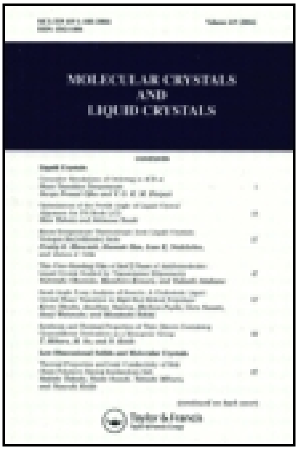

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# Contribution of Fluorescence Spectroscopy to the Determination of Binary Phase Diagrams of Mesomorphic Mixtures. Part II. Investigation of the Induced Smectic $A_1$ Phase of the System Nonylcyanobiphenyl/ Phenylcyclohexanecarboxylate

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# Contribution of Fluorescence Spectroscopy to the Determination of Binary Phase Diagrams of Mesomorphic Mixtures. Part II. Investigation of the Induced Smectic $A_1$ Phase of the System Nonylcyanobiphenyl/Phenylcyclohexanecarboxylate

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*Keywords: injected smectic phases, binary phase diagrams, fluorescence spectroscopy*

The fluorescence intensity and the wavelength distribution of binary mesomorphic mixtures composed of 4-nonyl 4'-cyanobiphenyl (9CB) and 4-pentylphenyl 4'-cyclohexane carboxylate (5H5) have been recorded as a function of the temperature in the isotropic, nematic and induced smectic mesophases ($S_{A1}$, $S_B$ and $S_G$).

Two types of fluorescence can be observed in these systems: monomer fluorescence and excimer fluorescence. Their intensity ratio ranges from 0 to $\infty$ as a function of the composition, of the temperature and of the nature of the phase involved. Monomer fluorescence ($I_M$) is characteristic of materials of low molecular mobility and high degree of order. It is found in $S_B$ and $S_G$ mesophases. Excimer fluorescence ($I_D$) on the other hand is predominantly observed in less-ordered and more fluid phases like $S_{A1}$, nematic and isotropic phases.

It has been shown in this work that band shape modifications and shifts of the λ max of the fluorescence spectra can be related to changes in the relative importance of radiative and non-radiative deactivation processes of the excited state and that intensity changes allow us to detect phase transitions. A new type of isoemissive point which has the nature of the phase as the variable parameter has also been discovered for these mixtures.

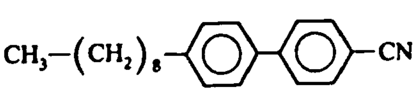
## INTRODUCTION

This paper is part II of a general study of the fluorescence of binary mesomorphic mixtures. Mixtures of alkyl-cyanobiphenyl derivatives with alkyl-phenylcyclohexane esters which give an injected $S_{A1}$ phase on heating and injected $S_{A1}$, $S_B$ or $S_G$ phases on cooling are investigated. The phenomenon of induced smectic phase formation has become one of the most interesting topics in relation to the applications of liquid crystals. Induced smectic phases are usually formed when weakly or non polar l.c. are mixed with nematogens with a strong polar terminal group such as —CN or —$NO_2$. The purpose of this work is the study by fluorescence spectroscopy of the high ester weight fraction range of the mesomorphic 9CB-5H5 mixture when the injected or induced smectic phase occurs. Alkylcyanobiphenyl derivatives (9CB) give, in the neat mesomorphic phase, excimer fluorescence resulting from the radiative deactivation of two neighbouring 9CB chromophores associated as a "dimer" in the excited state; monomer fluorescence is emitted in the crystalline state,[1] but the alkylphenylcyclohexane ester (5H5) is not fluorescent. In mixtures, the non-fluorescent compound breaks up the molecular pairing and consequently the dimer association of the cyanobiphenyl molecules: monomer and excimer fluorescence can thus be observed simultaneously and ratios $I_{FM}/I_{FD}$ (where $I_{FM}$ and $I_{FD}$ are the intensity of monomer and excimer) ranging from 0 to $\infty$ can be obtained as a function of the composition of the mixture, of the temperature and of the nature of the phase involved. It was shown in part I[2] that, for a mixture of a given composition (15 weight% of 9CB in 5H5), the measurement of the fluorescence intensity as a function of the temperature, at two wavelengths, one in the monomer range, the other one in the excimer range shows two types of discontinuity at the phase transitions. The first type could arise from changes in the refractive index on passing from one phase to another, the second type, to monomer-excimer fluorescence interconversion. This conversion gives information concerning the rigidity and the degree of order of the different phases involved. The study of the spectral distribution and intensity fluorescence, measured as a function of temperature, is presented in this work as a convenient method for obtaining phase diagrams of binary mesomorphic mixtures.

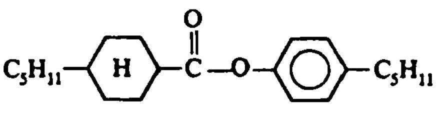
## EXPERIMENTAL

The mixtures studied were 9CB/5H5

9CB :



5H5 :



Their characteristics have been described previously in Reference 2.

The phase diagram is compiled from the results of optical microscopy, DSC analysis and fluorescence spectroscopy according to the following conditions:

THE PHASES were identified using a *LABOVAL* (Zeiss) polarising microscope equipped with a *METTLER FP 52* hot-stage and a *FP 5* control unit (3°C/min).

THE PHASE TRANSITION TEMPERATURES were determined using a *PERKIN-ELMER DSC* (2°C/min).

THE FLUORESCENCE EMISSIONS were measured with a *MPF-2A PERKIN-ELMER* spectrofluorimeter. The frontal excitation wavelength is 280 nm.

The compositions of the mixtures studied cover the range 0–50 weight% of 9CB in 5H5. For typical compositions, the phase transition temperatures and the corresponding enthalpies are listed in TABLE I.

## RESULTS AND DISCUSSION

### 1. Phase diagram

A schematic phase diagram based on optical microscope observations of the 9CB-5H5 binary mixture, kindly supplied by GRAY,[3] is shown in Figure 1. In this

TABLE I

| | | T°C | ΔH (J/gr) |
|---|---|---|---|
| 5H5 | 1st heating run | C–N : 36.3 | 83.9 |
| | | N–I : 46.2 | 1.6 |
| | 2nd heating run | $S_G$–N : 27.3 | 10.2 |
| | | N–I : 46.2 | 2.2 |
| 5% CB | 1st heating run | Eutect: 20.2 | |
| | | End of the melting : 33.9 | |
| | | N–I : 46.8 | |
| | 2nd heating run | $S_G$–$S_{A1}$ : 31.7 | 10.4 |
| | | $S_{A1}$–N : 32.5 | |
| | | N–I : 46.8 | 2.46 |
| 20% CB | 1st heating run | Eutect: 20.2 | |
| | | End of the melting : 27.0 | |
| | | $S_{A1}$–N : 39.7 | 2.2 |
| | 2nd heating run | N–I : 46.7 | 1.86 |
| | | $S_B$–$S_{A1}$ : 23.0 | — |
| | | $S_{A1}$–N : 39.3 | 3.0 |
| | | N–I : 46.5 | 2.2 |
| 35% CB | 1st heating run | Eutect: 21.4 | |
| | | $S_{A1}$–N : 38.9 | 0.9 |
| | | N–I : 47.4 | 1.1 |
| | 2nd heating run | $S_{A1}$–N : 38.9 | 0.9 |
| | | N–I : 47.5 | 1.0 |
| 50% CB | 1st heating run | Eutect: 20.6 | |
| | | End of the melting: 28.4 | |
| | | S–N : | 1.66 |
| | | N–I : | |
| | 2nd heating run | N–I : | 2.43 |

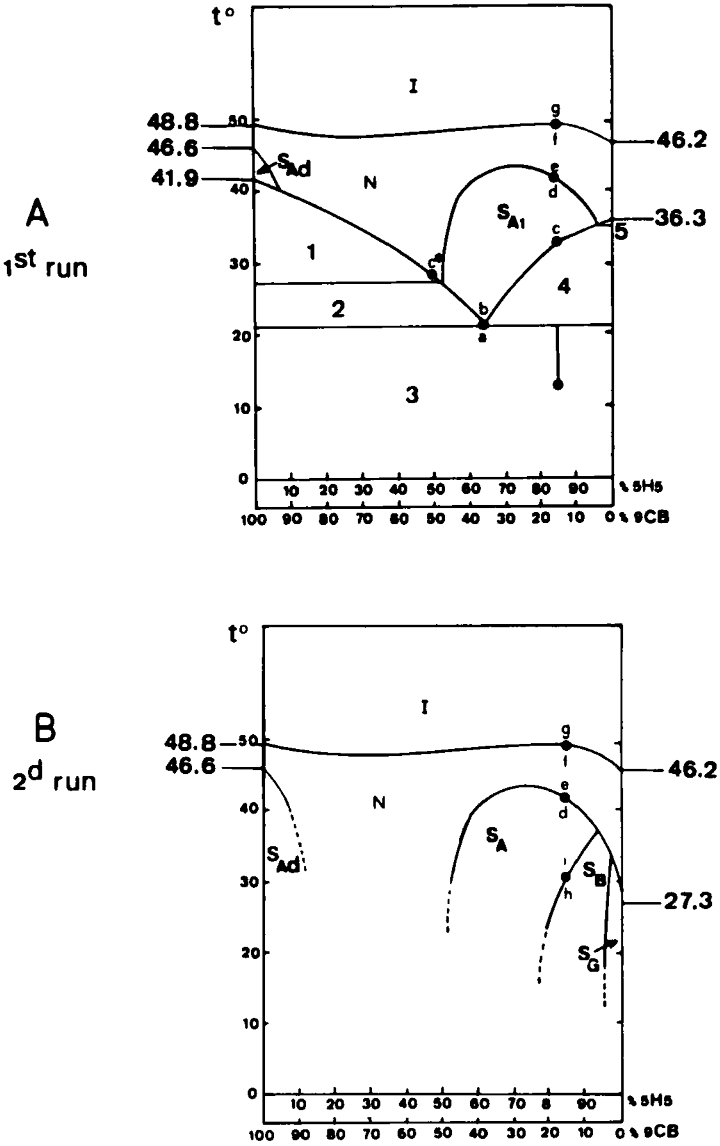


FIGURE 1 Temperature-composition diagram for the system 9CB/5H5 (weight %) obtained by microscope examination, compilation of DSC and fluorescence measurements

