

### Assignment of far infrared absorptions in liquid crystalline 4-n-heptyl-4'-cyanobiphenyl

by C. J. REID and M. W. EVANS

Chemistry Department, University College of Wales,  
Aberystwyth SY23 1NE, Wales

(Received 26 November 1979; revision received 15 April 1980)

Our aim is to clarify by experimental methods the nature of the far infrared absorption of the nematogen 4-n-heptyl-4'-cyanobiphenyl (7CB). This was first studied in the far infrared in the nematic and glassy states by Evans *et al.* [1], and a subsequent note [2] has dealt with the effect of an applied electric field on the nematic phase absorption. The effect of an electric field is well understood in terms of the generation of a macroscopically ordered system, but on a molecular level the mechanism of alignment is still to be evaluated in detail. The spectroscopic effects in the far infrared are pronounced and to understand these in molecular terms it is of interest to investigate the origin of the various peaks observed in the far infrared spectrum. Some of the earlier interpretations in this field [3] (such as that on 4-methoxybenzylidene 4'-n-butyl aniline (MBBA), in various phases) may then be revised. The theoretical indications are that the equivalent of the Poley absorption in nematogens is split, in rational accord with the recent findings of Price *et al.* [4, 5] in the microwave.

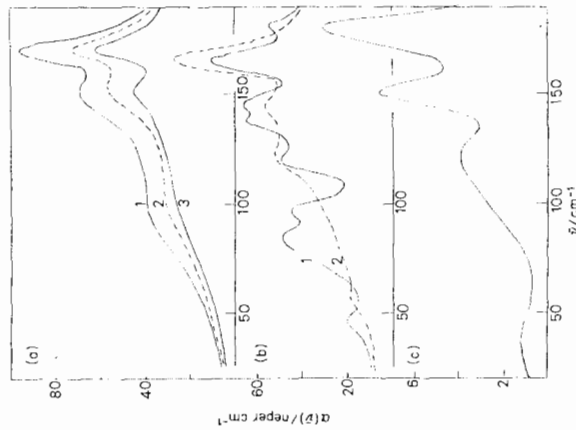
In addition to dielectric relaxation the nature of the liquid crystal phases has been investigated by a variety of techniques, including [5] Raman, Brillouin and neutron scattering, ultrasonic attenuation and N.M.R. Purely hydrodynamic theories cannot be expected to explain the results from such a wide range of experiments, and particularly in the far infrared we are able to focus on the details of molecular behaviour at short times and over short distances, comparable with the intermolecular spacing. We have therefore attempted to use molecular theories [6] to explain the spectra of nematic MBBA, cholesteryl oleyl carbonate (OCC) and nematic 7CB. For MBBA and OCC the low frequency bands (at  $130\text{ cm}^{-1}$  and  $78\text{ cm}^{-1}$  respectively) were assigned in the absence of contrary evidence as the respective unsplit Poley modes in these liquid crystals. In the light of the microwave results [4] these interpretations need revision with the aid of a rigorous molecular theory of nematic phase diffusion currently under development. Models due to Brot [7] and Wylie [8], adapted by Larkin [9] were used to assess the well depth of libration. A Mori approximant [10] for the reorientational (dipolar) autocorrelation function has more recently been used with 7CB to assess semi-empirically the equilibrium mean square torque from some of the observable spectral features. The complexity of these latter calls for more precise measurement and interpretation than has hitherto been possible.

Here we present far infrared spectra of 7CB in various environments in an attempt to analyse the complete spectrum for vibrational (proper) modes and

the intermolecular modes which represent the Poley absorption in the nematic as opposed to the isotropic phase.

Spectra were recorded using a phase modulated Grubb-Parsons/N. P. L. Michelson Cube interferometer, with cells as described elsewhere. One experimental difficulty encountered in obtaining the spectrum for the nematic phase of pure 7CB was that the absolute intensity depended on the thickness of the sample and so the technique of ratioing thick to thin samples cannot be used. For a 0.8 mm path length of sample the reproducible spectrum of the nematic at 298 K is shown in the figure as the broken curve, while for a 0.3 mm sample the intensity has increased uniformly over the range as in curve (2). In each case the spectrum emergent through the same cell containing decalin is used as background. Clearly the untreated poly(4-methyl pent-1-ene) window surfaces are aligning the samples, an effect which can be observed visibly, the thinner samples appearing almost transparent without the scatter (opalescence) that arises from non-uniform bulk samples. In view of this our path lengths are quoted.

