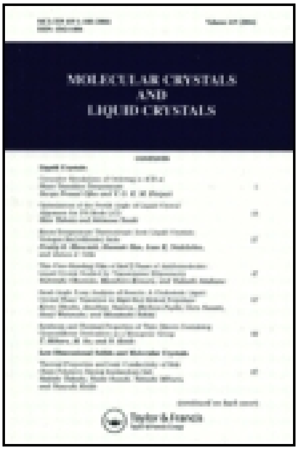

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Energy Transfer and Migration in Liquid Crystalline Systems. II-4-Octyl-4′-Cyanobiphenyl, 1 -Heptyl-4-(4′-Cyanophenyl) Cyclohexane and 4-Pentyl-4′-Methylbiphenyl[†;]

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Energy Transfer and Migration in Liquid Crystalline Systems. II—4-Octyl-4′-Cyanobiphenyl, 1-Heptyl-4-(4′-Cyanophenyl) Cyclohexane and 4-Pentyl-4′-Methylbiphenyl†

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The photophysical processes occurring in the mesomorphic and isotropic phases of two thermotropic liquid crystals, an alkylcyanobiphenyl and an alkylcyanophenylcyclohexane, have been investigated and compared to those of the alkoxycyanobiphenyls previously reported.[1] Rate constants of transfer to diphenyloctatetraene have been measured for the different phases and interpreted according to Voltz's model to obtain the migration coefficients. Two types of transfer have been shown to occur in these systems.

INTRODUCTION

The present paper is Part II of a more general study undertaken in order to investigate the effect of liquid crystal (LC) organization on energy migration and transfer.

In Part I of the study[1] we showed that

- the emission of 4-alkoxy-4′-cyanobiphenyl derivatives (8COB and 3COB) is of excimer type in the smectic, nematic and isotropic phases.
- in COB derivatives, where the electronic coupling between neighbouring aromatic units is efficient, energy migration is very important whatever the phase involved.

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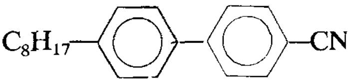
†Part I: *Mol. Cryst. Liq. Cryst.*, **106**, 45 (1984).

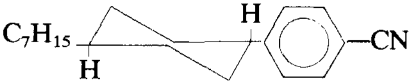
- the migration coefficient is of the same order of magnitude as that for neat aromatic phases ($\Lambda = 10^{-5}$ cm^2 s^{-1}) indicating that the order revealed by the migration coefficient Λ in smectic and nematic liquid crystals is much more similar to that of a neat aromatic liquid than a crystal.
- residual short range nematic ordering still persists into the isotropic phase.

The three derivatives studied in this paper are

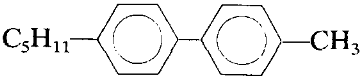
- 4-octyl-4′-cyanobiphenyl (8CB)



- 1-heptyl-4-(4′-cyanophenyl)cyclohexane (7PCH)



- 4-pentyl-4′-methylbiphenyl (5MB)



They were chosen in order to investigate the relationship between excimer and singlet energy migration, i.e., is singlet energy migration consistant with an excimer formation-dissociation mechanism or on the contrary, are excimers an efficient trap to it? We have studied:

- 8CB as alkyl analogue of the alkoxy derivatives previously studied
- 7PCH as a liquid crystal where the electronic coupling between neighbouring aromatic molecules is less important, since a highly polarizable phenyl group of the biphenyl structure is replaced by a cyclohexane group which has negligible polarizability. Furthermore, antiparallel association as observed in the CB's and COB's series

could be less favourable for excimer formation in the PCH's compounds: the substitution of a phenyl by a much bulkier ring system should have a marked effect on the packing of pairs of molecules in the excited state.

- 5MB as a compound in which the 4-CN substituent is replaced by a CH_3 and the 4'-alkyl chain has only 5 C instead of 8 in 8CB. As a consequence, the 5MB has no LC character and the lowest excited state is different.

This study involves the analysis of the fluorescence emission and decay, and energy transfer experiments to diphenyloctatetraene in normal solvents, neat phases and LC solvents.

EXPERIMENTAL

Neat phases

- 8CB was purchased from B.D.H. Chemicals Ltd, Poole, Dorset, U.K. When excited at 280 nm, the fluorescence spectrum exhibits a small contribution from an impurity with λ_{max} at 355 nm. This impurity can be selectively excited at 320 nm and was in a previous work tentatively assigned to an α,β-unsaturated derivative.[2] The 8CB was therefore carefully purified by one recrystallization from n-hexane and three recrystallizations from spectrophotometric grade MeOH. It was then shown to be free from impurities by HPLC and by spectrofluophosphorimetry.
- 7PCH is a Merck product shown to be free from impurities after recrystallization from n-hexane (1x) and spectrophotometric grade MeOH (3x).
- 5MB is a Hoffmann La Roche product, shown to be free from impurities and used without further purification.

The phase transitions of the neat LC compounds are given below

	—S_A C—N (°C) —I	S_A—N (°C)	N—I (°C)
8CB	21.5	33.5	40.5
7PCH	30	—	57
5MB	40	—	—
5H5	—	29	47.5

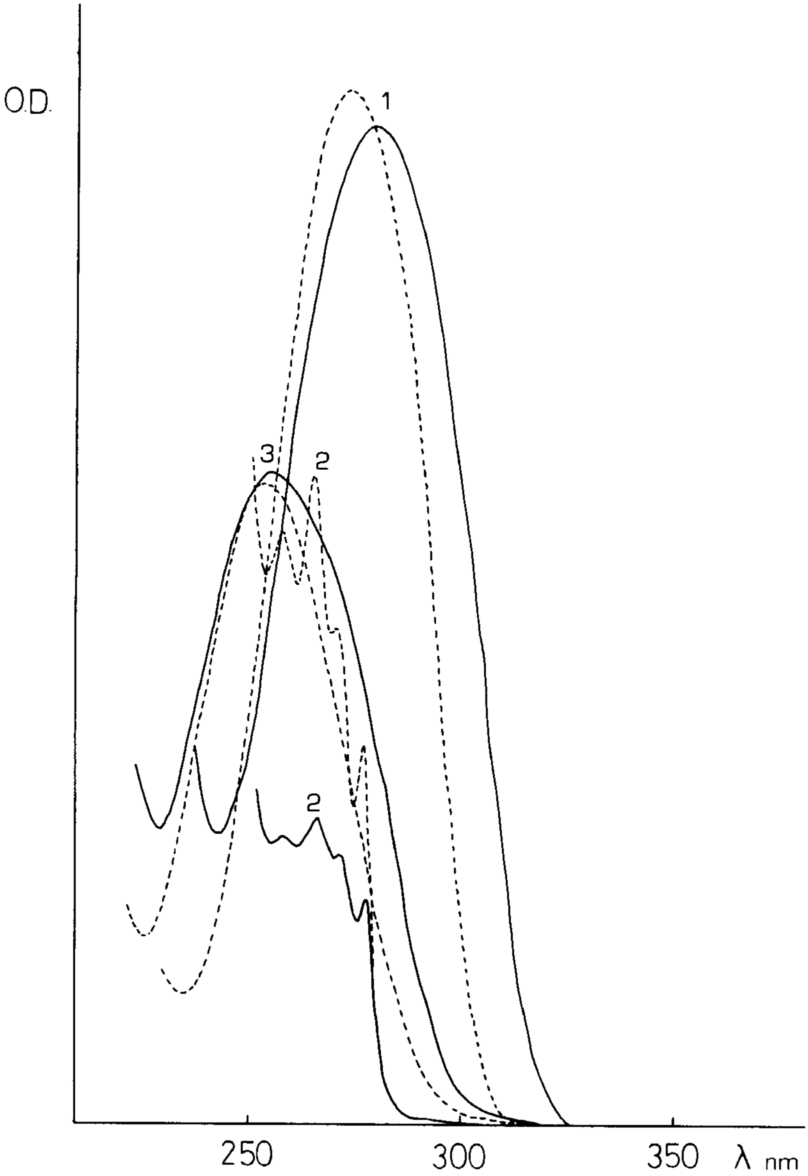
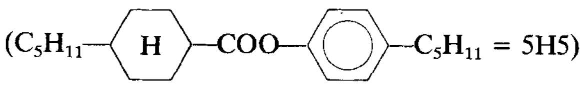