A. First heating run
B. Second heating run
1. Crystal 9CB + nematic phase
2. Crystal 9CB + $S_{A1}$ phase
3. Crystal 9CB + Crystal 5H5
4. Crystal 5H5 + $S_{A1}$ phase
5. Crystl 5H5 + nematic phase

system, two types of smectic phase are obtained. An $S_{Ad}$ "bilayer" phase is obtained for high concentrations of 9CB while for low concentrations, an $S_{A1}$ monolayer phase is observed. This injected $S_{A1}$ phase covers the weight fraction range which will be investigated in this work *i.e.* from 0 to 50 weight% 9CB in 5H5. The injected $S_{A1}$ phase is observed during a first heating run *i.e.* when the sample is warmed up from the crystalline state to the isotropic melt. If the sample is allowed to cool to room temperature before a second heating run is performed on the same sample, crystallization does not occur and other smectic phases are formed. For these supercooled samples $S_B$ and $S_G$ monotropic phases are observed in a second heating run, for sample with compositions between 0 and 20 weight% of 9CB.

## 2. DSC and fluorescence spectroscopy as a function of temperature

Mixtures of 5H5 and 9CB containing different weight fractions of 9CB have been systematically investigated in their successive phases by DSC, optical microscopy with polarized light and fluorescence spectroscopy. Two types of experiments were performed:

*IN A FIRST HEATING RUN*, the mesomorphic mixture is warmed up in the isotropic phase and then allowed to cool and crystallize in a refrigerator. Different properties are then measured on heating the sample at a controlled rate from the crystalline to the isotropic phase:

THE PHASE TRANSITIONS are determined by DSC analysis (2°/min) and controlled by microscopic examination (3°/min).

THE FLUORESCENCE INTENSITY is measured respectively at $\lambda a = 310$ nm (in the frequency range of the monomer) and at $\lambda a = 470$ nm (in the frequency range of the excimer) as a function of the temperature (3°/min).

THE SPECTRAL DISTRIBUTION OF THE FLUORESCENCE is recorded at different temperatures.

The sample used here above in the first heating run is allowed to cool from the isotropic phase (75°C) to room temperature. At this temperature, crystallization does not occur. The sample is then reheated. The phase transition temperatures, the fluorescence intensity and the spectral distribution of the fluorescence are measured again as summarized above; this constitutes *the second heating run.*

### 2.1. First heating run

*2.1.1. DSC analysis.* The phase transition temperatures measured by DSC are given in Figure 2 and in Table I. The transitions from the crystal to the $S_{A1}$ phase will be considered first. For the mixtures containing 5–20 and 50% 9CB, two melting peaks are observed. The first sharp peak at 21°C corresponds to partial melting at the eutectic temperature; a second broad peak corresponds to the melting of the excess solid. The maximum of the broad peak indicates the end of the C–$S_{A1}$ transition. For 5 and 50wt%, the second peak also contains C–N transitions. For the mixture containing 35% 9CB, only one melting peak is observed in the thermogram, indicating that we are not far from the eutectic composition which was

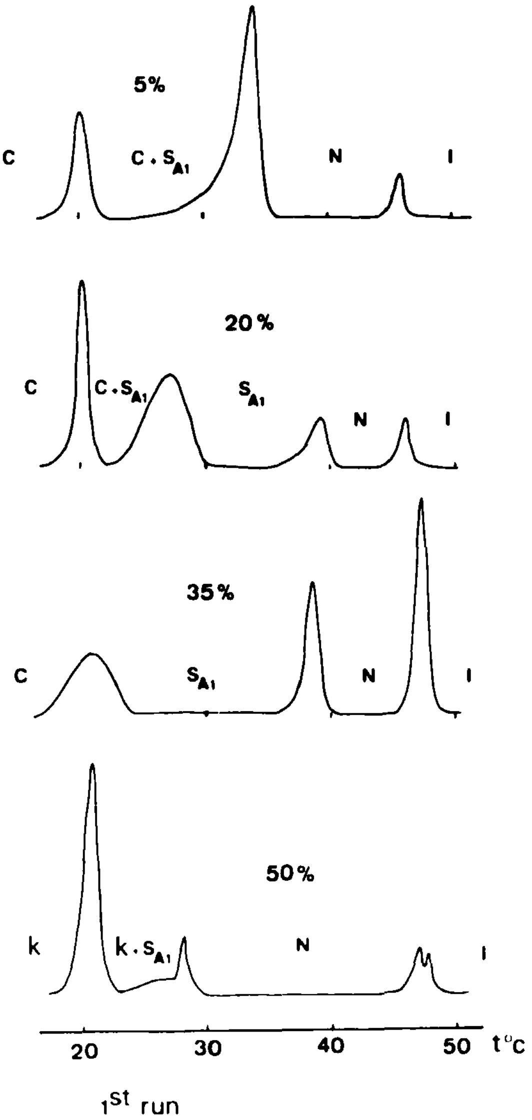


FIGURE 2 DSC thermograms—first heating run 9CB/5H5 mixtures—composition in weight % 9CB
C : 5H5 crystal
K : 9CB crystal

calculated by the Schroeder-Van Laar equation, to correspond to 38% 9CB. The $S_{A1}$–N transition temperature strongly depends on the composition of the mixture. It follows immediately after the end of the melting of the excess 9CB (C–$S_{A1}$ transition) for mixtures below 50%, passes through a maximum between 20 and 30% and then decreases with decreasing 9CB content. For the 5% 9CB mixture, the transition to the nematic phase immediately follows the end of the melting of the excess 5H5. The N–I transition is rather constant in temperature and is observed between 48 and 49°C in the whole composition range. All the DSC data are in agreement with the microscope examinations of the samples.

*2.1.2. Continuous recording of the fluorescence intensity at constant wavelength as a function of the temperature.* The fluorescence intensities recorded continuously as a function of the temperature in the frequency range of monomer and excimer emission (respectively 310 and 470 nm) are given in Figure 3 for the seven mixtures investigated. Different discontinuities corresponding to the phase transitions observed by DSC are present. The sensitivity of the method results from the selective measurement of the monomer fluorescence intensity in the short wavelength range of the spectrum (310 nm) and of the excimer fluorescence intensity in the long wavelength range of the spectrum (470 nm).

For mixtures near or below the eutectic composition (5 to 35 wt% 9CB).

Small letters a to k will be used later in the text to characterize the temperature ranges of interest. Range a–b of Figure 3 is characteristic of the crystal–$S_{A1}$ transition corresponding to the partial melting at the eutectic temperature. At b, the system is composed of a non-fluorescent crystalline phase (5H5) and a fluorescent $S_{A1}$ phase at the eutectic composition which consists predominantly of excimer emission. After b, (range b–c) when the temperature of the sample rises, the concentration of 9CB decreases in the $S_{A1}$ phase when the weight% 9CB of the initial mixture is different from the eutectic composition, in agreement with Figure 1A. As a consequence, monomer fluorescence increases while excimer fluorescence decreases according to the equation:

$$I_D/I_M = [k_{FD}/k_{FM}] * [(k_{DM}[M])/(k_{MD} + k_D)] \qquad (1)$$

where $I_M$ and $I_D$ are the monomer and the excimer fluorescence intensities.[2,4] Equation 1 has been obtained for steady-state illumination under photostationary conditions using the monomer–excimer kinetic scheme proposed by Birks:[4]

| | | | |
|---|---|---|---|
| $M \xrightarrow{h\nu} M^*$ | $I_a$ | excitation | |
| $M^* \rightarrow M + h\nu_{FM}$ | $k_{FM}$ | radiative deactivation of M*<br>emission of monomer fluorescence | $k_M$ |
| $M^* \rightarrow M + kT$ | $k_{GM}$ | non radiative deactivation of M* | |
| $M + M^* \rightarrow D^*$ | $k_{DM}$ | excimer formation | |
| $D^* \rightarrow M + M^*$ | $k_{MD}$ | excimer dissociation | |
| $D^* \rightarrow M + M + h\nu_{FD}$ | $k_{FD}$ | radiative deactivation of D*<br>emission of excimer fluorescence | $k_D$ |
| $D^* \rightarrow M + M + kT$ | $k_{GD}$ | nonradiative deactivation of D* | |

