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# FTIR of liquid crystals. Organization and phase transitions in binary mixtures of nonylcyanobiphenyl and phenyl-cyclohexanecarboxylate

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# FTIR of liquid crystals

## Organization and phase transitions in binary mixtures of nonylcyanobiphenyl and phenyl-cyclohexanecarboxylate

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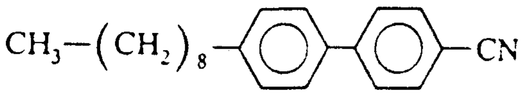
The FTIR spectra of the isotropic and mesomorphic N, $S_{A_d}$, $S_{A_i}$, $S_B$ and $S_G$ phases of 4-*n*-nonyl-4′-cyanobiphenyl (9CB), 4-*n*-pentylphenyl-trans-4′-*n*-pentylcyclohexane-1-carboxylate (5H5) and their binary mixtures have been recorded and analysed. Changes in absorbance related to spontaneous reorientation of the molecules at the phase transitions have been observed and assigned to the orientation of the transition dipoles of typical vibrations. The results are discussed in terms of the phase diagram obtained by D.S.C. and by optical microscopy.

## 1. Introduction

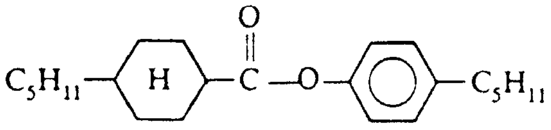
Infrared spectroscopy is a powerful tool for the study of molecular orientation and interactions. The recent development of FTIR with its high calculation potential has stimulated considerable interest in the study of orientational and conformational changes in adsorbed monolayers [1–3]. This method also offers many possibilities for structural investigations of mesomorphic phases. The previous literature on thermotropic systems has been reviewed [4–5]. Dodecylcyanobiphenyl has been investigated by Zerbi *et al.* [6]. Other studies have also been concerned with lyotropic phases [7, 8].

The binary mesomorphic system 4-*n*-nonyl-4′-cyanobiphenyl (9CB) and 4-*n*-pentylphenyl-trans-4′-*n*-pentylcyclohexane-1-carboxylate (5H5)

9CB :



5H5 :



has been extensively investigated in our laboratory [9, 10]. In this interesting system, nematic and various smectic phases ($S_{A_d}$, injected $S_{A_i}$, monotropic $S_B$ and $S_G$ phases) have been identified as a function of temperature and composition. The phase diagram has been established using DSC and polarizing microscopy [9]. The fluorescence spectrum of 9CB in the non-fluorescent 5H5 has been thoroughly investigated as a function of temperature and composition and related to the nature of the different

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mesophases involved [9, 10]. Fluorescence spectroscopy has been shown to be a convenient technique to detect phase transitions. This well-known binary system appears therefore to be particularly convenient for an exploratory study of phase transitions by FTIR.

The change of absorbance of unpolarized infrared light as a function of temperature has been related to the change of orientation of the main axis of the molecule with respect to the direction of incident ray. Vibrations corresponding to transition dipoles with well-defined orientation with respect to the main axis of the molecule have to be used. An example is the $-C \equiv N$ stretching of cyanobiphenyl derivatives with its transition dipole parallel to the main axis of the molecule. Transition dipoles parallel to the direction of propagation of incident rays do not absorb light while absorbance is maximum when they are perpendicular to it. As a consequence, reorientation with respect to the direction of incident light involves a change in absorbance.

## 2. Experimental

9CB was purchased from BDH Ltd, Poole, Dorset, UK. After three recrystallizations from methanol, it was shown to be free from impurities by HPLC and spectrofluophosphorimetry. The ester 5H5 purchased from E. Merck, Darmstadt was used without further purification. The two components were mixed under stirring in the isotropic phase and then allowed to cool down. This operation was repeated two or three times before use.

The phase diagram of the binary system 9CB/5H5 was obtained using a polarizing microscope Laboval (Zeiss) equipped with a Mettler FP 52 heating stage and a FP 5 control unit (3°C/min) and by D.S.C. analysis (DSC 2 Perkin-Elmer, 3°C/min). Two types of experiments have been performed. In a first heating run (see figure 8 (*a*)), the mixtures, crystallized in a refrigerator, are studied as a function of increasing temperature either with the microscope or by DSC. The sample was then allowed to cool to room temperature. At this temperature, crystallization does not occur. The supercooled sample is then reheated; this constitutes the second heating run (see figure 8 (*b*)).

The FTIR spectra were recorded using a IFS 44 Brucker Spectrophotometer equipped with a Brucker I.R. microscope and the Mettler heating stage described here. The I.R. spectra of circular spots with a diameter of 80 $\mu$m were recorded. The I.R. spectra are independent of the spot size. The same spectra were obtained either during heating or cooling programmes (3°C/min). They do not depend on the number of heating or cooling cycles applied to the sample. $CaF_2$ windows were used.

## 3. Results and discussion

### 3.1. *I.R. spectra of neat 9CB and 5H5 in the isotropic phase at 60°C. Assignment and polarization of the transitions with reference to the main axis of the molecule*

The spectra of 9CB and 5H5 in the isotropic phase at 60°C are given in figures 1 and 2. The main absorption bands have been assigned tentatively to characteristic vibrational modes (see table 1). The directions of the transition moments associated with these vibrations with reference to the long axis of the aromatic part of the molecules are also given. The assignments given for 9CB agree with those proposed by Zerbi *et al.* for 12 CB [6]. Examination of the data in table 1 shows that the direction of the long molecular axis of 9CB in unambiguously determined if the

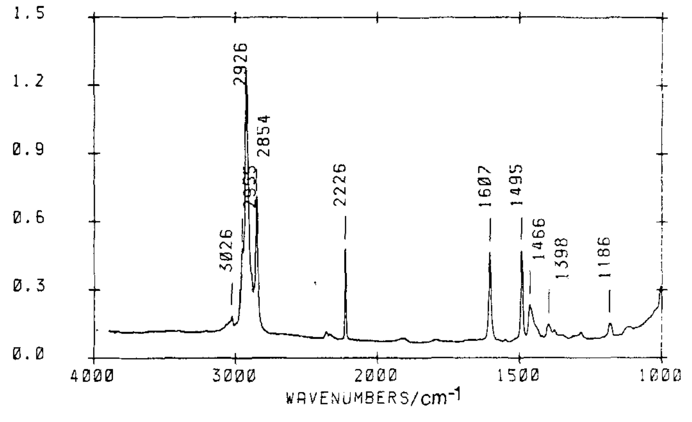


Figure 1. I.R. spectrum of pure 9CB in the isotropic phase at 60°C–$CaF_2$ cell.

