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Vibrational Spectra of Liquid Crystals. XII

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Raman Spectroscopic Study of the Crystalline Forms and the Crystal-Smectic Transition of 4-Cyano 4′-Octyloxybiphenyl

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Recent papers by Gray *et al.*[1] have discussed the synthesis, structure, and properties of the mesomorphic 4-cyano, 4′-alkyl (or alkoxy) biphenyls. The reports on these materials have made mention of the existence of solid state dimorphism for certain homologs. This paper discusses this dimorphism as it manifests itself in the Raman spectrum of the octyloxy homolog (hereinafter referred to as 8OCB) in the CN stretching region.

The approach used involves direct measurement of the Raman spectrum as a function of temperature, as well as computation of a correlation function obtained from the Raman band envelope by means of Fourier transformation. The application of this correlation function technique to this system has been discussed by us recently in detail.[2,3]

Gray and Mosley,[4] in a recent study of the Raman spectrum of 4-cyano, 4′-pentylbiphenyl note that the CN stretch of this compound is a doublet in the solid phase (2224 and 2233 cm^{-1}), but only the 2224 cm^{-1} band appears in the nematic phase. They further report that only a single band appears in the CN stretching spectrum of solid 4′-heptyl-, -hexyl-, and -butyl-derivative. They speculate that the doublet might appear in the spectrum of the metastable solid phase of the heptyl homolog.

In this work, we show that for 8OCB this is not the case. Rather, a doublet is observed for the stable solid but not for the metastable. The origin of this doublet is discussed, and all of the CN stretches for stable solid, metastable solid, and smectic liquid crystal are analyzed from the viewpoint of the vibrational relaxation correlation function.

EXPERIMENTAL

The experimental set up used has been described in detail previously (3). Experiments were run using both the Spex and J-Y Instruments SA spectrometers described in the previous paper. 80CB was purchased from BDH

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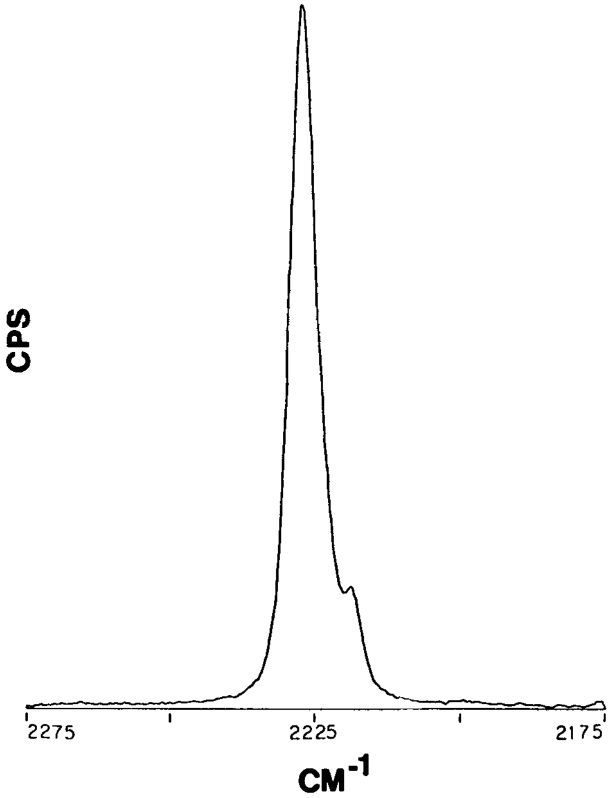

FIGURE 1 Raman spectrum of polycrystalline 8OCB in the CN stretching region. Note that intensity of the shoulder may vary from sample to sample. This spectrum shows minimum height of shoulder, obtained in annealed sample. Spectrum taken at 27°C.

Chemicals, England. The specified purity was 99.5 %. The samples were used without further purification. Each of the spectroscopic measurements has been made at least six times. The errors in wavenumber measurements given in the Results section are standard deviations computed from these sets of measurements.

RESULTS

Figure 1 shows a Raman spectrum of polycrystalline 8OCB at 27°C in the CN stretching region. This band is well isolated from other modes of the molecule. There is a strong peak with a maximum at 2227.6 ($\pm$0.8) cm^{-1} and a shoulder at 2218.0 ($\pm$1.1) cm^{-1}. When this sample is heated into the