FIGURE 1 Absorption spectra of 1 8CB
2 7PCH
3 5MB
---- in dilute heptane
—— in the mesomorphic or isotropic phase
Optical density in arbitrary units.

The transition temperatures were monitored by DSC and by microscopic examination in a Mettler microfurnace FP52 between crossed polars.

Solvents

- Heptane and ethanol are spectroscopic grade solvents from Janssen Chimica
- 4-pentylphenyl *trans*-4-pentylcyclohexane-1-carboxylate



is a carboxylate ester which was used without further purification as a LC solvent.

Additives

- 1,8 diphenyloctatetraene-all trans (DPOT) is a *purissimum* grade product from Fluka.

The fluorescence and absorption spectra, the quantum yields and the decay-time data were obtained according to the experimental methods described in ref. 1. The excitation wavelengths are respectively 260 nm for 7PCH and 280 nm for 8CB and 5MB.

RESULTS

1. Absorption spectra of 8CB-7PCH and 5MB in thermotropic phase

The absorption spectra of 8CB, 7PCH and 5MB are given in Figure 1 and compared to those obtained in dilute solution. For 8CB and 5MB, an intense non-structured absorption band is observed at 290 and 255 nm respectively with ϵ values of 30,100 and 20,600 in cyclohexane. The lowest transition is of ^1L_a-type for 8CB while it is of ^1L_b type for 5MB. In the case of 7PCH, a structured absorption band characteristic of the phenyl ring is observed with a λ_{max} at 265 nm and a ϵ value of 610 l/mol cm in cyclohexane. Whatever the compound studied, no new absorption indicative of the presence of stable dimers or aggregation is detected in the spectra of neat phases.

2. Fluoresence spectra of 8CB, 7PCH and 5MB

2.1. In dilute solution

The fluorescence of 8CB was previously studied in dilute solution in different solvents.[2] A shift to longer wavelength and a loss of vibrational structure are observed at room temperature when the polarity of the solvent increases. The shift is however less important than in the analogous COB derivatives (Figure 2). It was assigned to an orientation relaxation process of the solvent cage induced by an increase of the dipole moment of the solute in the excited state (μ_g = 4.98 D − μ_e^* = ~20 D). The life-time is very short ~1 ns and the quantum yield is high: 0.54 ± 0.05 in degassed cyclohexane and ethanol.

Fluorescence spectra of 7PCH and 5MB are structured and insensitive to solvent polarity. Their λ_{max} are respectively 292 and 325 nm (Figure 2). In degassed cyclohexane the life-time of 7PCH is about 2.5 ns and the quantum yield is low (~0.01). For 5MB the life-time is 15.5 ns and the quantum yield is 0.35 ±0.05.

2.2. In concentrated solution

As for 3COB and 8COB, excimer fluorescence is observed for 8CB for concentrations exceeding 5 10^{-2} M, in polar and non-polar solvents. It consists of a broad unstructured emission with λ_{max}^D not very sensitive to solvent polarity (λ_{max}^D: 380 nm in cyclohexane and 385 in ethanol) (Figure 3). The excimer life-time was measured to be 22 ns in cyclohexane. Excimer fluorescence is also observed in 7PCH but only for concentrations exceeding 5 10^{-1} M in polar and non-polar solvent. No excimer fluorescence similar to that seen for cyano biphenyls could be obtained for 5MB even for very high concentrations ($\gg$5 10^{-1} M) and whatever the solvent involved (Figure 3). Lack of excimer fluorescence has also been observed and previously discussed in the case of biphenyl.[2]

2.3. In neat phase and LC solvent

The fluorescence spectra of 8CB, 7PCH and in the crystalline, mesomorphic and isotropic phases are given in Figures 4 and 5.

8CB. At room temperature, the fluorescence of 8CB in the S_A phase is that of the excimer. It is a large unstructured band centered at 380–385 nm, identical to that obtained in concentrated solution and with an identical life-time (21 ns). The quantum yield in the S_A phase was estimated to be 0.10 ± 0.05. The same emission is observed

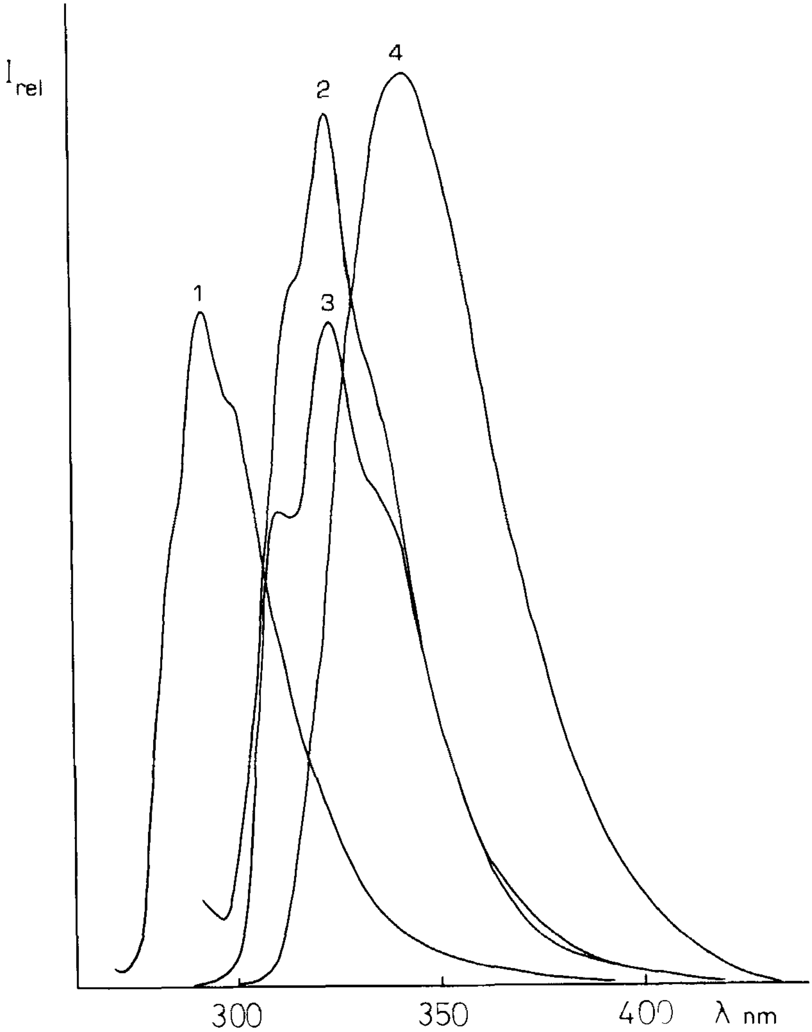


FIGURE 2 Emission fluorescence spectra at room temperature of dilute solutions.
1 7PCH } in polar or non polar solvent
2 5MB }
3 8CB in heptane
4 8CB in dimethylformamide
Intensity is in arbitrary units.

