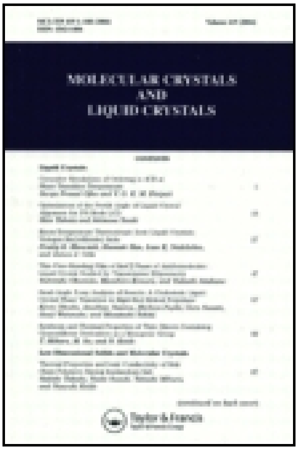

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Absorption and Fluorescence Spectra of 4-Cyanobiphenyl and 4'-Alkyl- or 4'-Alkoxy-Substituted Liquid Crystalline Derivatives

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Absorption and Fluorescence Spectra of 4-Cyanobiphenyl and 4′-Alkyl- or 4′-Alkoxy-Substituted Liquid Crystalline Derivatives

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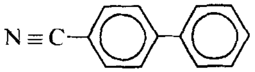
The fluorescence spectrum of 4-cyanobiphenyl, 4-cyano-4′-propyloxybiphenyl, 4-cyano-4′-octylbiphenyl and 4-cyano-4′-octyloxybiphenyl has been analyzed as a function of solvent polarity and solute concentration.

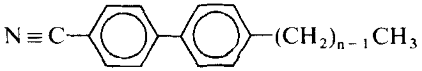
The fluorescence originates from the planar ^1L_a state polarized along the long axis of the molecule. A red shift of the emission and loss of vibrational structure is observed by increasing the solvent polarity in fluid solution but these effects are absent in glassy ethanol at 77°K. This red shift 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. Excimers are formed in concentrated solutions.

I INTRODUCTION

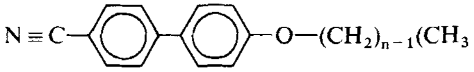
The purpose of the present work is the investigation of the photo-physical processes in solutions of 4-cyanobiphenyl (CB), 4-cyano-4′-propyloxybiphenyl (3 COB), 4-cyano-4′-octylbiphenyl (8 CB) and 4-cyano-4′-octyloxybiphenyl (8 COB).



(CB)



(nCB)



(nCOB)

These p-substituted cyanobiphenyls belong to an important class of thermotropic liquid crystals.

The absorption and fluorescence spectra of these compounds are very different from those of biphenyl and other substituted biphenyls previously reported in the literature.

Absorption and fluorescence of biphenyl have been thoroughly investigated.[1-9]. The fluorescence is structured while the absorption does not show any vibronic structure. A large Stokes loss (3310 cm^{-1}), low fluorescence yield (0.18) and rather long life-time (16 nsec) are observed. Early work of Berlman[2] has assigned the broad structureless absorption to three superimposed transitions: a weak $^1A \rightarrow {}^1L_b$ transition polarized perpendicular to the long axis of the molecule and two stronger transitions $^1A \rightarrow {}^1L_a$ and $^1A \rightarrow {}^1B$ respectively polarized parallel and perpendicular to the long axis. From the value of the ratio of life-time to quantum yield the author assigned the fluorescence of biphenyl and of some derivatives to the ^1L_b (biphenyl and methyl or methoxysubstituted biphenyl), ^1L_a (fluorene) or ^1B transition (vinylbiphenyl or p-terphenyl). A contribution of the ^1B transition to the first absorption band has been dispelled in recent works. A general agreement has however been obtained concerning the assignment of the two lowest transitions of biphenyl observable in the one-photon spectroscopy.[3,4] In biphenyl, the absorption in the region 32,000–40,000 cm^{-1} is due to the superposition of the strong ^1L_a transition with a small contribution of ^1L_b polarized respectively parallel and perpendicular to the long axis. The fluorescence results from deactivation of the ^1L_b level and this results in the lack of "mirror relationship" between absorption and fluorescence and in a large Stokes loss. A weak contribution of $^1B_{3g}$ as the lowest excited state has been reported by Hochstrasser in biphenyl crystals.[9] Recently planar ^1L_a state and slightly twisted (20–30°) ^1L_b state have been proposed for biphenyl, vinylbiphenyl and p-terphenyl.[7,8] Fluorescence would originate from the planar ^1L_a state in vinylbiphenyl and p-terphenyl. This justifies the appearance in the fluorescence spectrum of a long progression in the vibrational mode that carries the geometry of one state into another. It corresponds to 1300 cm^{-1} in vinylbiphenyl and p-terphenyl and has been assigned to the stretching vibration of the interannular bond. According to these authors, introduction of the stretching and twisting vibrational modes of the interannular bond in the calculation of the Franck–Condon distribution gives a structureless absorption and structured fluorescence for vinylbiphenyl and p-terphenyl. The progression of the vibrational mode is only 1000 cm^{-1} in biphenyl and this last interval has been associated with the ground state ring breathing vibration indicating that in this compound, the geometry of the ground state is not very different from that of the lowest excited ^1L_b state (twisting angle of 20–30°).

The fluorescence spectrum, quantum yield and life-time of biphenyl is weakly dependent on solvent polarity in agreement with a ^1L_b lowest excited state characterized by a weak dipole moment. No excimer formation has been reported in concentrated solution of this compound.

