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A. Ghanem [a] & C. Noël [a]

[a] Laboratoire de Physicochimie Structurale et Macromoléculaire ESPCI, 10 rue Vauquelin, 75231, PARIS Cedex 05, France

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FTIR Investigation of Two Alkyl-*p*-Terphenyl-4,4″-Dicarboxylates in Their Crystalline, Smectic and Isotropic Phases

A. GHANEM and C. NOËL

Laboratoire de Physicochimie Structurale et Macromoléculaire ESPCI, 10 rue Vauquelin, 75231 PARIS Cedex 05, France

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Fourier transform infrared spectroscopy is used for studying the conformational changes occurring in the crystalline (K), smectic (S) and isotropic (I) phases of diethyl *p*-terphenyl-4,4″-dicarboxylate (DETC) and di-n-propyl *p*-terphenyl-4,4″-dicarboxylate (DPTC). Additional bands observed at the solid-smectic phase transition are interpreted in terms of symmetry and conformational changes both in the aliphatic part and the rigid core. Spectroscopic evidence for modifications of the latter is also observed at the crystal$_1$-crystal$_2$ phase transition in DETC. Wavenumber shifts as well as changes in band intensity and halfwidth are analysed in terms of variations of intra- and inter-molecular interactions.

Keywords: FTIR, liquid crystals, phase transitions, conformational changes

INTRODUCTION

Vibrational spectroscopy has proved to be useful in studying the structure and physical properties of liquid crystals. For the interpretation of infrared and Raman spectra we can separate the atomic displacements approximately into internal and external vibrations. The internal vibrations are based on those of the isolated molecule perturbed by the molecular field of neighbouring molecules. The external vibrations are approximately the translational and rotational displacements of the rigid molecule about its centre of mass. The analysis of internal vibrations is expected to provide a good picture

of the conformational changes, which show up in terms of wavenumber shifts, changes in intensity and band shape, while the low-frequency region yields information about the intermolecular forces and the structure.

In this paper we present an infrared spectroscopic study of two liquid crystal materials having the general structure:

The investigated compounds show the following transitions[1,2]:

$$n = 2 \text{ (DETC) } K_1 \xrightarrow{154^\circ C} K_2 \xrightarrow{177^\circ C} S_E \xrightarrow{191^\circ C} S_A \xrightarrow{263^\circ C} I$$

$$n = 3 \text{ (DPTC) } \quad K \xrightarrow{123^\circ C} S_E \xrightarrow{139^\circ C} S_A \xrightarrow{240.8^\circ C} I$$

The smectic E phase, like the smectic A phase, exhibits a layer structure with the molecules orthogonal to the layer planes. However, the E modification has a higher degree of order of the molecules within the layers. Indeed, an additional ordering is obtained through a two-dimensional herring-bone packing of the molecules which extends over long distances.[1-3] Besides, the layers in the smectic E phase are correlated with each other which gives rise to a three-dimensional crystal-like structure. This does not prevent, however, motions of the molecules such as oscillations about their long axes and deformation. To our knowledge, no infrared study of this ordered mesophase has been previously reported.

The objective of this paper is to investigate by vibrational spectroscopy the structural differences of DETC and DPTC which occur in going from one phase to another. Wavenumber shifts and intensity modifications are interpreted in terms of symmetry and conformational changes. The solid crystalline polymorphism in DETC is also discussed.

EXPERIMENTAL

DETC and DPTC were prepared by standard methods. The transition temperatures were checked using differential scanning calorimetry and optical microscopy.

Infrared spectra were recorded with a Nicolet 7199 Fourier transform infrared spectrometer with a $2 cm^{-1}$ resolution. The sample was

placed between two KBr windows and the sandwich cell was then heated by using a Mettler hot stage compatible with the FTIR spectrometer. Solid samples in KBr pellets were also studied. The evolution of the spectra with temperature was qualitatively identical in both cases. Thus, unless mentioned, the results shown and discussed in this paper are those obtained from the samples in KBr cells. In order to carry out quantitative measurements on bands of different absorption coefficients, the thickness of the cell was varied. Because of the Beer-Lambert Law and instrumental restrictions, only bands of absorbance less than 0.7 could be considered.[4,5]

Infrared spectra were also investigated for dilute solutions in chloroform and carbon disulfide.

Peak frequencies were determined with cubic spline peak picker software available with the spectrometer.

Raman spectra of DETC in the K_1 crystalline phase, and in chloroform solution were recorded with a Coderg T 800 spectrometer using about 500 mw of the 5145 Å line of an ionized Argon laser as the exciting line. The resolution was 2.5 cm^{-1}.

RESULTS AND DISCUSSION

From the infrared spectra of DETC and DPTC in their crystalline (K), smectic (S) and isotropic (I) phases, it appears that the most prominent changes occur at the K_1-K_2 and the K_2-S_E transitions for DETC and at the $K-S_E$ transition for DPTC. In contrast to this, the transitions S_E-S_A and S_A-isotropic liquid occur smoothly without noticeable alteration of the spectrum. This is especially true for the appearance in the S_E phase spectra of additional bands at 1210, 1180, 860, 778 and 729 cm^{-1} (Figures 1 and 2). The appearance of new infrared bands at the crystal–liquid crystal transition is consistent with previous spectroscopic studies on liquid crystals.[6,7] This could result from a change in the unit cell symmetry and/or the molecular symmetry as chemical groups rotate within the molecule. In the investigated compounds, such an intramolecular process could be due to rotations of the benzene rings, the ester groups and/or the aliphatic groups. A deeper insight into the temperature dependence of the spectra points out that all these chemical groups are involved in the phase transition.

X-ray data reported for diethyl terephthalate in the crystalline state indicate that the conformation of the carboxyl groups relative to the aromatic ring is "trans".[8] Stokr *et al.*[9] observed a band at 1174 cm^{-1}

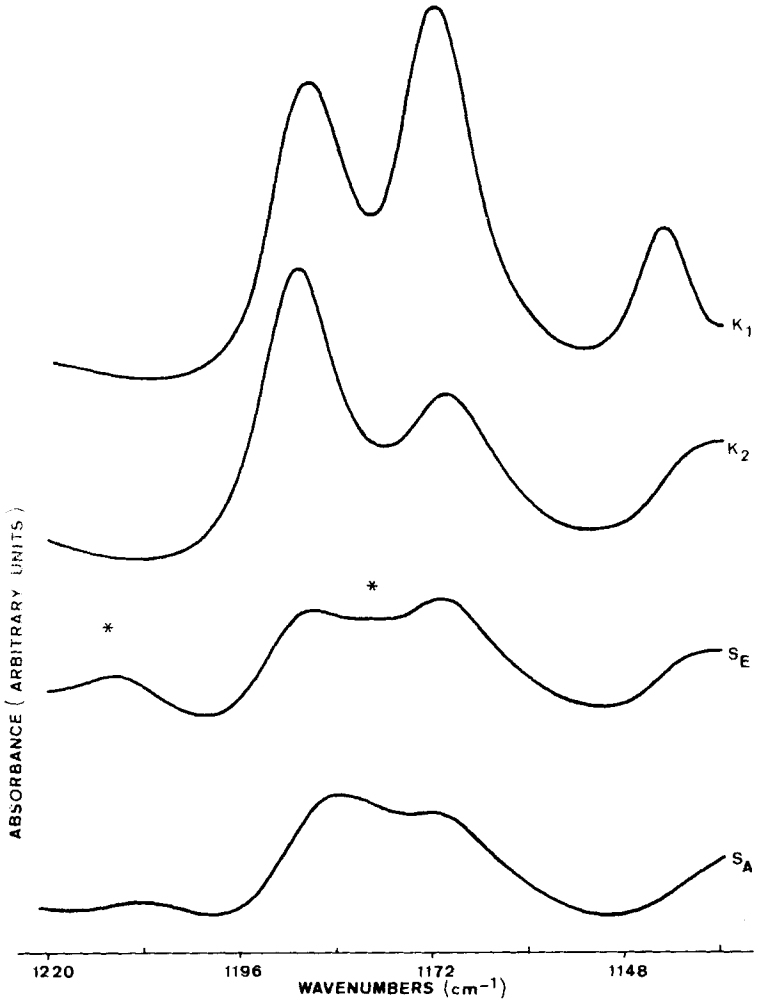


FIGURE 1 FTIR spectra of DETC in the crystalline, smectic and isotropic phases (*a*) 1136–1220 cm^{-1} region (*b*) 705–880 cm^{-1} region.