in the nematic and isotropic phases. However, above the N—I transition, the λ^{D}_{max} of emission is progressively shifted to the blue when the temperature increases and an isoemissive point is observed. Such an isoemissive point is obtained if the spectrum consists of contri-

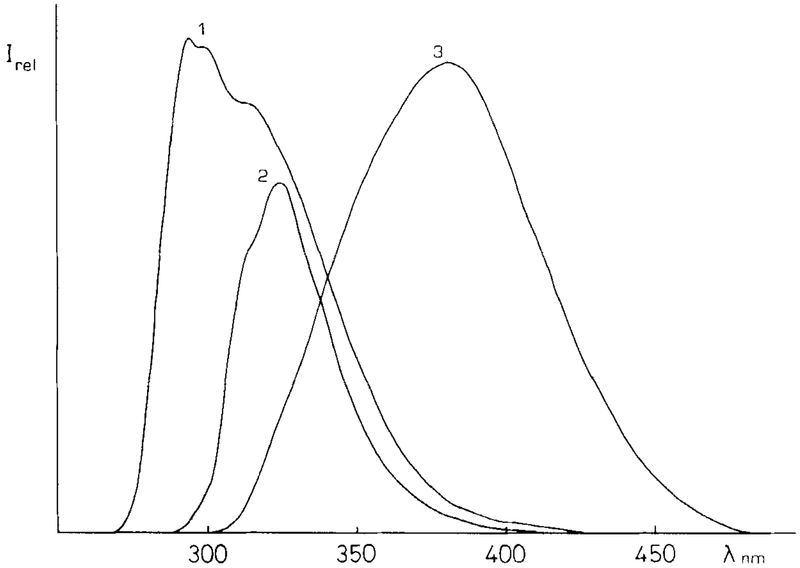


FIGURE 3 Emission fluorescence spectra at room temperature of concentrated solutions (heptane)
1 7PCH
2 5MB
3 8CB
Intensity is in arbitrary units.

butions due to only two components interconverting into each other.[3] It is in the present case characteristic of excimer and monomer conversion (Figure 4). It indicates that the relative importance of excimer formation and deactivation pathways is modified according to the nature of the phase. Monomer emission alone is never obtained in the neat phase below 85°C but is observed at room temperature in mesomorphic solution when the 8CB is dilute in a cyclohexanoate ester (5H5) which can disrupt the associated 8CB pairs. It is a slightly structured emission centered at 337 nm in a mixture containing 2% 8CB and 98% 5H5. Its life-time was measured by single photon counting to be ≤ 1 ns and the quantum yield measured in the S_A phase is identical to that obtained in solution (0.60). The fluorescence λ_{max} values of the monomer of 8CB (337 nm) and of 8COB (355 nm)[1] are indicative of the polarity of the LC solution. The emission intensity of 8CB, measured at 380 nm as a function of temperature, shows discontinuities at the phase transitions owing to the modification of the refractive index. This effect is particularly well observed at the N—I transition (Figure 6) and is in agreement with the refractive

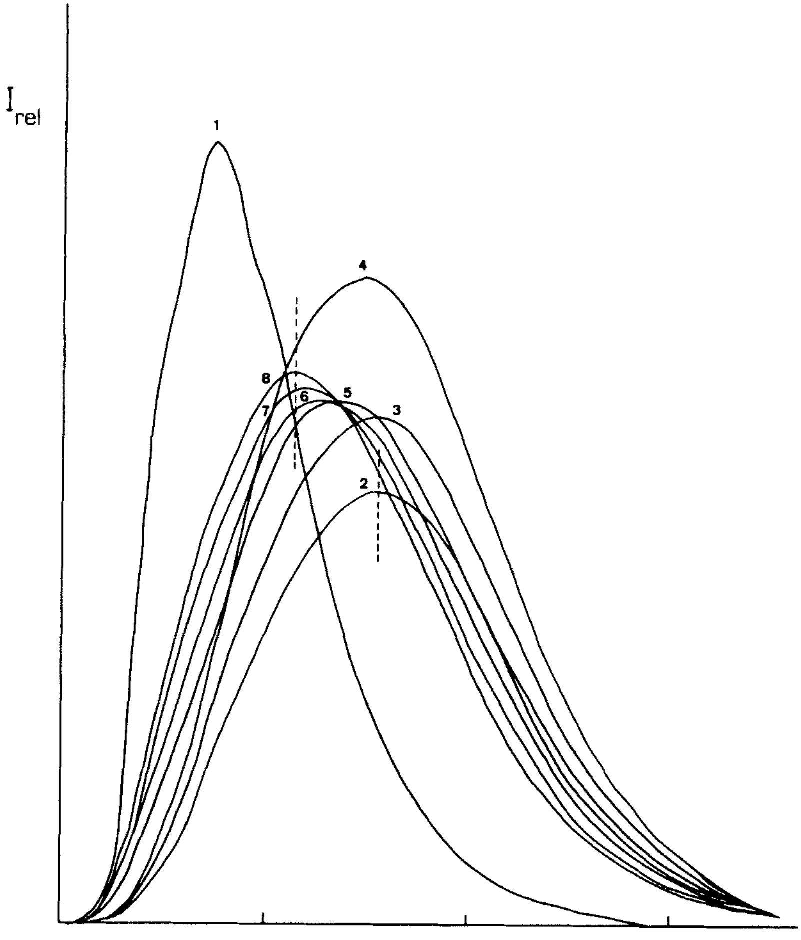


FIGURE 4 Emission fluorescence spectra of 8CB in the neat phase
1 $T° < 20°C$: crystal monomer
2 22°C: S_A
3 34°C } N
4 37°C
5 45°C
6 65°C } I
7 75°C
8 85°C
Intensity is in arbitary units.

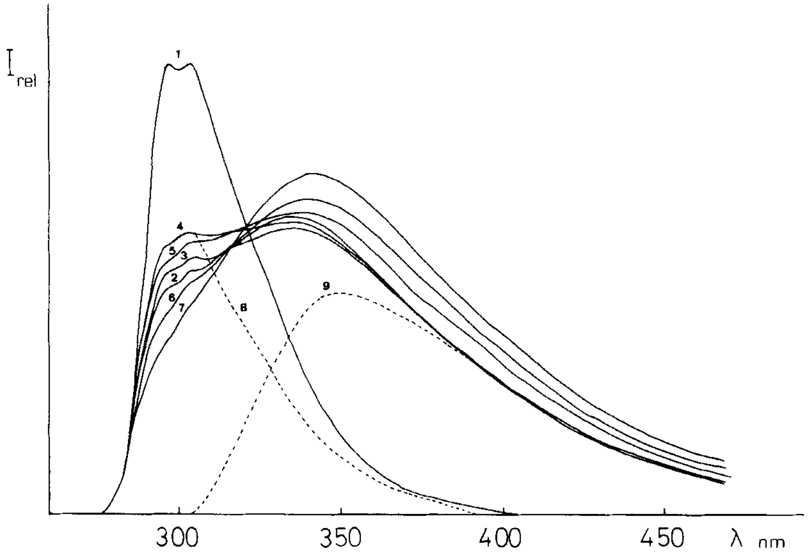


FIGURE 5 Emission fluorescence spectra of 7PCH in the neat phase
1 $T° < 30°C$: crystal
2 30°C
3 41°C } N
4 50°C
5 58°C
6 65°C } I
7 82°C
8 monomer and
9 excimer emission obtained by decomposition of spectrum 3
Intensity is in arbitrary units.

index discontinuities measured by Bradshaw[4] and Ibrahim[5] for the CB compounds. The decay of the excimer emission measured by single photon counting at 380 nm in the smectic, nematic and isotropic domains is mono-exponential (Figure 7). The life-time data derived from these curves are reported below.

