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SOLVENT DYNAMICS AND INTRAMOLECULAR CHARGE TRANSFER IN 4-CYANO-4'-BUTYLOXYBIPHENYL (4COB).

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Abstract

The photophysical properties of 4-cyano-4'-butyloxybiphenyl (4COB) in diluted solutions at room temperature are reported. From this study it is clear that 4COB forms an I(ntramolecular) C(harge) T(ransfer) state. Furthermore, the influence of the temperature on the formation of the ICT state of 4COB in 1-butanol and diethylether is investigated to study the role of the solvent dynamics on the stabilization of the ICT state. Finally the importance of hydrogen bonded clusters in the stabilization of the ICT state of 4COB has been examined in 1-butanol/butyronitrile mixtures.

1. Introduction

Since the observation of dual fluorescence for dimethylaminobenzonitrile (DMABN) in polar solvents, numerous investigations into the details of this phenomenon have appeared.[1-8] Solvent studies as well as recent picosecond experiments conclude that the Stokes-shifted emission arises from a twisted intramolecular charge transfer (TICT) state. Since, numerous other compounds were found to exhibit the same photophysical characteristics.[9-14]

The photophysical properties of 4-cyano-4'-alkyl-and 4'-alkyloxybiphenyl were first examined by David et. al.[15] They observed a red shift of the emission by increasing the solvent polarity. This red shift was assigned to an orientation relaxation process of the solvent cage in the electric field of the excited molecule. Mataga and coworkers[16,17] found a similar behaviour for 8COB and they attributed the shift to the formation of an intramolecular charge-transfer state which is stabilized in polar solvents. In order to obtain a better understanding of the processes involved in the excited state of 4COB, more detailed experiments were performed in solvents with different polarity.

Furthermore the influence of the solvation dynamics in the stabilization of the ICT state of 4COB have been studied. The ICT formation of 4COB in 1-butanol and in diethylether was studied in the temperature region of 77K to 293K by means of time resolved and steady state fluorescence experiments. In a final step the role of hydrogen bonded clusters in the stabilization of the intramolecular charge transfer state of 4COB was investigated in 1-butanol/butyronitrile mixtures. The time resolved data are correlated with the data obtained from the infrared O-H stretch of the corresponding mixtures.

2. Experimental.

4COB (4-cyano-4'-butyloxybiphenyl) was obtained from BDH. It was shown to be free from impurities by H.P.L.C.. The solvents (hexane, isooctane, diethylether, dibutylether, tetrahydrofuran, methanol, 1-butanol, ethylacetate, butylacetate and acetonitrile) used are spectroscopic grade UVASOL and obtained from MERCK. All the samples (conc. < 10^{-4}M) were studied in 1-cm quartz cells, and degassed by repeated freeze-pump-thaw cycles.

Infrared absorption spectra were recorded on a PERKIN-ELMER 882 infrared spectrophotometer. The absorption spectra were recorded on a SLM AMINCO DW-2000 U.V. spectrophotometer. The fluorescence spectra were taken on a SPEX fluorolog with excitation near the maximum of the long wavelength absorption band. The data were transmitted to an Olivetti M28 for data manipulation by a program, developed in the laboratory, using the Asyst 2.0 language and plotted on a HP7475A. Time resolved decay measurements were obtained with single photon timing equipment using a synchronously pumped, cavity-dumped dye laser as excitation source[18a,b].

A global iterative reweighted reconvolution program based on the nonlinear least squares algorithm of Marquardt[19] was used to estimate the unknown parameters α_j and τ_j. The entire decay profiles, including the rising edge were analyzed. Fluorescence decay curves at different wavelengths and time increments were analyzed simultaneously according to equation 1, the sample and reference decay time parameters (fluorescence response function of the detection system about 80 ps) were linked.

$$\left[\begin{array}{l} f_1 = \sum_j \alpha_j^{1} \exp(-t/\boxed{\tau_j}) \\ f_2 = \sum_j \alpha_j^{2} \exp(-t/\boxed{\tau_j}) \\ f_3 = \sum_j \alpha_j^{3} \exp(-t/\boxed{\tau_j}) \\ \quad\vdots \\ f_i = \sum_j \alpha_j^{i} \exp(-t/\boxed{\tau_j}) \end{array}\right. \qquad \text{(eq.1)}$$