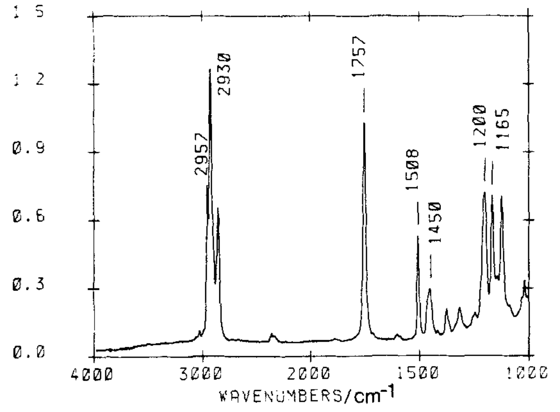


Figure 2. I.R. spectrum of pure 5H5 in the isotropic phase at 60°C.

direction of the transition moments corresponding to the 2226, 1607, 1495 and 1007 cm$^{-1}$ vibrations is known. The direction of the dipole moments associated with the $CH_2$ and $CH_3$ stretching vibrations of 9CB depends on the conformation of the aliphatic part of the molecule. For $CH_2$, they are approximately perpendicular to the main direction of the chain if the alkyl chain is in the all-trans conformation.

The case of 5H5 is more complex since the molecule is less rigid. The 1508 cm$^{-1}$ vibration is polarized parallel to the long axis of the substituted aromatic ring. The transition dipole associated with the $C=O$ stretch depends on the conformation of the molecule. In the most extended conformation, it is approximately perpendicular to the long axis of the aromatic part (see figure 3 (*a*)). Another conformation showing the $C=O$ bond parallel to this long axis is also shown (see figure 3 (*b*)). The transition dipoles associated with the $CH_2$ and $CH_3$ stretching vibrations also depend on the conformation of the aliphatic part of the molecule.

### 3.2. *The I.R. spectra of mixtures of 9CB and 5H5 in the isotropic phase at 60°C*

The spectra are given in figures 4 to 7. Identical spectra are obtained either with unpolarized or with polarized light. The absolute absorbance of the $C=O$ and $C\equiv N$

Table 1. Tentative assignment of the infrared spectrum of 9CB and 5H5.

| No | Frequency/cm$^{-1}$ | 9CB Vibration | 9CB Polarization† | 5H5 Vibration | 5H5 Polarization† |
|---|---|---|---|---|---|
| 12 | Near 3026 | Stret CH arom | Perpendicular | Stret CH arom | Perpendicular |
| 11 | 2924 | As. stret $CH_2$ | Conformation dependent | As. stret $CH_2$ | Perpendicular to the chain axis in the all-trans zig-zag conformation |
| 10 | 2854 | S. stret $CH_2$ | Conformation dependent | S. stret $CH_2$ | Perpendicular to the chain axis in the all-trans zig-zag conformation |
| 9 | 2226 | Stret $C\equiv N$ | Parallel | — | — |
| 8 | 1757 | — | — | Stret $C=O$ | Conformation dependent |
| 7 | 1607 | Stret ring $C=C$ | Parallel | Very weak | — |
| 6′ | 1508 | — | — | Stret ring $C=C$ | Perpendicular |
| 6 | 1495 | Stret ring $C=C$ | Parallel | — | — |
| — | Near 1450 | Complex absorption | — | Complex absorption | |
| 2 | 1200 | — | — | COO stret | Same as 6′ perpendicular |
| | 1165 | — | — | COO stret | Same as 6′ perpendicular |
| | 1124 | — | — | COO stret | Same as 6 perpendicular |
| | 1007 | Interring C–C stret | Parallel | — | — |

† With reference to the long axis of the aromatic part of the molecule.

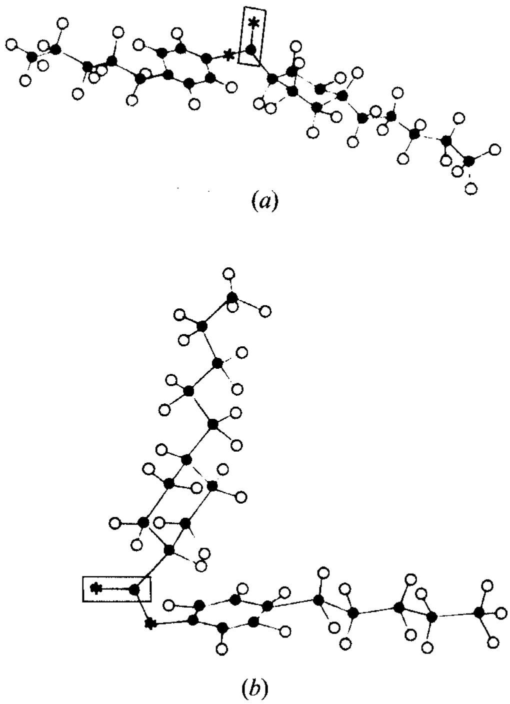


Figure 3. Conformation of the ester (5H5): (*a*) with the C=O group perpendicular to the aromatic ring, (*b*) with the C=O group parallel to the aromatic ring. The * symbol represents oxygen atoms.