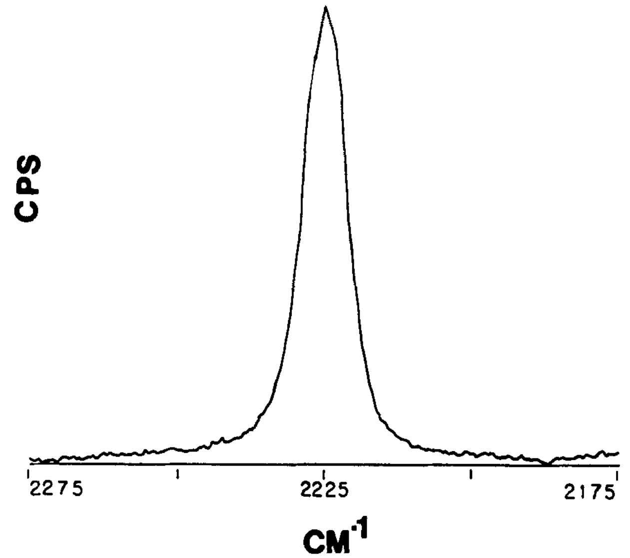

FIGURE 2 Raman spectrum of smectic 8OCB in the CN stretching region. $T = 60°C$.

smectic phase, the spectrum seen in Figure 2 is obtained. This consists of a single band with maximum at 2225.1 (± 0.4) cm^{-1}. If this sample is now cooled back into the crystalline phase, and the Raman spectrum examined at once, the spectrum (Figure 3) still consists of a single band, but with maximum at 2222.4 (± 0.4) cm^{-1}. The shape of the band is also considerably different from that observed in the smectic phase. This will become clearer from the correlation function studies reported below.

When a freshly crystallized sample is allowed to remain at room temperature for about 3 days, the shoulder on the CN stretching peak reappears. This process can be speeded up by annealing at higher temperatures (in the solid state). The metastable crystalline form has an appreciably lower melting point (48°C) than does the stable form (54.5°C).

There are many possible reasons why a peak in this spectral region may shift in frequency, grow or lose a shoulder, change shape, etc. The phenomenon occurring here is partially clarified by an experiment shown in Figure 4. Here the stable solid is examined at a series of temperatures close to the crystal-smectic phase transition, but still within the crystalline phase. As the *c-s* transition is approached, the shoulder appears to grow in intensity at the expense of the higher frequency band. Actually, the positions of the maxima are also changing. Lowering the temperature slightly indicates that there is reversibility characteristic of a rather mobile equilibrium of some sort in this phase.

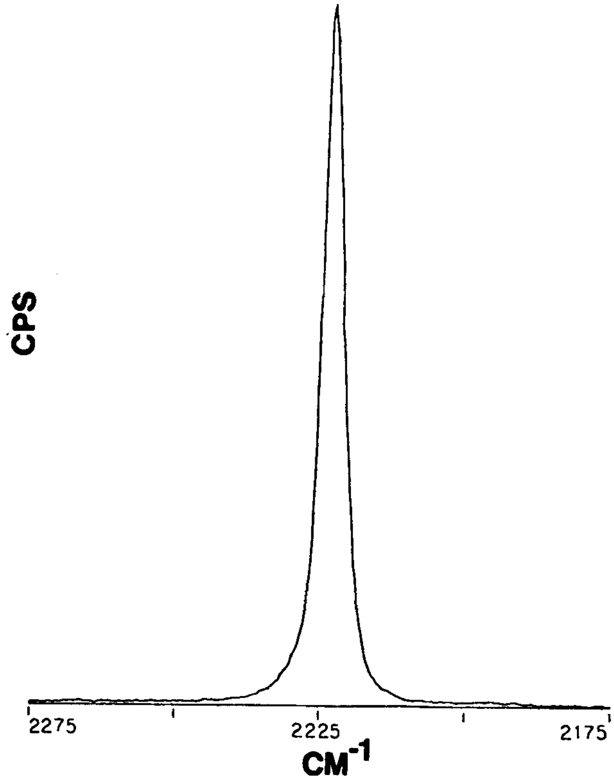

FIGURE 3 Raman spectrum of metastable polycrystalline 8OCB, quenched rapidly from the smectic phase $T = 27°C$.

As discussed in our earlier papers,[2,3] it is useful to examine the processes involved here in the time as well as frequency domains. This is done by computing a normalized correlation function, $C(t)$

$$C(t) = \frac{\int_{\text{band}} I(\omega) e^{i(\omega + \omega\ )t} \mathrm{d}\omega}{\int_{\text{band}} I(\omega)\, \mathrm{d}\omega}$$

from the Raman band. As shown previously[3] there is no doubt that this correlation function is a pure vibrational relaxation function, with no reorientational component. It is likely to be due to dephasing processes.

Figure 5 shows the correlation functions for the CN stretching band of the smectic liquid crystal, stable crystalline, and metastable crystal phases. The $C(t)$ for the metastable crystal indicates that this phase relaxes much less efficiently than does the stable crystal. The relaxation here is in turn much slower than that of the smectic liquid crystal.

