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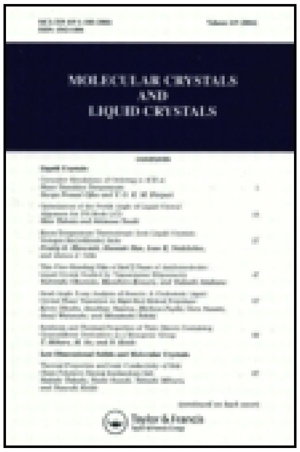

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Energy Transfer and Migration in Liquid Crystalline 4-Cyano 4′-Alkoxybiphenyls

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Energy Transfer and Migration in Liquid Crystalline 4-Cyano 4′-Alkoxybiphenyls

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An investigation of photophysical processes occurring in the pure isotropic liquid and thermotropic liquid crystal phases of 4-cyano-4′-propyloxybiphenyl and 4-cyano-4′-octyloxybiphenyl is described.

INTRODUCTION

The purpose of this work is the investigation of photophysical processes in the neat thermotropic phases of 4-cyano-4′-propyloxybiphenyl (3 COB) and 4-cyano-4′-octyloxybiphenyl (8 COB) in order to see the effect of liquid crystalline organization on energy migration and transfer. The liquid crystal state is characterized by orientational ordering of the molecules; transitions from one type of mesophase to another and, in particular, transition from L.C. to isotropic liquid, are accompanied by changes in the degree of molecular order. Order is expected to modify the interaction parameters between neighbouring excited and non-excited chromophores and thus the efficiency of transfer or migration.

The photophysical processes in 3 COB and 8 COB have been previously studied using dilute solutions.[1] The main conclusions of this work can be summarized as follows:

—The fluorescence spectra of 3 COB and 8 COB in solution are shifted toward longer wavelength when compared with biphenyl. The

λ_{max} are respectively 340 and 315 nm in cyclohexane. Furthermore, the λ_{max} of the COB derivatives are strongly dependent on the polarity of the solvent in fluid solution at room temperature, while they are independent of it in the glassy state at 77 K. The progression in the vibrational structure (1300 cm^{-1}) is also different from that of biphenyl (1000 cm^{-1}). The life-time is shorter (~ 1 ns) and the quantum yield is high (0.54 ± 0.05).

—Therefore, the fluorescence of COB's has been assigned to the emission from the planar ^1L_a state to the non-planar ground state, the transition moment being parallel to the long axis of the molecule. The red shift of the emission in a polar solvent has been assigned to an orientation relaxation process of the solvent cage in the electric field of the excited solute that has a higher dipole moment than the ground state.[1] The fluorescence of biphenyl, which is only weakly solvent dependent and is characterized by a longer life-time (15 ns) and lower quantum yield (0.18) is generally assigned to a transition from the lowest ^1L_b state characterized by a weak dipole moment.

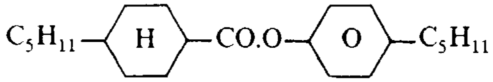
—As the concentration of the solution increases (from 3 COB 5.10^{-2} to 10^{-1} mol.l^{-1}), excimer fluorescence can be observed for 3COB and 8 COB while it has never been reported for biphenyl. The λ_{max} of the excimer is situated at 380 nm and its life-time is 11 ± 0.5 ns in cyclohexane.

EXPERIMENTAL

3 COB and 8 COB were purchased from BDH Chemicals Ltd, Poole, Dorset. They were both shown to be free from impurities by H.P.L.C. and by spectrofluophosphorimetry. The phase transitions of these thermotropic liquid crystals are given below:

	C → S or I	S_A → N	N → I
3 COB	74.5 °C (I)		(64 °C) monotropic phase
8 COB	54.5 °C (S_A)	67 °C	80 °C

These temperatures were monitored by DSC and by microscope examination between crossed polarizers using a microfurnace (Mettler FP 52). The 1,8-diphenyl-octatetraene (DPOT) and perylene (P) were *purissimum* grade products of Fluka and Aldrich respectively. The 4-pentylphenyl *trans*-4-pentylcyclohexane-1-carboxylate:



(5H5)

(5H5) is an ester and was used without further purification. The absorption spectra were recorded with an Hitachi Perkin Elmer 124 double beam spectrophotometer. To obtain accurate spectra (OD < 1), the liquid crystalline or isotropic phases were spread as very thin layers between two quartz plates (< 1 μm thick). The fluorescence spectra of 3 COB and 8 COB were measured by reflection with a Perkin Elmer MPF 2A spectrofluorimeter. A thin layer of liquid crystal was spread between two quartz plates ($\sim$ 10 μm thick) which were inserted in a thermostated copper block. The exciting wavelength was 280 nm. Fluorescence quantum yields were estimated by comparing the area under the fluorescence spectrum of the sample (relative number of quanta/wavenumber *versus* wavenumber) with that of thin layers of 8 COB in DMF dilute solution, measured under the same experimental conditions. The quantum yields were calculated according to the method described by Parker[2] using for the refractive index of the sample and of the solution values of 1.43 and 1.57 respectively. For energy transfer measurements, the acceptor was dissolved in the pure isotropic phase. The exact molar concentration was obtained by dissolving a given amount of L.C. containing the additive in CH_2CL_2 and measuring the OD at 400 nm (DPOT). Long decay times have been measured by a single photon counting at the University of Leuven and all the results were analyzed according to the method of Van Bockstaele *et al.*[3] The short decay times were measured with a mode-locked ruby laser at the Ecole de Chimie de Mulhouse.

RESULTS

1. Absorption spectra of 3 COB and 8 COB in their thermotropic phases

The absorption spectra of 3 COB and 8 COB are given in Figure 1 and compared with those obtained using dilute solutions. In all cases, an intense absorption band is observed at 290 nm. (ϵ values are respectively 26,000 and 30,000 l.mole^{-1} cm^{-1} at λ_{max} for 3 COB and 8 COB in dilute ethanolic solution). A broad intense absorption develops below 240 nm. No new absorption which would be indicative of the presence of stable dimers is observed in the case of neat 3 COB and 8 COB.