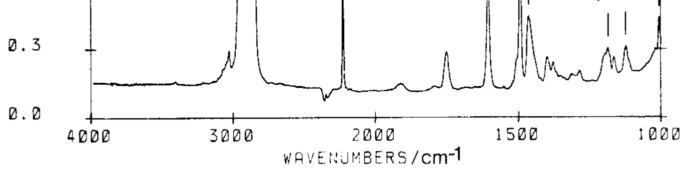


Figure 4. I.R. spectrum of the mixture 90 wt % 9CB in 5H5 at 60°C in the isotropic phase.

peaks at 1757 and 2226 $cm^{-1}$ are related to the thickness of the samples which are slightly different in each case. The ratio of C=O to C≡N is proportional to the mole ratio of the corresponding molecules in the mixtures.

### 3.3. *The phase diagram of the 9CB–5H5 binary mixture*

The phase diagram has been compiled by DSC and optical microscopy (see figure 8) and has been discussed previously [9]. A $S_{A_d}$ and an injected $S_{A_i}$ phases

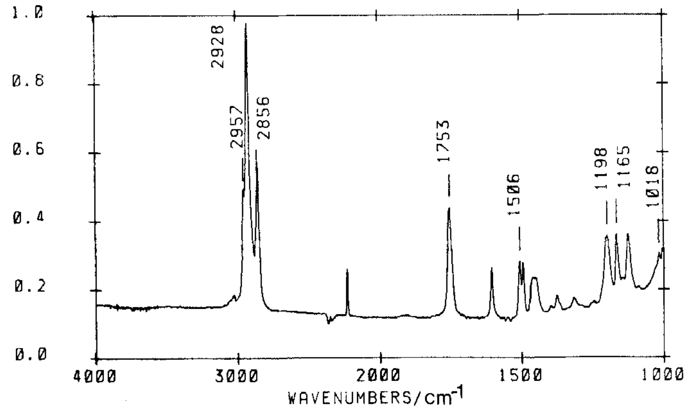


Figure 5. I.R. spectrum of the mixture 50 wt % 9CB in 5H5 at 60°C in the isotropic phase.

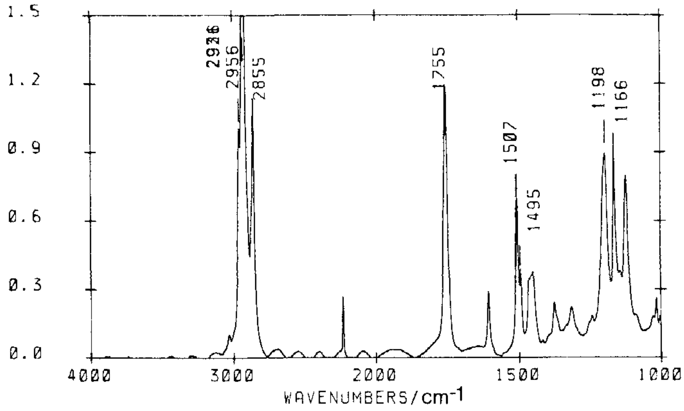


Figure 6. I.R. spectrum of the mixture 35 wt % 9CB in 5H5 at 60°C in the isotropic phase.

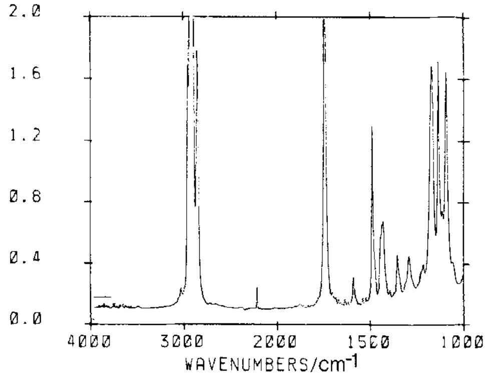
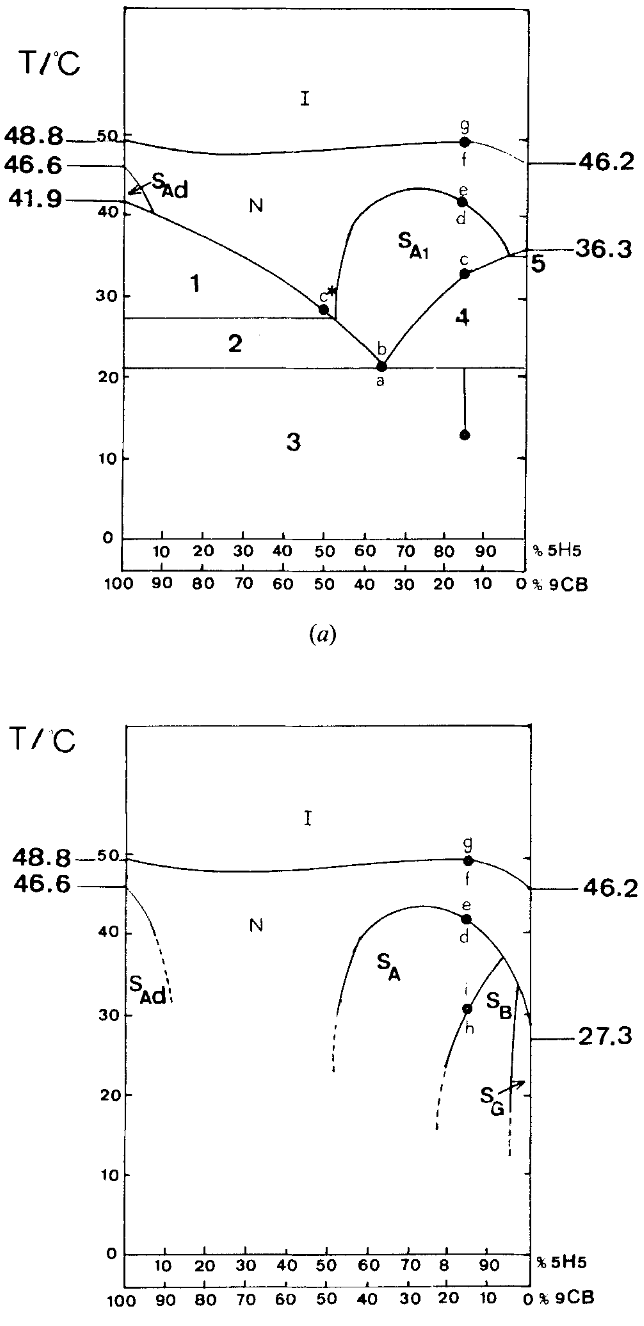


