarding the molecular interactions or local field effects. In this light, the agreement between the present data and the diamagnetic anisotropy results over the entire temperature range is a further indication that possible corrections to our data from local field effects are well within our experimental uncertainties.

Following an initial suggestion by McMillan that the A–N transition in CBOOA may be of second order,[31] considerable experimental[13,14,32,33] and theoretical[34] work has been devoted towards understanding the nature of this transition. Near a second order A–N transition, the orientational order parameter is expected to vary continuously, but it may exhibit a discontinuity in slope. On the other hand, when the A–N transition is distinctly of first order, a discontinuous change in the order parameter is expected at the transition.[5,35] The NMR results of Cabane *et al.*[27] show that the discontinuity in the order parameter at the A–N transition in CBOOA is less than 0.3% and on this basis, they suggest that this transition may be of second order. Our data shown in Figure 3 do not reveal a measurable discontinuity at the A–N transition. However, it must be noted that the possible scatter in our data amounts to ~5% and hence our data do not permit any conclusions to be drawn regarding the order of this transition.

B Near Infrared Spectra

Figure 4 shows the near infrared spectra of the different phases of CBOOA, in the range 2–15 μ. Spectra of solid Phase II are not shown because except for minor intensity changes, no significant differences were observed as compared to the spectra of Phase I. In the internal mode region, the Raman spectra of the two phases also show a similar behaviour.[16] This is consistent with the expectation that when the crystal symmetry of a complex molecular crystal changes due to a polymorphic transition, the intra-

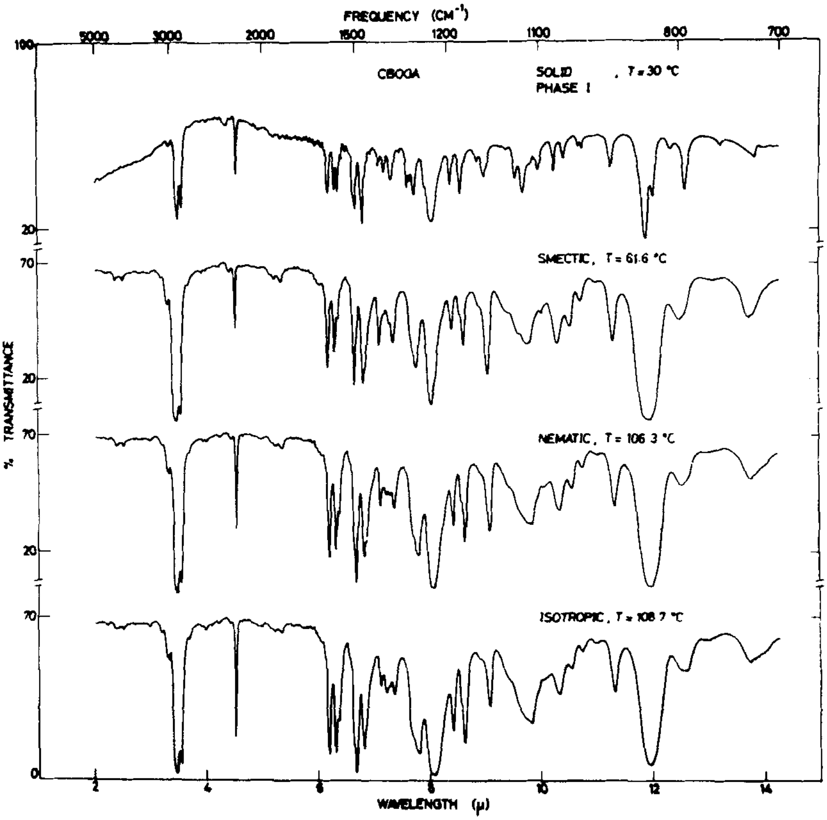

FIGURE 4 Near infrared spectra of CBOOA in the solid (Phase I), smectic A, nematic and isotropic phases. The temperature corresponding to each phase is also shown.