8CB	T°c	τ_D ns
S_A	25	21.0
N	33	16.0
I	60	9.6
concentrated solution (cyclohexane)	25	22.0

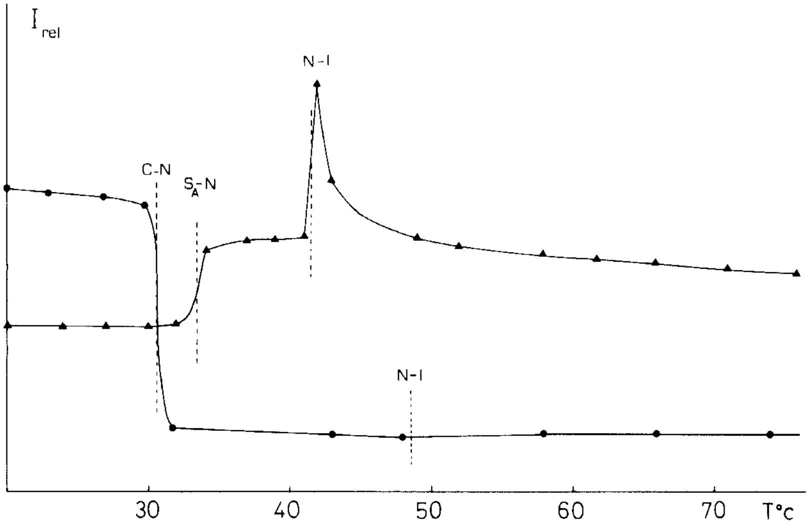


FIGURE 6 Fluorescence intensity of ▲ 8CB and ● 7PCH as a function of temperature
8CB: $C \xrightarrow{21.5°C} S_A \xrightarrow{33.5°C} N \xrightarrow{40.5°C} I$ $\lambda_a = 380$ nm
7PCH: $C \xrightarrow{30°C} N \xrightarrow{57°C} I$ $\lambda_a = 340$ nm
Intensity is in arbitrary units.

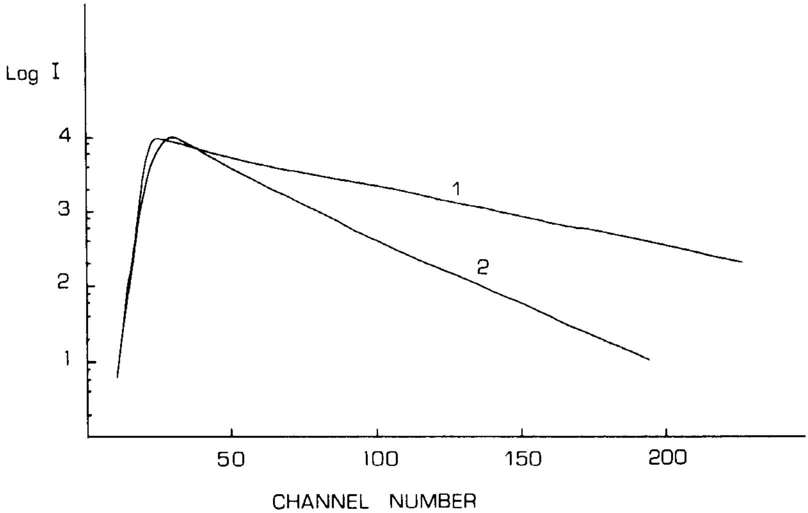


FIGURE 7 Decay curves of 1 8CB in the S_A phase $\lambda_a = 380$ nm
Channel width: 0.406 ns
2 7PCH in the N phase $\lambda_a = 340$ nm
Channel width: 0.203 ns

Growth of the excimer intensity I_D is never observed, indicating that excimer formation is very rapid. Recent measurements of picosecond time resolved fluorescence on 8COB have indeed shown that the excimer could be formed from the monomer within 200 ps.[6] As for 8COB, the life-time depends on the phase: it is 21 ns in the S_A phase, 16 ns in the N phase and 9.6 ns in the isotropic phase.

7PCH. The fluorescence of 7PCH at room temperature is composed of monomer (I_M: λ^M_{max} = 295 nm) and excimer fluorescence (I_D: λ^D_{max} = 340 nm). Monomer emission alone is observed in the crystalline phase (Figure 5). The ratio I_M/I_D is modified when the temperature is raised. The proportion of monomer grows in the nematic phase, but decreases in the isotropic phase. A temperature independent isoemissive point is observed in the two phases. It is associated with the monomer-excimer conversion. The decay-curves measured at 300 nm (λ^M_{max}) and 340 nm (λ^D_{max}) were fitted with mono-exponential functions. In this system, the signal is difficult to analyze by single photon counting owing to the low quantum yield of 7PCH [ϕ_M (monomer) = 0.01 − ϕ_D (excimer) = 0.005] and the corresponding short decay-time (<5 ns). No significant intensity changes are observable at the phase-transition; this could be due to the lower birefringence of a PCH (0.09) compared with a CB (0.16).[7]

5MB. 5MB exhibits the same fluorescence spectra in the neat phase as in dilute and concentrated solutions. It is a structured monomer fluorescence centered at 325 nm (Figure 3). The decay curve is mono-exponential and the derived life-time is 7.6 ns in the neat isotropic phase (45°C). The quantum yield is impossible to measure for the isotropic phase owing to a rapid photodecomposition of the 5MB.

3. Energy transfer in neat phase

Energy transfer has been studied in the same way as for 8COB and 3COB, i.e., to DPOT as acceptor, in the mesomorphic and isotropic phases. DPOT was chosen for its good solubility in the LC medium, its elongated shape and its highly directional transition moment.