Figure 7. I.R. spectrum of the mixture 15 wt % 9CB in 5H5 at 60°C in the isotropic phase.

are observed at high and intermediate 9CB content, respectively. Monotropic $S_G$ and $S_B$ phases have been identified in neat 5H5 and in mixtures with a high 5H5 content, respectively. In the present study, only supercooled samples have been studied. As a consequence the crystalline phases are not considered and figure 8 (*b*) has been used.



(a)

(b)

Figure 8. The phase diagram for the system 9CB/5H5 (wt %) obtained by microscopic examination, compilation of DSC and fluorescence measurements. (*a*) First heating run. (*b*) Second heating run. (1) Crystal 9CB + nematic phase. (2) Crystal 9CB + $S_{A_1}$ phase. (3) Crystal 9CB + crystal 5H5. (4) Crystal 5H5 + $S_{A_1}$ phase. (5) Crystal 5H5 + nematic phase.

### 3.4. *Infrared spectra as a function of phase transitions and transition dipole orientation*

The degree of order of oriented nematic phases has been quantitatively related to the absorption of linearly polarized [11] and unpolarized [12] I.R. light.

The change of absorbance of unpolarized light by a given vibration mode characterized by a dipole transition moment can be visualized very simply qualitatively by examination of figure 9. The thin sample layer is held between two plates parallel to the *XOZ* plane. The direction of the incident unpolarized ray is perpendicular to the cell walls. Its associated electric vectors vibrate in planes parallel to *XOZ* and do not have any component in the *OY* direction. Each transition dipole absorbs radiation according to its component along the electric vectors. For a given transition dipole, the absorption of light will thus be a maximum if it is oriented parallel to the electric vectors associated with the incident light. On the contrary, no absorption will occur if it is perpendicular to the electric vectors. This means that a transition dipole aligned parallel to *OY* in figure 9 will not absorb unpolarized light (i.e. a hidden transition). If the incident radiation is linearly polarized either parallel to the *OX*, or to the *OZ* axis, the electric vectors associated with the incident radiation will vibrate either parallel to *OX* in planes parallel to *XOY*, or parallel to *OZ* in planes parallel to *YOZ*. From this it can be concluded that:

a transition dipole parallel to *OZ* will not absorb light polarized parallel to *OX*
a transition dipole parallel to *OX* will not absorb light parallel to *OZ*
a transition dipole parallel to *OY* will absorb neither polarized nor unpolarized light

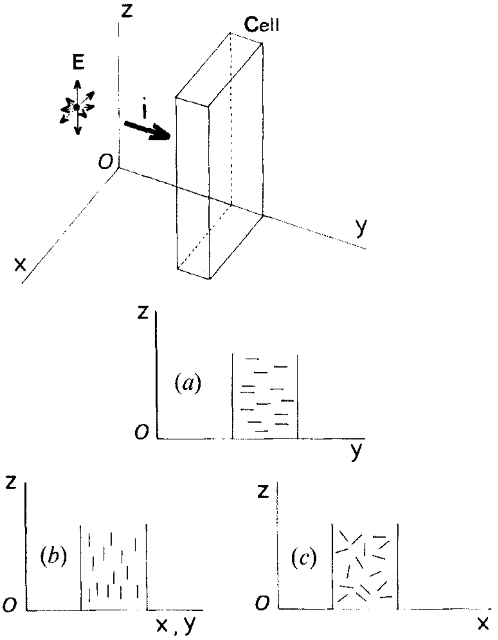


Figure 9. Cell orientation ($CaF_2$). i, incident ray; E, electric vectors associated with unpolarized incident rays. Assignment of the molecular orientation in the cell; – – –, long axis of the molecule. (*a*) Homeotropic nematic alignment. (*b*) Homogeneous nematic alignment. (*c*) Planar nematic alignment.

Table 2. Summary of the qualitative changes of I.R. unpolarized absorption of typical vibrations on passing from the isotropic to the organized phases.

|  | No | 12 | 10 | 9 | 8 | 7 | 6′ | 6 | 2 |
|---|---|---|---|---|---|---|---|---|---|
| System | Frequency/cm$^{-1}$ | 3026 | 2850 | 2226 | 1757 | 1607 | 1508 | 1495 | 1165 |
| Pure | 9CB (*a*) | Few changes observed |  |  |  |  |  |  |  |
| Pure | 5H5 (*b*) | ↘ | ↗ | — | ↗ | — | ↘ | — | ↘ |
| 90 per cent | CB (*c*) | ↘ | ↗ | ↘ | ↗ | ↘ | ↘ | ↘ | ↘ |
| 50 per cent | CB (*d*) | — | Unch. | ↘ | ↗ | ↘ | ↘ | ↘ | ↘ |
| 35 per cent | CB (*e*) | ↘ | ↗ | ↘ | ↗ | ↘ | ↘ | ↘ | ↘ |
| 15 per cent | CB (*f*) | ↘ | ↗ | ↘ | ↗ | ↘ | ↘ | 0 | ↘ |

(*a*) Data from figure 1.
(*b*) Data from figures 2, 10 and 11.
(*c*) Data from figures 4, 12 and 13.
(*d*) Data from figures 5, 14 and 15.
(*e*) Data from figures 6, 16 and 17.
(*f*) Data from figures 7, 18, 19 and 20.

a large number of randomly oriented dipoles will absorb with equal probability unpolarized light, light polarized parallel to $OZ$ and light polarized parallel to $OX$.