Electronic and vibrational states of biphenyl crystals and solutions have also been studied using two-photon excitation spectroscopy.[10, 11]

II EXPERIMENTAL

Cyanobiphenyl was synthesized in the laboratory by reaction of CuCN on 4-Bromobiphenyl.[12] It was purified by vacuum distillation followed by five recrystallizations from hexane. 4-Bromobiphenyl was prepared from *p*-bromoaniline and benzene[13] purified by chromatography on silicagel and recrystallization from ethanol. It was purified by crystallization up to the disappearance of any impurity fluorescence. The substituted cyanobiphenyls were purchased from BDH. They are of high purity grade and were used without further purification. Spectroscopy grade solvents were used in all cases. The emission spectra were recorded with a MPF 2A Perkin-Elmer spectrofluophosphorimeter and are uncorrected for the response of the photomultiplier.

III RESULTS AND DISCUSSION

III.1 Absorption spectra as a function of solvent polarity

The absorption spectra of cyanobiphenyls in ethanol are given in Figure 1. The specific absorption coefficient for CB, 3 COB, 8 CB and 8 COB at λ_{max} are respectively: 22,300, 25,600, 30,100 and 25,300 $1 \cdot \text{mole}^{-1}\,\text{cm}^{-1}$. A small shift of λ_{max} with solvent polarity is observed (Table I). Broad absorption bands without vibrational structure are recorded in all solvents.

III.2 Fluorescence spectra as a function of solvent polarity in dilute solution

The fluorescence spectra strongly depend on solvent polarity. The emission spectra of the cyanobiphenyls in cyclohexane are given in Figure 2. The separation between vibrational structures is 1300 cm^{-1} while it is only 1000 cm^{-1} in biphenyl. A shift of the emission spectra to longer wavelength is also observed in $-$R and $-$OR substituted cyanobiphenyl derivatives but the Stokes loss is smaller than for biphenyl (Table I).

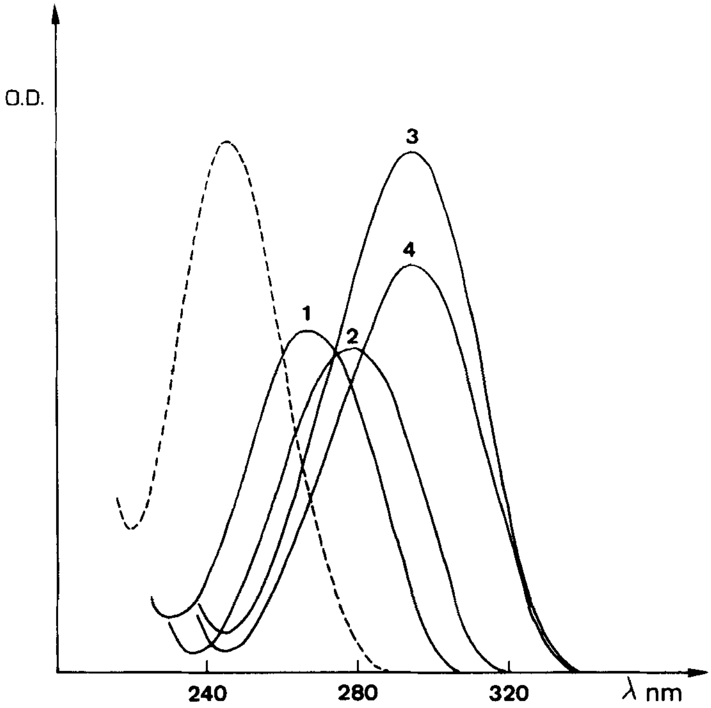


FIGURE 1 Absorption spectra of cyanobiphenyls in ethanol. 1, CB; 2, 8CB; 3, 3COB; 4, 8COB; -------biphenyl C = 10^{-5}M.

TABLE I

Absorption maximum and emission maximum as a function of solvent polarity

Solvent polarity functions			Solvents (RT)	CB		8CB		3COB		8COB	
F_1	F_2	F_3		λ_{abs}^{max} (nm)	λ_{em}^{max}	λ_{abs}^{max} (nm)	λ_{em}^{max}	λ_{abs}^{max} (nm)	λ_{em}^{max}	λ_{abs}^{max} (nm)	λ_{em}^{max}
0.001	0.001	0.254	n. hexane	262.5	311	–	–	–	–	289	340
-0.001	-0.003	0.286	cyclohexane	263	312	272	324.5	290	339	291	339
0.165	0.378	0.427	diethyl ether	264	317.5	274	330	–	–	291	350
0.201	0.489	0.494	ethyl acetate	265.5	320	276	333.5	292	358	292	358
0.290	0.811	0.649	ethanol	266.5	324	278	337	294	366	294	367
0.274	0.765	0.637	isopropyl alcohol	–	–	277.5	338.5	293	367	294	367
0.307	0.866	0.665	acetonitrile	–	–	–	–	–	–	292	370
0.276	0.837	0.708	dimethyl-formamide	271	328	281	343	296	374	297	374
–	–	–	ethanol at 77°K	–	316	–	329	–	343	–	344