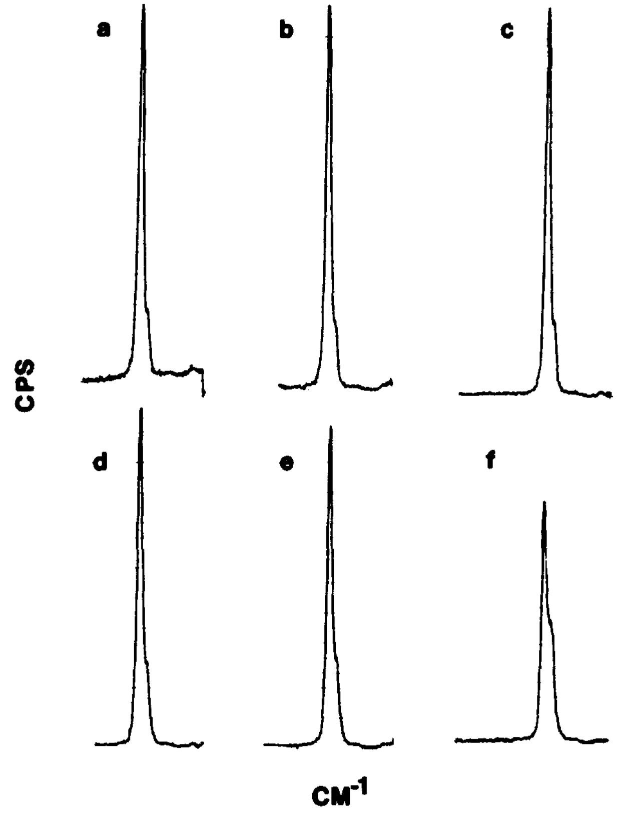

FIGURE 4 Raman spectra of polycrystalline 8OCB, taken in the 2175 to 2275 cm^{-1} region (as in Figure 1-3). Spectra (a)-(c) are at 27°, 37° and 50°C respectively and show no variation in shoulder/main peak ratio. Spectra (d) at 51°, (e) at 53° and (f) at 54°C show increasing shoulder/main peak intensity ratio. Changes are reversible, i.e. if sample is cooled back to 50° shoulder returns to lower intensity.

To summarize these results, each of the three phases discussed here has a distinct Raman spectrum in the CN stretching region. Both the position of the frequency maximum or maxima and the band shape differ. By contrast, as shown in Ref. 3, the CN stretching region spectra of smectic, nematic, and isotropic 8OCB are identical both in frequency and band shape.

DISCUSSION

While the crystal structure of 8OCB has not been reported, it seems reasonable to expect, based on crystal structures of other mesogens, that the molecules will be arranged in the crystal with their long axes parallel. There may

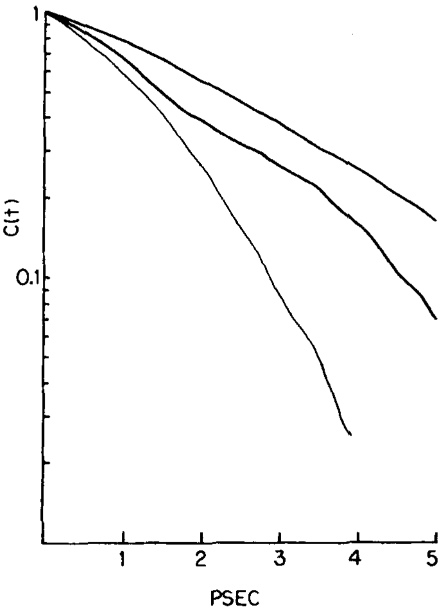

FIGURE 5 Correlation functions obtained from the Fourier transform of the Raman spectra shown in Figures 1–3. The uppermost curve (most slowly relaxing sample) is from the metastable crystal (Figure 3). The intermediate curve is from the stable crystal (Figure 1) and the lower curve, most rapidly relaxing sample, is the smectic liquid crystal (Figure 2).

also be an approximate layer structure. In making the transition from crystal to smectic, a relatively small change in molecular position will be necessary. Some degrees of freedom will, of course, change from hindered rotations and translations, to free. As there is only one smectic phase for this molecule, these will include both motions within and between layers. In this general context we can try to interpret the above results.

In the stable crystalline form, at 27°C, the ratio of intensity of the main peak to shoulder averages to 5.7. However, this shows some scatter (5.1 to 6.0) from sample to sample, never rising above 6.0, however, in a sample that has been equilibrated. It has already been pointed out that thermal history affects this equilibration.