3. Results and discussion.

3.1. Photophysical properties of 4COB in neat solvents.

Steady state fluorescence

The basic optical properties of 4COB were first examined in isotropic media, e.g. hexane, diethylether, dibutylether, ethylacetate, butylacetate, tetrahydrofuran, acetonitrile, butyronitrile, methanol and 1-butanol. The absorption spectrum of 4COB in hexane (figure 1) exhibits two absorption bands, the first one at 292.2 nm and a second one at 220 nm. The maximum of the long-wavelength absorption band shifts to the red with increasing solvent polarity . The absorption maximum shifts from 292.2 nm in hexane to 297.4 nm in 1-butanol (table I).

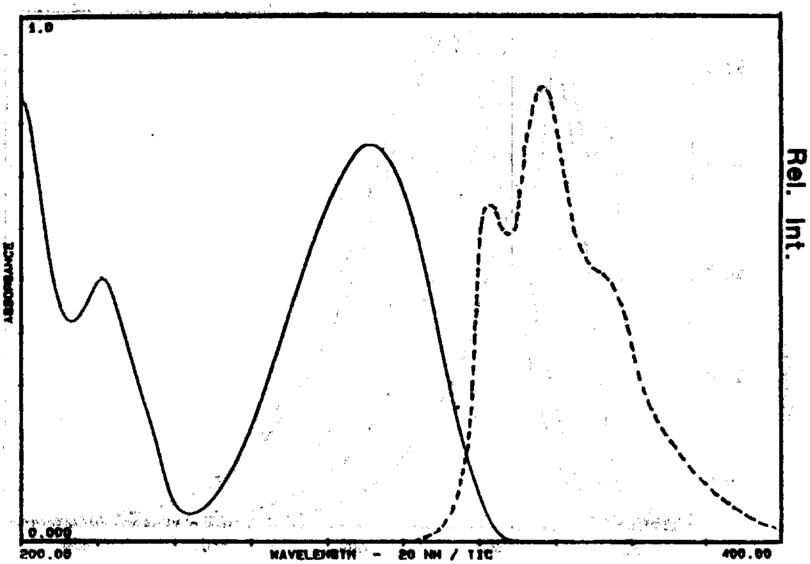

Figure 1: Absorption and emission spectrum of 4COB in hexane (R.T.).
(——) (- - -)

Fluorescence measurements were carried out by excitation into the long wavelength absorption band (290 nm). The fluorescence spectrum of 4COB in solution strongly depends on the solvent polarity. Figure 2 shows the fluorescence spectra of 4COB in hexane, diethylether, ethylacetate, 1-butanol and acetonitrile. In table I the emission and absorption maxima together with the quantum yields of fluorescence are listed. Upon increasing the polarity the spectrum undergoes a bathochromic shift and the shift to longer wavelengths is accompanied with a loss in vibrational fine structure.

Table I: Emission maxima ($\lambda_{max,F}$), absorption maxima ($\lambda_{max,A}$) and quantum yields of fluorescence for 4COB in solution.

Solvent	$\lambda_{max,A}$	$\lambda_{max,F}$	Φ_F
Hexane	292.2 nm	323 nm 338 nm	0.76
Diethylether	293.2 nm	340 nm 352 nm	0.51
Dibutylether	294.0 nm	339 nm 349 nm	0.73
Ethylacetate	294.1 nm	357 nm	0.83
1-Butanol	297.4 nm	367 nm	0.86
Acetonitrile	295.2 nm	375 nm	0.79