At point c, whatever the mixture involved, the melting of the crystals is complete: the systems are homogeneous $S_{A1}$ phases. Range d–e and f–g are characteristic of the $S_{A1}$–N and N–I transitions respectively. They can be interpreted as resulting

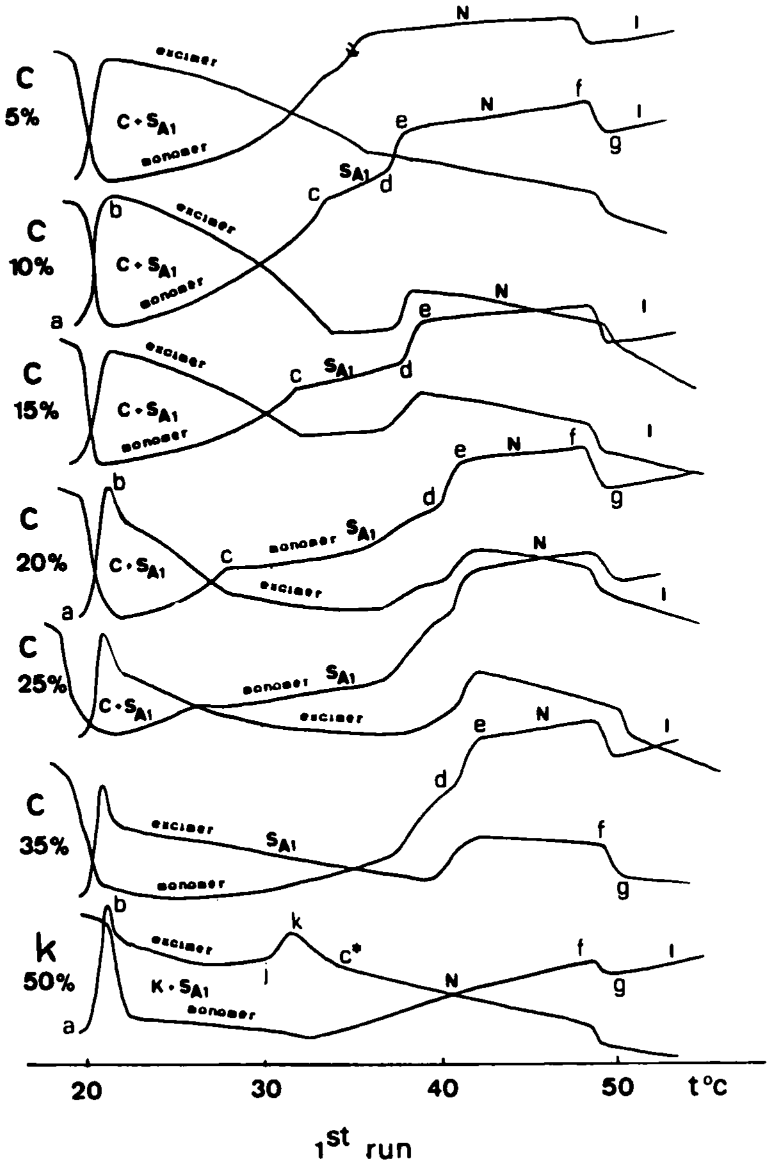


FIGURE 3 Fluorescence intensity at constant wavelength as a function of the temperature for the system 9CB/5H5 (composition in weight % 9CB)—first heating run
C : 5H5 crystal
K : 9CB crystal
λa = 310 nm (monomer) – λa = 470 nm (excimer)
Scan rate 3°C/min.

from changes of intensity correlated with changes of the refractive index on passing from one phase to another. The $S_{A1}$–N transition temperatures are a function of the concentration of the mixtures; they are depressed when the 9CB content decreases in the sample. The N–I transitions occur between 48–49°C. For some mixtures in the composition range (20–25–35) weight% of 9CB, unexpected discontinuities which could be assigned to "transitional" effects are observed below the $S_{A1}$–N transition. These effects need however some further investigation before a definitive explanation can be given. For the mixtures with concentrations greater than 20wt%, immediately after point b, a very steep decrease of the intensity is observed at the wavelength of the excimer. This could be due to a rapid modifcation of the specific absorption coefficient of 9CB resulting from the reorientation of the cyanobiphenyl molecules of the mixture, perpendicular to the quartz surface of the cell. The cyanobiphenyl derivatives have indeed a very strong tendency to homeotropy in the mesomorphic phases.

For the mixture above the eutectic composition (50 wt% 9CB).

At the eutectic melting (range a–b of Figure 3), the system is composed of a fluorescent solid (9CB crystal) and the same fluorescent $S_{A1}$ phase at the eutectic composition as described above. After b, when the temperature of the sample rises, the concentration of the 9CB increases in the $S_{A1}$ phase in agreement with Figure 1A and the initial weight% CB (range b–c*). As a consequence, the monomer fluorescence decreases while excimer fluorescence increases according to Equation 1. Just before point c*, a $S_{A1}$–N (range j–k) transition is observed. Range f–g is characteristic of the N–I transition. (N.B.: this transition is not clearly detected in the frequency range of the monomer).

*2.1.3. Spectral distribution of the fluorescence as a function of the temperature.* Two types of experimental observations require discussion:

discontinuities of either the fluorescence intensities or of the $I_M/I_D$ values at the phase transitions

the evolution of the same parameters as a function of temperature in each phase.

Table II summarizes the results obtained for the seven mixtures investigated in the present work. The fluorescence spectra given in Figures 4, 5, 8 and 9 will be related to the temperature ranges of stability of the different phases defined in Figure 3 using small letters.

Up to 25 weight% CB in 5H5, the spectral distribution at some characteristic temperatures are the following. Below 21°C (below point a in Figure 3), the structured fluorescence is that of the crystalline 9CB (Figures 4A and 5A). Between b and c (Figures 4B and 5B), the fluorescence is emitted by the $S_{A1}$ phase initially at the eutectic composition; at this composition the spectrum is mainly excimer fluorescence with a small contribution of monomer fluorescence at 330 nm. As the temperature rises, a progressive decrease of the 9CB weight fraction in the $S_{A1}$ phase is observed up to point c which corresponds to the end of melting of 5H5, according to the phase diagram given in Figure 1A. Between b and c excimer fluorescence is thus progressively converted to monomer fluorescence according to equation 1. An isoemissive point which is concentration dependent is obtained. This corresponds, at constant temperature and in a narrow frequency range, to the following condition[5,6,7]:

$$i = i_M + i_D \qquad \text{and} \qquad di/d[\mathrm{M}] = 0 \tag{2}$$

TABLE II

| WT % CB | First heating run | | Second heating run | |
|---|---|---|---|---|
| 5% | C + $S_{A1}$ | Fluorescence of the eutectic mixture (predominantly excimer)<br>M–D conversion (20–31°C)<br>[a]isoem point (C) : ~ 368 nm | $S_G$–N | monotropic phase<br>monomer fluorescence<br>M–D conversion at the phase<br>[c]transition isoem. point (P) |
| | $S_{A1}$ | important increase of intensity | | |
| | N | no significant change | N | no significant change |
| | I | M–D conversion (50–85°C)<br>[b]isoem. point (T) : ~ 350 nm | I | M–D conversion (48–85°C)<br>[b]isoem. point (T) : ~ 350 nm |
| 10% | C + $S_{A1}$ | M–D conversion (20–30°C)<br>[a]isoem. point (C) : ~ 366 nm | $S_B$ | monotropic phase (predom. monomer)<br>M–D conversion (32–36°C)<br>[c]isoem. point (P) : ~ 370 nm |
| | $S_{A1}$ | increase of intensity | $S_{A1}$ | no change of intensity |
| | N | no significant change | N | no significant change |
| | I | M–D conversion (48–85°C)<br>[b]isoem. point (T) : ~ 350 nm | I | M–D conversion (48–85°C)<br>[b]isoem. point (T) : ~ 350 nm |
| 20% | C + $S_{A1}$ | M–D conversion (22–31°C)<br>[a]isoem. point (C) : ~ 358 nm | $S_B$ | monotropic phase (predom. monomer)<br>M–D conversion (20–25°C)<br>[c]isoem. point (P) : ~ 378 nm |
| | $S_{A1}$ | small increase of intensity | $S_{A1}$ | no change of intensity<br>M–D conversion (25–48°C)<br>[b]isoem. point (T) : ~ 372 nm |
| | N | no significant changes | N | |
| | I | M–D conversion (48–85°C)<br>[b]isoem. point (T): ~ 364nm | I | M–D conversion (48–85°C)<br>[b]isoem. point (T) : ~ 364 nm |

| | | | | |
|---|---|---|---|---|
| 25% | C + $S_{A1}$ | M–D conversion (20–30°C)<br>[a]isoem. point (C) : ~ 352 nm | | |
| | $S_{A1}$ | small increase of intensity | $S_{A1}$ | M–D conversion<br>[b]isoem. point (T) |
| | N | no significant change | N | |
| | I | M–D conversion<br>[b]isoem. point (T) : ~ 364 nm | I | M–D conversion (48–85°C)<br>[b]isoem. point (T) : ~ 364 nm |
| 35% | Eutect. | no isoem. point | | |
| | $S_{A1}$ | small increase of intensity | $S_{A1}$ | M–D conversion (20–40°C)<br>[b]isoem. point (T) |
| | N | | N | |
| | I | blue shift of the $\lambda_{max}$ of the excimer | I | blue shift of the $\lambda_{max}$ of the excimer |
| 50% | C + $S_{A1}$ | fluorescence of the eutectic mixture (predominantly the excimer) + structured fluorescence due to crystalline 9CB | | |
| | N | no significant change | N | M–D conversion (20–48°C)<br>[b]isoem. point (T) : ~ 378 nm |
| | I | blue shift of the $\lambda_{max}$ and decrease of the excimer intensity | I | blue shift of the $\lambda_{max}$ and decrease of the excimer intensity |

[a]: isoem (C) : the variable parameter is concentration.
[b]: isoem (T) : the variable parameter is temperature.
[c]: isoem (P) : the variable parameter is the nature of the phase.