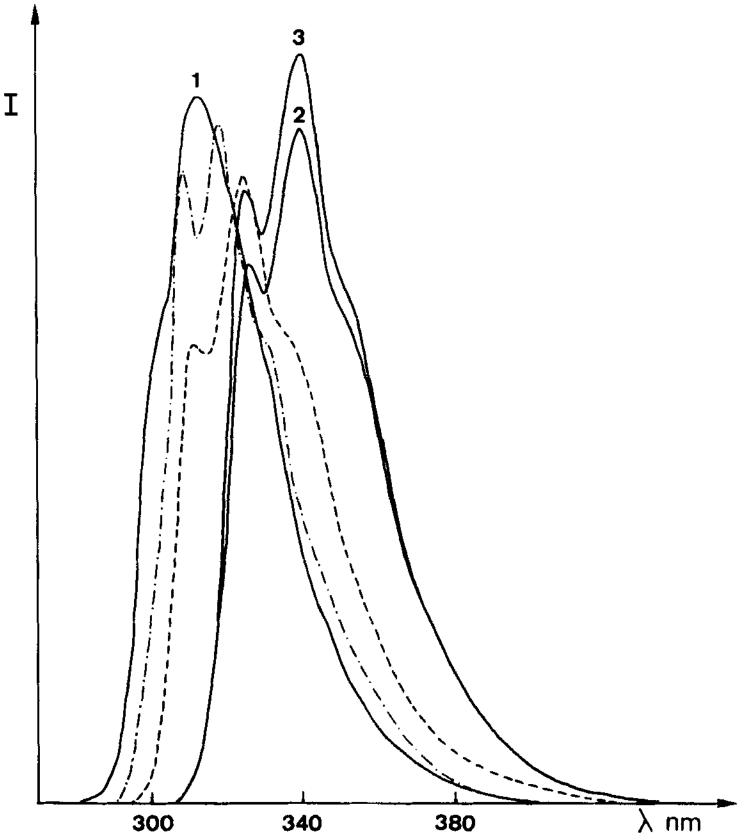


FIGURE 2 Emission spectra of cyanobiphenyls in cyclohexane at RT. 1, CB; 2, 3COB; 3, 8COB. –·–·–biphenyl; -------8CB, C = 10^{-5} M; λ_{exc} = 280 nm.

More interesting is the shift to longer wavelength and loss of vibrational structure observed at room temperature (RT) when the polarity of the solvent increases (Figure 3 and Table I). In glassy ethanolic solution at 77°K, on the contrary, the spectra are not very different from those obtained in cyclohexane at RT: the vibrational structure is maintained and a bathochromic shift of only 5 nm is measured. The same behaviour is observed for the four *p*-substituted cyanobiphenyls studied. Their fluorescence quantum yield is high (0.36 for CB and 0.54 for 8 CB, 3 COB and 8 COB in cyclohexane at RT). Their life-time is very short (<1 nsec in hexane) and could not be measured by single photon counting.

If vibrational progressions, life-time, quantum yield, Stokes loss in cyclohexane and shift of emission spectra as a function of solvent polarity of biphenyl and cyanobiphenyls are compared, it becomes clearly evident that

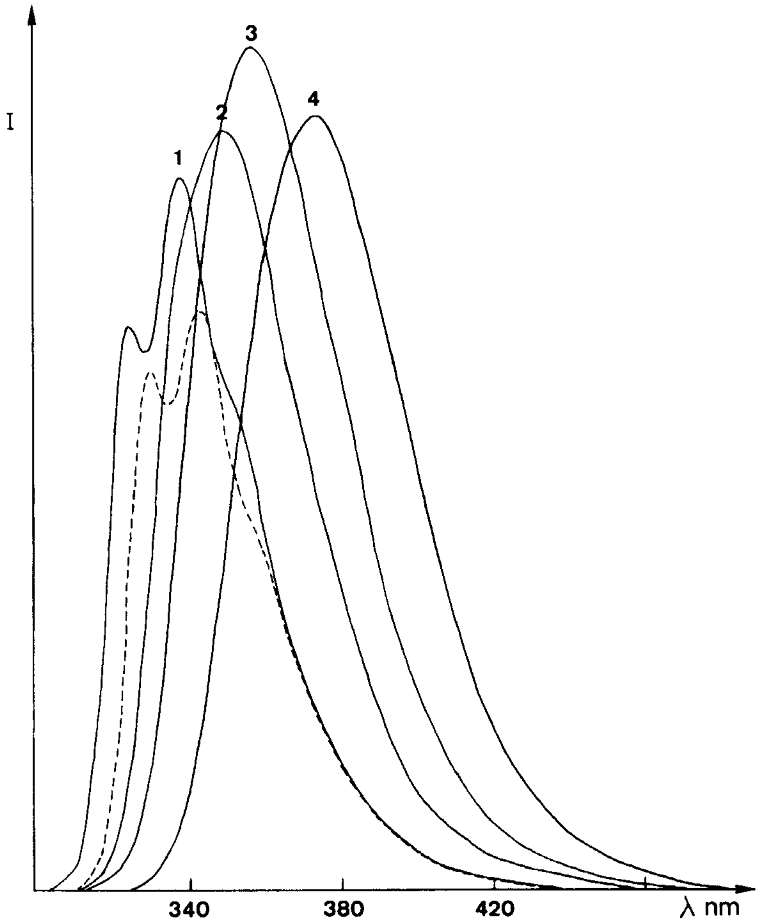


FIGURE 3 Solvent effect on the emission spectrum of 8COB at RT. 1, heptane; 2, diethyl ether; 3, ethyl acetate; 4, dimethylformamide. ------- ethanol at 77°K, C = 10^{-5} M; λ_{exc} = 280 nm.