As a consequence, a phase transition accompanied by a change of orientational distribution of one or several transition dipoles could be detected by changes in the IR absorption. This occurs even with unpolarized light if the orientational distribution along the $Y$ axis changes. Any tendency to either homeotropic, homogeneous or planar orientation on passing from the isotropic to a mesomorphic phase could be detected, therefore, as a change in absorbance. The system 9CB–5H5 which shows a strong tendency to spontaneous homeotropic alignment in the mesophases is thus particularly well adapted to this study. Increase or decrease of typical absorption bands will be considered on passing from the isotropic to the mesomorphic phases. The isotropic phase will be taken as reference and unpolarized light will be used. A summary of the results is given in table 2.

### 3.4.1. *Pure 9CB*

Bands 6, 7, 9 and 10 will be considered (see table 1 and figure 1). The first three, together with the weak absorption at 1007 cm$^{-1}$, are polarized parallel to the main axis of the molecule. Band 10 assigned to sym $CH_2$ stretching is perpendicular to the main axis of the molecule if the alkyl chain is in the all-trans conformation. Only minor changes in the absorbance of the most characteristic bands are observed as a function of temperature: reorientation of the molecules on passing from the isotropic to the nematic (48·6°C) and to the $S_{A_d}$ (46·6°C) mesomorphic phases is thus unimportant in pure 9CB, in agreement with [6]. Perfect homeotropic alignment of the molecule in the $S_{A_d}$ or N phases (parallel to $OY$ in figure 9) would indeed cause the disappearance of the absorptions corresponding to transition dipoles parallel to the long axis of the molecule (6, 7 and 9).

### 3.4.2. *Pure 5H5*

Comparison of figures 2 and 10 shows that the ratio of 6′ to 8 is very different in the isotropic and in the $S_G$ phases. The intensity of 6′ decreases on passing to the organized phase indicating a tendency to alignment of the long axis of the aromatic

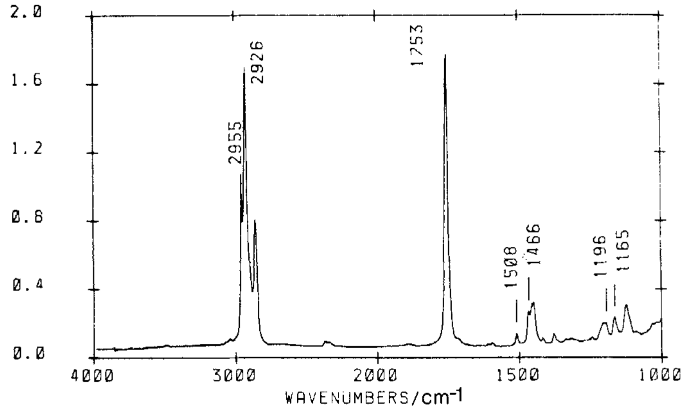


Figure 10. I.R. spectrum of pure 5H5 in the smectic $S_G$ phase at 26°C.

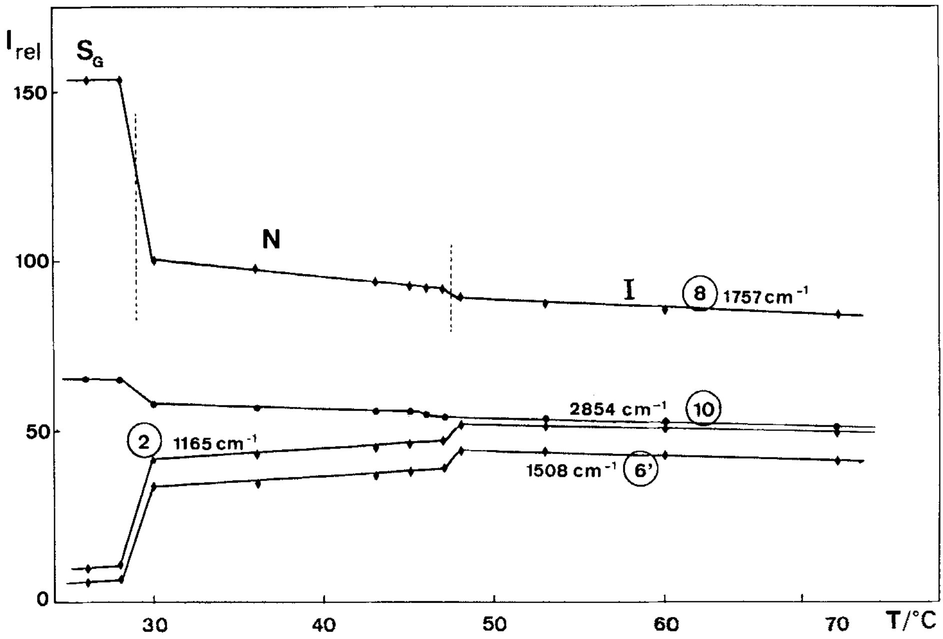


Figure 11. Relative intensity of different IR peaks of pure 5H5 as a function of temperature. (2) 1165 cm$^{-1}$. (6′) 1508 cm$^{-1}$. (8) 1757 cm$^{-1}$. (10) 2854 cm$^{-1}$.

part parallel to *OY*. This is accompanied by an increase of the C=O absorption indicating that this bond aligns perpendicular to *OY*. An example of a conformation of the 5H5 molecule which obeys both requirements is given in figure 3 (*a*). Figure 11 gives the absorbance corresponding to typical vibrations as a function of temperature and shows that the degree of order along *OY* increases according to $I < N < S_G$.