molecular modes would be affected much less compared to the intermolecular modes. From Figure 5 we note that in a few cases, the characteristic splittings observed in the solid (Phase I) disappear in the fluid phases. The spectra of smectic A and nematic phases were obtained using homoeotropically aligned samples. The flat baseline at wavelengths shorter than 3 μ indicates that the alignment is very good. Comparing the intensities of the different bands in the fluid phases, the "dichroic" ratio R, as defined earlier, is less than unity for certain bands, while it is greater than unity for some others. This is indicative of the fact that the transition dipole moments of these bands have their major component along the long axis or perpendicular to the long axis of the molecule, respectively. The observed "dichroic" ratio of each band is hence useful in ascertaining the predominant polarization direction of that band. Along with the observed frequencies of the bands, the polarization features of the bands are also useful in making vibrational assignments to the spectra. To consider some examples, the strong modes at $\sim$970 and 838 cm^{-1} are assigned to out-of-plane C—H vibrations of the benzene rings and all of these do have $R > 1$. In contrast, the mode at $\sim$1160 cm^{-1} which is assigned to a skeletal mode of the octyl tail (ω_c) may be expected to have $R < 1$ and this is what is observed. Of course, the —C≡N stretching mode itself provides another clear illustration of this type of behaviour.

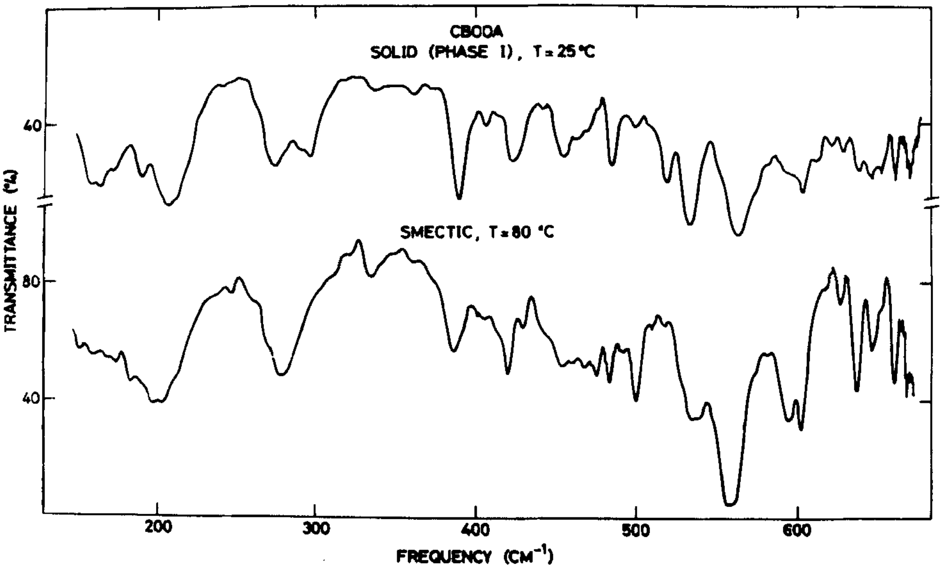

FIGURE 5 Far-infrared absorption spectra of CBOOA in the solid (Phase I) and smectic A phases. The temperature corresponding to each phase is also indicated.

The vibrational assignments to the Raman and far-infrared spectra of the solid phases of CBOOA were reported earlier.[16] As noted in that study, there is some overlap between the frequency regions of the various possible modes arising from the different molecular units constituting CBOOA. In addition, designations such as rocking and twisting modes are only approximate as considerable coupling between these motions can occur in a complex molecule. For these reasons, complications can arise in the assignments of some of the modes. However, from a comparison of the present spectra with those of other liquid crystals[36–38] and 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 observed infrared frequencies together with the assignments proposed on this basis are listed in Table I. The frequencies below 650 cm^{-1} were obtained from the far-infrared measurements which are discussed below.

C Far Infrared Spectra

(i) *Crystal-Mesophase Transition*: The far-infrared spectra of the solid (Phase I) and smectic A phases, in the range 150–650 cm^{-1}, are shown in Figure 5. Spectra of the nematic and isotropic phases were almost identical to that of the smectic A phase and hence they are not shown here. Owing to an upper limit of ~40 μ on the average particle size in samples of Phase II, strong scattering was present in the range above 300 cm^{-1} and this made it difficult to obtain meaningful spectra of Phase II at higher frequencies.