different photophysical processes are involved in the excitation and de-excitation of the unsubstituted and CN-substituted biphenyls. The lowest excited state in cyanobiphenyls is the ^1L_a state, the $^1A \rightarrow {}^1L_a$ transition being polarized parallel to the long axis. The weak $^1A \rightarrow {}^1L_b$ transition is hidden by the more intense $^1A \rightarrow {}^1L_a$ transition in absorption. The $^1L_a \rightarrow {}^1A$ transition is responsible for the fluorescence spectrum and results in shorter fluorescence life-time, higher fluorescence yield and smaller Stokes shift than in biphenyl. Most likely the ^1L_a state is planar since the interannular vibration corresponding to 1300 cm^{-1} [12] appears in the emission spectrum.

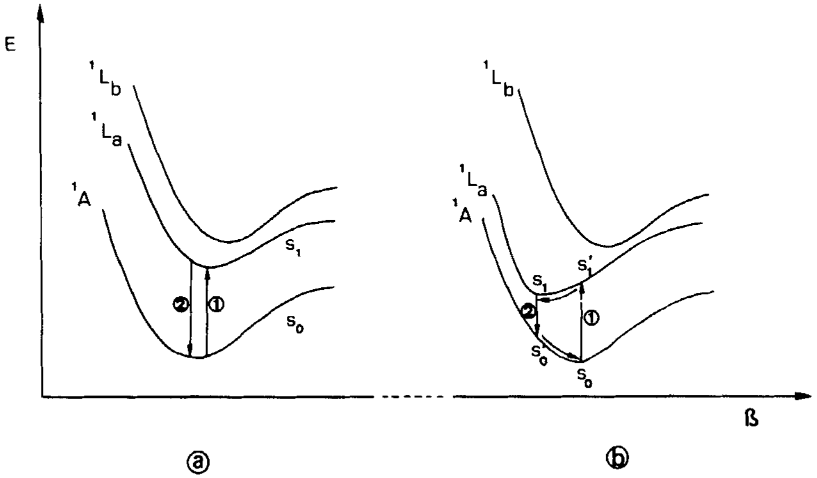


FIGURE 4 Schematic diagram of the activation-deactivation processes in cyanobiphenyl derivatives (a) non polar solvents; (b) polar solvents. β = mean degree of orientation of the dipoles of the nearest neighbour solvent molecules relative to the dipole moment of the solute, according to (19). (1) = $h\nu_a$; (2) = $h\nu_f$.

This vibrational mode carries the geometry of the non-planar ground state into the planar ^1L_a state.

This transition is very sensitive to solvent polarity. Indeed, the dipole moment of these molecules is higher in the excited ^1L_a state than in the ground state. Absorption of light thus induces an orientation relaxation process of the solvent cage in the internal electric field of the excited solute. The solute molecule first excited to a Franck–Condon S_1' state relaxes to an equilibrium S_1 state and fluorescence is emitted from this state to a non-equilibrium S_0' state with loss of vibrational structure (Figure 4a and b) and a shift in the fluorescence spectrum with solvent polarity is thus observed. Such a bathochromic shift in the emission spectrum with solvent polarity has also been reported for indole and some derivatives.[14–21] A schematic diagram of the process responsible for absorption and emission of indole is given in Figure 5 (a and b) and compared with that we proposed for nCOB and nCB. From the numerous and extensive studies of indole,[14–17] it appears that in non-polar solvents ^1L_a and ^1L_b are situated near to each other, ^1L_b being the lowest one. These states are in thermal equilibrium as revealed by the non-exponential decay and the emission spectrum contains components of ^1L_a and ^1L_b fluorescence. When the polarity of the solvent increases, the ^1L_a fluorescence shifts to the red and thermal equilibrium is more difficult to attain. Simultaneously, photoionization from the ^1L_a state is favoured in polar solvents. A dual fluorescence resulting from the

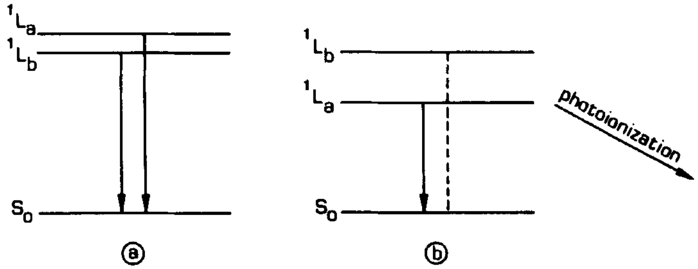


FIGURE 5 Schematic representation of the energy levels in indole, anilino-naphthalene sulfonate and alkylaminocyanobenzene. (a) non polar solvents: dual fluorescence; (b) polar solvents.

same scheme of deactivation has been reported for alkylaminocyanobenzene.[18–19] Fluorescence from ^1L_a and ^1L_b states are characterized by a different degree of polarization. Their relative importance and the position of the ^1L_a band strongly depends on solvent polarity. 1,8-anilinonapthalene sulfonate[20–21] presents strong similarities with indole and alkylaminocyanobenzene. In those three compounds, the fluorescence yield decreases in polar solvents owing to the increasing importance of photoionization.