2. Fluorescence spectra of 3 COB and 8 COB in neat phase

The fluorescence of 3 COB and 8 COB in the crystalline, mesomorphic and isotropic liquid phases are given in Figures 2 and 3. The λ_{max} in

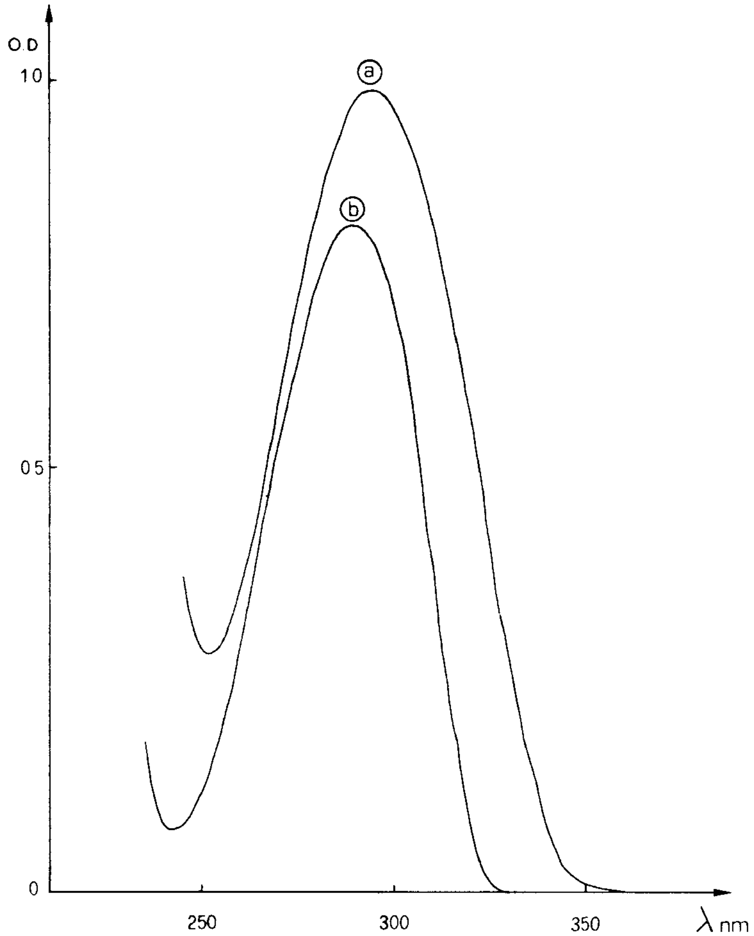


FIGURE 1 Absorption spectra of 8 COB; (*a*): in neat phase; (*b*): in dilute ethanolic solution. The absorption spectra are identical for 3 COB.

the smectic (S), nematic (N) and isotropic (I) phases correspond to the λ_{max} observed using concentrated solutions. The decay curves are exponential in all cases (S, N or I) for 3 COB and 8 COB. The life-time of 8 COB is 10.7 ns in the smectic phases (60 °C) and 7.6 ns in the nematic phase (72 °C). For 3 COB, the life-time is 7.7 ns in the isotropic phase (75 °C). The life-time of the excimer of 8 COB in solution was measured as 11 ns. Owing to the similarity of the λ_{max} and of the decay-times observed using concentrated solutions and neat phases, and to the absence of any new absorption band in this last case, the emission in the neat phase has been assigned to excimer

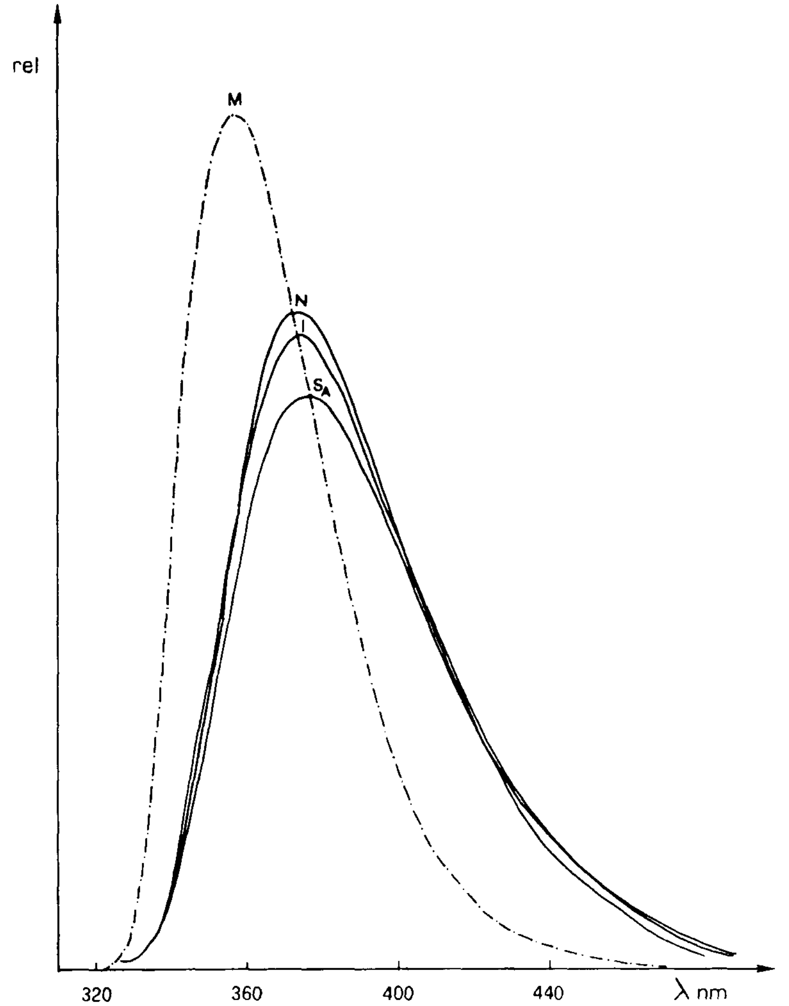


FIGURE 2 Emission fluorescence spectra for the neat phases of 8 COB (λ_e = 280 nm) M: monomer emission (mixture 8 COB/5H5)

$\left.\begin{matrix} S_A \\ N \\ I \end{matrix}\right\}$ excimer emission in the smectic (S) nematic (N) and isotropic phases (I)

(the S_A phase of 8 COB is a bilayer phase). Intensity is in arbitrary units.