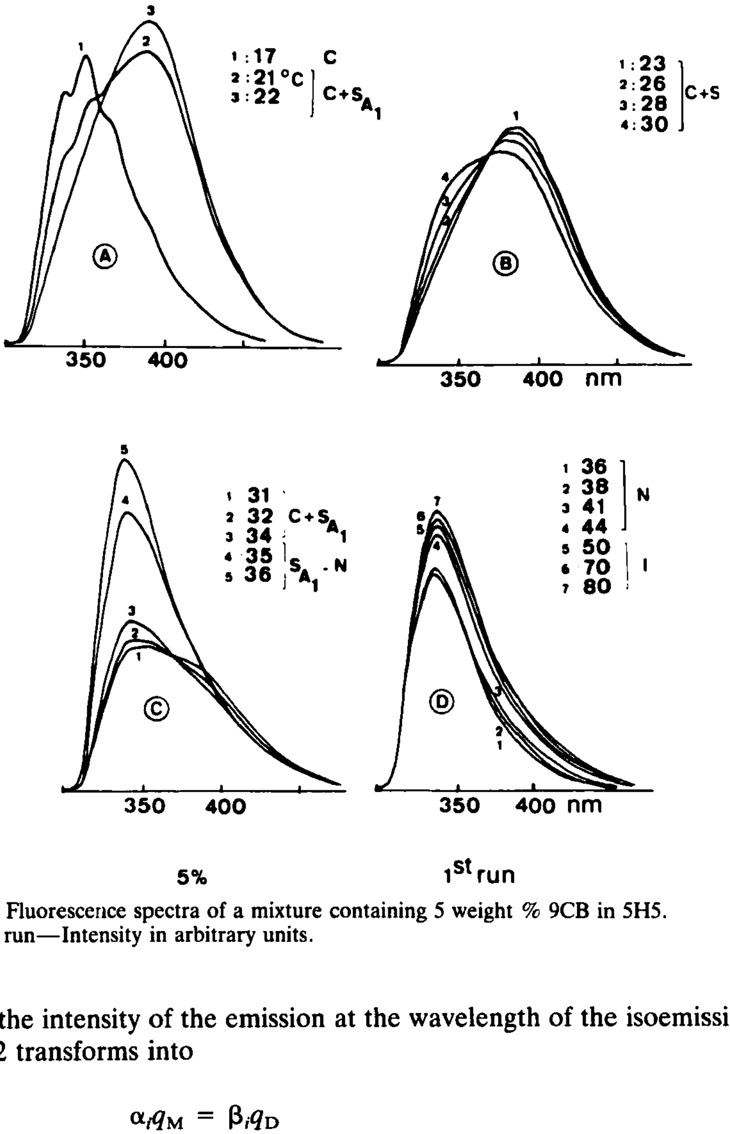


FIGURE 4 Fluorescence spectra of a mixture containing 5 weight % 9CB in 5H5. First heating run—Intensity in arbitrary units.

where $i$ is the intensity of the emission at the wavelength of the isoemissive point. Equation 2 transforms into

$$\alpha_i q_M = \beta_i q_D$$

where

$$\alpha_i = i_M/\phi_M \quad \text{and} \quad \beta_i = i_D/\phi_D$$

$\phi_M$ and $\phi_D$ are the quantum yield of monomer and excimer fluorescence and $q_M$ and $q_D$ are the quantum efficiencies, respectively defined by:

$$\phi_M = k_{FM}/[k_M + k_{DM}[M]] - \phi_D = k_{FD}/[k_{DM}[M]]$$

and

$$q_{FM} = k_{FM}/k_M - q_{FD} = k_{FD}/k_D$$

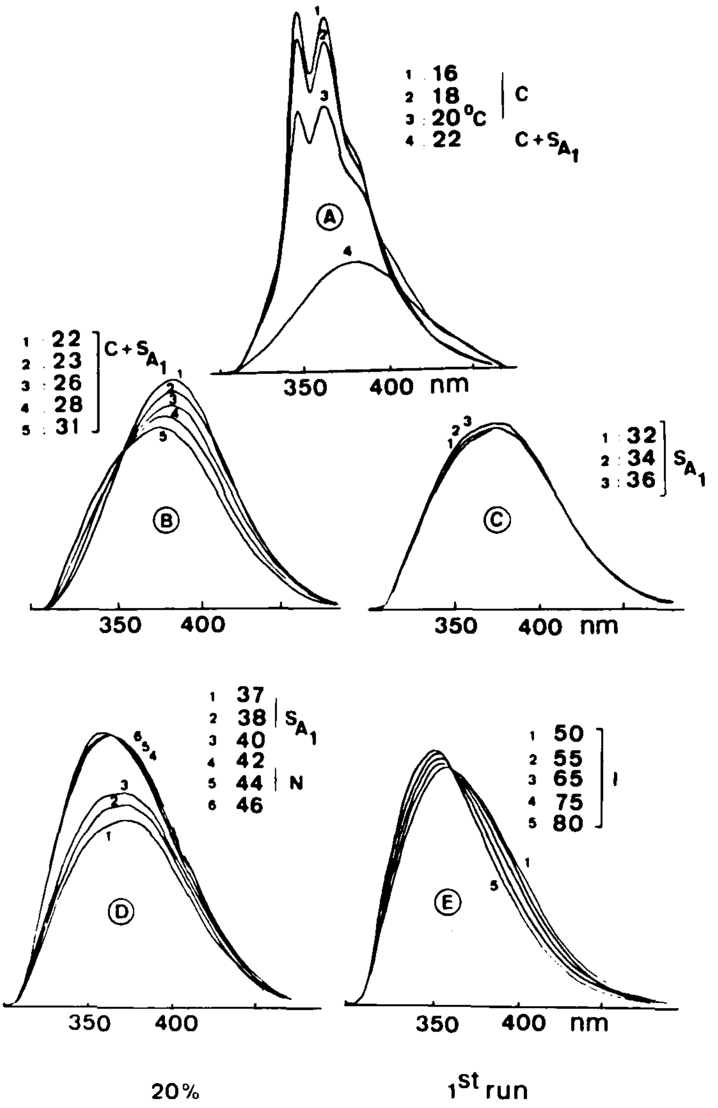


FIGURE 5 Fluorescence spectra of a mixture containing 20 weight % 9CB in 5H5. First heating run—Intensity in arbitrary units.

From point c, the weight fraction of 9CB in the fluorescent phase is constant and the subsequent modifications of the emission spectrum are functions of only the temperature and/or the organization of the phase. At the $S_{A1}$–N transition, an enhancement of intensity of both $I_M$ and $I_D$ is observed whilst in the $S_{A1}$ and nematic phase, no significant changes of intensity occurs (Figures 4C–D and 5C–D). Also the ratio $I_M/I_D$ in the nematic phase is not very different from that of the $S_{A1}$ phase. A decrease in the total emission intensity reveals the N–I transition (range f–g) in agreement with the measurements at one wavelength reported in Figure 3. In the isotropic phase beyond g, an increase of $I_M/I_D$ does occur as the temperature rises (Figures 4D and 5E). At 75°C, the fluorescence spectrum is predominantly that of the monomer. An isoemissive point is observed in the isotropic phase. In this temperature range, the concentration is constant and the variable parameter is temperature. The conditions to be obeyed for the existence of an isoemissive point having temperature as the variable parameter are very complex when the basic equations

$$i = i_M + i_D \quad \text{and} \quad di/dT = 0 \tag{3}$$

are developed as a function of the different parameters involved in the kinetic scheme usually obeyed in excimer-forming systems. Several examples of such high temperature isoemissive points have been reported in the literature.[8,9] Under these conditions, the rate constant for excimer dissociation $k_{MD}$ is generally larger than the rate constant $k_D$ for deactivation of the excimer so that:

$$\begin{aligned} I_D/I_M &= [k_{FD}/k_{FM}] * [(k_{DM}[M])/k_{MD})] \\ &= k * [k_{DM}/k_{MD}] \end{aligned} \tag{4}$$

where $k$ is a constant provided $k_{FD}$, $k_{FM}$ and [M] are temperature invariant. A state of equilibrium is obtained in the high temperature region and the dependence of ln $(I_D/I_M)$ on 1/T yields an estimate of the binding energy of the excimer. The value of B ~ 15 kJ/mole, obtained from Figures 4D and 5E and given in Figure 6, is in quite good agreement with those of other aromatic compounds.[10] In the $S_{A1}$ phase studied in the present work, the steady-state fluorescence spectra do not provide any evidence for the existence of two different excimers as it has been