Returning to nCOB and nCB dual fluorescence does not seem to be present since the degree of fluorescence polarization has the same positive value in the whole spectrum in ethanol at 77°K (0.20 ± 0.01). It must be noted however that the fluorescence polarization in biphenyl is also positive (0.20 ± 0.01) whereas it should have to be negative since excitation results mainly from the ^1L_a transition and emission from the ^1L_b. This was also reported by Dörr several years ago.[22] Photoionization in polar solvents is not important in nCOB and nCB since the quantum yield does not significantly depend on solvent polarity.

Quantitative correlation of the spectral red shift of the fluorescence with the polarity of the solvent have been proposed in several theoretical treatments.[18, 19, 23–29] They relate the shift of the O–O transition in absorption and emission ($\bar{v}_a$ and $\bar{v}_f$) to the dipole moment of the ground and excited state μ_g and μ_e, the dielectric constant D, the refractive index n of the solvent and the cavity radius a in Onsager's theory of reaction field. The dipole moment of the excited state can thus be calculated if the other physical parameters are known.

Different theories leading to final Eqs. (1),[24, 25] (2)[26, 27] and (3)[28] have been proposed.

$$\bar{v}_a - \bar{v}_f = \frac{2\,\Delta\mu^2}{a^3hc}\left[\left(\frac{D-1}{2D+1}\right) - \left(\frac{n^2-1}{2n^2+1}\right)\right] \tag{1}$$

where $\Delta\mu^2 = (\mu_e - \mu_g)^2$

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2\,\Delta\mu^2}{a^3hc}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right)\frac{2n^2+1}{n^2+2} \tag{2}$$

where $\Delta\mu^2 = (\mu_e - \mu_g)^2$

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -\frac{2\,\Delta\mu^2}{a^3hc}\left[\frac{2n^2+1}{2(n^2+2)}\cdot\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) + \frac{3(n^4-1)}{2(n^2+2)^2}\right] \tag{3}$$

where $\Delta\mu^2 = \mu_e^2 - \mu_g^2$.

The problem of non-spherical molecules has been discussed by Lippert[24] and Marcus.[30] Lippert has calculated the excited dipole moment of substituted stilbenes and other ellipsoidal derivatives using Eq. (1) in which the radius a was taken as half the length of the axis of the ellipsoidal molecule.

Quantitative correlation of the difference between absorption and emission maxima of 8 CB, 8 COB, 3 COB and CB as a function of the solvent functions

$$F_1 = \frac{2(D-1)}{2D+1} - \frac{2(n^2-1)}{2n^2+1}$$

$$F_2 = \frac{2n^2+1}{n^2+2}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right)$$

$$F_3 = \frac{1}{2}F_2 + \frac{3}{2}\,\frac{(n^4-1)}{(n^2+2)^2}$$

according to Eqs. (1), (2) and (3) are given in Figures 6, 7 and 8 where $\bar{\nu}_a$ and $\bar{\nu}_f$ correspond to the maximum of absorption and emission. The $\Delta\mu = (\mu_e - \mu_g)$ values can be obtained from (1), (2), if reasonable values are assumed for a. The length of the fully extended molecule for CB, 3 COB, 8 CB and 8 COB are respectively 1.1–1.3–2.0 and 2.2 nm. The effective length of the hydrocarbon substituent chain depends on the nature of the solvent. Therefore the parameters $\Delta\mu$ and μ_e were calculated for different values of a. The results given in Table II show that these parameters are weakly dependent on small changes of a for a given equation. In any case, the dipole moment of the excited state is much larger than in the ground state.

Sun and Song[29] have recently proposed to use a combination of Eq. (2) and (3) to allow the calculation of μ_e if the value of μ_g is unknown.

$$\mu_e = \frac{1}{2}\left(\frac{a^3hcS_2}{2}\right)^{1/2}\left(1 - \frac{S_3}{S_2}\right) \tag{4}$$