While some intensity differences are apparent between the two spectra shown in Figure 5, the observed frequencies in the solid and smectic A phases are almost identical except for two interesting features, which we consider below in further detail. First, the distinct mode observed in the crystal at 518 cm^{-1} is absent in the smectic A phase. We have followed the intensity change of this mode in relation to the neighbouring line at 530 cm^{-1}, as a function of temperature, and this is shown in Figure 6. The mode at 530 cm^{-1} undergoes some broadening and attenuation in intensity as the temperature approaches the crystal-smectic A transition and such a behaviour was noticeable in the cases of other neighbouring lines also. However, the mode at 518 cm^{-1} is seen to exhibit a much more rapid change in intensity in comparison to the line at 530 cm^{-1}. The former nearly disappears at the crystal-smectic A transition, whereas the mode at 530 cm^{-1} persists in the smectic A phase, although with reduced intensity. From an infrared study of *p*-azoxyanisole and its higher homologues, Bulkin *et al.* reported a similar behaviour;[39] the intensity of certain mid-infrared bands was found to decrease continuously as the crystal–nematic transition was

TABLE I.

Infrared absorption frequencies (in cm^{-1}) of CBOOA in the solid (Phase I) and smectic A phases, in the range 30–3100 cm^{-1} and their proposed assignments[a]. The absorption frequencies of solid (Phase I) below 220 cm^{-1} are also listed[16] here for comparison. Wavelengths corresponding to frequencies above 700 cm^{-1} are accurate to ±0.01 μ; below 700 cm^{-1} the frequencies are accurate to ±2 cm^{-1}.

Solid (Phase I)	Smectic A	Proposed Assignment		
45 (vw)	50	∠C—C—C bend (C_8H_{17})	τ(CH_2CH_2)	Lattice modes (solid)
70 (sh)	65 (sh)			
84 (sh)	80			
88		Libration C_6H_4		
93 (sh)				
98				
101	100			
	110			
128	130 (sh)	τ(CH_2CH_2)		
157				
166				
	174	τ(CH_3)		
187				
204	200			
219 (sh)				
274	278	Accordion mode (C_8H_{17})	∠C—C—C bend (C_8H_{17})	
294				
336 (vw)	334			
361 (vw)	361 (vw)	Libration CHN		
389	386			
406				
423	420			
454	457		C_6H_4—C≡N interaction; Γ	
462 (sh)	466			
470 (sh)	474	∠C—C—C bend (C_8H_{17})		
484	482			
499	499			
518				
532	536			
563	559			
592 (sh)	594			
602	602			
638	637	Γ		
647	646			
662	662			
671	671			
	712 (sh)			
721	720 (sh)	ρ(CH_2)		
	728			
754	771			
792	795	ω		
809	802 (sh)			
830	825 (sh)	γ		
840	838			

TABLE I (*Continued over*)

Solid (Phase I)	Smectic A	Proposed Assignment					
848 (sh)				$\rho(CH_2)$	ω_C		
886	884	$\rho(CH_3)$					
	912 (vw)						
927							
933	931						
956	947		γ				
973	970						
1000	999 (sh)		δ				
1015 (sh)	1018						
1028	1029 (sh)						
1043							
1062 (sh)	1063 (sh)						
1075 (sh)							
1104 (sh)	1103		δ				
1109							
1127	1126 (sh)	$\tau(CH_2)$					
1166	1161	ω_C				$\tau(CH_2)$	
	1172 (sh)						
1191	1192						
1217 (sh)		$\gamma(CH_2)$					$\gamma(CH_2)$
1244	1247	C—O—C stretch	ω				
1261 (sh)							
1292	1285						
1305 (vw)	1305 (sh)						
1315							
1340 (vw)							
1369	1365		$\delta(CH_3)$				
	1380 (sh)						
1391	1391						
1412	1411						
1459 (sh)	1463 (sh)		$\delta(CH_2)$; $\delta(CH_3)$				
1470	1472						
1500	1507	ω; $\delta(CH_3)$					
	1524 (sh)						
1558 (vw)	1561 (sh)						
1575	1578 (sh)						
1589	1591		ω; C=N stretch				
1620	1624						
	1885 (vw)						
	1938 (vw)						
2028 (vw)	2018 (vw)						
2077 (vw)							
2212	2233	C≡N stretch					
	2460 (vw)						
	2527 (vw)						
	2746 (vw)						
2827	2849		C—H stretch (C_8H_{17})				
2891	2919						
3025 (vw)	3036	C—H stretch (C_6H_4)					