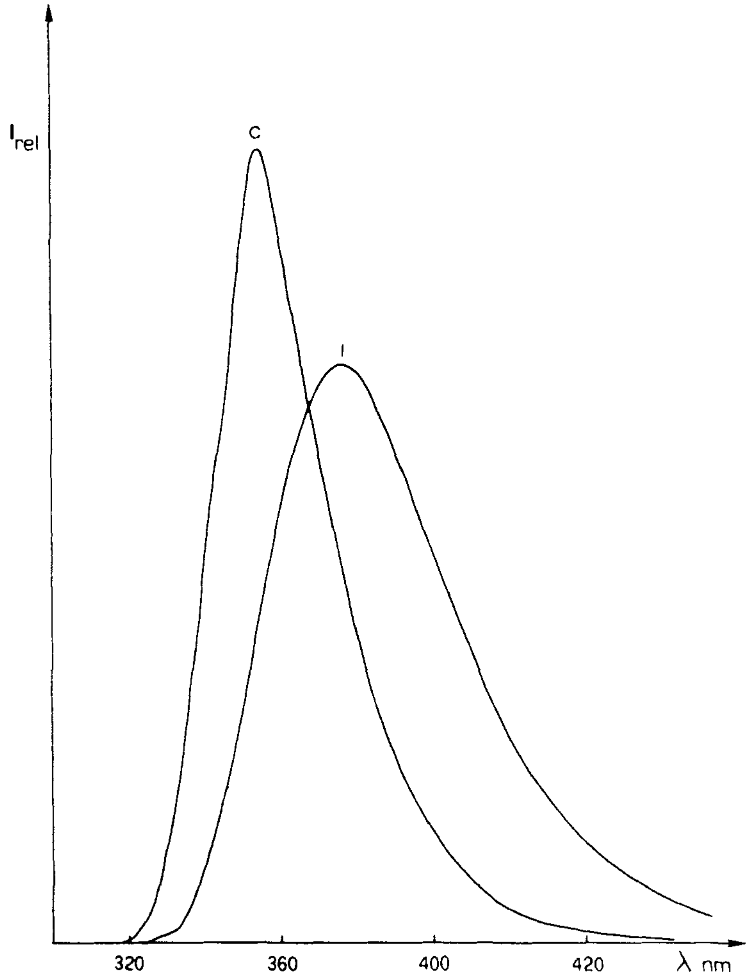


FIGURE 3 Emission fluorescence spectra for the neat phases of 3 COB (λ_e = 280 nm) C: crystalline emission I: excimer emission in the isotropic phase. Intensity is in arbitrary units.

deactivation. Indeed, dimers contrary to excimers, have a stable ground state and an additional absorption would have to be observed. The fluorescence quantum yield was estimated to be 0.15 ± 0.05 for 8 COB in the smectic phase and of the same order of magnitude in the other phases and for 3 COB.

The excimer fluorescence intensity of 8 COB has been measured as a function of temperature between 20 and 90 °C.[4] Discontinuities (less

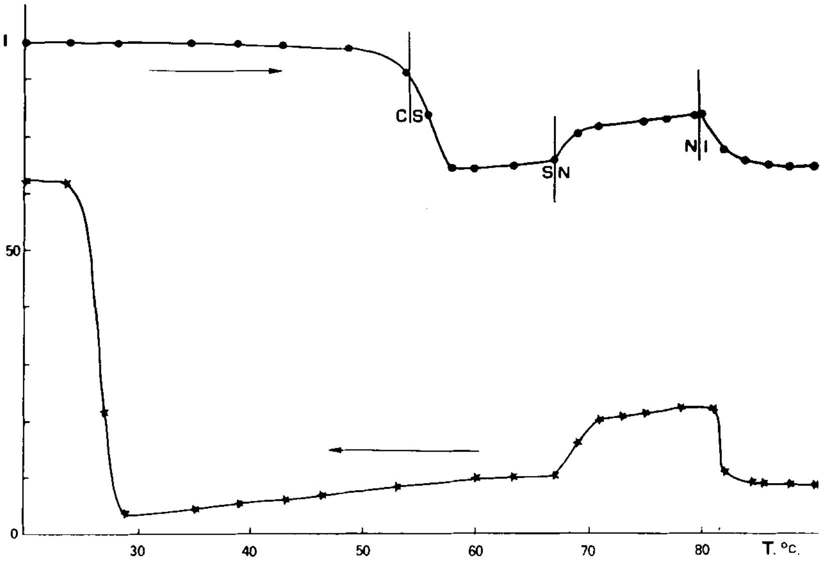


FIGURE 4 Fluorescence intensity of 8 COB as a function of temperature ● increasing temperature ★ decreasing temperature

$$C \xrightarrow{54.5°C} S \xrightarrow{67°C} N \xrightarrow{80°C} I$$

Intensity is in arbitrary units.

than 20%) corresponding to small differences in fluorescence intensities appear at the transitions S → N → I (Figure 4). Monomer emission of 3 COB and 8 COB is never observed for the neat phase. Monomer emission can however be observed when the pairing of the cyano-compounds is gradually broken up by increasing the concentration of a cyclo-hexanoate ester such as 5H5. It is a non-structured emission analogous to that obtained with polar solutions. Its λ_{max} is situated at 355 nm (Figure 2). The monomer life-time is 1.1 ns and the quantum yield has not yet been determined owing to orientational problems with thin films of mixtures.

3. Energy transfer in the L.C.

Energy transfer has been studied from donors (3 COB and 8 COB) to different acceptors in the smectic, nematic or isotropic phases as a function of temperature, by measuring:

—the fluorescence intensity of the donor as a function of acceptor concentration under steady-state illumination and

—the fluorescence decay of the donor as a function of acceptor concentration under flash excitation.