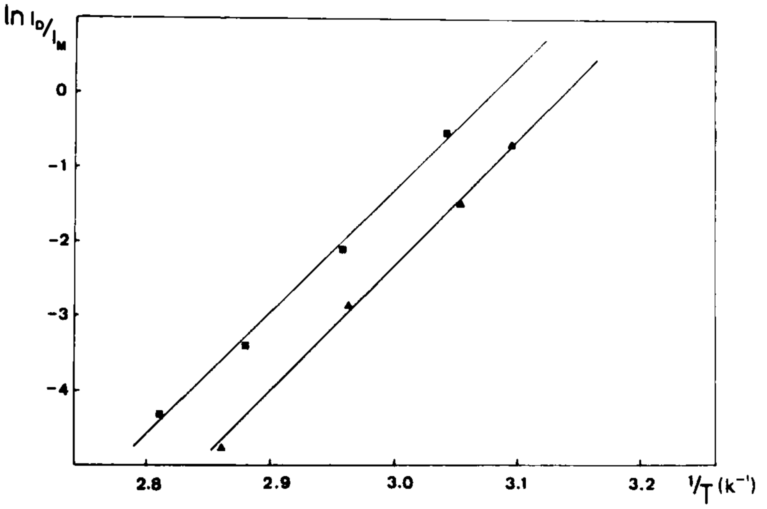


FIGURE 6 Variation of $I_D/I_M$ as a function of temperature for mixtures containing 15 ▲ and 20 ■ weight % 9CB in 5H5.

proposed by Markovitsi *et al.*[11] for 8CB in the $S_{Ad}$ phase using time-resolved fluorescence measurements. In this $S_{Ad}$ phase, both, partial and/or complete overlapping of the rigid aromatic cores could be possible, according to a structural model proposed by Guillon and Skoulios[12,13] for mesophases obtained with dissymetric and highly polar mesogens (Figure 7). Exciplex formation between the cyanobiphenyl and the ester compound has also to be ruled out in the present work: the fluorescence of mixtures assigned to the excimer has indeed the same $\lambda$ max, the same spectral distribution and the same lifetime as the emission observed in neat cyanobiphenyl. (*N.B.* an exciplex is an excited molecular complex of definite stoichiometry formed from two different species, which is dissociated in the ground state.[4])

For the mixture in the range of the eutectic composition (35% CB)

The only spectral modifications after the eutectic melting (range b–d), consist of a small enhancement of the intensity in the $S_{A1}$ phase (Figure 8B–C) and a pro-

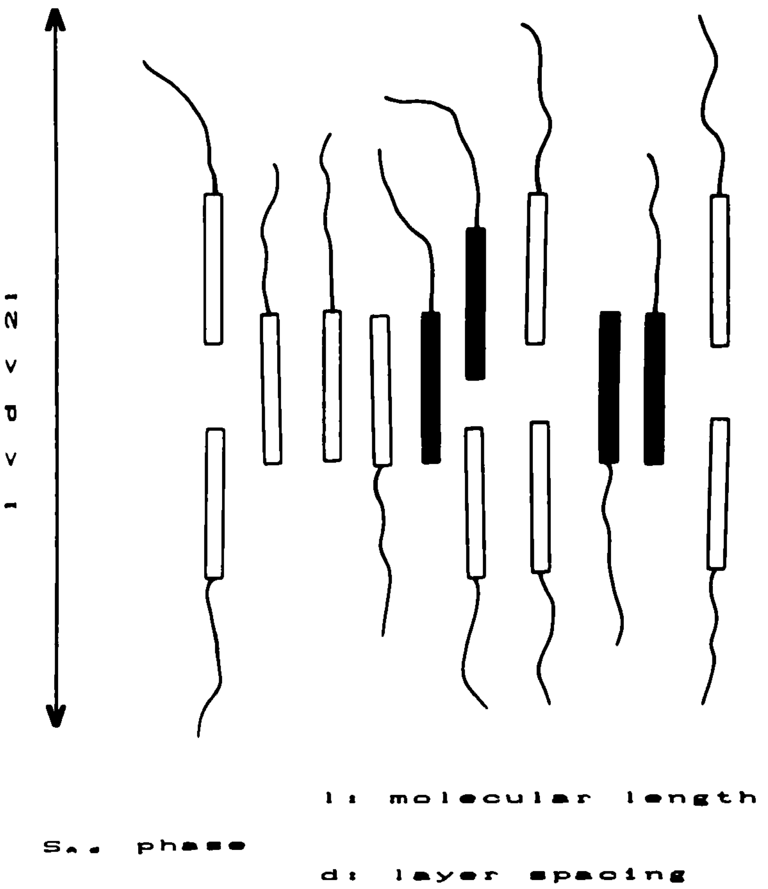


FIGURE 7 Proposed model for fully and partially overlapped excimers in the $S_{Ad}$ phase of 8CB.[13]

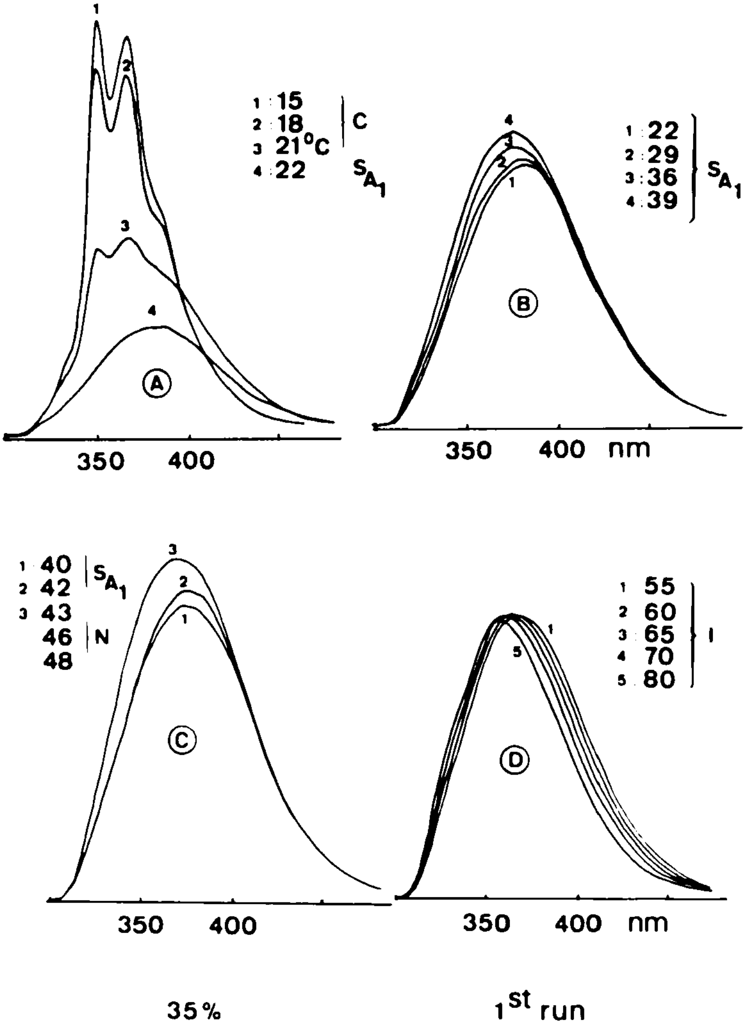


FIGURE 8 Fluorescence spectra of a mixture containing 35 weight % 9CB in 5H5. First heating run—Intensity in arbitrary units.

gressive blue shift of the wavelength of the maximum in the isotropic phase (Figure 8D). No isoemissive point having temperature as the variable parameter is detected in this phase as it is for systems containing low CB wt%. The observed shift of the λ max of the fluorescence can be assigned either to monomer–excimer conversion without isoemissive point or to a change of the potential energy curves of the excimer and/or of a paired chromophore in the ground state (Figure 9). The existence of several different excimers characterized by varying degrees of overlap of the aromatic rings could also explain the results.