in the spectrum of diethyl terephthalate in the molten state. By considering the vibrational spectrum of ethyl benzoate,[10] they assigned this band to the aromatic frame, its appearance being an indication of the loss of the symmetry centre of the molecule as a result of the rotation of the two carboxyl groups out of their planar "trans" conformation. Support for such an interpretation is obtained from experimental observations on dimethyl terephthalate. Indeed, the mo-

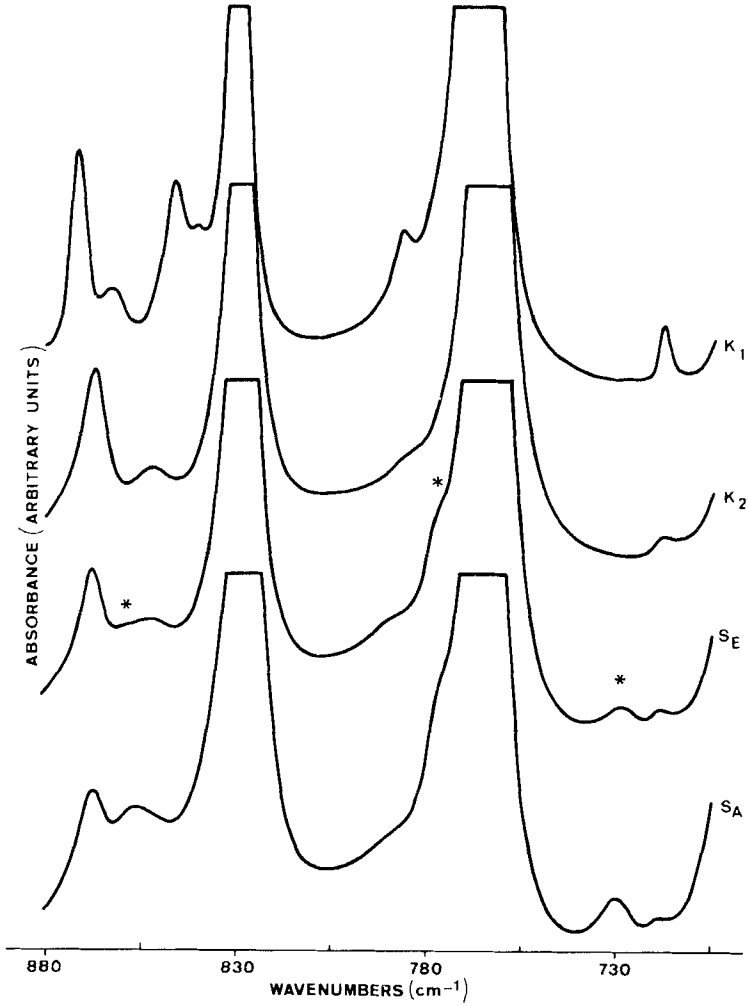


FIGURE 1 (*con't.*)

lecular conformation in the crystalline state was found to be "trans," the phenyl ring standing at an angle 4.7° to the plane of the carboxyl group.[11] However, infrared and Raman studies[12] indicated that the populations of the "cis" and "trans" conformers are nearly the same in the melt. As the chemical structures of these compounds resemble those of DETC and DPTC, we assign the 1180 cm^{-1} band to the aromatic frame, its appearance in the smectic E phase being due to the loosening of the selection rules.

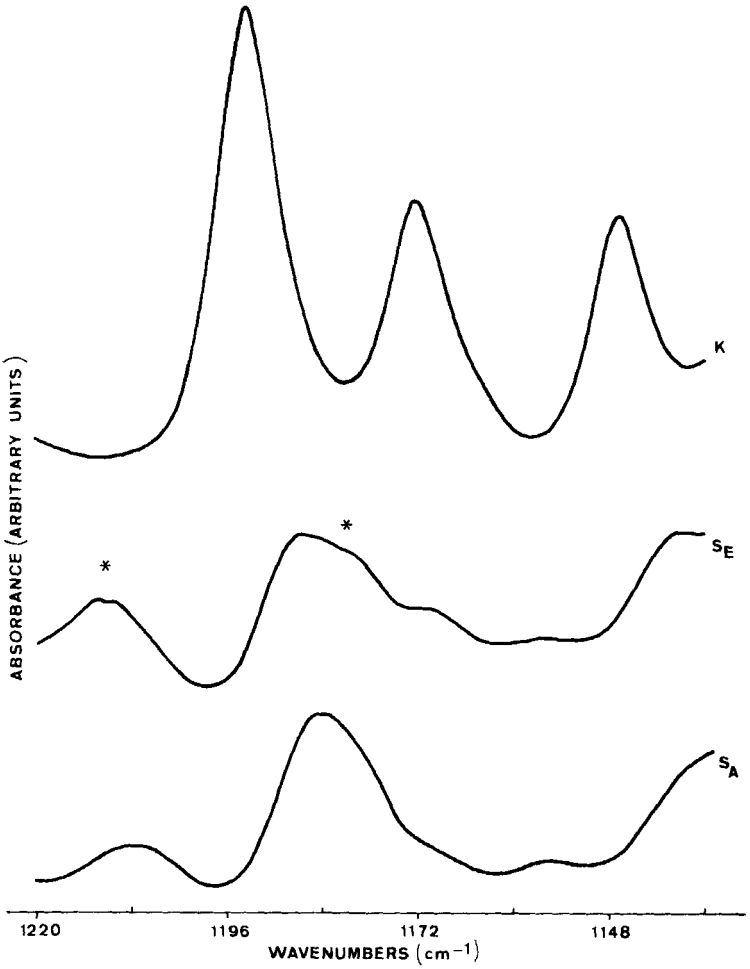


FIGURE 2 FTIR spectra of DPTC in the crystalline, smectic and isotropic phases (*a*) 1136–1220 cm^{-1} region (*b*) 705–880 cm^{-1} region.

In the carbonyl stretching region, two bands are observed at 1707 and 1717 cm^{-1} in the K_1 crystalline phase of DETC and at 1710 and 1717 cm^{-1} in the crystalline phase of DPTC (Figure 3). These peak frequencies are those determined after resolution enhancement was obtained either by deriving the spectra in the Fourier space or by using self-deconvolution software available with the Nicolet FTIR spectrometer as described in Reference 13. Upon heating to the K_2

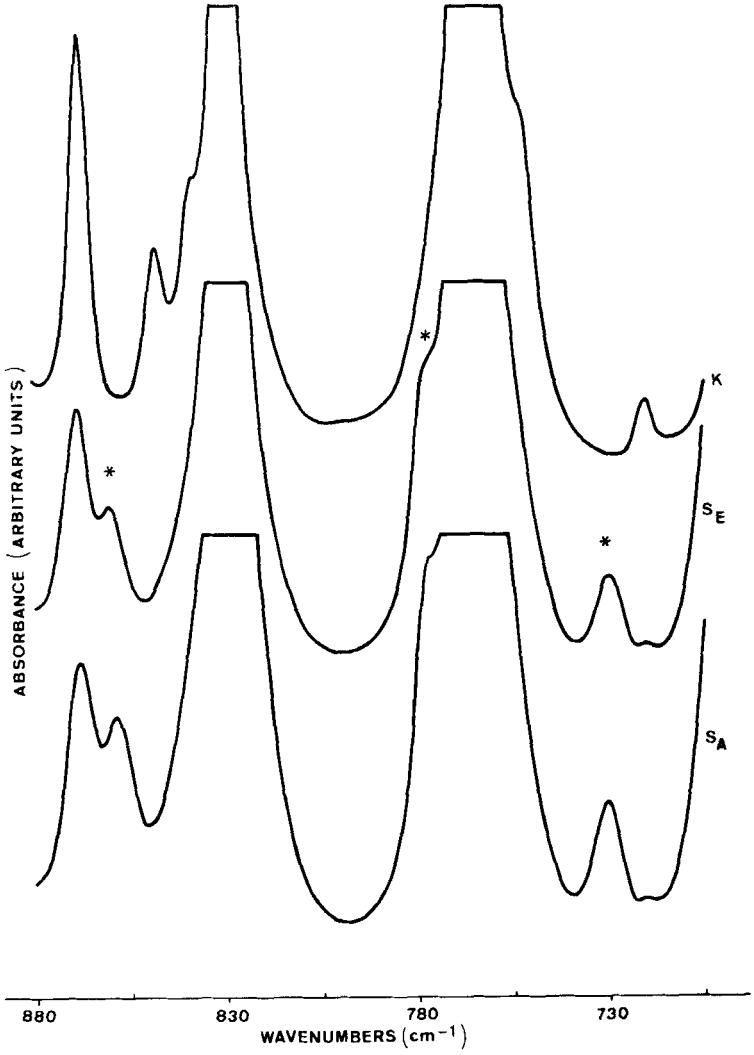


FIGURE 2 (*con't.*)

phase of DETC and the S_E phase of DPTC, these two bands coalesce into a single one which cannot be resolved by the resolution enhancement techniques. This single peak shifts to higher frequency with increasing temperature, passing through abrupt changes at phase transitions. A number of explanations could be offered for the pres-