The results have been plotted according to Stern-Volmer's kinetics.[5a] The equations used for the fluorescence intensity and life-time are respectively:

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

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

where

$k_Q = k_{YM}\tau_{0M}$ according to the nature of the donor

or $k_{YD}\tau_{0D}$ (monomer or excimer)

I_0 and τ_0 are the fluorescence intensity and the life-time of the donor in the absence of acceptor

I and τ are the fluorescence intensity and the life-time of the donor in the presence of acceptor

k_{YM} and k_{YD} are the rate constants for energy transfer

$[Y]$ is the acceptor concentration

(see discussion)

3.1 Energy transfer under steady-state illumination

The emission intensity of 8 COB in the smectic, nematic and isotropic phases and of 3 COB in the isotropic phase has been measured as a function of acceptor concentration. Two acceptors were chosen: 1,8 diphenyloctatetraene (DPOT) and perylene (P). They were chosen not only for their required optical properties, but also for their shape (rod-like for DPOT and bulky for P) and their ability to dissolve in the organized phases. The ratio I_0/I of the fluorescence intensity measured at 380 nm (maximum of the excimer emission) in the absence (I_0) and in the presence (I) of acceptor is nearly identical in the smectic, nematic and isotropic phases up to 40 °C above the N → I transition for a given acceptor concentration. Linear Stern-Volmer's plots are obtained when I_0/I is measured as a function of the acceptor concentration (equation 1). Straight lines with identical slopes were obtained with DPOT as acceptor whatever the phase involved. A somewhat smaller slope is obtained when P is used as

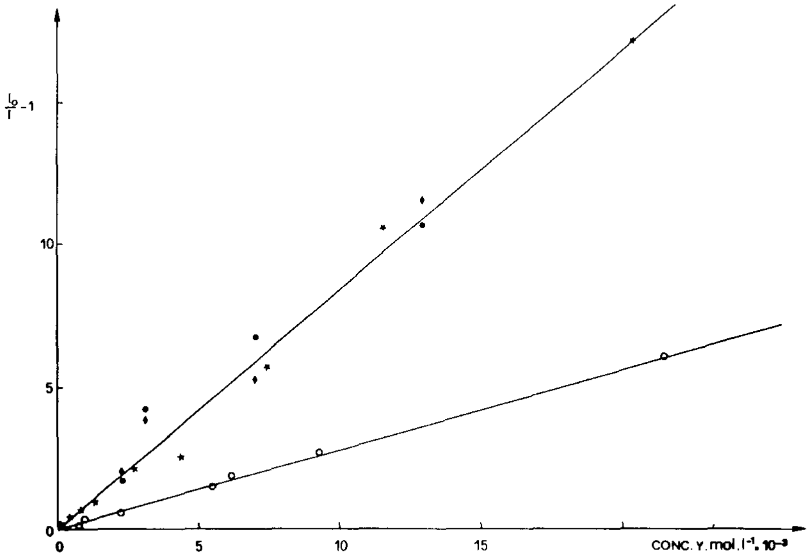


FIGURE 5 Stern-Volmer's plots $I_0/I - 1$ as a function of the acceptor concentration $\lambda_e = 280$ nm; $\lambda_a = 380$ nm (excimer emission):

◆: 8 COB in the smectic phase: uncovered plates } 60 °C
●: 8 COB in the smectic phase: covered plates } 60 °C
★: 8 COB in the nematic phase: 72 °C, with DPOT as acceptor;
○: 8 COB in the nematic phase: 72 °C, with perylene as acceptor.

acceptor (Figure 5). The k_Q values calculated in the case of 8 COB are respectively of 840 and 258 $\mathrm{l.mol^{-1}}$ for DPOT and P. The k_Q value calculated for the system 3 COB/DPOT in the isotropic phase is 1063 $\mathrm{l.mol^{-1}}$ (Figure 6). No surface orientation effects are observed with thick L.C. layers. The ratio I_0/I is the same for samples covered with a quartz glass plate or uncovered (Figure 5).

Energy transfer was also studied using mixtures of 8 COB and the ester (5H5) (8 COB : 2% – 5H5 : 98%), where only monomer emission of the COB derivative is observed (λ_{max} : 355 nm) and a k_Q value of 1160 $\mathrm{l.mol^{-1}}$ is obtained for DPOT (Figure 6). The bimolecular k_{YM} and k_{YD} rate constants were calculated according to (1) by dividing the k_Q values by the respective life-times given in section 2. When the excimer is donor, the bimolecular rate constants are rather similar whatever the phase involved (S, N or I) when DPOT is used as acceptor. In a given phase, a five times lower value is however obtained for k_{YD} when perylene is used instead of DPOT. When the monomer is donor, k_{YM} is about ten times greater. All these results are summarized in Table I.

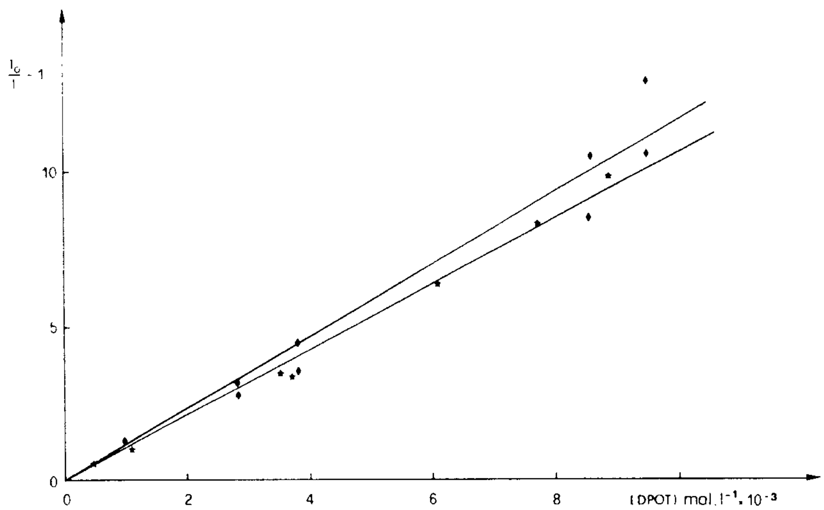


FIGURE 6 Stern-Volmer's plots $I_0/I - 1$ as a function of the acceptor concentration (DPOT) ★: 3 COB in the isotropic phase: 75 °C $\lambda_e = 280$ nm; $\lambda_a = 380$ nm (excimer emission) ◆: 8 COB/5H5 mixture in the smectic phase: 25 °C (smectic A phase with monolayer arrangement) $\lambda_e = 280$ nm; $\lambda_a = 355$ nm (monomer emission).