For the mixture at 50 weight% CB (above the eutectic composition)

At the eutectic melting (range a–b of Figure 3), the spectral distribution corresponds predominantly to the excimer with a contribution of the structured fluo-

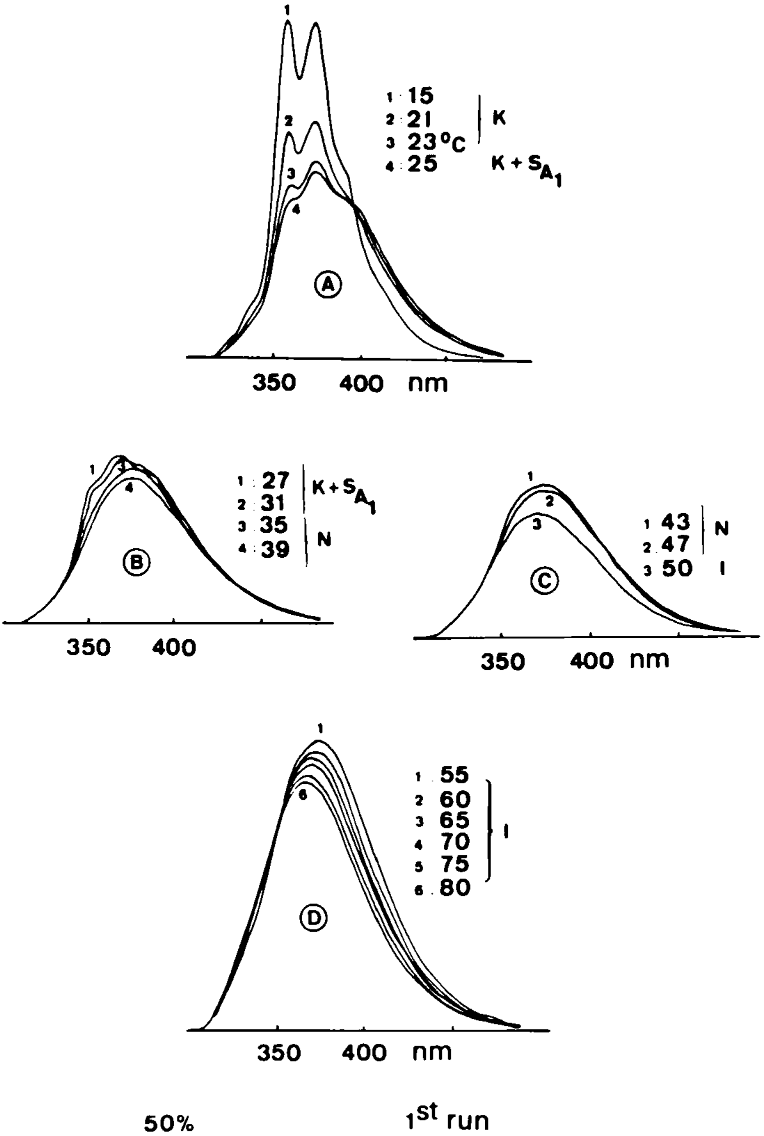


FIGURE 9 Fluorescence spectra of a mixture containing 50 weight % 9CB in 5H5. First heating run—Intensity in arbitrary units.

rescence of the crystalline 9CB (Figure 9A). The structure is maintained up to 32°C (Figure 9B). This temperature corresponds to the end of melting of the crystalline 9CB as confirmed by microscopy; between 29 and 30°C the fan-like texture of the $S_{A1}$ phase coexisting with the crystalline solid changes into the nematic state and almost simultaneously the excess solid (crystalline 9CB) melts; this transforms the system to a homogeneous nematic phase. When the temperature increases in the isotropic phase, the λ max of the emission is now progressively shifted to shorter wavelength with a simultaneous decrease in the intensity (Figure 9D). No iso-emissive point with temperature as the variable parameter is observed in this phase. Simulation of spectra for different values of the photophysical parameters have shown that a decrease of intensity coupled to a blue shift of the λ max is observed in the fluorescence spectra as a function of the temperature if non-radiative deactivation processes become more important than dissociation.[14]

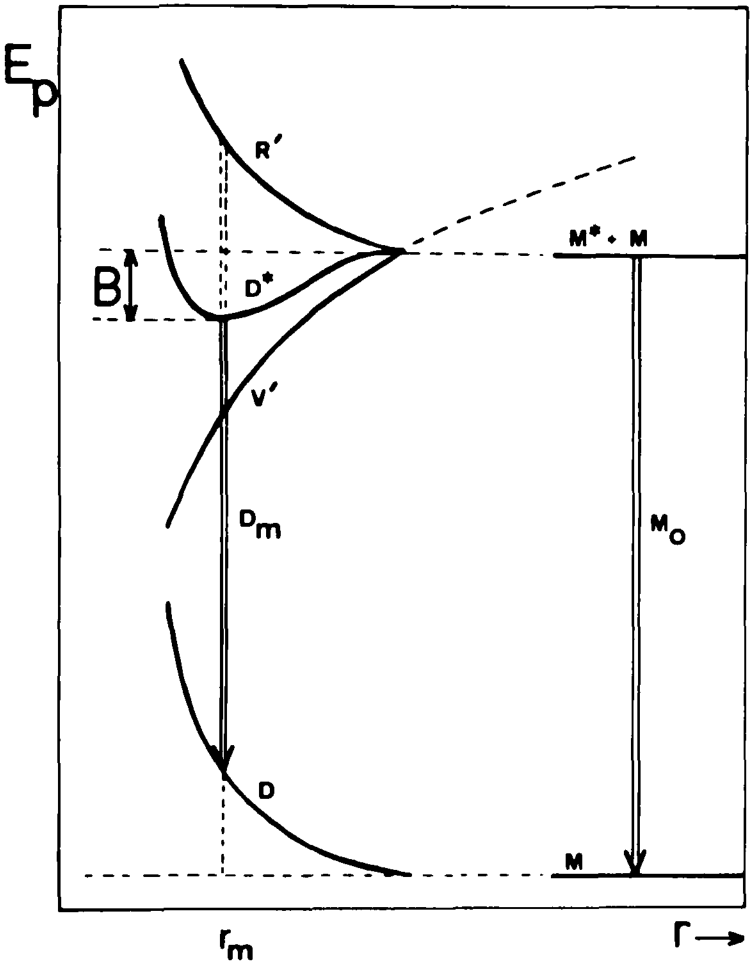


FIGURE 10 Schematic potential energy diagram of pair of parallel molecules M and M* as a function of intermolecular separation r
R' : repulsive potential in the excited state
V' : excimer interaction potential
D : repulsive potential in the ground state
D* (= V' + R') : resultant excimer energy
$M_o$ : molecular O–O transition
$D_m$ : peak excimer transition
$r_m$: excimer separation
(after Birks[4]).

## 2.2 Second heating run

*2.2.1 DSC analysis* When the sample used during the first heating run is allowed to cool from the isotropic phase and then reheated, many endotherms are present (Figure 11).

For the 5 wt% CB, a first endotherm is observed at ≈32°C. This endotherm is composed of two peaks which could be the successive $S_G$–$S_B$ and $S_B$–N transitions as indicated by microscopy (a monotropic $S_G$–N is also observed for the neat ester). The second peak at 47°C indicates the N–I transition. When the amount of 9CB

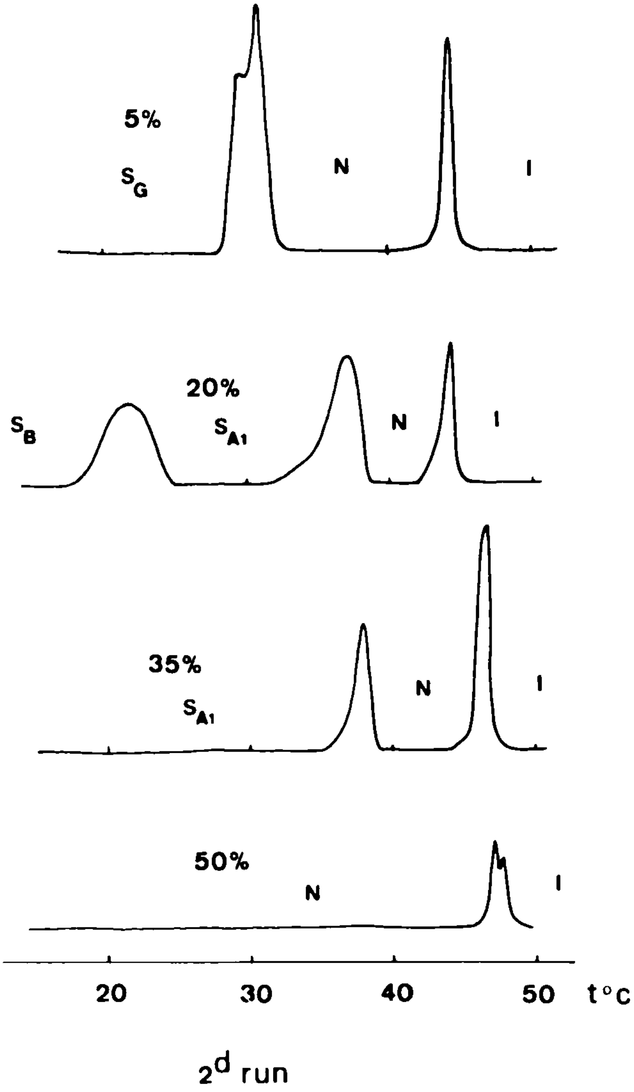


FIGURE 11 DSC thermograms—Second heating run. 9CB/5H5 mixtures-composition in weight % 9CB

increases in the sample, a first peak is observed at 33°C (10 wt%), at 31°C (15 wt%) (see also reference 1), and at 24°C (20 wt%). In this case, the peak is the $S_B$–$S_{A1}$ transition. Between 20 wt% and 35 wt%, this peak, if present, would be observed far below room temperature. For these systems the second peaks are the $S_{A1}$–N transitions and the third peaks the N–I transitions. For the 50 wt% mixture,