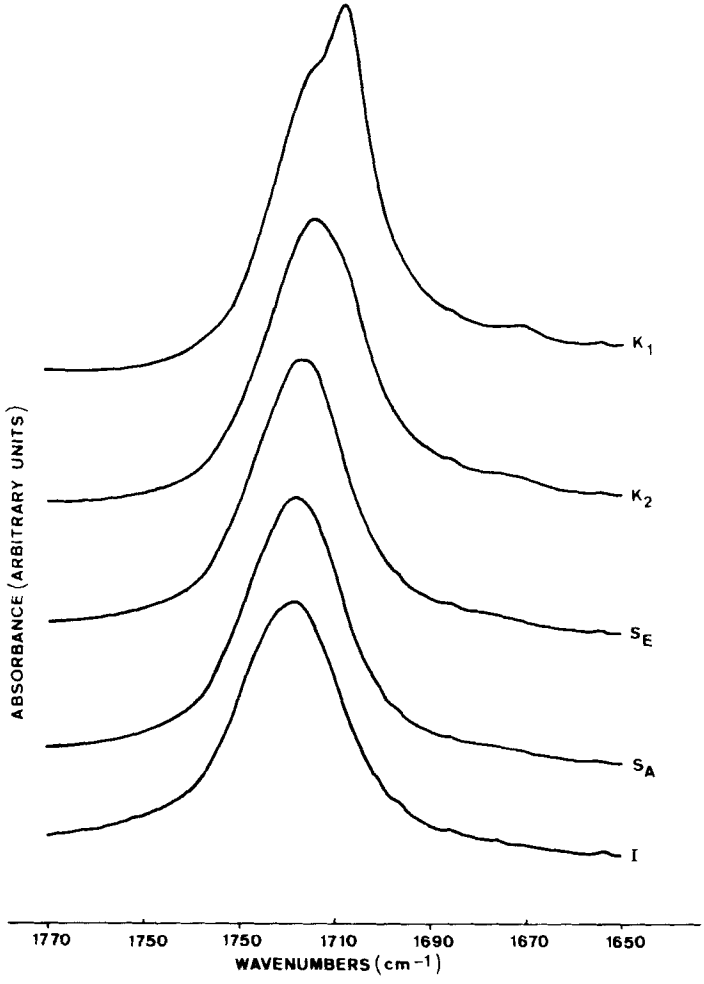


FIGURE 3 FTIR spectra of DETC (*a*) DPTC (*b*) in the C=O stretching range. (in KBr pellets).

ence of the double carbonyl band in the lower temperature crystalline state spectra including i) Davydov splitting, ii) hydrogen bonding and iii) the possibility of the existence of two different conformations for the ester groups. Davydov splitting can be discarded unequivocally because it is absent from the other regions of the spectra and because the resultant single band is not centered midway between the two initial components, but is closer to the higher frequency one (Figure

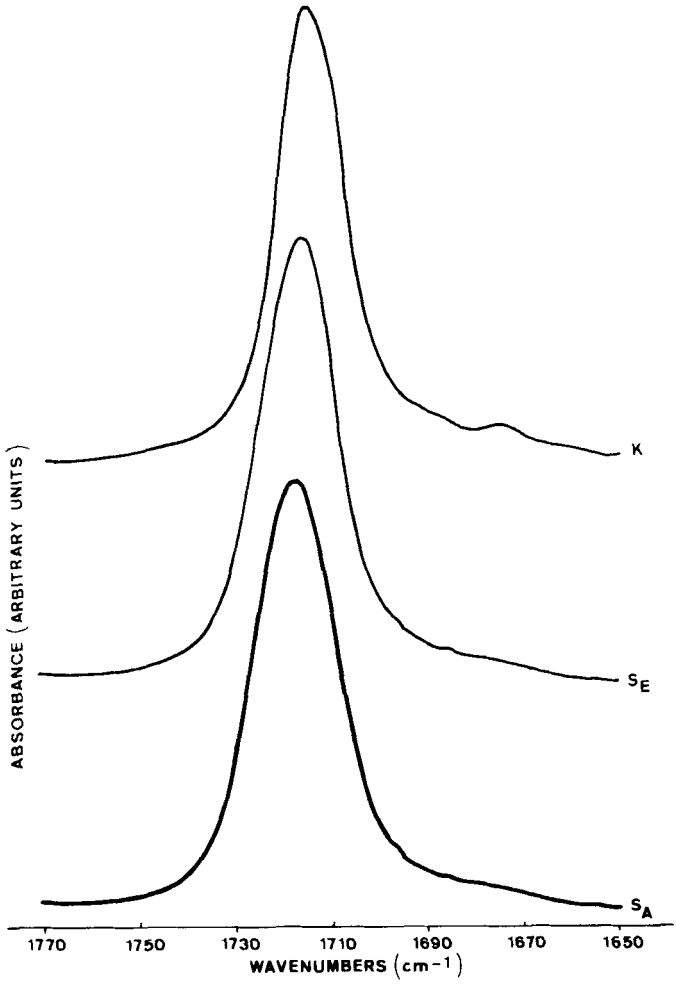


FIGURE 3 (*con't.*)

4). Another possibility is that hydrogen bonds might be formed between the aromatic hydrogens and the C=O of the repeating unit. The capability of forming such hydrogen bonds between aromatic hydrogens and electronegative atoms has been discussed in References 14 and 15. It is commonly accepted that when a hydrogen bond is formed, the C=O stretching vibration shifts to lower frequency. Thus, the double carbonyl band in the crystalline state might originate

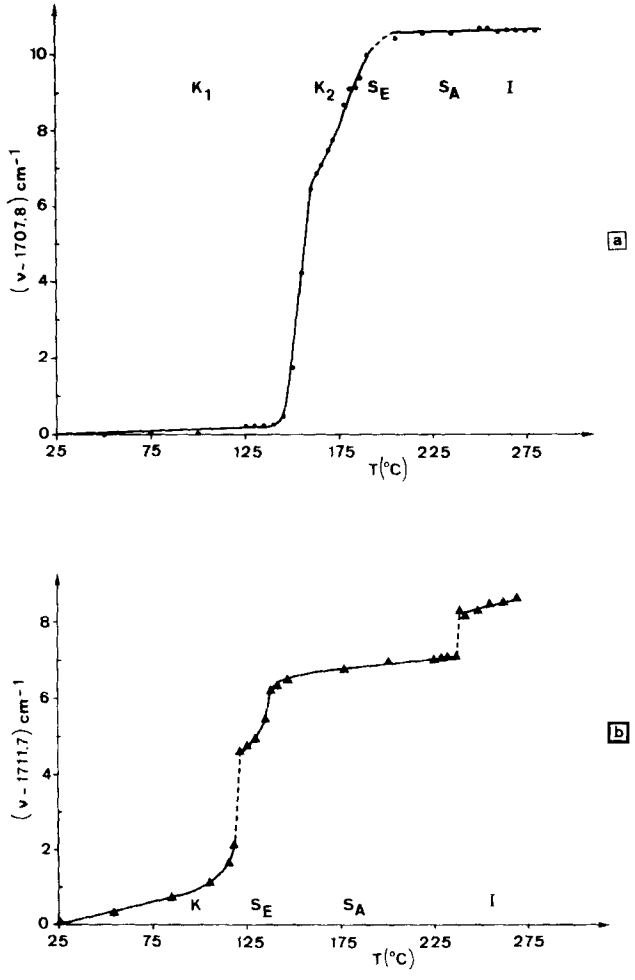
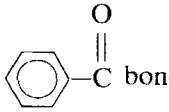