To assign the peaks we recall that the dipole in 7CB is almost entirely along the biphenyl linkage. However the heptyl chain is predominantly trans (not completely so from N.M.R. results [11]) so that rotation of the molecule as a whole about the *A* inertia axis (the smallest) is far infrared active, i.e. produces dielectric loss at this and lower frequencies. This mechanism has been treated



Far infrared absorption spectra of 7CB in the nematic, crystal and solution states. (a) Nematic phase at 298 K. (1) Unaligned, path length = 0.8 mm; (2) homeotropic alignment by cell windows (untreated poly(4-methyl pent-1-ene), 0.3 mm); (3) partial homogeneous alignment of (2) by 15 kV/cm electric field perpendicular to the beam. (b) Single crystal at 290 K. (1) *Z* axis perpendicular to the plane of polarization; (2) *Z* axis parallel to the plane of polarization. (c) 10 per cent v/v 7CB in decalin glass at 110 K.

with a Smolchowski equation by Price and Evans [4]. In view of the far greater hindrance to libration about the *B* and *C* axes, that about the *A* axis is associated with a low activation energy with a different Poley peak frequency  $\nu_{\text{max}}$  in the far infrared. All three modes are therefore infrared active, i.e. libration about the *A*, *B* and *C* principal inertia axes. To complicate the complete far infrared spectrum there are in addition two C-N torsional modes of different frequency which give fluctuating dipole components normal to the *A* axis. These two can be identified by comparison with the far infrared spectrum of 4-cyano-biphenyl, which does not form a nematic phase but does have an identical pair of peaks in the 140 to 180  $\text{cm}^{-1}$  region. Augmenting this information is the single isolated benzonitrile proper mode at 170  $\text{cm}^{-1}$ . Using this argument the peaks in the figure can be assigned as C-N torsions at 150  $\text{cm}^{-1}$  and 170  $\text{cm}^{-1}$ . The two peaks in the nematic phase do not change their frequencies either on warming to the isotropic phase above 308 K or on dilution in non-dipolar solvents. These isotropic and solution state spectra are not sufficiently accurate to distinguish changes in the Poley shoulder although solvent shifts are expected, paralleling those found [12] amongst isotropic solutes such as acetonitrile or  $\text{CH}_2\text{Cl}_2$  in various solvents. However, there is some evidence in our spectra that the relative intensity of the two peaks changes on dilution so that it is possible that part of the absorption in this region is due to dipole-dipole interaction of C-N groups.

To characterize further the 7CB far infrared absorption, spectra of the crystalline state were recorded at 290 K and at 110 K; the former is shown in the figure (b). The crystal was formed in a 0.2 mm cell by cooling an isotropic sample through the ordered nematic phase to a temperature 2 K below the melting point. By attempting to avoid supercooling an almost perfect single crystal was grown through trial and error, the growth occurring slowly at this temperature. Several peaks are now apparent, the two at highest frequency, C-N torsions, remaining similar to the liquid state doublet. The other features in the single crystal appear to be remnants of the Poley band shifted to lower frequency upon solidifying and resolved into two (or more) lattice modes at 85 and 97  $\text{cm}^{-1}$ .

These differences on crystallization reflect well-known structural changes through the phase transition. Inspection of the single crystal at its edges indicated a unique axis with the plane of the sample implying absence of cylindrical symmetry along the optic axis. Using this direction as a reference, referred to here as the *Z* axis, spectra were recorded in polarized light for both parallel and perpendicular orientations of *Z*. In the perpendicular orientation the resulting spectrum is very similar to curve (1) of the figure (a), but for *Z* parallel to the plane of polarization curve (2) indicates a suppression of the peaks at 85 and 97  $\text{cm}^{-1}$ . There is also evidence that the torsional modes above 140  $\text{cm}^{-1}$  have changed their relative intensities.