The emission intensities and the decay-times for 8CB (λ^D_{max}: 380 nm) (Figure 8), for 7PCH (λ^D_{max}: 340 nm) and for 5MB (λ^M_{max}: 325 nm) (Figure 9), have been measured as a function of acceptor concentration in the different mesomorphic phases. According to Stern-Volmer's kinetics which applies to dynamic quenching in fluid solutions,[8a]

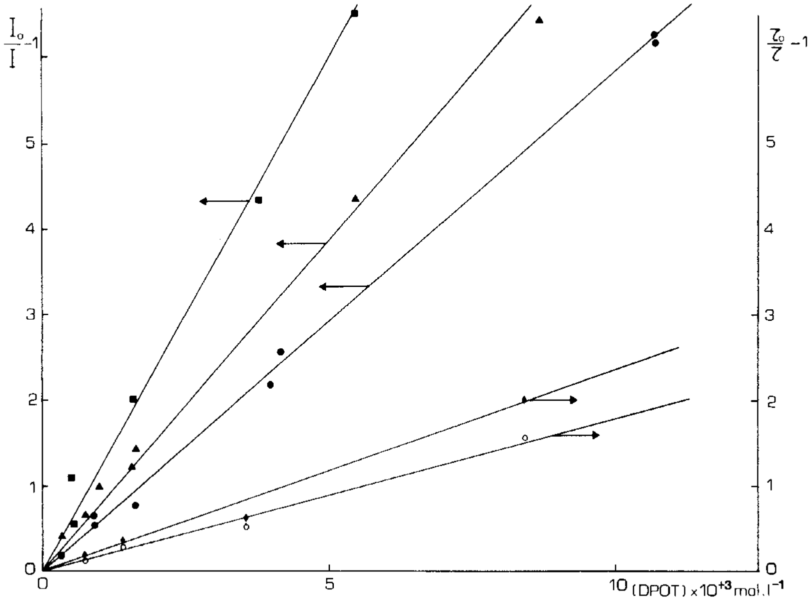


FIGURE 8 Stern Volmer's plots for 8CB as a function of DPOT concentration

$\frac{I_0}{I} - 1$
- ●: in the S_A phase 28°C
- ▲: in the N phase 38°C $\lambda_a = 380$ nm
- ■: in the isotropic phase 60°C

$\frac{\tau_0}{\tau} - 1$
- ○: in the S_A phase 28°C
- ♦: in the N phase 38°C

under steady-state excitation:

$$\frac{I_0}{I} = 1 + k_Q[Y] \tag{1}$$

where k_Q is a quenching constant

I_0 and I the fluorescence intensities in the absence and presence of acceptor

$[Y]$ is the acceptor concentration

under flash excitation:

$$\frac{\tau_0}{\tau} = 1 + k_Q[Y] \tag{2}$$

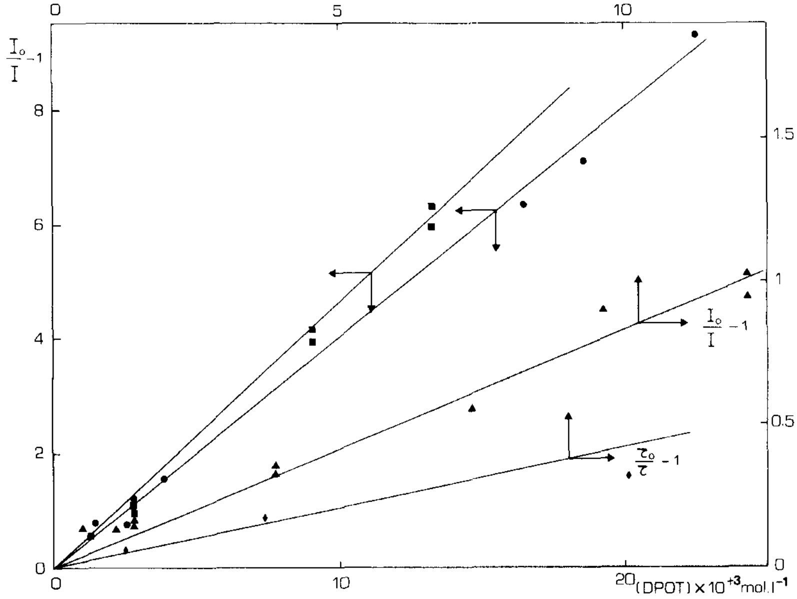


FIGURE 9 Stern Volmer's plots for 8CB-5H5, 7PCH and 5MB as a function of DPOT concentration.

$\frac{I_0}{I} - 1$ ●: 5MB in the I phase 45°C λ_a = 325 nm
■: 8CB/5H5 in the S_A phase 28°C λ_a = 340 nm
▲: 7PCH in the N phase 45°C λ_a = 340 nm

$\frac{\tau_0}{\tau} - 1$ ◆: 7PCH in the N phase 45°C λ_a = 340 nm

where τ_0 and τ are the life-times of the donor in the absence and presence of acceptor.

In all cases, the fluorescence intensity and the life-time derived from the decay-curves decrease when the acceptor concentration increases. The bimolecular transfer constants k_{YM} and k_{YD} can be obtained from the k_Q's values by dividing k_Q by the appropriate life-time given in section 2.

$$k_{YM} = \frac{k_Q}{\tau_M} \qquad \text{if the monomer is the donor}$$

$$k_{YD} = \frac{k_Q}{\tau_D} \qquad \text{if the excimer is the donor}$$

The results obtained are given in Table I. The bimolecular rate constants k_{YD} are of the same order of magnitude ($\sim 10^{10}$ l mol^{-1} s^{-1} for the three systems studied and agree well with those previously found for 8 and 3COB. For 8CB however the k_{YD} value is different according to the phase involved. It increases on passing from S_A to N and from N to I. The values obtained for k_{YD} under flash excitation are lower than those measured under steady-state illumination, as already pointed out for the COB series. The k_{YM} value of 8CB in 5H5 when the monomer is the donor is also much higher.

DISCUSSION

1. Excimer formation

The ability to form excimer in neat LC and isotropic phases is dependent on the nature of the molecules involved as indicated below

8COB–8CB: excimer emission is dominant up to 85°C;

7PCH: excimer and monomer emission are simultaneously present;

5MB and 8CB/5H5: monomer emission only is observed.

TABLE I

Fluorescence quenching and rate constants for energy transfer from 8CB, 7PCH and 5MB to DPOT

		STEADY-STATE EXCITATION		FLASH EXCITATION		
		k_Q (l mol^{-1})	k_{YM} (1) or k_{YD} (2) (l mol^{-1}s^{-1}) × 10^{-10}	k_Q (l mol^{-1})	k_{YM} (1) or k_{YD} (2) (l mol^{-1}s^{-1}) × 10^{-10}	τ ns
8CB	S_A	581	2.84$^{(2)}$	188	0.92$^{(2)}$	21
	N	777	5.51$^{(2)}$	216	1.53$^{(2)}$	16
	I	1200	12.40$^{(2)}$	—	—	9.6
8CB/5H5	S_A*	685	45.6 $^{(1)}$	—	—	1
7PCH	N	82	1.64$^{(2)}$	40	0.80$^{(2)}$	5.0
5MB	I	402	5.23$^{(1)}$	—	—	7.6

*S_A phase with monolayer arrangement.

X ray diffraction[9-10] and dielectric permittivity studies[11] suggest an overlapping core packing as the preferred local structure in the N and S_A phases of the alkyl- and alkoxy-cyanobiphenyl compounds. According to Leadbetter *et al.*,[10] dimer overlap involves the CN group and the two aromatic rings of the biphenyl nucleus in the CB's and COB's (Figure 10). In neat 8CB, 95% of the molecules could be associated in such an antiparallel arrangement.[12] The presence of a very polar cyano-head group on the biphenyl is not only responsible for the existence of a bilayered mesophase, but also for the shift of the ^1L_b transition to higher energies. As a consequence, the lowest excited state corresponds to the ^1L_a transition. It is planar and excimer formation is possible between neighbouring units. The alkoxy and alkyl chains which respectively substitute the COB and CB derivatives in position 4′ induce differences between these two families of LC. Interaction between the more polar and polarizable alkoxy group and the CN substituent induce a larger dipole moment and a higher stability of the pairs in the COB series. This could be related to the absence of monomer emission in these derivatives in the whole range of temperature investigated, while a contribution of monomer emission is observed for the CB's at the highest temperature studied (Figure 4). When 4-alkylbiphenyl is substituted by a non polar CH_3 group instead of a cyano-group, the mesophase does not form and excimer formation is hindered owing to the non-planarity of the lowest excited ^1L_b transition.