TABLE I

Quenching constants of fluorescence and rate constants of transfer for neat 3 COB and 8 COB using various quenchers

	k_Q (l/mol.)	k_{YM} or k_{YD} (l/mol.s) (steady-state excitation)	k_{YD} (l/mol.s) (flash excitation)
3 COB/DPOT	1063	$1.4\ 10^{11}$ I	—
8 COB/DPOT	840	$7.8\ 10^{10}$ S_A	$5.1\ 10^{10}$ S_A
		$1.1\ 10^{11}$ N	$7.2\ 10^{10}$ N
8 COB/P	258	$2.6\ 10^{10}$ N	—
8 COB/5H5/DPOT 2%-98%	1160	$1.1\ 10^{12}$ S_A	—

3.2 Energy transfer under flash excitation

The decay curves are exponential in all cases (S, N or I) for 3 COB and 8 COB as shown in Figure 7 and remain exponential whatever the acceptor concentration. Plots of $\tau_0/\tau - 1$ as a function of acceptor concentration, where τ_0 is the life-time of 8 COB without acceptor and τ the life-time of 8 COB in the presence of DPOT, can thus be interpreted according to the simple Stern-Volmer's kinetics (equation 2). The k_Q value obtained in the case of 8 COB/DPOT is about 550 l.mol^{-1} in the smectic and the nematic phases (Figure 8). This value is

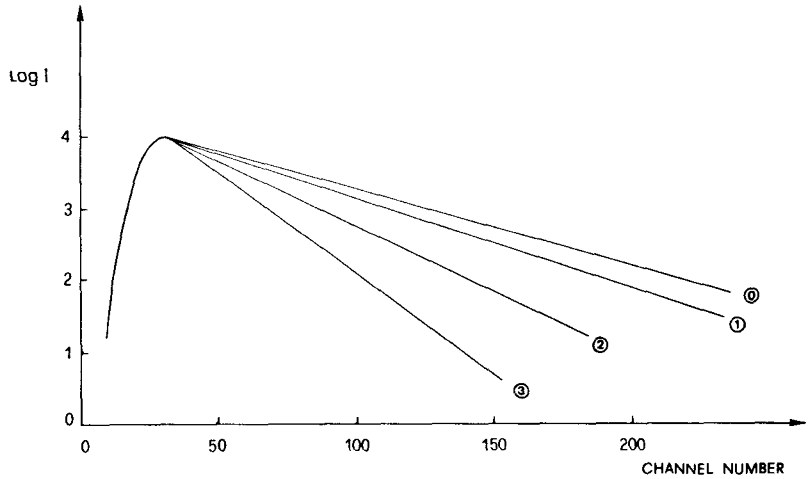


FIGURE 7 Decay-curves of 8 COB in the nematic phase as a function of DPOT concentration 0: 0 mole/l; 1 : 4.11 10^{-4} mole/l; 2: 2.30 10^{-3} mole/l 3: 3.63 10^{-3} mole/l; $\lambda_e = 280$ nm – $\lambda_a = 380$ nm.

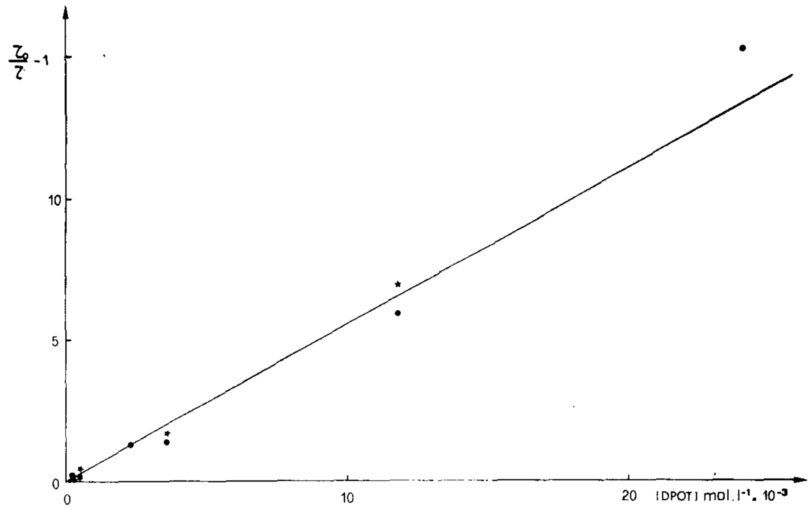


FIGURE 8 Stern-Volmer's plots $\tau_0/\tau - 1$ for 8 COB as a function of DPOT concentration ●: in the smectic phase: 60 °C; ★: in the nematic phase: 72 °C $\lambda_e = 280$ nm $\lambda_a = 380$ nm.

smaller than that obtained under steady-state illumination for the same system.

Bimolecular k_{YM} and k_{YD} values can thus be calculated from the Stern-Volmer's plots according to (2) and the life-time values given in the section 2. They are given in Table I.

DISCUSSION

These systems are thus characterized by:

—Excimer formation in the mesomorphic and isotropic liquid phases.

—Stern-Volmer's kinetics and very high values of k_{YM} and k_{YD} in the S, N and I phases.