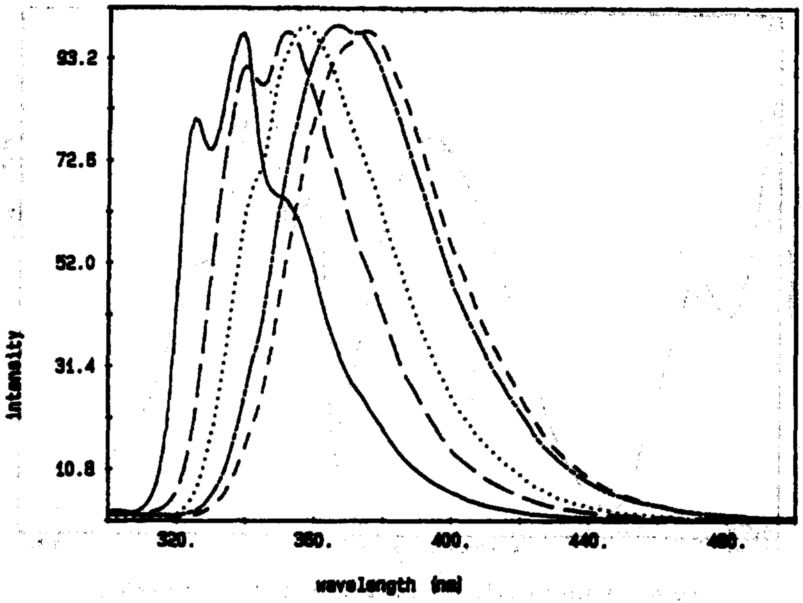

Figure 2: Fluorescence spectra of 4COB in (——) hexane, (– –) diethylether, (.....) ethylacetate, (–.–) 1-butanol and (-----) acetonitrile (R.T.).

The fluorescence shift obtained in highly polar solvents like acetonitrile could be attributed to a TICT-state[20,21] (Twisted Intramolecular Charge Transfer), which is stabilized in polar solvents resulting in a large Stokes shift. However the absence of fine structure in the absorption spectrum of 4COB in hexane and the observation of this fine structure in emission suggests an enhanced planarity of the emissive state. The amount of vibronic structure in a nonpolar solvent can even be used to monitor the relaxation towards a planar emissive conformation as shown by Swiatkowski et al.[22] for the case of biphenyl and terphenyl. The allowedness of the emission (high Φ_f, Table I and short lifetime, Table III) also points to the planarity of the emission state. In more polar solvents this vibrational structure disappears for 4COB due to solvent interactions stabilizing ^1S and destabilizing the Frank-Condon ground state. This also holds for bridged model compounds of cyanobiphenyls[23].

Quantitative correlation of the spectral shift of the fluorescence with the polarity of the solvent has been proposed in several theoretical treatments[24]. They relate the 0-0 transition in absorption and emission (ν_a and ν_f) to the dipole moment of the ground and excited state μ_g and μ_e, the dielectric constant ε, the refractive index n of the solvent and the cavity radius ρ 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 (equation 2).

$$\nu_a - \nu_f = \frac{2\Delta\mu^2}{4\pi\varepsilon_0 hc\rho^3} \cdot f(\varepsilon,n) \qquad \text{(eq.2)}$$

with

$$f(\varepsilon,n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

and $\Delta\mu = (\mu_e - \mu_g)$.

The $\Delta\mu$ values can be obtained from equation 1, if reasonable values are assumed for ρ (Figure 3). The length of the fully extended molecule for 4COB is 1.4 nm. The effective length of the hydrocarbon substituent chain depends on the nature of the solvent. Therefore, the parameter $\Delta\mu$ was calculated for different values of ρ. The results given in table II show that $\Delta\mu$ is only moderately dependent on small changes of ρ. But in any case the dipole moment of the excited state is much larger than the dipole moment of the ground state consistent with earlier results[15].