In the PCH's, the pseudo-layer spacings measured by X-ray diffraction[9] in the nematic phase also exceed the molecular length by about the length of the cyclohexyl chain suggesting a core overlapping structure similar to that of the cyanobiphenyls. According to Leadbetter,[10] only the cyanophenyl groups overlap. The extra bulkiness of the cyclohexane ring dominates the packing by requiring the low area cyano-group to be adjacent to the cyclohexyl ring and reduces consequently the overlap of the phenyl units and the possibility of excimer formation.The molecular arrangement given in Figure 10 is thus the most probable local packing for the nematic phase. A contribution of excimer fluorescence is however observed in the emission spectra in spite of this poor overlap. Indeed, owing to the liquid character of this phase, many PCH molecules are displaced from this most probable packing. Excimers could thus form at defects present in the layer where phenyl ring overlapping could be favoured. The proportion of excimer is low in the nematic phase, but increases in

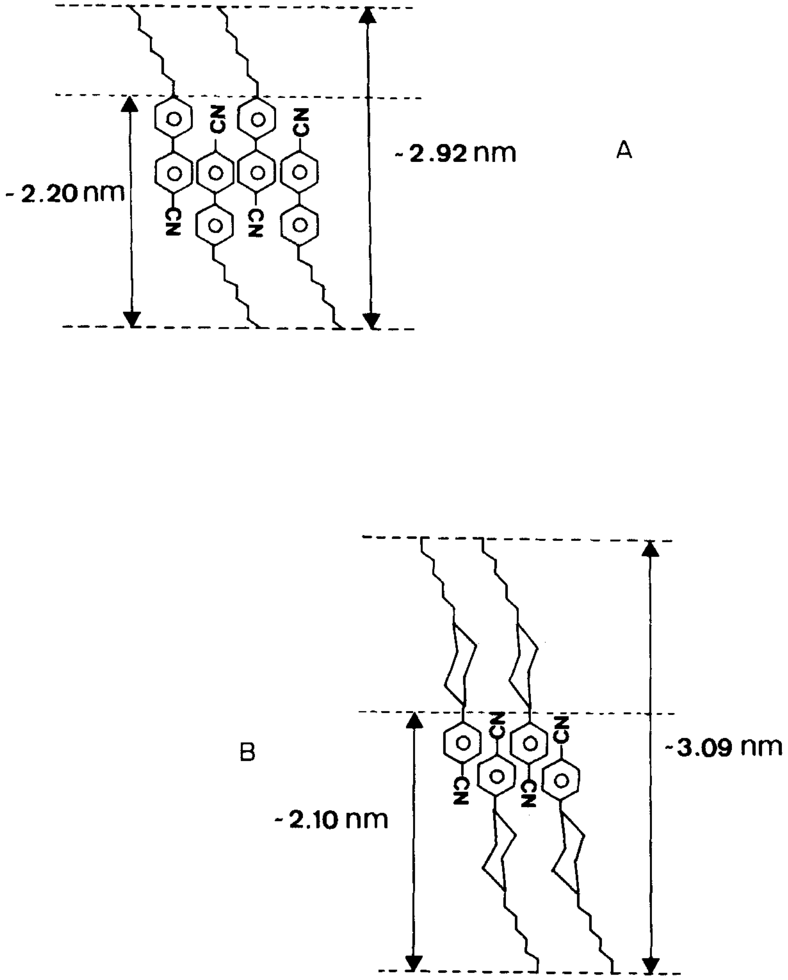


FIGURE 10 Schematic drawing of proposed local packing in
A 8CB[10]
B 7PCH[10-23]

the isotropic phase owing to the higher mobility of these molecules which can then overcome steric hindrance.

2. Energy transfer

Assuming stationary state conditions for the excited states and negligible dissociation of excimers in the mesomorphic phases,[1] Stern-

Volmer's kinetics allows the bimolecular rate constants k_{YM} and k_{YD} to be obtained:

$$\left.\begin{aligned} \frac{I_0}{I} &= 1 + k_Q[Y] \\ \frac{\tau_0}{\tau} &= 1 + k_Q[Y] \end{aligned}\right\{ \begin{aligned} &\text{with } k_Q = k_{YD}\,\tau_D && (3a) \\ &\text{or } k_Q = k_{YM}\,\tau_M && (3b) \end{aligned}$$

According to Voltz,[13,14,15] the bimolecular constants k_{YM} and k_{YD} in fluid media, for a process controlled by dipole-dipole interactions, diffusion, and migration, are given by:

$$k_{Y(M \text{ or } D)} = 2\pi N'(D + \Lambda)R_0^{th}[1 + 0.5\, R_0^{th}(\pi(D + \Lambda)t)^{-1/2}] \qquad (4a)$$

where

D is the diffusion coefficient

Λ is the migration coefficient

N' is the number of molecules per millimole

R_0^{th} is the theoretical Förster's critical transfer distance

When

$$t^{1/2} \gg \frac{0.5\, R_0^{th}}{\pi(D + \Lambda)^{1/2}}$$

this reduces to

$$k_{Y(M \text{ or } D)} = 2\pi N'(D + \Lambda)R_0^{th} \qquad (4b)$$

Voltz's model combines Förster's and Stern-Volmer's kinetics: it supposes that singlet energy diffuses and migrates from donor to donor in the medium up to a donor-acceptor distance equal to the critical transfer distance R_0, where long range transfer resulting from dipole-dipole interactions between the transition moments of the donor and the acceptor, occurs with a probability $p = 0.5$. Voltz's equation allows the migration coefficient Λ to be calculated if D and R_0^{th} are known. The theoretical value of R_0 can be calculated according to Förster's theory of weak interactions by:[16]

$$R_0^6 = \frac{9000 \ln 10\, K^2 \phi}{128\, \pi^5\, n^4\, N_A} \int_0^\infty F_D(\bar{\nu})\, \epsilon_A(\bar{\nu})\, \frac{d\bar{\nu}}{\bar{\nu}^4}$$

where n is the refractive index of the sample
K^2 is an orientation factor equal to ⅔ when the acceptor is randomly distributed
ϕ is the emission quantum yield of the donor
$F_D(\bar{\nu})$ is the emission spectrum of the donor
$\epsilon_A(\bar{\nu})$ is the absorption spectrum of the acceptor
N_A is the Avogadro's number

The theoretical R_0 values are 2.9 nm for 8CB/DPOT (in the S_A, N and I phases) and 1.6 nm for 7PCH/DPOT assuming the excimer to be the donor, and excimer emission quantum yields (ϕ_D) of respectively 0.10 and 0.05. For 5MB and 8CB/DPOT, the R_0^{th} are 2.8 nm and 3.4 nm with the monomer as donor, and monomer emission quantum yields of 0.35 and 0.60. These values are much lower than the experimental values obtained by plotting the transfer efficiency $f = (I_0 - I)/I_0$ as a function of the logarithm of the acceptor concentration.[1] This discrepancy is relevant to the presence of an additional important migration mechanism which is characterized by Λ values. The R_0 and the migration coefficients Λ are summarized in Table II. The migration coefficients Λ calculated from the bimolecular rate constants k_{YD} or k_{YM} from steady-state measurements (I_0/I) for the different systems (CB, PCH, and 5MB) are similar to those reported in the literature for neat aromatic liquids, measured under the same conditions (1–$5\ 10^{-5}$ cm^2 s^{-1}),[17] except for the 8CB-5H5 mixture where the Λ value obtained from the k_{YM} is much higher. However, two different Λ coefficients are obtained, according to the nature of the excitation (steady-state or flash) for 8CB and 7PCH systems, since two different Stern-Volmer's slope are observed. In the case of flash excitation, the migration coefficients Λ are calculated from the k_{YD} values obtained by decay-times measurements according to eq. (3b). The importance of the energy migration observed and the difference between the steady-state and flash excitation will be tentatively interpreted by adding to the energy migration and transfer mechanisms previously discussed and described by equations 3a, 3b, 4a and 4b, a second type of transfer which involves only monomer