Energy transfer has never been studied for neat LC systems where the LC is the solvent and the donor. No theory being thus available, the results of the present study will be interpreted using Stern-Volmer's kinetics valid for collisional transfer in dilute solution,[5a] Förster's theory valid for long-range transfer between donors and acceptors randomly distributed and orientated in a rigid medium[6] and Voltz's theory which has been successfully applied to neat aromatic systems and polymers where energy migration is operative.[7-9]

Excimer formation and energy transfer are generally described by the following sequence of elementary steps:[5b]

$$\begin{array}{ll}
{}^1M \xrightarrow{h\nu} {}^1M^* & I_a \\
\begin{array}{l} {}^1M^* \rightarrow {}^1M + h\nu_M \\ {}^1M^* \rightarrow {}^1M \end{array} & \left.\begin{array}{l} k_{FM} \\ k_{GM} \end{array}\right\} k_M \\
{}^1M^* + {}^1M \rightarrow {}^1D^* & k_{DM} \\
{}^1D^* + {}^1Y \rightarrow {}^1Y^* + {}^1M + {}^1M & k_{YD} \\
{}^1D^* \rightarrow {}^1M^* + {}^1M & k_{MD} \\
\begin{array}{l} {}^1D^* \rightarrow {}^1M + {}^1M + h\nu_D \\ {}^1D^* \rightarrow {}^1M + {}^1M \end{array} & \left.\begin{array}{l} k_{FD} \\ k_{GD} \end{array}\right\} k_D \\
\begin{array}{l} {}^1Y^* \rightarrow {}^1Y + h\nu_A \\ {}^1Y^* \rightarrow {}^1Y \end{array} & \left.\begin{array}{l} k_{FY} \\ k_{GY} \end{array}\right\} k_Y
\end{array}$$

symbols ^{1}M and ^{1}D* refer to the monomer and the excimer state of the donor, ^{1}Y to the monomer state of the acceptor.

Assuming stationary state conditions for the excited states, elementary kinetics gives:

$$\frac{I_M}{I_D} = \frac{k_{FM}}{k_{FD}} \times \frac{(k_{MD} + k_D)}{k_{DM}[^1M]} \tag{3}$$

Since k_{FM} and k_{FD} are usually of the same order of magnitude and no monomer fluorescence is observed in neat 8 COB and 3 COB, excimer formation ($k_{DM}[^1M]$) is assumed to be much larger than excimer dissociation (k_{MD}). Using this approximation one obtains (1) where τ_{0D} is $1/k_{MD} + k_D$ with $k_{MD} \ll k_D$ and thus negligeable if the excimer is the donor as indicated in the present case by the decay of τ in the presence of acceptor.

At a subsequent time t after excitation, the rate equations are[5c]

$$\frac{d[^1M^*]}{dt} = k_{MD}[^1D^*] - \left(k_M + k_{DM}[^1M]\right)[^1M^*] \tag{4}$$

$$\frac{d[^1D^*]}{dt} = k_{DM}[^1M][^1M^*] - (k_D + k_{MD})[^1D^*] \tag{5}$$

Since excimer dissociation is negligeable, the term k_{MD} can be suppressed from (4) and (5).

Solving (4) and (5) and applying the initial conditions $[^1M^*] = [^1M^*]_0$ and $[^1D^*] = 0$ at $t = 0$, we obtain

$$\begin{aligned} I_D(t) &= \frac{k_{FD}[^1D^*]}{[^1M^*]_0} \\ &= \frac{k_{FD}k_{DM}[^1M]}{k_D - \left(k_M + k_{DM}[^1M]\right)}\left\{e^{-(k_M + k_{DM}[^1M])t} - e^{-(k_D)t}\right\} \end{aligned} \tag{6}$$

with $(k_M + k_{DM}[^1M]) > k_D$

At sufficiently long time, the term $\exp - (k_M + k_{DM}[^1M])t$ is much smaller than $\exp - (k_D)t$. The decay of I_D is then exponential as experimentally observed and the measured parameter is k_D or more precisely the decay-time we need in (1).

Evidence from dielectric permittivity studies[10] as well as from X-ray and neutron diffraction experiments[11-13] show that there is a statistical anti-parallel pairing of the molecules of the alkoxy series of cyano compounds in the smectic phase as shown in Figure 9. Excimer or

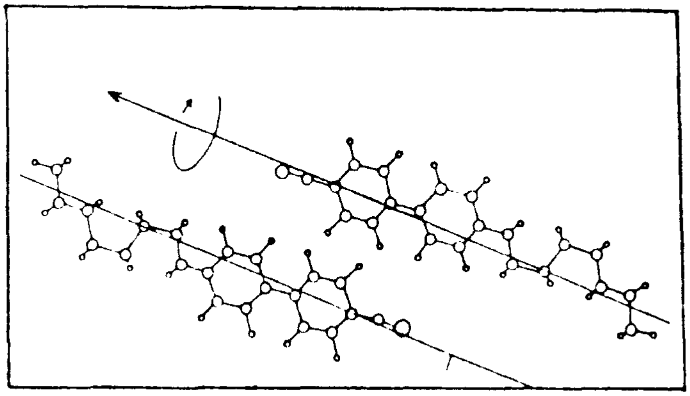


FIGURE 9 Approximate arrangement of the cyanobiphenyl units in the smectic A bilayer phase.

dimer interactions between pairs of neighbouring chromophores are thus highly probable. Excimer emission is indeed the only emission observed in the isotropic, nematic or smectic phase of 3 COB and 8 COB. This means that the number of excimer sites is sufficiently high even in the isotropic state to allow quantitative trapping of the excitation energy after efficient migration.

The Stern-Volmer's mechanism of energy transfer operative in dilute solution results from diffusion-controlled collisions between donors and acceptors.[5a] Elementary kinetics give a linear relationship between I_0/I or τ_0/τ and the acceptor concentration, (equations 1 and 2) the slope of which is the rate constant k_{YM} or k_{YD} given by the theory of diffusion controlled reactions. The rate parameter for a process controlled by diffusion and migration is:

$$k_{YM} = 4\pi N'DpR\left(1 + pR(\pi Dt)^{-1/2}\right) \qquad (7)$$

where N' is the number of molecules per millimoles;
D is the sum of the diffusion coefficients;
R is the sum of the collision radii;
p is a probability factor

In the present case, diffusion-limited collisional quenching only is very improbable. The rate constants for transfer are indeed weakly dependent on the phase, whereas the coefficient for self-diffusion in the mesomorphic phases increases from 10^{-7} to 10^{-5} $cm^2 \cdot s^{-1}$ on passing from smectic to isotropic phase. Furthermore, the values for the diffusion coefficient D obtained from the k_{YM} or k_{YD} values of Figures 5 and 6 are much too high for 3 COB and 8 COB when compared with D values given in the literature for L.C. and other aromatic systems. Since the Stern-Volmer mechanism cannot therefore explain the experimental results, although a linear relation is found between I_0/I and $[Y]$, we have tried Förster's mechanism.