FIGURE 4 Apparent frequency changes observed for the C=O stretching vibration of DETC (*a*) and DPTC (*b*). (in KBr pellets)

from "free" and hydrogen bonded carbonyls. Upon heating up to the less ordered phases, the hydrogen bonds might tend to break as a result of the decrease in intermolecular interactions. Abrupt frequency shifts of the C=O stretching band (Figure 4) might reflect changes in the distribution of hydrogen bonds. Such an interpretation has been recently proposed to account for similar spectroscopic changes observed for thermotropic liquid crystalline polyesters in the C=O stretching region.[16] Alternatively, the existence of two different con-

formations for the ester groups is an equally plausible explanation. Both theoretical and experimental studies on aromatic esters and poly(alkylene terephthalates) have shown that the two coplanar arrangements (trans and cis) of the carbonyl groups and the benzene ring in the terephthaloyl residue are equally likely and are the most probable conformers.[11,12,17–19] However, instead of being confined predominantly to these two planar conformations, rotations about the  bonds resulting in non-planar conformations are also highly probable.[19] A laser-Raman study of polyethylene terephthalate carried out by Melveger[20] supports this prediction of non-planar terephthaloyl residue conformations. From the observed broadening of the C=O stretching band with a decrease in crystallinity, this author inferred that the carbonyl groups may be rotated out of the plane of the benzene ring in amorphous polyethylene terephthalate. In the light of these findings, we believe that the two C=O stretching bands observed in the crystalline state originate from differences in the value of the angle which defines the orientation of a carbonyl group and the adjacent phenyl ring. It is obvious that in the conjugated systems investigated an increase in the dihedral angle will correspond to a lesser extent of delocalization so that the frequency will rise.[21] An increase in temperature is expected to favour the higher-energy non planar conformations and thereby shift the C=O stretching band to higher frequency, which is actually observed (Figure 4).

Of special interest is the band at 463 cm^{-1} which has been assigned to out-of-plane vibrations implying[22] a $\bar{\gamma}_{CC}$ 16b mode.† This band shifts towards higher frequencies with increasing temperature (Figure 5). The same effect has been observed for biphenyl[22] and *p*-terphenyl[23] upon melting. Frequency calculations[22,24] have shown an extreme sensitivity of this mode to changes in the dihedral angles between the planes of the adjacent rings. On the basis of these calculations and previous observations, we interpret the frequency rise as an increase in the dihedral angles of the *p*-terphenyl moiety upon heating, passing through abrupt changes at phase transitions. The large shift observed for this band at the K_1-K_2 phase transition in DETC (from 463 cm^{-1} to 475 cm^{-1}) suggests that conformational changes of the terphenyl group are partly responsible for the solid crystalline polymorphism

†Wilson's notation is used for assignments: E. B. Wilson, *Phys. Rev.*, **45**, 706 (1934).

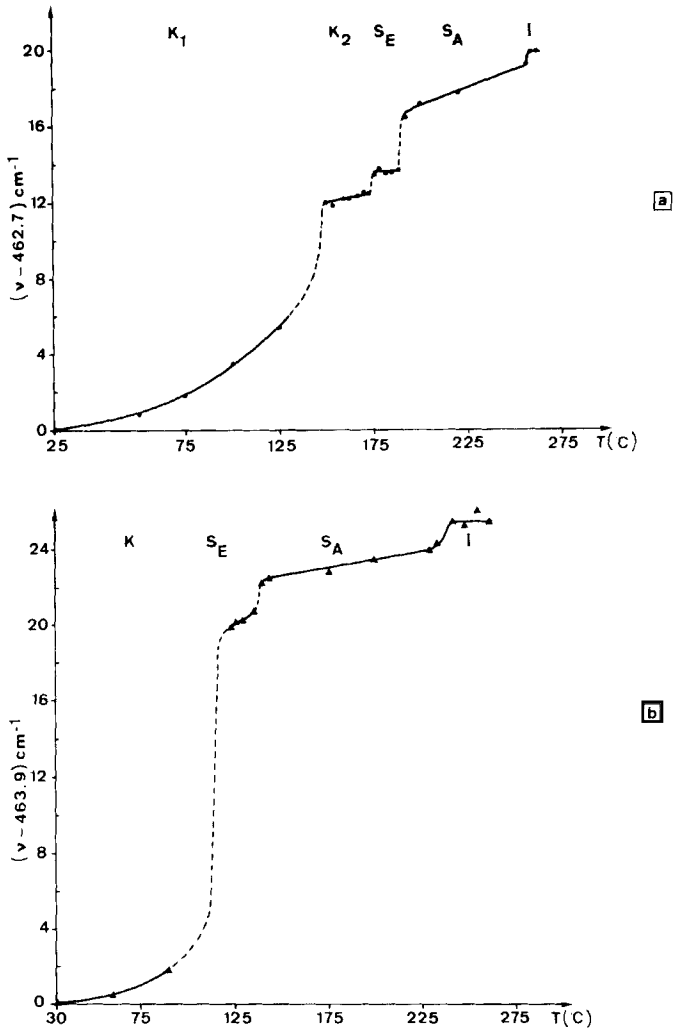


FIGURE 5 Frequency changes observed for the out-of-plane ring mode in DETC (*a*) and DPTC (*b*).

exhibited by DETC. These results as well as other spectroscopic studies[25-27] indicate that solid crystalline polymorphism is partly due to conformational changes in the rigid core of the molecules.

The other new bands which appear at 1210, 860 and 729 cm^{-1} in the S_E phase of DETC and DPTC are probably due to the terphenyl carboxylate part of the molecules. It is to be noted that Raman spectra

of DETC in the K_1 crystalline phase and in solution also reveal two lines at 1217 and 855 cm^{-1} which are polarized in the latter state. Similarly, the new infrared band at 1180 cm^{-1} has a corresponding Raman line at 1179 cm^{-1}. These observations argue for a symmetry change taking place at the crystal-S_E transition. This interpretation may also account for the development of an infrared band at 779 cm^{-1} in the S_E phase (Figures 1b, 2b and 6) which corresponds to a Raman line at 781 cm^{-1} for DETC in the K_1 crystalline state. This situation is quite similar to the activation of a silent mode at 770 cm^{-1} in the infrared spectrum of *p*-terphenyl in the molten state which has been interpreted in terms of changes in molecular symmetry.[23]

The symmetry change evidenced at the crystal-S_E transition is accompanied by modifications of the intermolecular interactions. As can be seen in Figure 7, the methyl deformation band ("umbrella" mode) of DETC displays a downward shift with increasing temperature, passing through an abrupt change at the K_2–S_E transition without further noticeable alteration. Similarly, the methyl deformation band of diethyl terephthalate moves from 1374 to 1369 cm^{-1} on going from the crystalline to the molten state.[9] These shifts indicate that the environment at the end of the molecule is changed. It is to be noted that a soap-like model, that is to say a head-to-head arrangement of the molecules, has been proposed for the di-n-alkyl *p*-terphenyl-4,4″-dicarboxylates in both the S_E and the S_A phases (which is not necessarily the case in the solid state). This could be the reason why the frequency shift of the methyl deformation band is negligible at the S_E–S_A transition but noticeable at the solid–S_E transition (Figure 7).

In the case of DPTC, the occurrence of the broad absorption in the region 1360–1400 cm^{-1} is the result of the overlapping of several bands (Figure 8). Nevertheless, from the temperature dependence of the infrared spectra it is apparent that no downward shift occurs for the methyl deformation band. In fact, this band moves from 1373 cm^{-1} in the crystalline state to 1375 cm^{-1} and 1378 cm^{-1} in dilute solution in carbon disulfide and chloroform, respectively. In the case of some n-hydrocarbons[28] and dodecylcyanobiphenyl[29] Zerbi *et al.* reported that an upward shift of the same order of magnitude takes place upon melting. These authors interpreted this shift of the umbrella deformation mode of the CH_3 group in terms of a general collapse of the "trans" aliphatic chain.