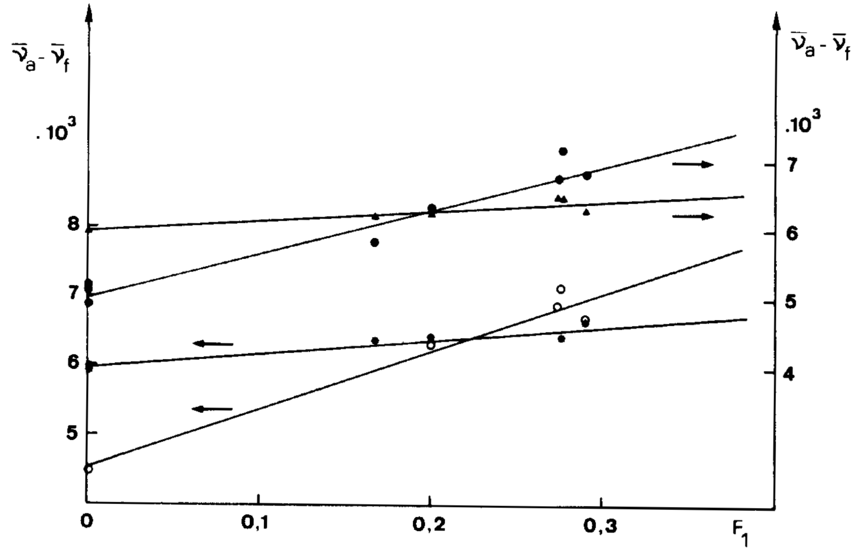


FIGURE 6 Spectral shift as a function of solvent polarity according to equation (1) ● CB ▲ 8CB ✱ 3COB ○ 8COB.

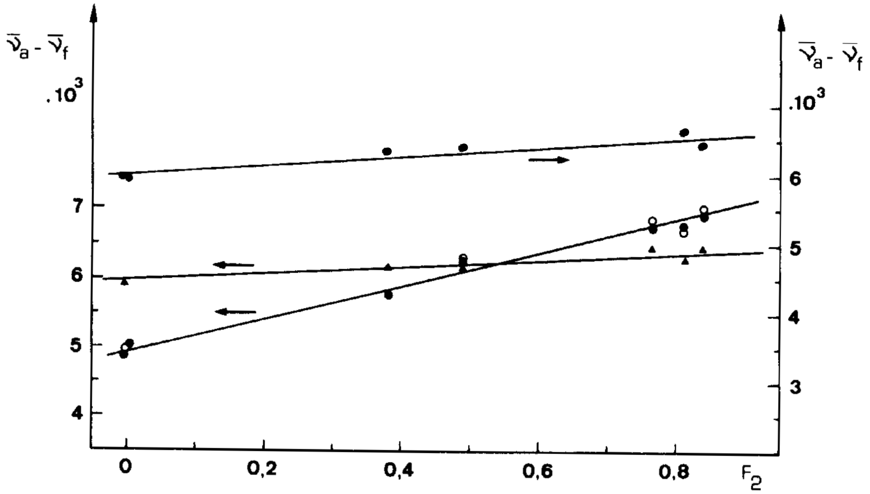


FIGURE 7 Spectral shift as a function of solvent polarity according to equation (2). ● CB ▲ 8CB ✱ 3COB ○ 8COB.

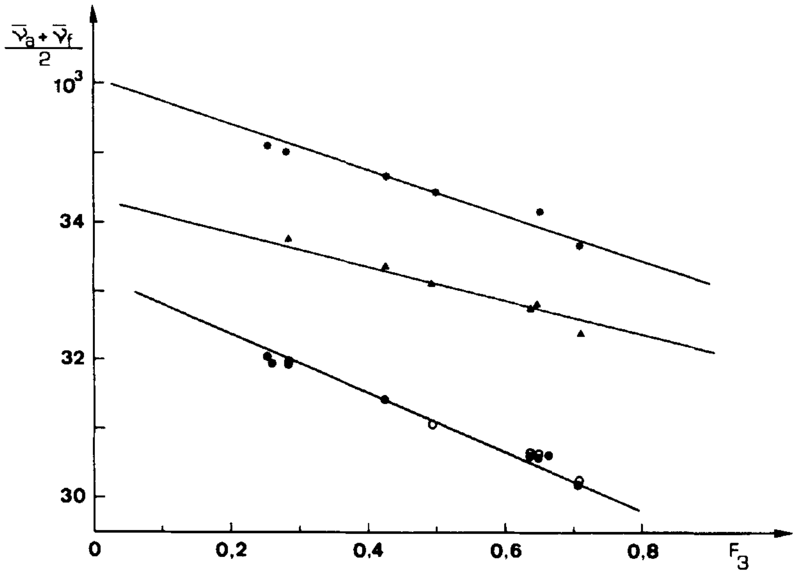


FIGURE 8 Spectral shift as a function of solvent polarity according to equation (3). ● CB; ▲ 8CB; ✱ 3 COB; ○ 8COB.

TABLE II

Values of $\Delta\mu$ and μ_e derived from equations (1), (2), (3) and (4).

		(1)		(2)		(3)		(4)
	a(nm)	$\Delta\mu^a$ (Debye)	μ_e	$\Delta\mu^a$ (Debye)	μ_e	$\Delta\mu$ (Debye)	μ_e	μ_e (Debye)
CB	0.5	5	9	3	7	–	8	8
	0.6	7	11	4	8	–	9	
8CB	0.8	9	14	5	10	–	12	15
	1.0	13	18	7	13	–	16	20
3COB	0.7	17	–	9	–	–	–	13
	0.8	21	–	11	–	–	–	16
8COB	0.8	18	–	11	–	–	–	16
	1.0	25	–	16	–	–	–	22

[a] Calculated assuming μ_g CB = 4.23 Debye[32].
μ_g 8CB = 4.98 Debye[32].