### 3.4.3. *90 per cent 9CB—10 per cent 5H5*

The spectra are very different in the I and $S_{A_d}$ phases (see figures 4 and 12). The bands associated with the vibration parallel to the main axis of 9CB (6, 7, 9) strongly decrease with decreasing temperature in agreement with a reorientation parallel to the

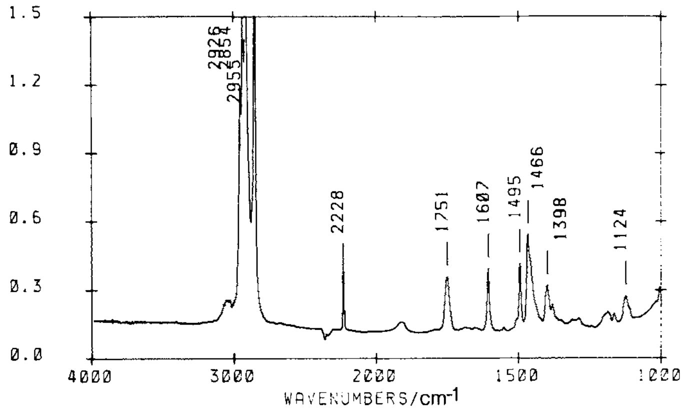


Figure 12. I.R. spectrum of the mixture 90 wt % CB in 5H5 at 27°C in the $S_{A_d}$ phase.

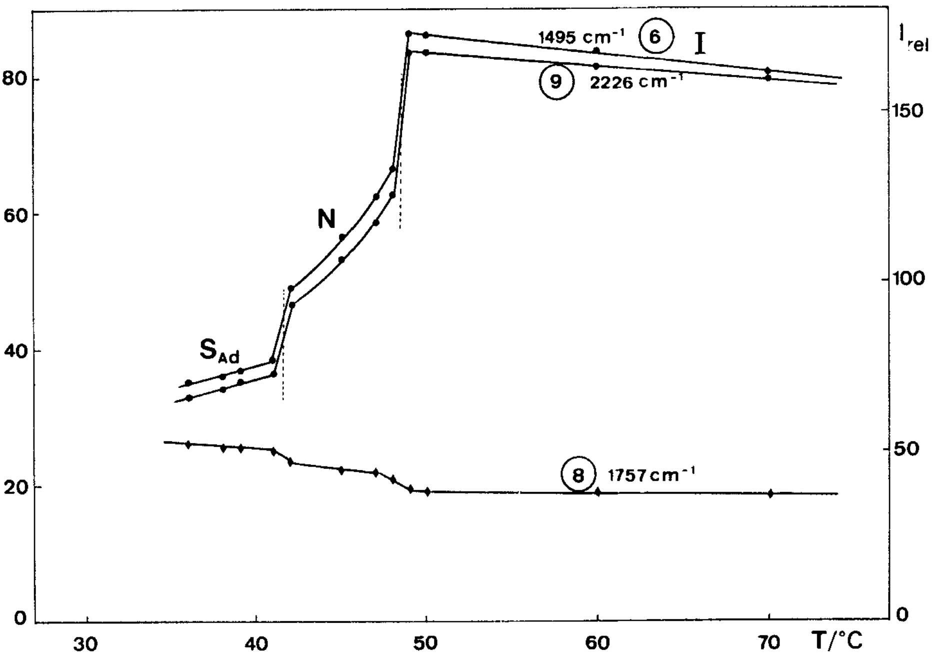


Figure 13. Relative intensity of different I.R. peaks of the mixture 90 wt % CB in 5H5 as a function of temperature. (6) 1495 cm$^{-1}$. (8) 1757 cm$^{-1}$. (9) 2226 cm$^{-1}$.

*OY* axis in the mesomorphic phase. The second compound is present at low concention and its absorptions are therefore weak. The C = O bond is only slightly modified in the organized phase while 6′ probably decreases. This would correspond to an alignment of the aromatic ring parallel to *OY* with a change of conformation of the O–C = O group. The aliphatic $CH_2$ sym stretching increases slightly. Phase transitions are clearly apparent from figure 13 in agreement with the phase diagram of figure 8.

### 3.4.4. *50 per cent 9CB—50 per cent 5H5*

No smectic phase is formed at this composition (see figure 8). At the N–I transition, a decrease of all the transitions associated with dipoles parallel to the main

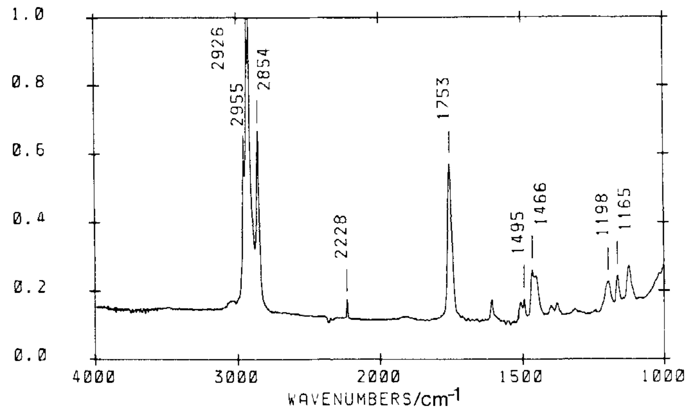


Figure 14. I.R. spectrum of the mixture 50 wt % CB in 5H5 at 27°C in the nematic phase.