Few spectroscopic studies have been made on smectic liquid crystals, and one cannot make any general statements concerning the origin of the frequency shifts observed in the region 1100–1400 cm^{-1}.

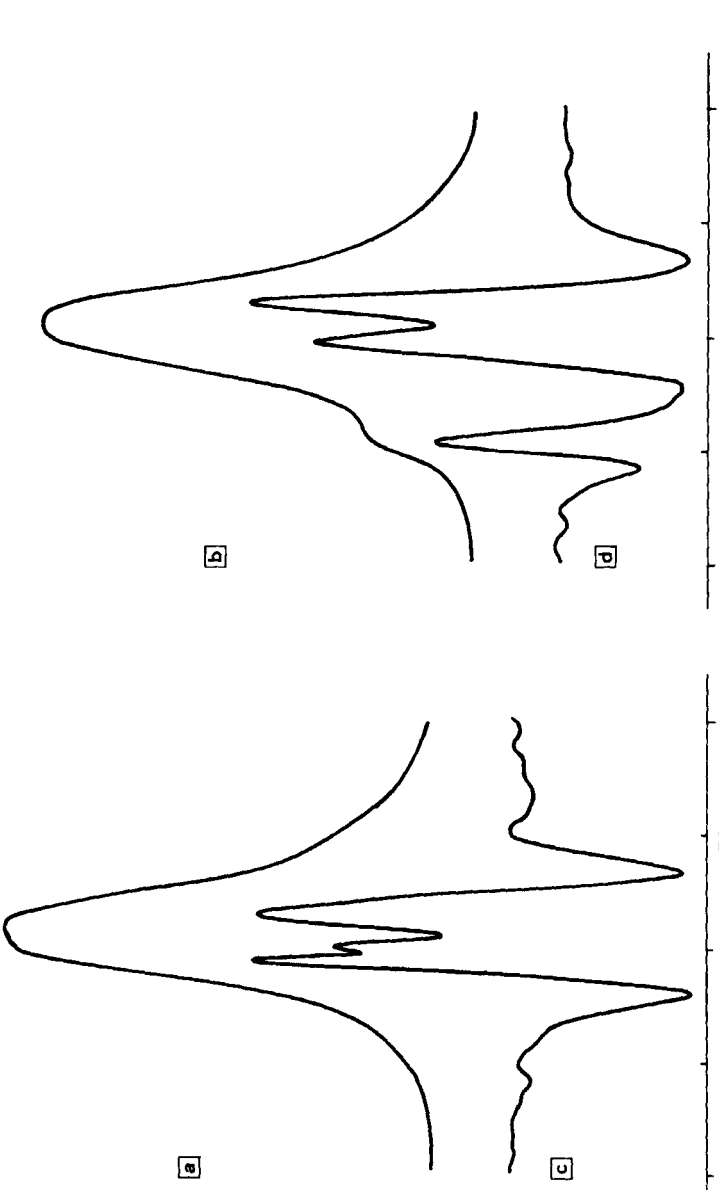


FIGURE 6 FTIR spectra of DPTC in the crystalline (*a*) and S_E (*b*) phases and their corresponding 4th derivatives (*c*, *d*) in the Fourier space: 738–794 cm^{-1}.

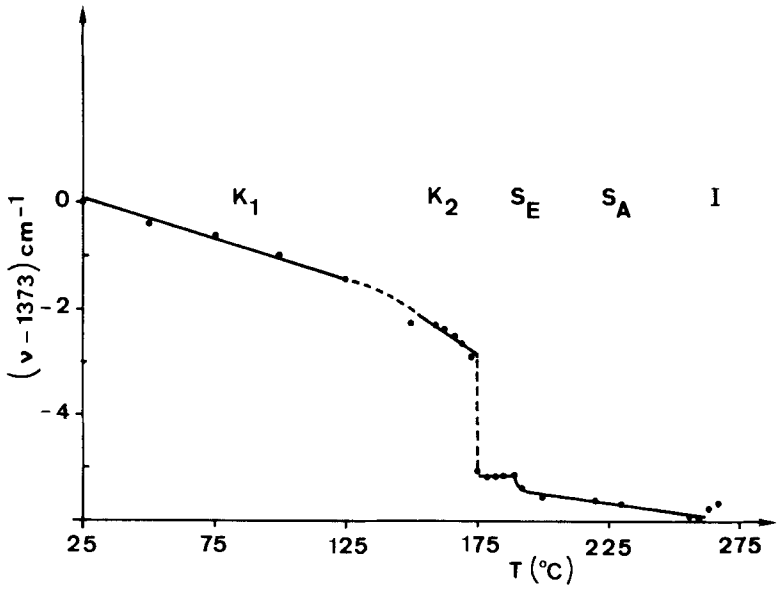


FIGURE 7 Frequency changes observed for the methyl deformation band ("umbrella" mode) in DETC.

Previous workers, by adopting a fairly common view, have interpreted such frequency shifts in terms of a significant change in nearest-neighbour intermolecular interactions at the phase transitions. However, the difference in behaviour of the methyl deformation mode observed between DETC and DPTC reflects the importance of the degree of flexibility of the terminal alkyl groups. As for the carbonyl stretching and the aromatic out-of-plane deformation bands previously discussed, the present results indicate that intramolecular effects such as the rotation of a group with respect to the other groups of the molecule must be taken into account. The same conclusions have been reached by Itoh *et al.*[30] from spectroscopic studies of related azoxy compounds exhibiting different types of crystalline and liquid crystalline phases.

Other examples of changes in intramolecular and intermolecular interactions are given by the frequency shifts of the in-plane ring modes at 1427 cm^{-1} and 1004 cm^{-1} (Figures 9 and 10) and the temperature dependence of the half bandwidth of the C=C stretching and the out-of-plane deformation ring bands (Figures 11 and 12). In passing from the crystalline state through the various mesophases to