TABLE III

Emission maximum for monomer ($\lambda^M_{\max}$) and excimer ($\lambda^E_{\max}$) fluorescence in cyclohexane and ethanol.

	Cyclohexane		Ethanol	
	$\lambda^M_{\max}$	$\lambda^E_{\max}$	$\lambda^M_{\max}$	$\lambda^E_{\max}$
	(nm)			(nm)
CB	312	I.S.	324	385
8CB	324	380	337	385
3COB	339	I.S.	366	non resolved
8COB	339	380	367	I.S.

where S_2 and S_3 are the slopes corresponding to Eqs. (2) and (3). The μ_e values obtained from (4) are given in Table II. Equation (2) gives lower values of $\Delta\mu$ and μ_e in any case. There is nevertheless a discrepancy between the values of μ_e obtained from (1) and (4) for the nCOB series (assuming μ_gnCOB > μ_gnCB) whereas it is satisfactory for CB and 8 CB. This cannot be explained at the present time.

These values obtained for the *p*-substituted cyanobiphenyls can be compared with the $\Delta\mu$ and μ_e determined by Lippert for 4-NH_2-4′-NO_2 biphenyl (respectively 12 and 18D).

III.3 Fluorescence spectra as a function of concentration

Since excimers are often formed in concentrated solution of fluorescent compounds, the emission spectrum of cyanobiphenyl derivatives was studied as a function of solute concentration in cyclohexane and ethanol. The results are summarized in Table III. Excimer fluorescence is observed for concentrations exceeding 5.10^{-2} M. It consists of a broad, unstructured emission with $\lambda^E_{\max}$ in the range 380–385 nm, almost independent of solvent polarity since the excited dipole moment of excimers has a very low or null value. Concentrations as high as 5.10^{-2}–5.10^{-1} M cannot be obtained in all cases owing to the low solubility of cyanobiphenyl derivatives. These compounds are mentioned as insufficiently soluble (I.S.) in Table III. The value of $\lambda^E_{\max}$ is also independent of the nature and length of subsituent chain in 4′ position.

Excimer fluorescence as a function of concentration is given in Figure 9, and 10 for CB in ethanol and 8 COB in cyclohexane. For 3 COB in cyclohexane, excimer could be detected as a broadening of the spectrum for C = 3.10^{-2} M but could not be resolved. The case of 8 CB is less clear. Indeed, the emission spectra in concentrated cyclohexane solution (C > 10^{-2} M) depends on the excitation wavelength. When excited at 280 nm, the

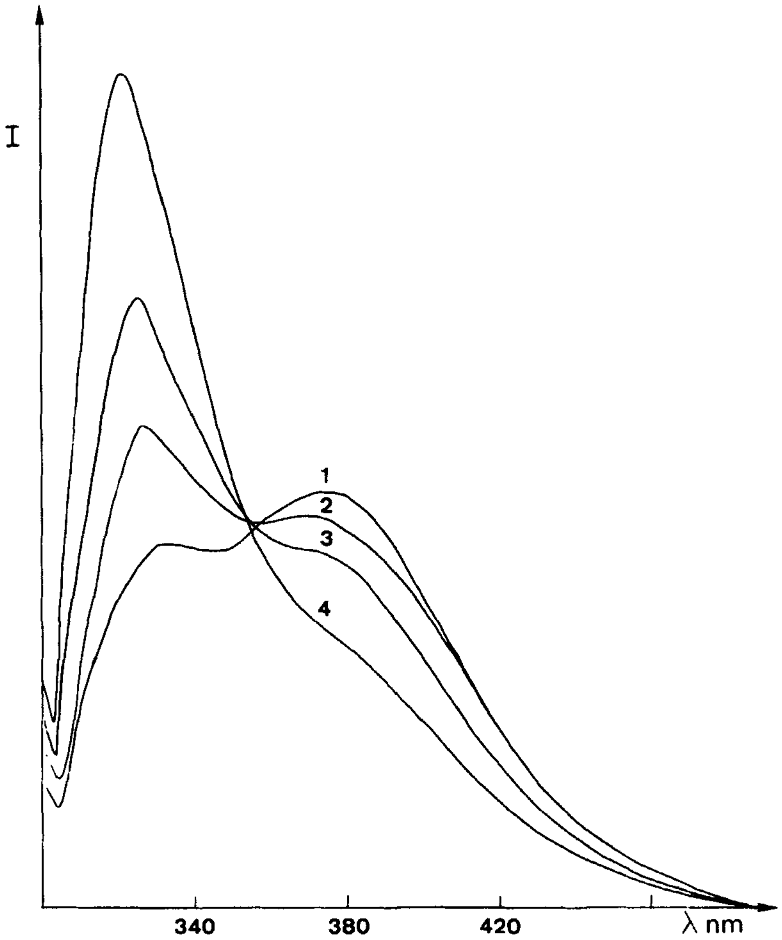
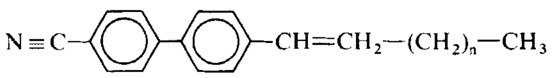