[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. In the case of the other symbols describing the proposed assignments, we follow here the notations given in Table 3 of Reference 36.

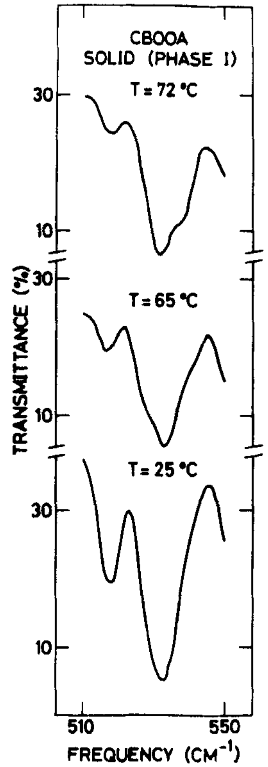

FIGURE 6 Temperature dependence of the far-infrared absorption of polycrystalline CBOOA (Phase I), in the range 500–550 cm^{-1}.

approached from below. However, they noted that this phenomenon could not be observed near a crystal–smectic transition. The present results show that such effects can occur near the crystal–smectic transition also.

In all these cases, the disappearing infrared bands occur at too high a frequency to correspond to typical lattice modes. Bulkin *et al.* suggested[39] that such bands could be combination modes between external and internal vibrations and related the disappearance of the bands to the onset of progressive disorder in the lattice. In the case of crystal–nematic transition, the pretransition effects observed in the infrared spectra were attributed to the movement of molecules from lattice to interstitial sites,[39] leading to positional disorder in the lattice. More recently, Kirov and Simiva[40] have also adopted the same reasoning. However, neutron scattering studies by Riste *et al.*[41] indicate that the pretransition effects in the vicinity of the crystal–nematic transition are caused by increasing rotational freedom of the molecules rather than positional disorder. During a study of *p*-azoxyanisole these authors noticed that with increasing temperature, the integrated intensity of several Bragg diffracted peaks decreased gradually and became zero at the crystal–nematic transition. Also, two broad, diffuse peaks characteristic of the nematic phase were seen to emerge in the crystalline phase itself nearly 10°C below the transition to the mesophase and their intensity was seen to increase as the transition point was approached from below. The *widths* of the disappearing Bragg peaks were found to be essentially *independent of temperature*. This implies that long range correlations of molecular centres of mass are maintained until the onset of the liquid crystalline phase and that these pretransition changes are not effected by positional disorder. On the basis of model calculations,[42] Riste *et al.* have concluded that the changes observed by them can be accounted for by assuming that the molecules execute uncorrelated, torsional oscillations about their long axes, the amplitude of the oscillations increasing as the temperature is raised towards the crystal–nematic transition. The molecules, however, were assumed to remain parallel and at the sites of a rigid lattice till the melting point was reached. This picture thus corresponds to progressive rotational disorder rather than positional disorder; it also suggests that the positional order is lost in such systems in a much more abrupt manner very close to the melting point. The latter notion is not inconsistent with the theory of melting presented by Kobayashi[6] for liquid crystalline materials. As emphasized by Kobayashi, the apparently gradual disappearance of the translational order parameter at the melting point, as seen from his calculations, is a consequence of certain simplifying assumptions and it is not essential to the theory.

The above model of rotational disorder may also be applicable to crystal–smectic transitions involving the less ordered smectic phases; in these cases also, as at the crystal–nematic transition, the molecules become nearly free to rotate about their long axes at the transition temperature.