A number of cells were used with which it was possible to apply electric and magnetic fields to the nematic phase. The electric field apparatus operated at 1 kHz, with fields of 2 kV/cm to 20 kV/cm. Because the compound has a positive dielectric anisotropy ( $\Delta\epsilon = 11$ ) the application of an electric field in the *x* or *y* direction across a measuring beam in the *z* direction perpendicular to the window surfaces should align the molecules in the opposite sense to that of the windows. For a 0.3 mm sample the integrated absorption intensity was decreased across the whole far infrared range by applying the electric field in this

sense. This decrease is approximately linear with field strength up to the maximum of about 15 kV/cm. A rapid and reversible realignment by the windows is observed on removing the field. The spectrum for an electric field alignment is shown in the figure (a), curve (3), for the same sample as in curve (2). An almost perfect uniform decrease has occurred except that the Poley band appears to have broadened. The comparison of curves (2) and (3) and the reversibility of the field effect again supports our assignments. When a magnetic field was applied in the  $x$  direction, parallel to the windows and perpendicular to the  $z$  axis of the measuring beam, the far infrared integrated intensity again decreased uniformly, being linear with a field strength of up to 1 T. No effect was found when a weaker magnetic field was applied in the  $z$  direction of the beam, suggesting that window alignment is already complete and the orientation of fields across the beam did not depend on its polarization plane.

Finally, to support the assignment made at ambient temperature a sample of 7CB was dissolved in decalin and its spectrum (figure (c)) recorded at 110 K in the decalin glass. This treatment might be expected to narrow and resolve the intramolecular proper modes. The Poley mode shoulder at 100  $\text{cm}^{-1}$  has narrowed at 110 K and peaks at higher frequency, as do most librational modes on supercooling dipolar solutions. In addition, a weaker peak has appeared in the solution at 35  $\text{cm}^{-1}$ . This is taken to be whole molecule libration about an axis perpendicular to  $C$ . The figure therefore brings out clearly the basic underlying features of the pure 7CB nematic phase spectra. These are summarized as follows:

- (i) a Poley (torsional oscillatory) mode split at 110 K into a 35  $\text{cm}^{-1}$  component and the major 100  $\text{cm}^{-1}$  shoulder;
- (ii) these features overlap two C-N torsions at 150  $\text{cm}^{-1}$  and 170  $\text{cm}^{-1}$ ;
- (iii) the complete far infrared cross section is affected by application of an electric or magnetic field parallel to the measuring beam and perpendicular to the cell windows.

A theory is being developed to account for the complete zero-THz features of 7CB, as described here, and elsewhere.

The Science Research Council is thanked for financial support.

#### REFERENCES

- [1] EVANS, G. J., and EVANS, M. W., 1977, *J. chem. Soc., Faraday Trans. II*, **73**, 285.
- [2] EVANS, G. J., and EVANS, M. W., 1978, *J. chem. Soc., Chem. Commun.*, p. 267.
- [3] EVANS, M. W., DAVIES, M., and LARKIN, I., 1973, *J. chem. Soc., Faraday Trans. II*, **69**, 1011.
- [4] PRICE, A. H., and EVANS, M. W., 1980, *J. chem. Soc., Faraday Trans. II*, **76**, 217.
- [5] OWEN, P. G., PRICE, A. H., and BUKA, A., 1979, *Molec. Crystals liq. Crystals*, **51**, 273, 295.
- [6] MOUTRAN, R., PRICE, A. H., and EVANS, M. W., 1975, *J. chem. Soc., Faraday II*, **71**, 1854.
- [7] BROU, C., 1967, *J. Phys. Radium, Paris*, **28**, 789.
- [8] WYLLIE, C., 1971, *J. Phys. C*, **4**, 564.
- [9] LARKIN, I., 1972, *Faraday Symp.*, **6**, 112.
- [10] MORI, H., 1965, *Prog. theor. Phys.*, **33**, 423.
- [11] LUCKHURST, G. R. (private communication). FABER, T. E., and LUCKHURST, G. R., 1975, *A. Rep. chem. Soc. A*, **72**, 31.
- [12] EVANS, M. W., EVANS, G. J., and DAVIES, A. R., 1980, *Adv. chem. Phys.*, **44**, 255.