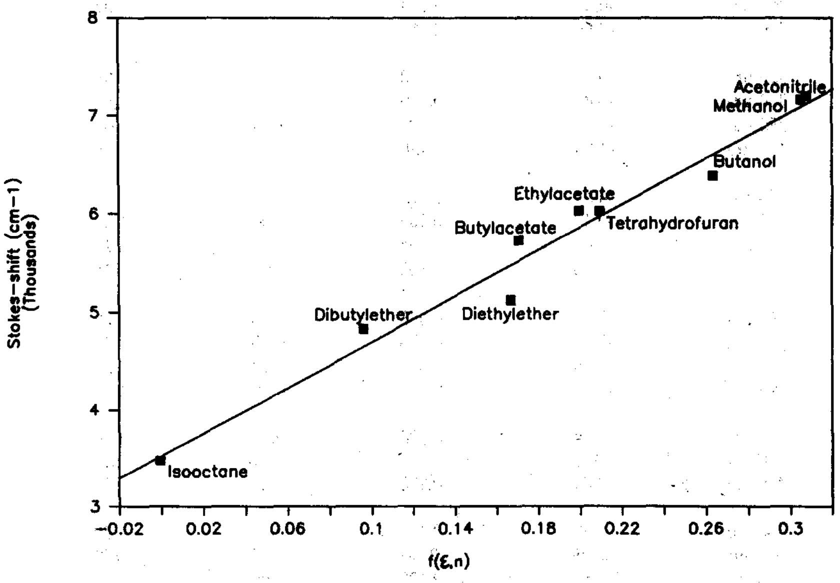

Figure 3: Spectral shift as a function of the solvent polarity according to equation 2

Table II: Values of $\Delta\mu$ and μ_e derived from equation 2.

	ρ/nm	$\Delta\mu$	μ_g	μ_e
4COB	0.5	12.4 D	4.5 D*	16.9 D
	0.6	16.5 D	4.5 D	21.0 D
	0.7	20.6 D	4.5 D	25.1 D

*Ref. 16.

Time-resolved fluorescence

The results of the time resolved measurements were analyzed by means of a global analysis program. In table III and IV the decay parameters and the statistical parameters are listed. The statistical parameters of the globally analyzed monoexponential decays are not within the confidence limits (i.e. global $Z(\chi^2) > 3$), while the statistical parameters of the globally analyzed two-exponential decays are within the confidence limits. David et al.[15] found that COB compounds in solution exhibit a monoexponential decay within the detection limit of their experimental setup. Analysis were also done on single curves, and the recovered parameters did not significantly change with emission wavelength, which justifies the use of global analysis as a more stringent method of analysis[25] especially useful for the short lifetime components encountered here.

Table III: Decay parameters [a] of the global analysis for 4COB in different solvents at room temperature.

Solvent	λ_{EM}	α_1	τ_1	α_2	τ_2	χ^2
Hexane	320 nm	-0.45	0.119	1.05	1.07	1.09
	340 nm	-0.55	0.119	1.06	1.07	1.14
	360 nm	-0.52	0.119	1.06	1.07	1.09
	380 nm	-0.66	0.119	1.10	1.07	1.16
Dibutylether	325 nm	-0.59	0.120	1.07	1.08	1.06
	350 nm	-0.47	0.120	1.08	1.08	1.15
	380 nm	-0.68	0.120	1.13	1.08	1.10
	400 nm	-1.13	0.120	1.13	1.08	1.13
Diethylether	330 nm	-0.54	0.105	1.04	1.16	1.13
	350 nm	-0.47	0.105	1.00	1.16	1.13
	370 nm	-0.46	0.105	1.01	1.16	1.12
	390 nm	-0.40	0.105	1.00	1.16	1.13
Butylacetate	330 nm	-0.44	0.083	0.96	1.26	1.14
	350 nm	-0.77	0.083	0.99	1.26	1.19
	370 nm	-0.64	0.083	0.99	1.26	1.13
	390 nm	-0.56	0.083	0.99	1.26	1.13
Tetrahydrofuran	350 nm	-0.54	0.120	0.98	1.26	1.08
$\tau_1 = 0.8$ps [b]	380 nm	-0.53	0.120	1.00	1.26	1.00
	420 nm	-0.86	0.120	1.03	1.26	1.11
Ethylacetate	330 nm	-0.61	0.109	1.01	1.30	1.14
$\tau_1 = 1.6$ps	350 nm	-0.49	0.109	0.98	1.30	1.18
	370 nm	-0.51	0.109	0.99	1.30	1.01
	390 nm	-0.50	0.109	0.98	1.30	1.04
1-Butanol	340 nm	+0.01	0.208	0.94	1.36	1.26
$\tau_1 = 132.9$ps	360 nm	-0.40	0.208	1.01	1.36	1.08
	380 nm	-0.62	0.208	1.06	1.36	1.02
	400 nm	-0.69	0.208	1.07	1.36	1.07
Acetonitrile	340 nm	-0.47	0.095	0.91	1.54	1.03
$\tau_1 = 0.2$ps	360 nm	-0.48	0.095	0.91	1.54	1.10
	380 nm	-0.52	0.095	0.92	1.54	1.09
	400 nm	-0.62	0.095	0.93	1.54	1.16

a) The decays were measured at 256 channels and at 512 channels. The rise times or short components τ_1 are accurate to about ± 20 ps.

b) τ_1 = longitudinal solvent relaxation time.