Förster's mechanism is responsible for S-S energy transfer in a rigid medium.[6] It is a long-range transfer resulting from dipole-dipole interactions between the transition moments of the donor and the acceptor according to

$$k_t = \frac{(9000 \ln 10) K^2}{128\, \pi^5 n^4 N_A r^6 \tau_0} \int_0^\infty F_D(\bar{\nu}) \cdot \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \tag{8}$$

where k_t: is the probability of transfer between a donor and an acceptor;
n: is the refractive index of the sample;
K^2: is an orientation factor equal to 2/3 when the acceptor is randomly distributed;
τ_0: is the life-time of the donor in the absence of additive;
$F_D(\bar{\nu})$: is the emission spectrum of the donor;
$\epsilon_A(\bar{\nu})$: the absorption spectrum of the acceptor.

The experimental parameter usually used to check Förster's model is the critical transfer distance R_0. The critical transfer distance is the distance at which energy transfer from donor to acceptor has the same probability as the other processes of deactivation of the donor. The experimental value of R_0 (R_0exp) can be obtained by plotting the experimental efficiency of transfer $f = I_0 - I/I_0$ as a function of the logarithm of the acceptor concentration. Although our results do not strictly obey Förster's theoretical curve, experimental R_0 values can be evaluated for comparative purposes. They are respectively 5.1 and 5.3 nm for the 8 COB and 3 COB/DPOT systems and 3.6 nm for the 8 COB/P system in the neat phase where only excimer emission is observed. When only monomer emission is obtained (8 COB/5H5 mixture), the value is 5.8 nm (Figure 10). These critical distances can also been calculated (R_0th) by substituting k_t according to (8), in equation (9)

$$k_t = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \tag{9}$$

where r is the donor-acceptor distance, to obtain the well-known

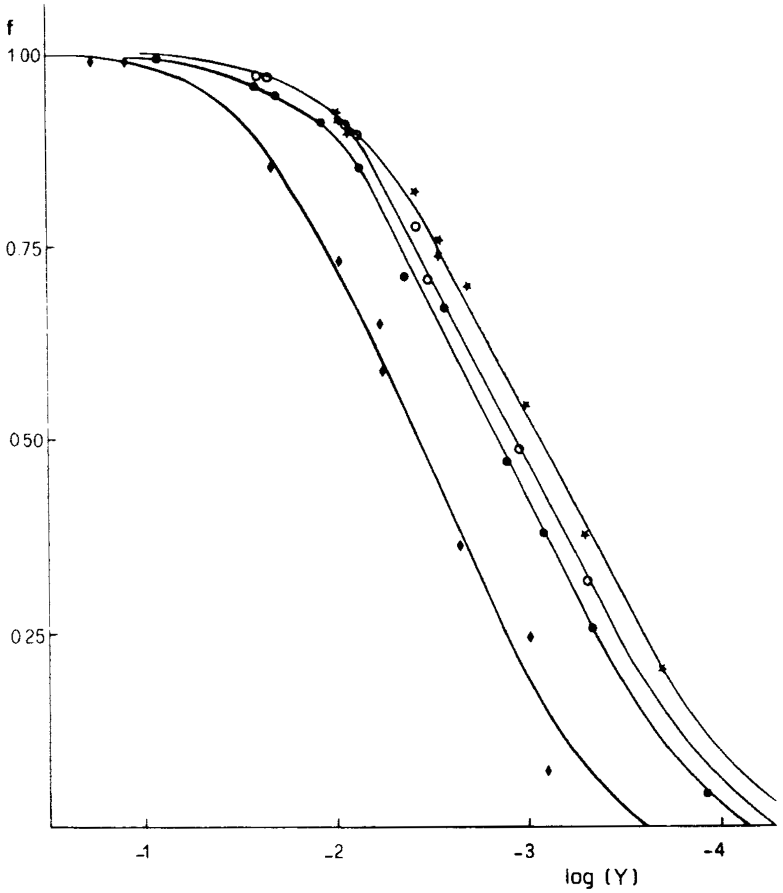


FIGURE 10 Transfer efficiency of 8 COB as a function of the logarithm of the concentration ◆: 8 COB/P (S_A); ●: 8 COB/DPOT (S_A); ○: 3 COB/DPOT (I); ★: 8 COB/5H5/DPOT (S_A).

equation

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

where ϕ_D: is the quantum yield for the donor
N_A: is the Avogadro number.

If the excimer is donor, R_0th is about 3.0 nm for 3 COB/DPOT and 8 COB/DPOT, and 2.5 nm for 8 COB/P($\phi_D \sim 0.15$). If the

TABLE II

Critical transfer distances and rate parameters for neat 3 COB and 8 COB.