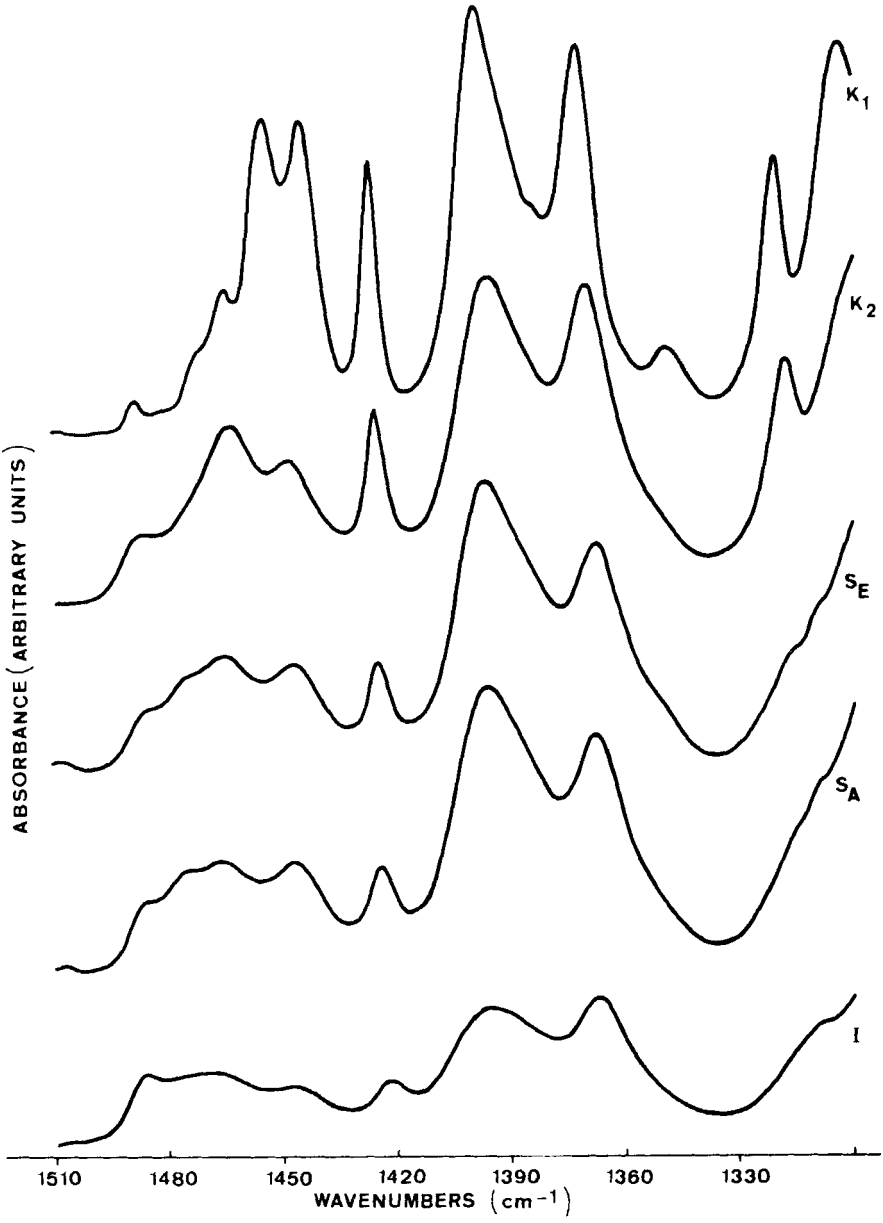


FIGURE 8 Temperature dependence of the infrared spectra of DETC (*a*) and DPTC (*b*) in the 1300–1510 cm^{-1} range.

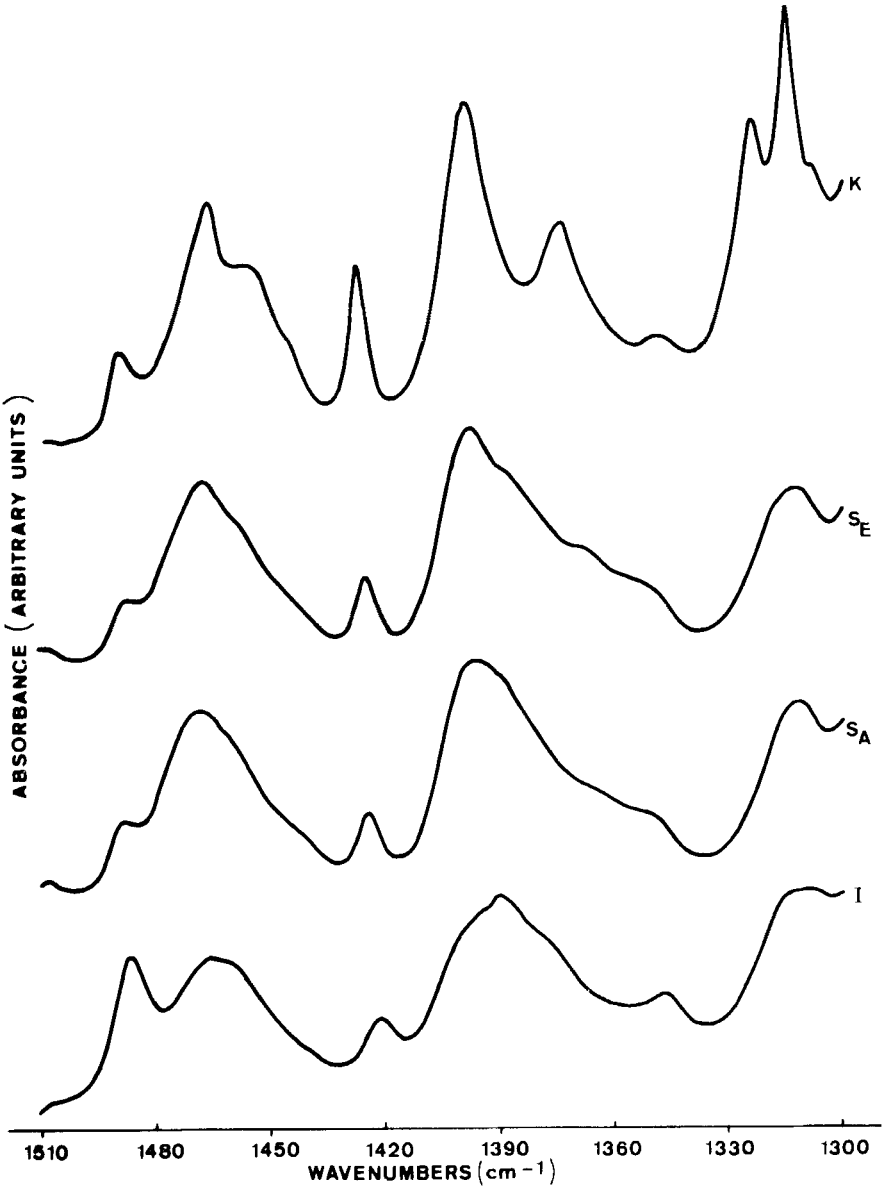


FIGURE 8 (*con't.*)

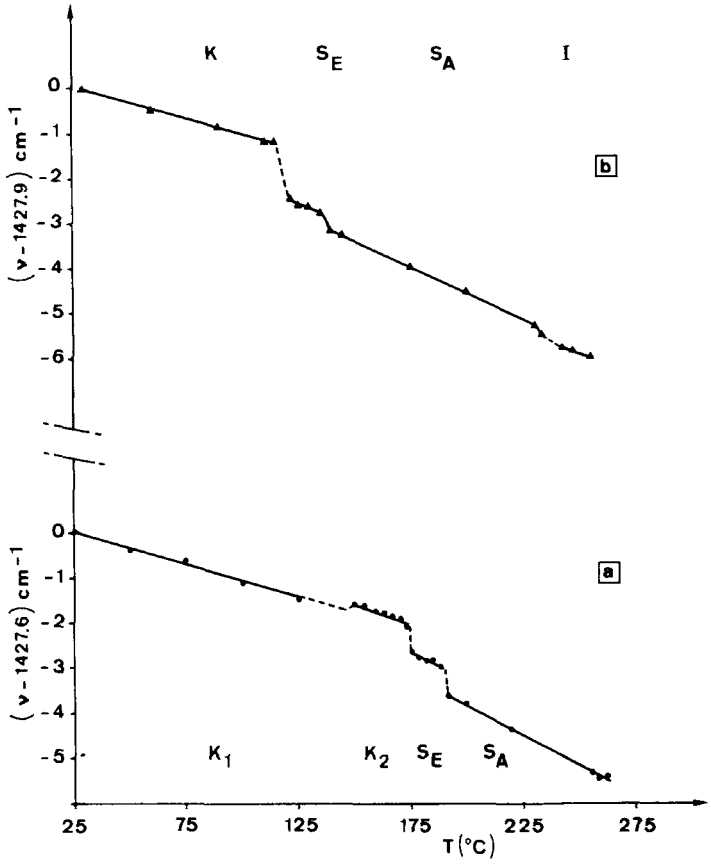


FIGURE 9 Frequency changes observed for the 1427 cm^{-1} in-plane ring mode in DETC (*a*) and DPTC (*b*).

the isotropic liquid, one might expect that the molecules would gradually become less rigidly confined to some definite equilibrium configuration. This increase in molecular mobility, if sufficiently pronounced, should be reflected in changes in the shapes of infrared absorption bands. In general, the broader the absorption band, the more mobile is the transition dipole giving rise to the absorption.[31] Such behaviour is observed for the out-of-plane deformation (γ(CH)) band. As the temperature is increased, this band continually broadens with clear breaks at the phase transitions. The situation is not as clear for the C=C stretching band which begins to broaden with increasing