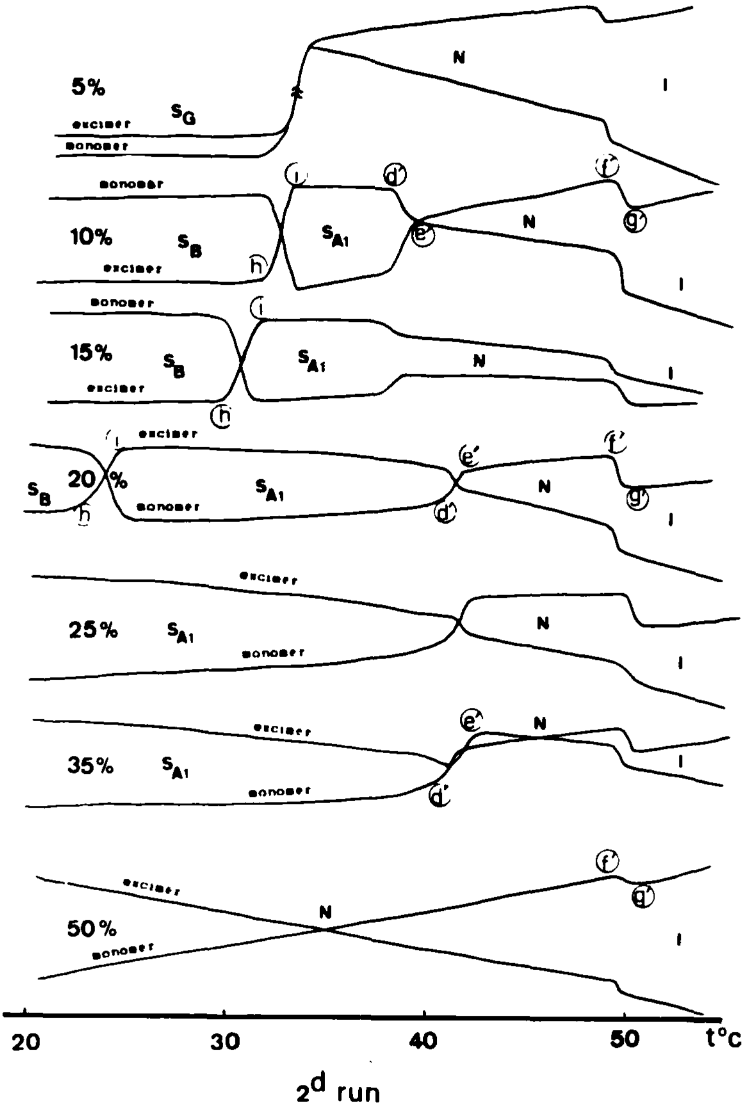


FIGURE 12 Fluorescence intensity at constant wavelength as a function of the temperature for the system 9CB/5H5
(composition of weight % 9CB)—Second heating run.
λa = 310 nm (monomer) – λa = 470 nm (excimer).
Scan rate 3°C/min.

no transition occurs before the N–I indicating that we are out of the injected $S_{A1}$ region as assumed during the first heating run.

All the $S_{A1}$–N and N–I transitions are observed in the same temperature range as those of the first heating run.

*2.2.2 Continuous recording of the fluorescence intensity at constant wavelength as a function of the temperture.* The fluorescence intensities measured in the monomer wavelength range (310 nm) and in the excimer wavelength range (470 nm) as a function of the temperature are given in Figure 12. Range h–i shows an important intensity change which corresponds, according to the amount of 9CB in the sample, to a $S_G$–N transition (5% CB) or to a monomer-excimer conversion associated with a $S_B$–$S_{A1}$ transition (10 to 25 wt% CB). Between d′ and e′ the

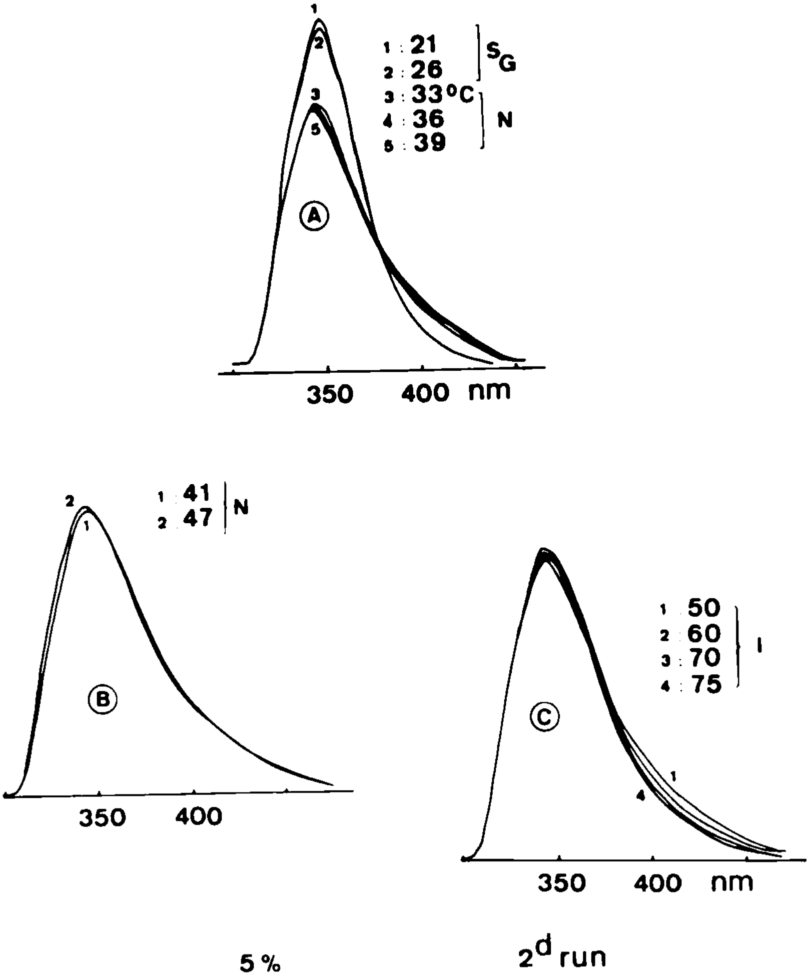


FIGURE 13 Fluorescence spectra of a mixture containing 5 weight % 9CB in 5H5. Second heating run—Intensity in arbitrary units.

expected $S_{A1}$–N transitions are present, except for the 50 wt% sample, which is out of the injected phase. Between f′ and g′ the expected N–I transitions do occur.

*2.2.3 Spectral distribution of the fluorescence as a function of the temperature.* All of the results obtained are summarized in TABLE II. The fluorescence spectra given in Figures 13, 14, 15, and 16 will be related to the temperature ranges of stability of the different phases defined in Figure 12 using small letters. Below h, the fluorescence of the sample is predominantly that of the monomer for mixtures up to 20 wt%CB (Figures 13A and 14A), beyond *i* excimer fluorescence is observed according to the concentration of the 9CB in the sample (Figures 14A and 15A).

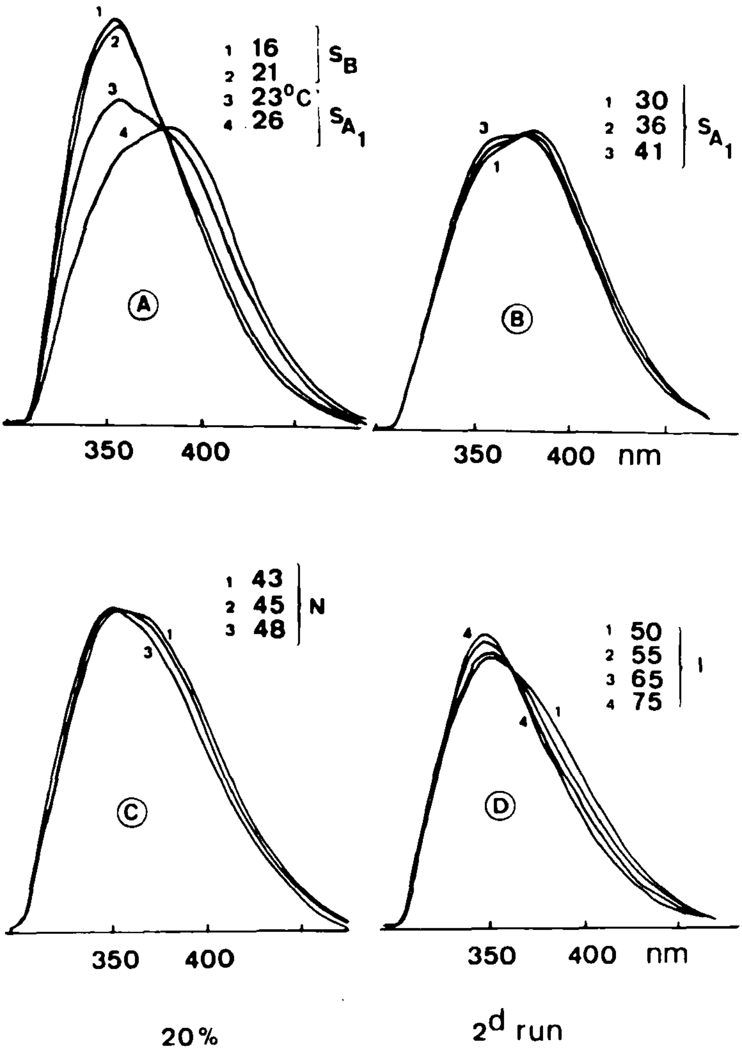


FIGURE 14 Fluorescence spectra of a mixture containing 20 weight % 9CB in 5H5. Second heating run—Intensity in arbitrary units.