As the external vibrations of a crystal would be sensitive to changes in lattice forces and intermolecular coupling, one might expect that their behaviour in the pretransition region would provide a direct check of either hypothesis. Far-infrared[21,38,43–45] and Raman spectra[37,46–49] of low-frequency modes have been reported for materials exhibiting crystal–nematic transition. In all these cases, the pretransition effects generally consist of broadening and intensity changes in the spectra. It should however be mentioned that the interpretation of the results as reported in these cases does not permit one to unambiguously conclude as to whether rotational or positional disorder is the dominant cause of these changes.

More definitive results have been reported in the low-frequency modes of mesogens exhibiting crystal–smectic transitions. The crystal structure of smectogenic compounds is known to exhibit a parallel, layered arrangement of molecules with some interpenetration between adjacent layers.[50,51] This is to be contrasted with the imbricated structure found in nematogenic materials. At the crystal–smectic transition, the coupling between the layers is weakened and the spacing between them increases, thus allowing them to glide freely, one on top of the other. An intermolecular mode arising from the coupling of molecules in adjacent layers is then expected to reflect these changes preceding the melting of the crystal. On this basis, Amer and Shen[52] as well as Dvorjetski *et al.*[53] have interpreted the softening of low-frequency Raman modes near the crystal–smectic transition as arising from a premelting relaxation of the bonding between layers. The latter authors also note that this process is probably accompanied by increased rotational motion of the molecules around their long axes.

From the foregoing considerations, the intensity variation of the band at 518 cm^{-1} in Figure 6 can be explained qualitatively if it is attributed to a combination between a "soft", low-frequency intermolecular mode and an internal vibration. The direct observation of the low-frequency mode in question has not yet been reported in this case. From earlier studies,[52,53] it seems likely that this mode can occur at a frequency below 30 cm^{-1}, a range not covered in our study of the vibrational spectra of CBOOA.[16] The softening of the intermolecular mode probably occurs due to the increased rotational freedom of the molecules accompanied by the weakening of inter-layer coupling, while approaching the crystal–smectic transition. The relative contribution of these two factors can be assessed only after crystal structural and neutron scattering data on CBOOA become available over a sufficient temperature interval preceding the crystal–smectic transition.

The role played by conformational changes in alkyl chains is also of considerable interest in the study of solid-fluid phase transitions. In the case of *n*-alkanes, the polymethylene chain is known to adopt the fully extended, trans conformation in the solid phase, while many possible gauche conformers resulting in chain shortened forms appear in the fluid phases. Schaufele[54] obtained evidence for such a behaviour from a study of the longitudinal, accordion like modes associated with the chain backbone. Also, Schnur[55] found a similar behaviour during a Raman study of alkoxyazoxybenzene series of liquid crystals. As compared to the solid phase, the intensity of the bands assigned to the accordion mode was seen to decrease markedly upon entering 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 octyl tail, we expect on the basis of previous results[54,55] that a similar accordion mode may be observable in the present case also; if so, it should occur in the frequency range between 250–300 cm^{-1}. Considering the molecular symmetry of CBOOA, the mode can exhibit infrared activity.

Figure 7 shows the detailed behaviour of the different phases in this range, as a function of temperature. Both Phase II and Phase I are seen to exhibit two absorption maxima at room temperature. The band at the higher frequency occurs at 288 cm^{-1} in Phase II and at 296 cm^{-1} in Phase I. The slight shift in the position of this band is probably related to the differences in the molecular environment and crystal structure[16] between the two solid phases. At temperatures above 65°C, the doublet is still clearly present in the solid (Phase I), although some broadening is evident. At the transition to the smectic A phase, the mode at 296 cm^{-1} virtually disappears, as was the case in the nematic and isotropic phases. This behaviour is in agreement with that already observed in alkoxyazoxybenzenes[55] and hence the mode at 296 cm^{-1} is tentatively identified as the "accordion" mode belonging to the octyloxy tail.