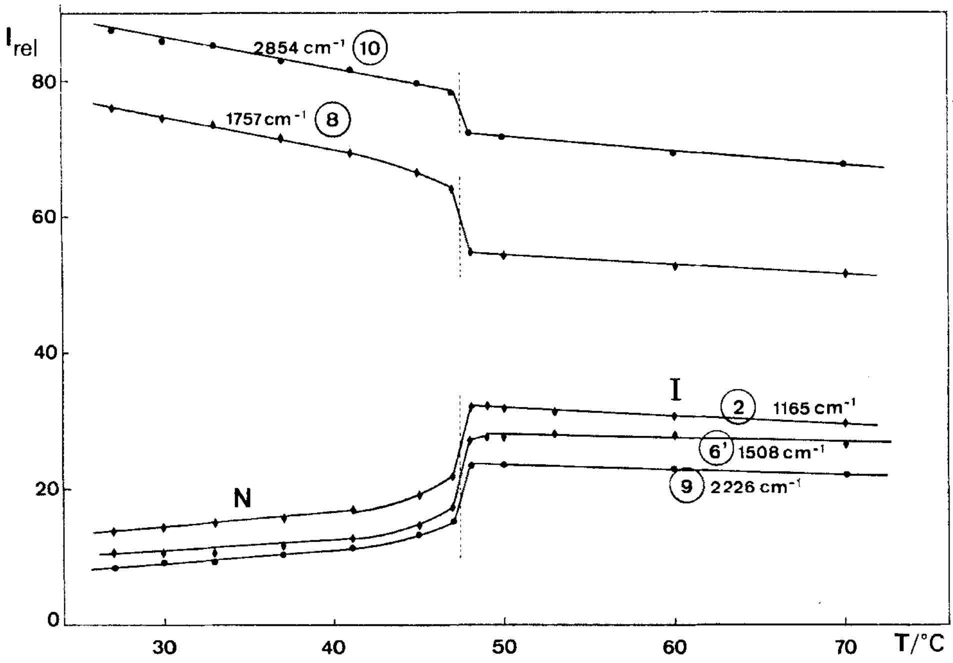


Figure 15. Relative intensity of different I.R. peaks of the mixture 50 wt % CB in 5H5 as a function temperature. (2) 1165 cm$^{-1}$. (6′) 1508 cm$^{-1}$. (8) 1757 cm$^{-1}$. (9) 2226 cm$^{-1}$. (10) 2854 cm$^{-1}$.

chain axis of the aromatic ring is observed (6, 7 and 9 for 9CB and 6′ for 5H5 in figures 5, 14 and 15). These decreases are accompanied by an increase for the C=O absorption indicating a tendency to homeotropic alignment of the long axis of the aromatic part of the molecules along *OY*, the C=O group being perpendicular to the aromatic ring of 5H5.

### 3.4.5. *35 per cent 9CB—65 per cent 5H5*

Comparison of figures 6 and 16 shows that in this case, the formation of a $S_{A_1}$ mesophase is also accompanied by a decrease of bands 6, 7 and 9 for 9CB and of

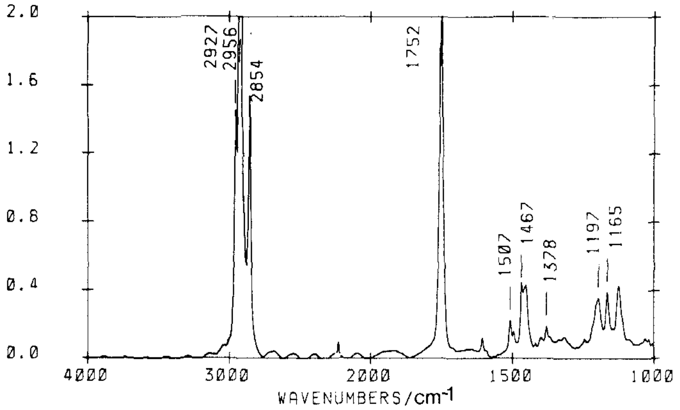


Figure 16. I.R. spectrum of the mixture 35 wt % CB in 5H5 at 27°C in the $S_{A_1}$ phase.

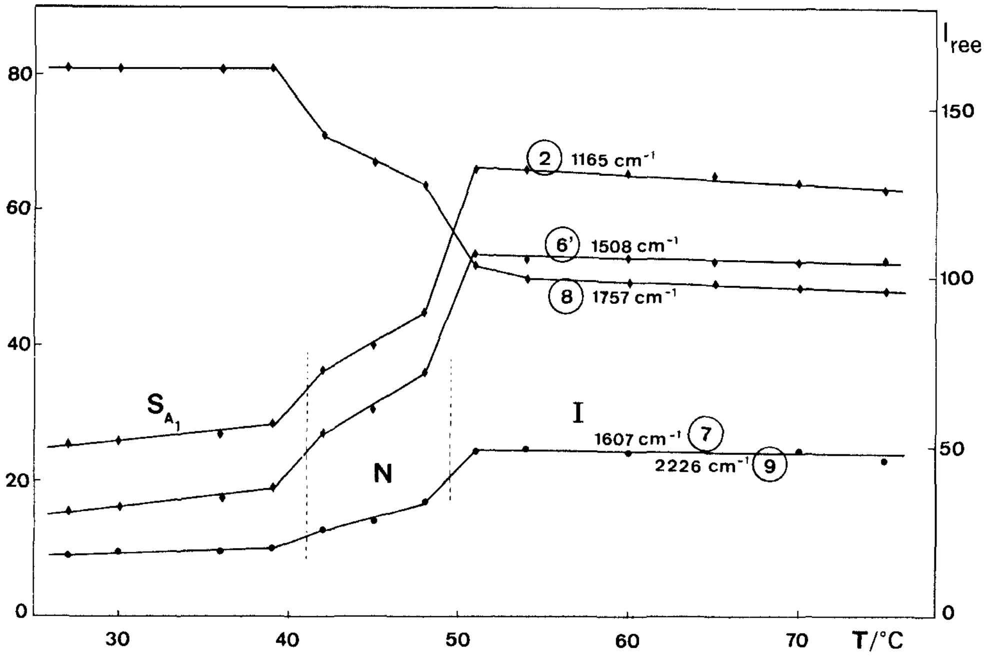


Figure 17. Relative intensity of different I.R. peaks for the mixture 35 wt % CB in 5H5 as a function of temperature. (2) 1165 cm$^{-1}$. (6′) 1508 cm$^{-1}$. (7) 1607 cm$^{-1}$. (8) 1757 cm$^{-1}$. (9) 2226 cm$^{-1}$.

band 6′ for 5H5 while C=O increases. The absorbance corresponding to $-CH_2$ sym stretching also increases, as usually observed, indicating a modification of the orientation of the aliphatic part of the molecules. The phase transitions appear clearly in figure 17.