	R_0th (nm)	R_0exp (nm)	$D + \Lambda$ cm^2/s	D cm^2/s	Λ cm^2/s
			$S_A \sim 4\ 10^{-5}$	10^{-7}[22]	$4\ 10^{-5}$
8 COB/DPOT	3.0	5.1	$N \sim 6.2\ 10^{-5}$	$4\ 10^{-6}$[23]	$5.8\ 10^{-5}$
			$I \sim 7.8\ 10^{-5}$	10^{-5}[24]	$6.8\ 10^{-5}$
8 COB/P	2.5	3.6	$S_A \sim 1.6\ 10^{-5}$		
			N —		
			I —		
3 COB/DPOT	3.0	5.3	$I \sim 9\ 10^{-5}$		
8 COB/5H5/DPOT 2%–98%	3.9	5.8	$S_A \sim 4.6\ 10^{-4}$		
Benzene					
Toluene					
p-Xylene	liquids				$4.5\ 10^{-5}$[8–9]
Mesitylene					
Methylnaphthalene					$1–5\ 10^{-5}$[25]
Naphthalene	crystal				$10\ 10^{-4}$[5d]
Anthracene	crystal				$1.5\ 10^{-3}$

monomer is donor, R_0th is about 3.9 nm for 8 COB/DPOT, assuming that the monomer quantum yield in the neat phase is identical to that obtained for a dilute solution. The comparison of the experimental and theoretical values of R_0 given in Table II indicates that Förster's mechanism is not sufficient to explain the experimental results, since R_0exp is much larger than R_0th. Larger values of R_0exp are usually explained in terms of energy migration.[9] Energy migration can be defined as a displacement of singlet energy in the system, without translational displacement of the molecules.

A simple manner to characterize migration efficiency quantitatively is to combine Förster's and Stern-Volmer's theories as proposed by Voltz.[7-9] Voltz's theory supposes that singlet energy diffuses and migrates from donor to donor in the medium. At a donor-acceptor distance equal to the critical transfer distance, long range dipole-dipole transfer to the acceptor occurs with a probability $p = 0.5$. The rate parameter for a process controlled by diffusion and migration is:

$$k_{\mathrm{YM}} = 2\pi N'(D+\Lambda)R_0\mathrm{th}\left[1 + 0.5R_0\mathrm{th}(\pi(D+\Lambda))t^{-1/2}\right] \quad (11)$$

and when

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

it reduces to

$$k_{\mathrm{YM}} = 2\pi N'(D + \Lambda)R_0\mathrm{th} \tag{12}$$

These equations allow Λ to be calculated if D is known. The values obtained for $(D + \Lambda)$, D and Λ in the different phases for 3 COB and 8 COB are given in Table II and compared with other neat aromatic liquids. From Table II we can see that the migration coefficient is about 5.10^{-5} $\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ for the three phases involved. This is of the same order of magnitude as values measured for other isotropic liquids and is very different from that for crystals.

It remains now to explain why migration is independent on the nature and the organization of the phase and why even the isotropic phase is characterized by such high migration efficiency, since it can reasonably be supposed that the interactions between neighbouring chromophores which are responsible for energy migration will decrease with the degree of order, i.e., an important requirement for energy transfer is the parallelism between the transition moment of the donor and acçeptor. An interpretation of this can be found in the local molecular organization: 3 COB and 8 COB exhibit strong molecular association due presumably to their high dipole moments. They have a structure with pronounced local ordering interpreted as arising from an overlapping head-to-tail arrangement of molecules resulting in a quasi-layer (smectic A) structure on a local scale. The results of this work thus prove that this local order is maintained in the nematic phase and still persists in the isotropic liquid.

Similar results can be found in recent experiments which are sensitive to long and short range order in the system. X-ray diffraction[14] from nematic and isotropic phases has shown that ordered structures of 100 to 150 molecules, similar to those observed in the smectic phase, still exist in the nematic and isotropic liquid phases even at temperatures that far exceed the N–I transition. The same conclusion was obtained by studies of dielectric relaxation in the nematic and isotropic phases.[15–17] By measuring the density as a function of temperature, Leadbetter *et al.*[18–19] showed that the changes in local molecular organization at the transitions are small, while changes in long-range order occur. Also, the order parameter determined by E.S.R. for other families of nematogens is maintained up to 40 °C above the N–I transition.[20]

The existence of efficient energy migration in neat 3 COB and 8 COB, either in the mesomorphic or the isotropic phase, is the main result of the present work. It is a very large effect which can be characterized even with approximate models such as those which have been used. In ref. 4, results concerning energy migration and transfer in 8 COB have been interpreted according to the hopping model[5e] generally used for crystals. It is another approximation, as valuable as the present one, which also indicates that energy migration is important in neat liquid crystals. It must be noted however that the τ_{0D} value used in this reference is 1 nsec, whereas the correct value (of the order of 10 nsec) is used in the present work.

The high k_{YM} value obtained for the mixture 8 COB/5H5, where the monomer is the donor, cannot be explained at the present time. Indeed, although a very high Λ value is obtained using equation (11), migration is expected to be less efficient in dilute than in neat 8 COB, if migration energy proceeds by excimer formation and dissociation. On the contrary, it could be more efficient when monomer only is observed if excimer sites act as energy traps. This is presently under investigation.

Other less important differences in the rate constants for transfer need tentative interpretation. The k_{YD} obtained for the system 8 COB/DPOT are five time larger than those obtained for the system 8 COB/P. This can be assigned to the relative orientation of the transition moments in both systems. If the mean orientation of the acceptor is supposed to be parallel to the director of the liquid crystal donor, the two transition moments lie on average parallel to each other in 8 COB/DPOT and perpendicular to each other in 8 COB/P. The energy transfer step will thus be more efficient in the first case, although a factor of 5 is larger than expected.[21] Also the difference in the k_{YD} values obtained using fluorescence intensity data and life-time data could be assigned to a small contribution of static quenching which occurs instantaneously and does not affect decay-time, whereas it decreases fluorescence intensity.

CONCLUSION

In the present work, we have shown that:

—the emission of the alkoxy-cyanobiphenyls (COB's) is of the excimer type in the smectic, nematic and isotropic phases.

—in COB's where the coupling between neighbouring units is very efficient, energy migration is important. It is independent of the nature of the phase involved, either S, N or I; migration is however less important than in crystals.

—No differences could be found in the rate constants of energy transfer to additives in the S, N and I phases, indicating that structures on a local scale similar to those existing in the smectic phase are still maintained in the nematic and isotropic liquids. The order parameter as measured by the migration coefficient is of the same order of magnitude as that for neat aromatic phases whether they are LC or not, whereas it is much higher for crystals. This means that the order revealed by the migration coefficient in smectic and nematic liquids is much more similar to that of a neat aromatic liquid than a crystal.

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