We suggest that the main peak represents the CN stretching frequency of the "pure" stable crystalline modification. The shoulder represents a second species of CN which exists, interstitially within the crystal to the extent of approx. 15%. The energy of the 8OCB on such sites must represent a local minimum with a small barrier from the stable energy sites. Hence a well defined CN stretching frequency results from each site. There is also a mobile equilibrium between sites which is observable near the phase transition.

Turn now to an interpretation of the metastable crystalline phase. It is noteworthy that the melting point of this phase is appreciably lower than that of the stable phase. This has already been mentioned by Gray[1] for several such polymorphs in this homologous series. For the metastable form to be lower melting, either it must be more ordered than the stable form, or the intermolecular interaction in the metastable form must be weaker, assuming that the enthalpy and entropy of the smectic phase at 48° are essentially the same as at 54°.

In the experiments reported here, only one aspect of the order and intermolecular forces is probed, namely that in the vicinity of the CN group. As pointed out by Bulkin and Grunbaum,[5] the dipolar interactions in a mesogenic crystal such as this one represent only a very small part of the intermolecular potential. Most of the energy is in interactions between the non-polar portions of the molecules.

The CN stretching frequency is hardly changed in the metastable crystal vis à vis the stable crystal. The observed frequency falls only about 5 cm^{-1} from the maximum in the stable form. Indeed, the perturbation in the stable solid form is greater than the shift to metastable solid. Thus we believe that there is no significant difference in intermolecular forces with respect to the CN group.

The correlation functions show that the ordering of molecules around the CN group is affected significantly, however, as we convert from metastable to stable phase. The reasoning behind this conclusion is based on work of Bratos,[6] Kubo,[7] and Rothschild.[8] It is analogous to the argument in frequency space that the change from a perfectly ordered environment for an oscillator to one which is disordered should be accompanied by a broadening of the band resulting from a superposition of overlapping bands, shifted from the frequency of the unperturbed oscillator. The result has a Gaussian shape. The effect of disorder on the correlation function is complicated by the possibility that molecular motion may mean that the instantaneous local fields do not exist long enough to significantly change the vibrational frequency. In this case a Lorentzian line shape ($C(t)$ linear as plotted in this paper) should result. Usually, this transition from Gaussian to Lorentzian band shape, known as "motional narrowing" is associated with liquids and solutions. However, it is possible that in comparing correlation functions from two solid phases, a difference in density could change the effect of collisions on the vibrational relaxation correlation functions.

The more rapid relaxation of the stable crystalline modifications is consistent with a greater number of distinct environments in this phase, compared to the metastable phase. Form this viewpoint then, the metastable phase is more ordered than the stable phase. Consistent with this is the much faster relaxation of the smectic phase, which is the most disordered of the three.

This conclusion relating to the relative order of the three phases leads back to the discussion of the two bands present in the stable solid. The interstitial imperfection in the stable crystal structure, manifesting itself as a shoulder on the CN stretching band, can be seen as the source of the disorder in this phase. In the metastable solid we must achieve order near the CN group through a freezing out of a single intermolecular structure, perhaps a "frozen smecticlike crystal". It should be stressed that this is an important observation because it is counterintuitive. The metastable solids are usually thought of as disordered, more like a "frozen liquid structure." In the one case (to our knowledge) examined via vibrational relaxation correlation functions,[9] *viz.* solid and glassy quinoline, it was indeed found that the correlation functions for the glassy phase decayed more rapidly than the crystalline. Further work is necessary to establish the nature of ordering in this metastable phase, and the extent to which similar observations may occur in other solid mesogenic polymorphs.

References

1. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1974), Vol. 2, p. 617.
2. K Brezinsky and B. J. Bulkin, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1978), Vol. 3, p. 355.
3. B. J. Bulkin and K. Brezinsky, *J. Chem. Phys.*, **69**, 15 (1978).
4. G. W. Gray and A. Mosley, *Mol. Cryst. Liq. Cryst.*, **35**, 71 (1976).
5. B. J. Bulkin and D. Grunbaum, *J. Phys. Chem.*, **79**, 821 (1975).
6. S. Bratos and E. Marechal, *Phys. Rev. A*, **4**, 1078 (1971).
7. R. Kubo, in *Fluctuations, Relaxation, and Resonance in Magnetic Systems*, edited by D. Ter Haar (Oliver and Boyd, Ltd., London, 1962), p. 23.
8. W. G. Rothschild, *J. Chem. Phys.*, **65**, 455 (1976).
9. W. G. Rothschild, in *Molecular Motions in Liquids*, edited by J. Lascombe (Reidel, Dordrecht, 1974), p. 247.