Table IV: Statistical parameters (χ^2_{glob} and $Z(\chi^2)_{glob}$) for the globally analysed monoexponential- and two-exponential decays.

	monoexponential		two-exponential	
	χ^2_{glob}	$Z(\chi^2)_{glob}$	χ^2_{glob}	$Z(\chi^2)_{glob}$
Hexane	5.729	102.079	1.118	2.546
Diethylether	4.206	69.470	1.120	2.590
Ethylacetate	5.972	107.737	1.089	1.927
1-Butanol	12.390	251.494	1.098	2.154
Acetonitrile	6.070	109.860	1.090	1.947

Table Va: Decay parameters of 4COB in n-butanol at room temperature for the global two-exponential analysis. $Glob_{Z(\chi 2)}$ = 10.762

λ_{EM}	α_1	β_1	α_2	β_2	Time Incr.	χ^2
340 nm	0.18	0.193	0.90	1.38	0.012	1.95
340 nm	0.26	0.193	0.90	1.38	0.018	1.82
340 nm	0.21	0.193	0.88	1.38	0.037	1.95
360 nm	-0.46	0.193	1.01	1.38	0.012	0.96
360 nm	-0.52	0.193	1.07	1.38	0.018	1.08
360 nm	-0.50	0.193	1.01	1.38	0.037	1.19
380 nm	-0.68	0.193	1.04	1.38	0.012	1.12
380 nm	-0.57	0.193	0.92	1.38	0.018	1.06
380 nm	-0.54	0.193	1.01	1.38	0.037	1.05
400 nm	-0.70	0.193	0.95	1.38	0.012	1.12
400 nm	-0.78	0.193	1.08	1.38	0.018	1.18
400 nm	-0.84	0.193	1.07	1.38	0.037	0.99

Table Vb: Decay parameters of 4COB in n-butanol at room temperature for the global two-exponential and three-exponential analysis. $Glob_{Z(\chi 2)}$ = 2.002

λ_{EM}	α_1	β_1	α_2	β_2	α_3	β_3	Time Incr.	χ^2
340 nm	-0.43	0.201	0.92	1.38	0.85	0.116	0.012	1.03
340 nm	-0.37	0.201	0.92	1.38	0.89	0.116	0.018	1.04
340 nm	-0.47	0.201	0.89	1.38	1.00	0.116	0.037	1.02
360 nm	-0.46	0.201	1.01	1.38			0.012	0.96
360 nm	-0.52	0.201	1.07	1.38			0.018	1.08
360 nm	-0.50	0.201	1.01	1.38			0.037	1.19
380 nm	-0.67	0.201	1.05	1.38			0.012	1.12
380 nm	-0.56	0.201	0.93	1.38			0.018	1.06
380 nm	-0.54	0.201	1.01	1.38			0.037	1.05
400 nm	-0.69	0.201	0.95	1.38			0.012	1.12
400 nm	-0.77	0.201	1.08	1.38			0.018	1.18
400 nm	-0.84	0.201	1.07	1.38			0.037	0.99

The time resolved decay measurements exhibit bi-exponential decays over the whole emission range, with a fast rise time and a decay time going from 1.07 ns in hexane to 1.54 ns in acetonitrile (Table III). In most cases, the relative weight of the risetime component is less than 50%, but in some cases, especially at the longest detection wavelengths they approach 50% indicative of a classical precursor - successor relationship. The fact that the ratio of the preexponential factor does not equal -1 at short wavelengths indicates that the process is more complex than indicated by the biexponential model used in our analysis but cannot be resolved within the experimental error. This is consistent with a model involving continuous red shift of the fluorescence due to solvent relaxation.