TABLE II

Critical transfer distances and rate parameters for neat 8CB-7PCH and 5MB

		R_0^{th} (nm)	R_0^{exp} (nm)	D $cm^2\ s^{-1}$	$(D + \Lambda)$[a] $cm^2\ s^{-1}$	Λ[a] $cm^2\ s^{-1}$	$(D + \Lambda)$[b] $cm^2\ s^{-1}$	Λ[b] $cm^2\ s^{-1}$
8CB	S_A	2.9	4.7	10^{-7}[25]	$1.8\ 10^{-5}$	$1.8\ 10^{-5}$	$4.3\ 10^{-6}$	$4.2\ 10^{-6}$
(excimer)	N	2.9	5.1	10^{-6}[26-27]	$3.7\ 10^{-5}$	$3.6\ 10^{-5}$	$7.7\ 10^{-6}$	$6.7\ 10^{-6}$
	I(45°C)	2.9	5.6	10^{-5}[28]	$8.7\ 10^{-5}$	$7.7\ 10^{-5}$	—	—
8CB/5H5 (monomer)	S_A[c]	3.5	3.9	10^{-7}	$2\ 10^{-4}$	$2\ 10^{-4}$	—[d]	—[d]
7PCH	N							
(monomer)		1.3						
(excimer)		1.6	2.4	10^{-6}	$1.7\ 10^{-5}$	$1.6\ 10^{-5}$	$7.0\ 10^{-6}$	$6.0\ 10^{-6}$
5MB (monomer)	I(45°C)	2.8	3.5	10^{-5}	$3.1\ 10^{-5}$	$2.1\ 10^{-5}$	—	—

[a] Values calculated from I_0/I Stern-Volmer's plots. } with equation 4a
[b] Values calculated from τ_0/τ Stern-Volmer's plots. } with equation 4a

[c] S_A phase with monolayer arrangement.
[d] Life-time measurements could not be made by single photon counting (too short life-time).

and is faster than the first one. Two possibilities will be discussed for this instantaneous type of transfer:

- it is the usual static quenching[8b-18]
- it involves instantaneous migration and transfer by very rapid Förster's medium interactions.[19]

A kinetic scheme which brings together this last case and the slower energy migration and transfer processes previously described will then be developed and applied to our results.

Let us first consider static quenching. Decay parameters are indeed recognized as insensitive to static quenching while fluorescence intensity is not. Static quenching is instantaneous. It occurs when ground state electron exchange interactions are operating between a donor and an acceptor situated within a sphere of action characterized by a radius R_Q. A contribution of static quenching introduces a correction to eq. (1) to give:[8b-20]

$$\frac{I_0}{I} = (1 + k_Q[Y])\, e^{+k'[Y]} \tag{6}$$

with $k' = vN'$
where v is the volume (in cm^3) of the active sphere of each quencher molecule

The radius of the active sphere for static quenching is then given by

$$R_Q = \left(\frac{3\,k'}{4\,\pi\,N'}\right)^{1/3} \simeq (400\,k')^{1/3}\ \text{Å} \tag{7}$$

Eq. (6) may introduce deviations from the Stern-Volmer's equation leading to curved Stern-Volmer's plots. These positive deviations are not observed in our systems while two different slopes are clearly measured using I_0/I and $2_0/2$. The R_Q, values calculated from (6) and (7) for 8CB in the different phases with $k_Q = k_{YD}\tau_D$ and k' accounting for initial transient quenching of those molecules adjacent to a quencher molecule at the moment of excitation, lead to a sphere of action with a radius value between 3 and 4 nm which is at odds with the fact that in fluid solution, a static quenching mechanism is assigned to ground state short range interactions.

However, instantaneous quenching involving transfer between donors and between donors and acceptors *via* stronger dipole-dipole interactions than those involved in classical Förster theory, could be concerned: large dipole moments in the lowest transition could be especially suited for the occurence of medium interaction and for wide range excitation transfer as in the case of some typical dye molecules.[19] This effect is not possible in most aromatic hydrocarbons: the weakly absorbing ^1L_b states which are the lowest for benzene, naphthalene and other hydrocarbons have only small or even no transition dipoles and will therefore interact weakly with acceptors. Only mixing with other states, due to vibrational perturbations, may enlarge this interaction to some extent. Stronger interaction between the donor and the acceptor could also afford an explanation for the additional splitting observed in the monomer fluorescence spectrum, when high DPOT concentrations are introduced in the LC medium. This splitting is particularly well observed in the monomer emission of COB derivatives characterized by an important dipole moment in the excited state (Figure 11). Charge-transfer perturbations arising from dipole interactions between guest and host molecules have also been observed with azo- and anthraquinoid dyes dissolved in eutectic liquid crystal mixtures composed of 4-cyanobiphenyl and 4-cyanoterphenyl alkyl derivatives.[21] According to these authors, the charge transfer could lie along a direction approximately parallel to the main geometric axis of the dye. Strong intermolecular attraction and close proximity could give rise to an extension of the π-electron system between neighbouring molecules, so leading to an extended dipole. A similar high, but not explained bimolecular rate constant has also been measured for DPOT/*para*terphenyl systems in bilayer membrane vesicles where considerable parallel donor-acceptor dipole orientation was also mentioned.[22] In the CB's and COB's, these interactions would be preferentially observed between DPOT and CB or COB molecules not involved in antiparallel pairing. Non-associated molecules are quite polar due to the high dipole moment associated with the nitrile bond of the CB's and COB's which is strongly reinforced in the excited state (μ_g = 5 Debye; μ_e^* = 20 Debyes). In contrast, antiparallel pairing of these molecules "neutralizes" the strong cyano(oxygen) dipole and progressively cancels this effect.[23] Fluorescence spectrum structures are indeed never observed in the neat phase were 95% of the molecules are shown to be associated and where the excimer does not dissociate. This hypothesis is reinforced by the fact that the relative importance of static quenching increases on passing from S_A to N and to I phase in the 8CB's system, as does the relative importance of monomer emission. Furthermore, these spectral modifications are completely absent in 7PCH/DPOT