FIGURE 9 Excimer fluorescence as a function of concentration for CB in ethanol. 1 : C $= 4.1\ 10^{-1}$ M; 2 : C $= 3.10^{-1}$ M; 3 : C $= 1.6\ 10^{-1}$ M; 4 : C $= 0.6.10^{-1}$ M.

fluorescence shows a small contribution of an impurity at 355 nm. This impurity can be selectively excited at 320 nm. It presents the same vibrational structure as 8 CB but is displaced at ~30 nm to the red. The emission spectrum of this impurity most probably loses its vibrational structure in ethanol and has the same λ_{max} as the excimer. It presents thus the same characteristics as those of the cyanobiphenyl derivatives and is also detected in 7 CB. The impurity can be tentatively assigned to an α, β unsaturated derivative



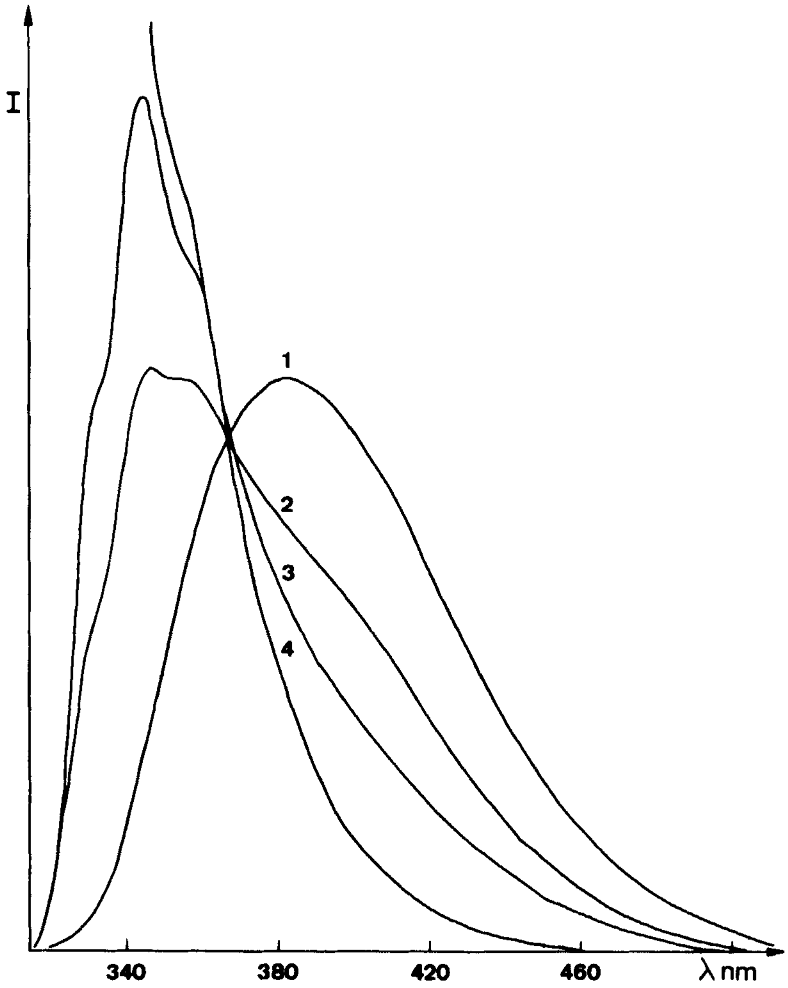


FIGURE 10 Excimer fluorescence as a function of concentration for 8COB in cyclohexane. 1:C = 5.2 10^{-1} M; 2:C = 2.9 10^{-1} M; 3:C = 9.4 10^{-2} M; 4:C = 4.6 10^{-3}M.

Assignment of this emission to a preformed dimer cannot be disregarded since the absorption and emission spectra of a dimer depend on its geometry. However, the absence of this type of emission in CB and nCOB derivatives lends to support the impurity hypothesis. This problem can be solved only by extensive purification of the alkyl CB derivatives but this is difficult to realize. The commercial "High purity" products is reported to have been purified by liquid chromatography.

Excimer formation was not detected upon photoexcitation of biphenyl which is non-planar in the ground and lowest excited state (^1L_b). The difference of behaviour between biphenyl and *p*-substituted cyanobiphenyls can be assigned to the nature of the dipole moment of the excited state involved: respectively non-planar ^1L_b polarized along the short axis and planar ^1L_a polarized along the long axis. Excimer were also reported to form in 1,3-dibiphenylpropane. In this last compound this has been assigned to the value of $-\Delta S$ which is generally lower for intramolecular than for intermolecular excimer formation.[31]

IV CONCLUSION

Fluorescence of cyanobiphenyl derivatives arises from deactivation of the excited planar ^1L_a state. Transition from the ground to the first excited state is accompanied by a large increase of dipole moment. This induces relaxation of polar solvent molecules resulting in an important red shift of the emission. Excimers which have never been reported to form in the first excited ^1L_b state of biphenyl, are observed in concentrated solution of cyanobiphenyl derivatives.

Acknowledgement

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