In table Va and Vb the time resolved fluorescence properties of 4COB in 1-butanol at room temperature were more intensively investigated because they showed a peculiar behaviour at hypsochromic wavelengths. A set of 12 fluorescence decays, analyzed at different wavelengths (340nm, 360nm, 380nm and 400nm) and at different time increments (12ps, 18ps and 37ps), was globally analyzed as two-exponentials (Table Va). It is clear from the χ^2 values that the decays measured at 340 nm are responsible for the high value of the glob$_{Z(\chi 2)}$. Analyzing the decays measured at 340nm as three-exponentials optimalizes the glob$_{Z(\chi 2)}$ to 2.002 which is within the confidence limit (Table Vb). From the global analysis three global decay parameters are obtained: a short rise time of 200ps and a decay time of 1.38ns over the whole emission range, and a small third decay time (with a positive contribution) of 116ps observed at hypsochromic wavelengths (<360nm). This more complex behaviour is probably a consequence of the slow solvent relaxation time of butanol. The relaxation time of the solvent becomes longer and within the resolution of the experimental setup. The larger bathochromic shift of the emission of the relaxed form observed in polar hydrogen bond forming solvents leads to a better resolution of the spectrum of the initial and the relaxed forms. As a consequence a positive preexponential factor is observed at short wavelengths for the fast decaying component (116 ps).

3.2. Influence of the solvation dynamics on the ICT stabilization.

In order to investigate the role of the solvent dynamics in the stabilization of the ICT state of 4COB, the formation of the ICT state of 4COB in a temperature region of 77K to 293K was examined in 1-butanol and in diethylether, both by steady state and time resolved measurements. These two solvents are chosen because their polarity strongly increases with decreasing temperature (from 293K to 190K), and they possess different relaxation characteristics : 1-butanol is a solvent with a slow relaxation time, while diethylether has a much faster relaxation time.

Steady state fluorescence

In figure 4, the fluorescence spectra of 4COB in 1-butanol in the temperature region of 292K to 77K are shown. The polarity of 1-butanol increases from 293K to 185K (Table VI), and this would normally result in a bathochromic shift of the ICT fluorescence upon cooling. However, a hypsochromic shift is observed upon cooling.

Since the polarity of diethylether also increases from 4.31 at 292K to 7.17 at 182K (Table VI), a bathochromic shift is also expected for the low temperature study. Experimentally a bathochromic shift is found for diethylether (Figure 5).

Formation of ICT states is usually accompanied with an increase of the magnitude of the dipole moment of the molecule. For 4COB, as indicated above, the dipole moment of the excited state is estimated to be around 20 D. Two limiting effects can be envisioned for the stabilization of the ICT state. If internal rotation and charge separation occurs rapidly compared to solvent relaxation, the solvent will not be in equilibrium with the excited molecule. As a result, relaxation and restructuring of the surrounding solvent will be manifested by a continuous Stokes shift of the emission spectrum. In this case, the rate of ICT formation is governed by the relaxation times associated with solvent motion. Time-dependent Stokes shifts have been observed in several molecules[26-30]. For 1-butanol at low temperature (see below table VII) the solvent relaxation is slow compared to the rotation and charge separation, and emission of photons will take place before the system is fully relaxed resulting in a hypsochromic shift upon cooling.

Table VI: Emission maximum (λ_{max}) for 4COB in 1-butanol and diethylether at different temperatures, and solvent dielectric constant.

	1-butanol			diethylether	
Temp.(K)	λ_{max}	ε	Temp.(K)	λ_{max}	ε
292	369 nm	19.0	292	350 nm	4.31
273	367 nm	20.6	273	352 nm	4.69
242	365 nm	24.0	260	353 nm	4.99
223	360 nm	26.5	224	355 nm	5.98
206	357 nm	29.1	203	357 nm	6.71
185	352 nm	33.1	182	359 nm	7.17
77	331 nm		77	333 nm	
	341 nm			344 nm	

On the other hand, if rotation and charge separation are slow compared to the solvent relaxation, equilibrium solvation will always be maintained during the rotation process. This will result in a rate of ICT formation which is slower than the relaxation times associated with the solvent motion. For diethylether, the solvent relaxation is of the same order or faster than the rotation and the charge separation kinetics, and the system is always in solvent conformational equilibrium, even at low temperatures (185K). However, at 77K the solvent relaxation becomes very slow and the system will not be relaxed before emission of photons takes place, and a hypsochromic shift is observed for both solvents (Figure 4 and 5).