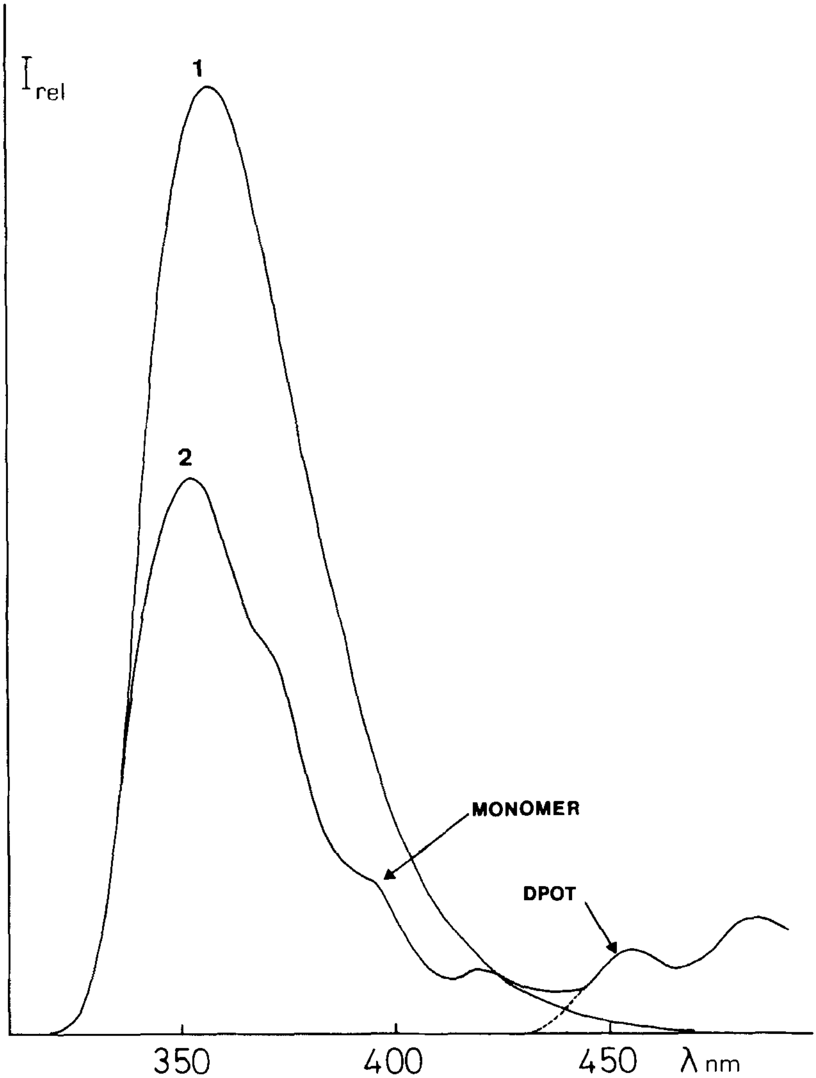


FIGURE 11 Emission fluorescence spectra of monomeric 8COB in 5H5
1 without acceptor
2 with 9.5 10^{-3} mol.1^{-1} of DPOT
Intensity in arbitrary units.

and 5MB/DPOT systems. Indeed they are recognized to be less polar in their fundamental and lowest ^1L_b excited state.

A kinetic scheme involving the fast transfer from monomer to DPOT and the slower transfer from excimer to DPOT will now be developed. The sequence of steps is given below:

$$
\begin{array}{rcll}
{}^1M & \xrightarrow{h\nu} & {}^1M^* & I_a \\
{}^1M^* & \longrightarrow & {}^1M + h\nu & k_{FM} \\
\begin{array}{r} {}^1M^* \\ {}^1M^* \end{array} & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \begin{array}{l} {}^1M + kT \\ {}^3M^* \end{array} & \left.\begin{array}{l} k_{GM} \\ k_{TM} \end{array}\right\} k_{IM} \\
{}^1M + {}^1M^* & \longrightarrow & {}^1D^* & k_{DM} \\
{}^1M^* + {}^1Y & \longrightarrow & {}^1M + {}^1Y^* & k_{YM} \\
{}^1D^* + {}^1Y & \longrightarrow & {}^1D + {}^1Y^* & k_{YD} \\
{}^1D^* & \longrightarrow & {}^1M^* + {}^1M & k_{MD} \\
{}^1D^* & \longrightarrow & {}^1M + {}^1M + h\nu & k_{FD} \\
\begin{array}{r} {}^1D^* \\ {}^1D^* \end{array} & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \begin{array}{l} {}^1M + {}^1M + kT \\ {}^3D^* \end{array} & \left.\begin{array}{l} k_{GD} \\ k_{ND} \end{array}\right\} k_{ID}
\end{array}
$$

Assuming stationary state conditions, the ratio I_D^0/I_D is given by

$$
\begin{aligned}
\frac{I_D^0}{I_D} &= \left(1 + \frac{k_{YM}}{k_M + k_{DM}\,M}[Y]\right)\left(1 + \frac{k_{YD}}{k_D + k_{MD}}[Y]\right) \\
&= (1 + k_{YM}\,\tau_M\,[Y])(1 + k_{YD}\,\tau_D\,[Y])
\end{aligned}
\tag{8}
$$

This expression shows that two types of energy transfer could be involved in the system. The first one could arise from monomer, the environment of which is not suitable for excimer formation. This transfer could result from an important migration of the excitonic type between neighbouring monomer units associated as aggregates, followed by long range medium dipole-dipole interaction and doesn't affect the decay-time. The second one could be observed when excitation energy reaches monomer units which have a configuration leading to excimer formation; transfer could occur after migration resulting from monomer-excimer dissociation up to a distance where weak resonant Förster's transfer can become operative. It is characterized by k_{YD} which can be derived from decay-time measurements. It is about 1 10^{10} 1 mol^{-1} s^{-1} as usually observed for neat aromatic liquids for reactions limited by diffusion or migration.[24]

Assuming in (8) values of 1 10^{10} and 5 10^{11} 1 mol^{-1} s^{-1} for k_{YD} and k_{YM}, and values of 9.6 and 1 ns for τ_{D} and τ_{M} in the isotropic phase, linearity is obtained for $I_0/I = f[Y]$ when the quencher concentration is lower than 6 10^{-3} mol 1^{-1} in agreement with our results. Different experiments to confirm these hypotheses are now under investigation using LC solutions and will be published soon.

CONCLUSION

The results described in this paper outline some features of two important classes of LC (CB's and PCH's):

- the emission spectrum of the CB's is of the excimer type in the S_A, N and I phases. In the isotropic phase however, some monomer component resulting from excimer dissociation is observable
- monomer and excimer fluorescence are always simultaneously present in the N and I phases of the PCH's
- the rate constants of energy transfer (k_{YD}) to diphenyloctatetraene (DPOT) are dependent on the phase. They increase on passing from S_A to N and from N to I in the two systems. Furthermore, the rate constants obtained are different according to the nature of the excitation (steady-state or flash). These differences are more important for the CB's than for the PCH's. They were related to the presence of monomer, to its dipole moment, and to the nature of its lowest excited state (^1L_a)
- in the CB systems, two types of transfer have been shown to occur. The first affects the intensity and could be an instantaneous quenching involving an excitonic migration between monomer units and efficient transfer between the highly polar monomer units and DPOT by medium dipole-dipole interactions. This transfer is characterized by a rate constant of about 5.10^{11} 1 mol^{-1} s^{-1} and an additional splitting of the monomer fluorescence. The second slower type of transfer affects only the decay time and is assigned to a less efficient migration involving the excimer up to a distance where Förster's weak dipole-dipole interactions can become operative. It is char-

acterized by a rate constant of about 1.10^{10} 1 mol^{-1} s^{-1}

- in the PCH's which have a ^1L_b lowest excited state, slow transfer occurs predominantly
- in all the LC systems investigated (COB's^1-CB's and PCH's) excimer formation slows down energy migration.

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