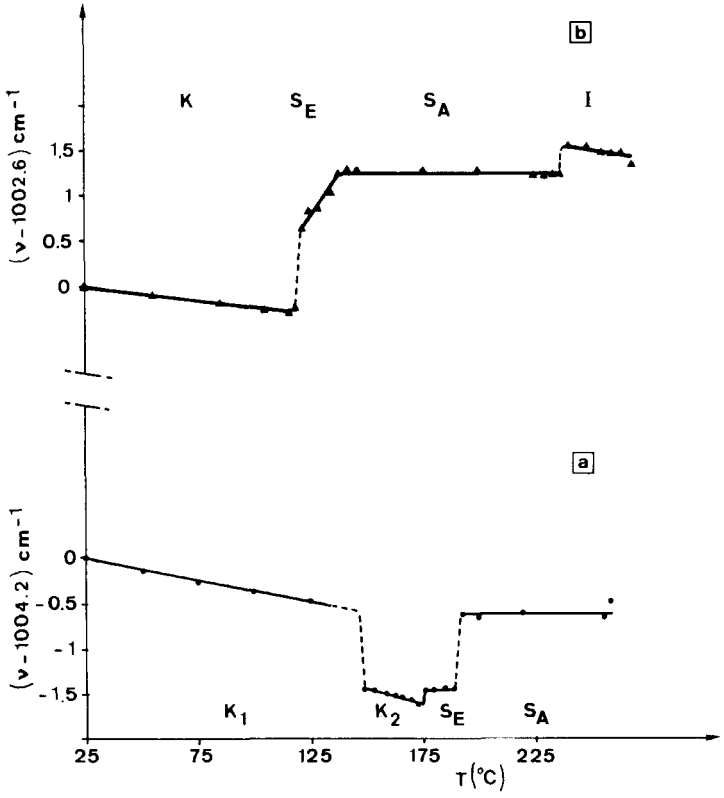


FIGURE 10 Frequency changes observed for the 1004 cm^{-1} in-plane ring mode in (*a*) DETC and (*b*) DPTC (in KBr pellets).

temperature but narrows sharply at the S_E–S_A transition. For comparison it is useful to cite a recent spectroscopic study of dodecylcyanobiphenyl carried out by Galbiati and Zerbi.[29] Very similar behaviour was observed for the same band at the S_A–Isotropic liquid transition. According to these authors, the sharp decrease of the band width of this ring mode indicates that "the energy relaxation into the manifold of librational and translational levels of the rigid portion of the molecule forced in an ordered cluster in the smectic phase ceases at the transition." In the case of DETC and DPTC, this would correspond to a sudden disappearance of the rigid core into a more disordered structure of the smectic liquid in which, however, some local order still persists.

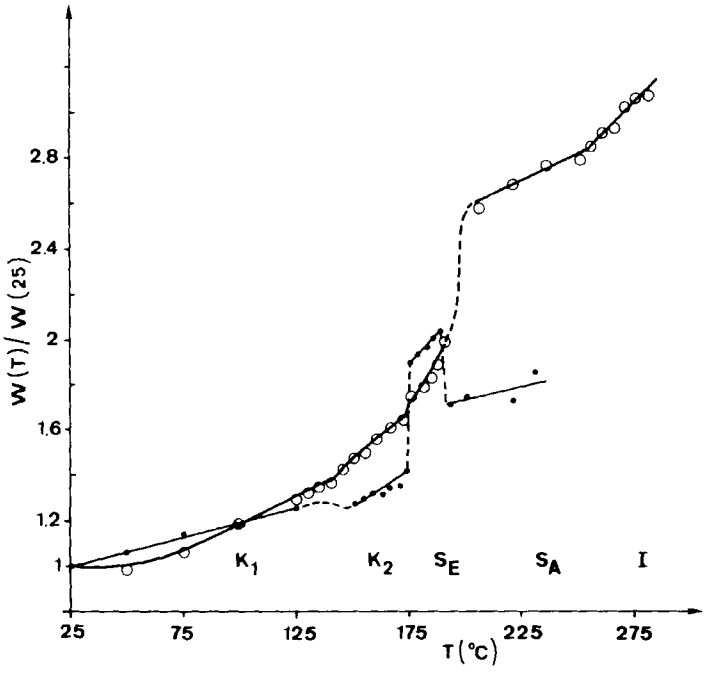


FIGURE 11 Temperature dependence of half bandwidth of the C=C stretching (●) and the out-of-plane γCH (○) ring bands in DETC.

Conformational changes in the terminal alkyl groups are expected to occur with increasing temperature. Figure 8 shows the temperature dependence of the infrared spectra of DETC and DPTC in the 1300–1510 cm^{-1} range. It is clear that, upon heating, bands definitely broaden and intensity changes occur. These effects are especially pronounced at the K_1–K_2 and K_2–S_E transitions for DETC and at the K–S_E transition for DPTC. Unfortunately, this region of the spectrum is complicated by the overlapping of many transitions including methylene and methyl deformation bands and benzene ring modes which makes it difficult to interpret the data.

More selective information on local conformations can be obtained by examining spectra in the 900–1000 cm^{-1} region where methylene rocking and C—C and C—O stretching bands are expected to appear. As shown in Figure 13, the general features of the infrared spectra of DPTC in this frequency range change drastically at the K–S_E transition. The 966 cm^{-1} band strongly decreases while the 937 cm^{-1} increases and shifts by about +4 cm^{-1}. This tendency is still observed

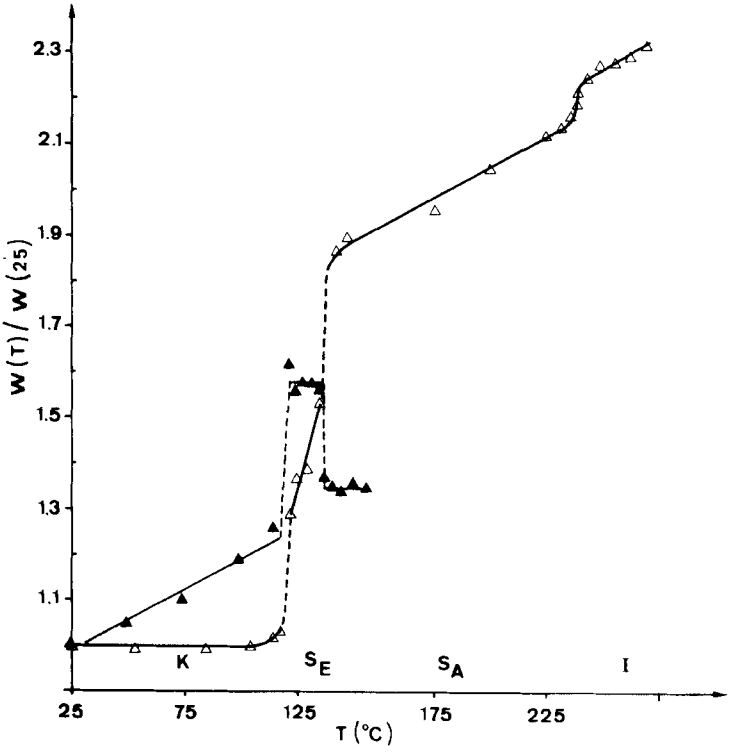


FIGURE 12 Temperature dependence of half bandwidth of the C=C stretching (▲) and the out-of-plane γCH (△) ring bands in DPTC.

in the higher temperature S_A and isotropic phases and in solution. Although most of the authors have focussed their attention directly on the mesophases, neglecting the structure in the solid, in general, for such liquid crystal materials, the alkyl chain is considered to be trans planar in the crystalline form. The observed decrease of the 966 cm^{-1} band must then be ascribed to a decrease in the all-trans conformers. The appearance of a large population of non-planar conformers is indicated by the development of the band at 941 cm^{-1}. In fact, as shown by the fourth derivative (Figure 14), the spectrum in the region 934–946 cm^{-1} is complicated by the overlapping of at least three bands at 937, 941 and 945 cm^{-1}. The first one corresponds to the band observed at the same frequency in the crystalline state and can be assigned to the all-trans conformer. This is in good agreement with the existence of a band at 935 cm^{-1} in the infrared spectrum of diethyl ether in the crystalline state, where the molecule is known to