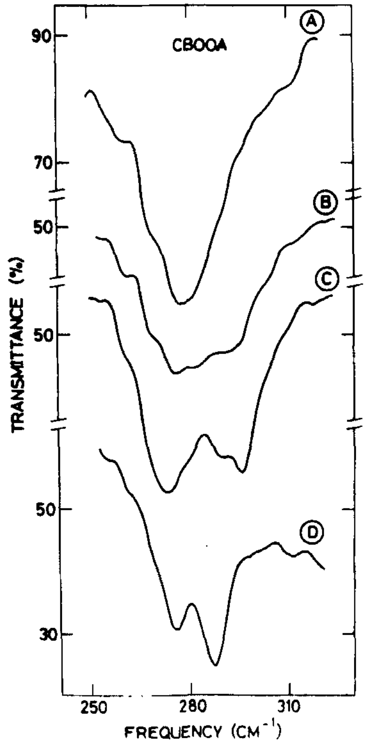

FIGURE 7 Far-infrared absorption spectra of the solid and smectic A phases of CBOOA in the range 250–330 cm^{-1}. (A) Smectic A (80°C); (B) Solid (Phase I) (72°C); (C) Solid (Phase I) (25°C); (D) Solid (Phase II) (25°C).

Additional evidence for conformational changes in the octyl tail is discernible from an inspection of Table I as well as Figure 4. Several other spectral features associated with the rocking, twisting and wagging progression modes of the $(CH_2)_7$ group as well as the aliphatic C—H stretching frequencies show interesting differences between the two phases. This would be as expected[56] if as compared to the solid, new conformations of the octyl tail are allowed in the smectic phase. The present results thus indicate that the crystal–smectic A transition in CBOOA is accompanied by intramolecular changes associated with the octyl tail and that such changes may be a general feature of solid-mesophase transitions, especially when the constituent molecules of the mesogen possess long, flexible end chains.

(ii) *Dichroic Effects*: We now turn to a discussion of the dichroic behaviour of the far-infrared absorption of liquid crystalline CBOOA. To our knowledge, no polarization studies on liquid crystals have been reported so far in the far-infrared region. Figure 8 shows the dichroic behaviour of homogeneously aligned samples in the range 30–250 cm^{-1}. As noted earlier, the alignment was not quite uniform over the entire sample in the nematic phase and it deteriorated noticeably in the smectic A phase. In spite of this departure from uniform alignment, the spectra do show evidence of a clear dichroic behaviour in both smectic A and nematic phases. At frequencies below 130 cm^{-1}, for incident radiation polarized perpendicular to the direction of alignment, ($\mathbf{n} \perp \mathbf{E}$), one observes a strong, broad absorption band centred at ~ 100 cm^{-1} in addition to a shoulder at ~ 65 cm^{-1}. In contrast, for radiation polarized parallel to the direction of alignment, ($\mathbf{n} \| \mathbf{E}$), three weak absorption maxima are present at 50, 80 and 110 cm^{-1}. It should be noted that without the aid of polarization studies, it would have been very difficult to establish the presence of these weak features, as the spectrum is otherwise dominated by the strong band centred at ~ 100 cm^{-1}. The modes at 175 and 200 cm^{-1} persist in both polarizations, although they are more intense for $\mathbf{n} \perp \mathbf{E}$.

The spectra do not show any significant changes between smectic A and nematic phases or as a function of temperature. The spectrum in the isotropic phase was essentially a superposition of the spectra shown here for the two different polarizations. This shows that the long range molecular ordering in the liquid crystalline phases has very little effect on the far-infrared absorption of CBOOA. Rather, the spectra appear to be more sensitive to the molecular structure and short range effects in the fluid phases. The broad absorption band at 100 cm^{-1} is similar to those observed earlier in other liquid crystals,[21,38,43,44] and organic liquids.[57] The weak, yet distinct low frequency structure seen here for $\mathbf{n} \| \mathbf{E}$ was not reported in previous studies. Earlier far-infrared studies on liquid crystals were limited to