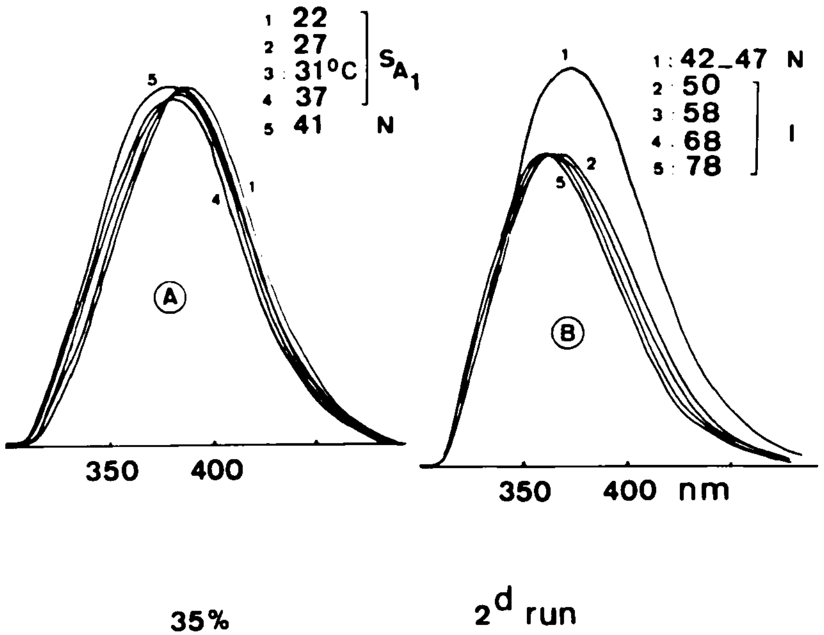


FIGURE 15 Fluorescence spectra of a mixture containing 35 weight % 9CB in 5H5. Second heating run—Intensity in arbitrary units.

The monomer fluorescence is representative of the $S_G$ and $S_B$ phases. In the $S_G$ phase the molecular axes are tilted with respect to the normal to the layers with hexagonal arrangement within the layers.[15] In the $S_B$ phase, the hexagonal arrangement is maintained but the molecular axes are now orthogonal to the layers. These two phases are ordered but rigid and are thus not favourable for the formation of excimers. In contrast, the disordered $S_{A1}$ phase with its random distribution of the molecular axes within the layers and its higher mobility is a much more favorable environment for the formation of excited dimers.

The $S_G$–N or $S_B$—$S_{A1}$ transitions are order–disorder phase transitions characterized by a monomer-excimer conversion. A new type of isoemissive point, having the nature of the phase as the variable parameter is obtained at ≈370 nm for the 5–20 wt% systems respectively (range h–i of Figure 12). This isoemissive point is observed in a small temperature range associated with the phase transition and has to be related to the disappearance of geometrical restrictions imposed by the in-plane organisation of the smectic B phase and by its low mobility. In the $S_{A1}$ phase, there is no change of intensity as observed during the first heating run; the ratio $I_M/I_D$ is constant in the $S_{A1}$ phase whatever the thermal history of the sample (first or second heating run) indicating that the $S_{A1}$ phases are well defined. For 20% CB, a first isoemissive point with the nature of the phase as variable parameter is observed between 20 and 26°C (Figure 14A) due to the $S_B$–$S_{A1}$ transition (range h–i of Figure 12). A second isoemissive point with temperature as variable parameter is now is observed in the range i–f′ *i.e.*: in the $S_{A1}$ and in the N phases (Figure

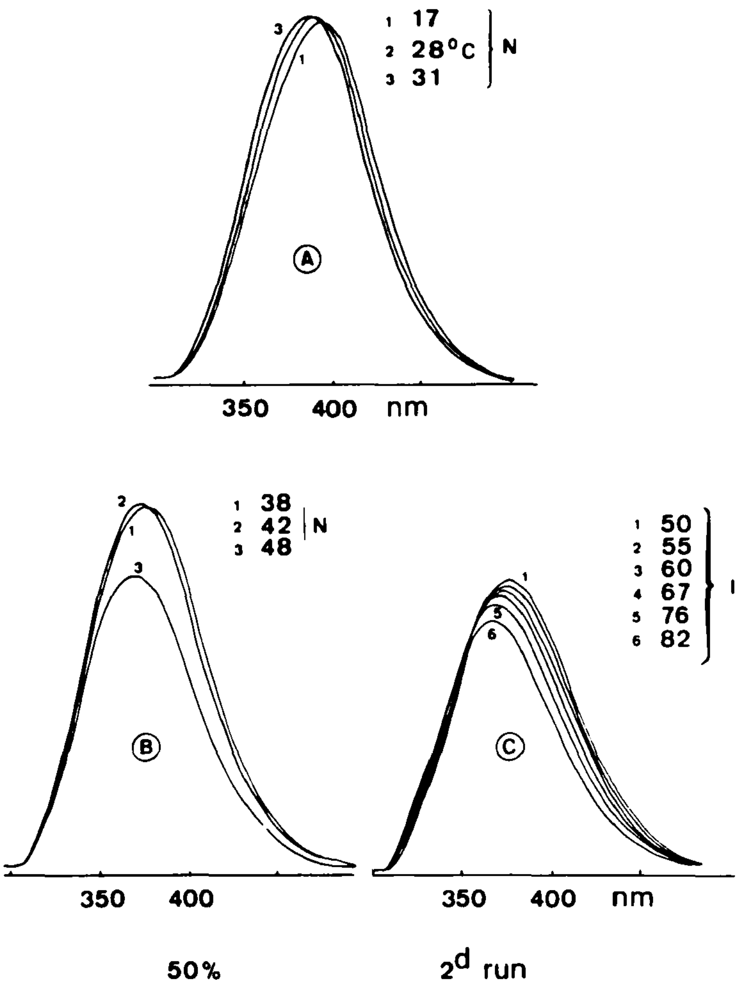


FIGURE 16 Fluorescence spectra of a mixture containing 50 weight % 9CB in 5H5. Second heating run—Intensity in arbitrary units.

14B and 14C). This isoemissive point appears also for all the other mixtures 25, 35 and 50 wt% CB (Figures 15A and 16A–B) where the $S_B$ phase does not form. In the isotropic phase (Figures 13C and 14C), the isoemissive points associated with excimer dissociation are again present in the same frequency range as in the first heating run for mixtures containing 5 to 25 wt% CB. For the two other mixtures (35 and 50 wt%) the λ max of the excimer emission shifts to the blue (Figure 15B) and simultaneously decreases in intensity (50 wt%) (Figure 16C).

## CONCLUSION

The spectral distribution and the intensity of the fluorescence of mesomorphic mixtures have been studied. These mixtures have the property to induce new mesomorphic phases which do not exist in the separate neat compounds. The study of these phases is attractive since it opens the possibility of understanding the specific interactions which develop in the mixtures of the two compounds. The system investigated is composed of a fluorescent polar 9CB derivative (4-nonyl-4'-cyanobiphenyl) and of a non-fluorescent and weakly polar ester 5H5 (4-pentyl-phenyl-trans-4'-pentylcyclohexane-1-carboxylate). It has been shown that it is possible to detect in very small samples (≈5 mg):

(i) the phase transitions by measuring the fluorescence intensity as a function of the temperature.

(ii) the molecular interactions existing in the excited state between 9CB and 5H5 in the different phases.

The emission spectra of these mixtures are composed, in the concentration range where the induced smectic phases appear, of monomer fluorescence resulting from the radiative deactivation of an excited 9CB chromophore and/or of excimer fluorescence, resulting from the radiative deactivation of two neighbouring interacting 9CB chromophores associated as a "dimer" in the excited state. The intensity ratio of these two emissions depends on:

the proportion of ester in the mixture

the temperature

the nature of the phase involved. As an example, the excimer does not form easily in the ordered rigid smectic B and smectic G phases, but forms predominantly in the smectic $S_{A1}$ and in the nematic phases. Our results have also shown that the band shape and λ max of the fluorescence spectrum can be related to changes of the relative importance of radiative and non-radiative deactivation processes of the excited state. In these mixtures a new type of isoemissive point which has the nature of the phase as variable parameter has been discovered.

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