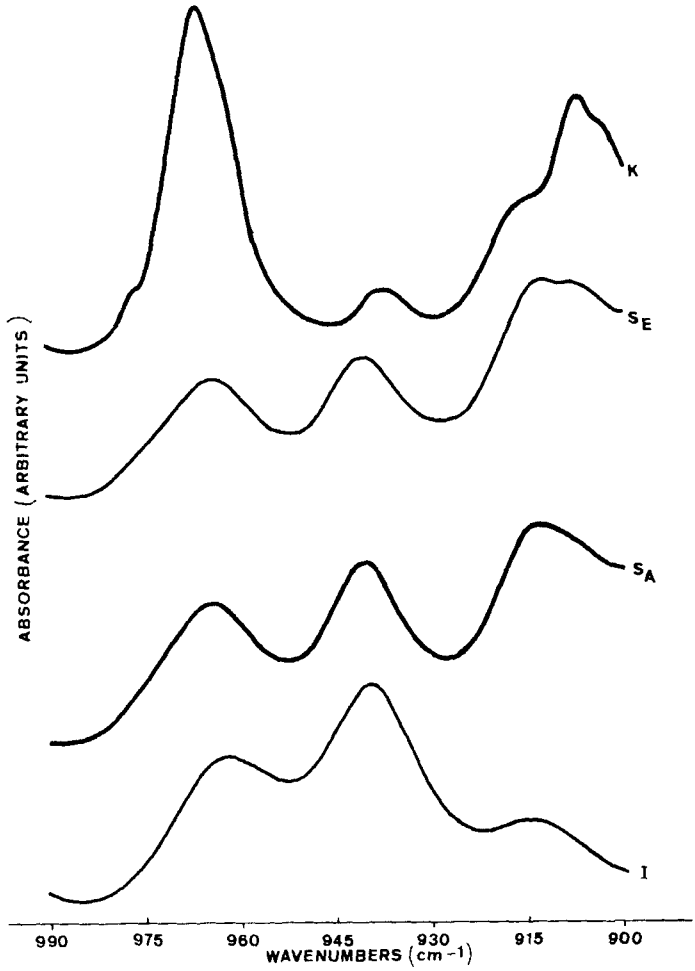


FIGURE 13 FTIR spectra of DPTC in the 900–990 cm^{-1} range.

adopt an all-trans conformation.[32] On the other hand, we believe that the bands at 941 cm^{-1} and 945 cm^{-1} are sensitive to the non-planar TG and GT conformations. Support for such an interpretation is obtained from the infrared band at 945 cm^{-1} in the spectrum of molten polyethylene glycol[33] which was assigned to gauche units. We note that for DPTC the TG and GT conformations of the terminal alkyl group are the only ones consistent with the X-ray investigation of the S_E phase[2]: the length of the molecule and the direction of the molecular long axis are almost the same as those for the all-trans

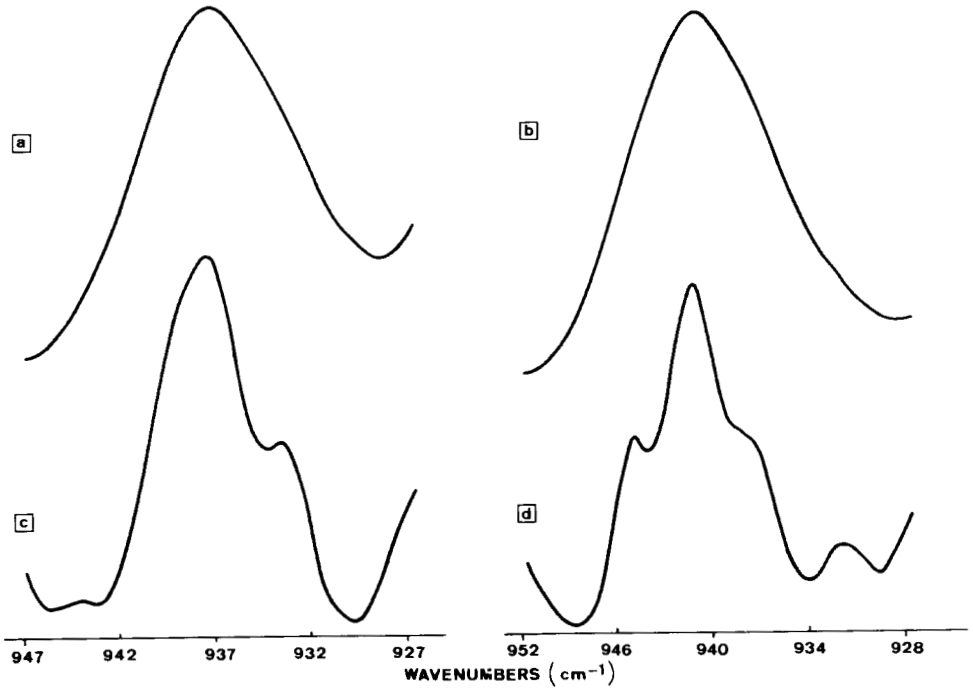


FIGURE 14 FTIR spectra of DPTC in the crystalline (*a*) and S_E (*b*) phases and the corresponding 4th derivatives (*c*, *d*) in the Fourier space. 927–950 cm^{-1}

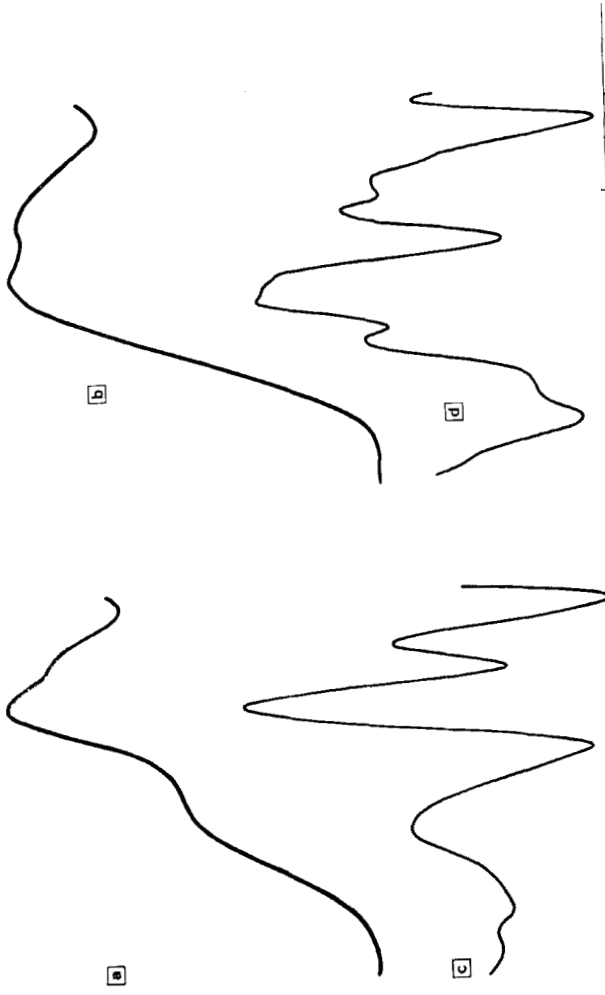


FIGURE 15 FTIR spectra of DPTC in the crystalline (*a*) and S_E (*b*) phases and the corresponding 4th derivatives (*c*, *d*) in the Fourier space: 898–930 cm^{-1}.

extended conformation. Since they do not fulfill these conditions, and because of their high energy, GG-type conformations can be discarded, especially in the highly ordered S_E phase. They might be responsible, however, for the appearance of weak shoulders at 883 and 896 cm^{-1} in the spectrum of DPTC in the isotropic liquid state. Finally, at the K–S_E transition, another band seems to develop at about 914 cm^{-1} (Figures 13 and 15). We believe that this band also originates from the non-planar GT and TG conformations. Indeed, a corresponding band assigned to a mode involving "gauche" conformations is observed at about the same frequency for liquid diethyl ether[32] and molten polyethylene glycol.[33]

CONCLUSIONS

From this work we conclude that conformational changes within the rigid core contribute to the solid crystalline polymorphism in DETC.

In the liquid crystals investigated, the most prominent changes occur at the crystal–S_E transition. They can be interpreted in terms of symmetry and conformational changes. The rigid core behaves in the same way in DETC and DPTC. The dihedral angles which define the orientation of a carbonyl group with respect to the adjacent ring and those between the planes of the adjacent rings in the terphenyl moiety increase upon heating.

The analysis of the spectra in the 900–1000 cm^{-1} region shows that the solid–S_E transition in DPTC is also associated with conformational disordering of the terminal alkyl group. In the S_E phase, the chain is not necessarily in the all-trans extended conformation: "gauche" conformers are also present.

In going from the smectic E to the isotropic liquid through the smectic A phase we find that the average conformational arrangement does not greatly change. We can conclude, however, from the temperature dependence of the spectra that the S_E–S_A and S_A–I transitions are both discontinuous.

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