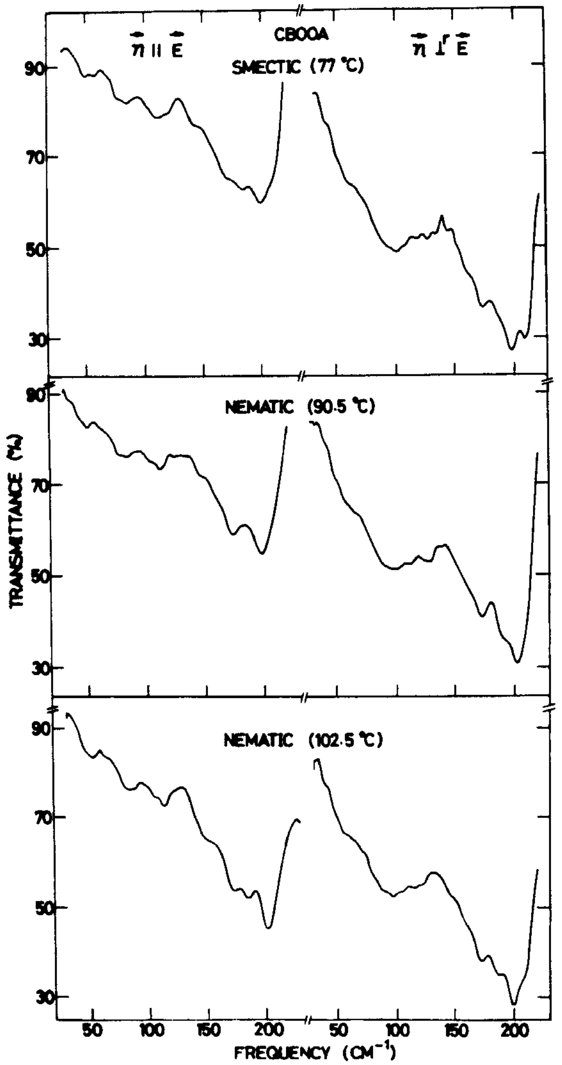

FIGURE 8 Dichroic behaviour of the far-infrared absorption of CBOOA in the smectic A and nematic phases. The sample was homogeneously aligned. The two traces at each temperature correspond to the electric vector being parallel (**n**∥E) and perpendicular (**n** ⊥ E) to the direction of alignment.

those with relatively shorter molecular end groups, whereas CBOOA possesses a long octyl tail. This suggests that some of the weak modes observed here may be characteristic of the octyl tail. In the case of *n*-alkanes, normal mode calculations by Schachtschneider and Snyder[58] indicate that such low frequency modes can arise from ∠ C—C—C bend and CH_2CH_2 torsional modes when the polymethylene chain is sufficiently long. Moreover, although *p*-azoxyanisole itself does not exhibit such modes, a preliminary study on higher members of its homologous series with hexyl and heptyl end chains indicates[59] that they too possess similar weak bands in this range. These considerations lend additional support to our assignment of these weak bands in CBOOA as originating from the octyl tail.

IV CONCLUDING REMARKS

The results reported in this paper illustrate the utility of vibrational spectra in the study of liquid crystals. From the temperature dependent changes in the intensity of the —C≡N stretching mode, it has been possible to determine the absolute orientational order parameter in both the smectic and nematic phases of CBOOA. Recently, Jen *et al.*[28] have shown that it is possible to determine S as well as the next higher order parameter describing the orientational order, $\langle P_4(\cos\theta)\rangle$, from Raman scattering studies. The latter was found to have negative values in a nematic phase[28] and this result could not be explained on the basis of existing theories of the nematic state. It is desirable to examine the variation of $\langle P_4(\cos\theta)\rangle$ in other nematic liquid crystals as well in order to understand the effects of molecular structure on this order parameter. In this connection, as the —C≡N vibration in CBOOA is also Raman active, it is of interest to carry out Raman scattering studies on CBOOA and compare the experimental values of $\langle P_4(\cos\theta)\rangle$ with theoretical predictions.

The far-infrared spectra of crystalline CBOOA give evidence of pretransition effects as well as intramolecular changes near the crystal–smectic A transition. In the fluid phases, the far-infrared absorption appears to be sensitive to the structures of the molecular end chain. In the case of polymesomorphic materials, this offers the possibility of investigating the influence of different types of molecular ordering on flexible end chains and the conformational changes associated with them in each phase.

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