### 3.4.6. *15 per cent 9CB—85 per cent 5H5*

The spectra of the I, $S_{A_1}$ and $S_B$ phases are given in figures 7, 18 and 19. The contribution of 9CB to the spectrum is very weak. Bands 7 and 9 are nevertheless

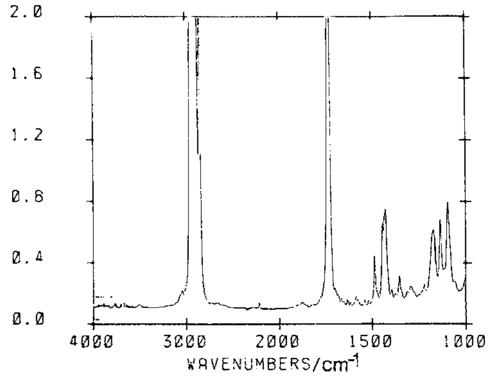


Figure 18. I.R. spectrum of the mixture 15 wt % CB in 5H5 at 36°C in the $S_{A_1}$ phase.

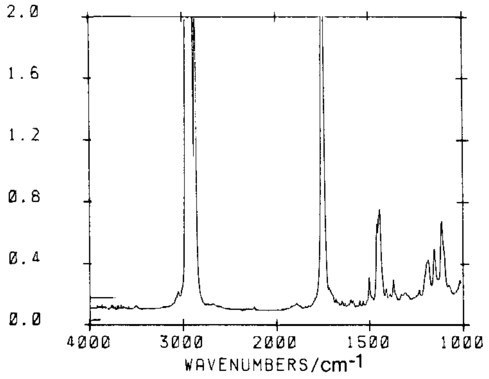


Figure 19. I.R. spectrum of the mixture 15 wt % CB in 5H5 at 27°C in the $S_B$ phase.

obviously smaller in the mesomorphic phases. Concerning 5H5, 6′ decreases very strongly and C=O increases when the degree of order increases, as in the other mixtures. The absorbance is given as a function of temperature in figure 20.

## 4. Conclusions

Phase transitions from the isotropic to the mesomorphic N, $S_{A_d}$, $S_{A_1}$, $S_B$ or $S_G$ phases induce important changes in the absorption of unpolarized I.R. light by 9CB, 5H5 and their binary mixtures. If the orientation of the transition dipoles of typical vibrations is considered (parallel or perpendicular to the main axis of the molecule), the changes can be assigned to some degree of spontaneous reorientation of the molecules perpendicular to the cell walls. The tendency to homeotropic alignment of the aromatic part of the molecule increases in the order $N < S_A < S_{B,G}$. The increase in the absorption of the C=O and of the aliphatic $CH_2$ sym-stretching mode in the organized phases is related to a conformation dependent increase of the component of C=O and C–H bonds perpendicular to the *OY* direction. Factors other than purely orientational or conformational can influence the absorption intensity. These include lateral expansion of the lattice for the polymethylene chains [13] or intermolecular interactions for the C=O and C≡N stretching [14]. Intermolecular interactions at the level of the C=O group certainly exist as indicated by the upward

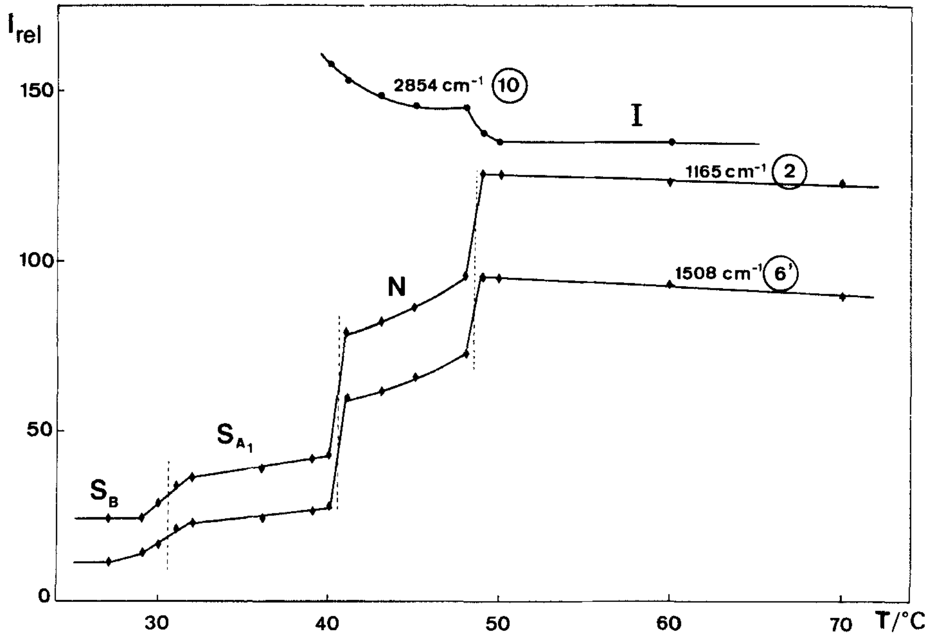


Figure 20. Relative intensity of different I.R. peaks of the mixture 15 wt % CB in 5H5 as a function of temperature. (2) 1165 cm$^{-1}$. (6') 1508 cm$^{-1}$. (10) 2854 cm$^{-1}$.

frequency shift of 4 cm$^{-1}$ observed on passing to the isotropic phase. These factors are most probably much less important than the orientational effects; they will be investigated in the near future. Infrared spectroscopy is a powerful method to detect phase transitions and the orientation of the molecules. All of these observations are in agreement with the phase diagram and with the direct observation of the phases, using a polarizing microscope.

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