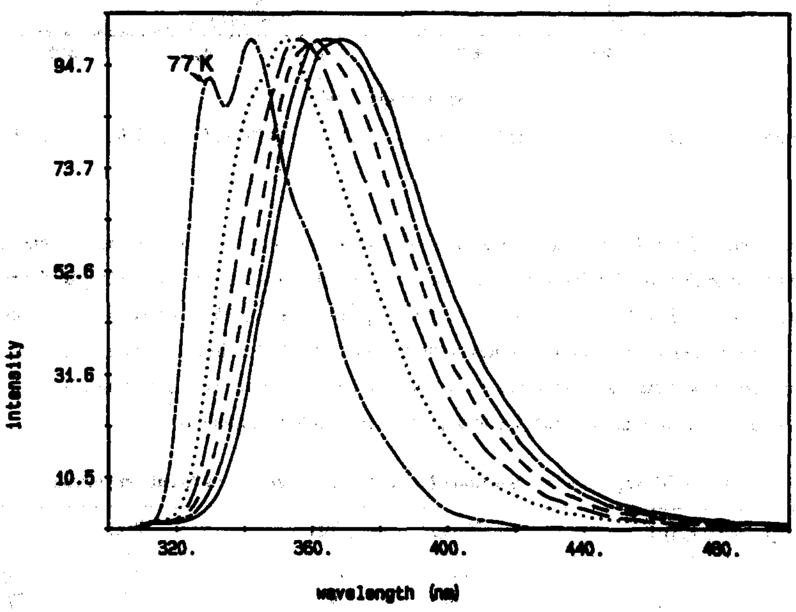

Figure 4: Fluorescence spectra of 4COB in 1-butanol at (——) 292K,(–.–) 273K, (-----) 242K, (– –) 223K and (.....) 206K.

Time-resolved fluorescence

At room temperature, the decays were globally analyzed as two-exponentials, with a very short rise time and a decay time of 1.07 ns in hexane to 1.54 ns in acetonitrile (Table III). For solvents with very short relaxation times, the observed rise time is about 100ps which is probably a consequence of the limited time-resolution of the experimental setup (about 100ps). Solvents with a slower relaxation time however, like 1-butanol and the higher alcohols, show a rise time of about 200 ps and longer.

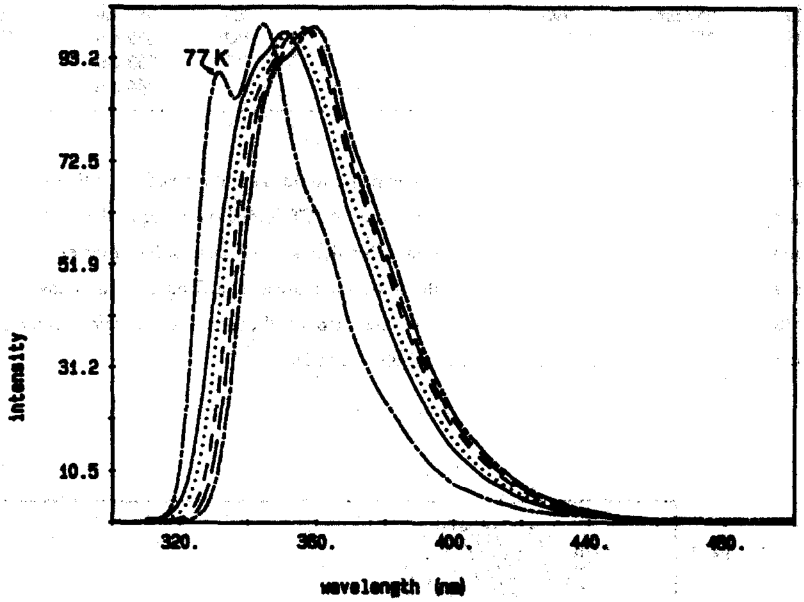

Figure 5: Fluorescence spectra of 4COB in diethylether at (——) 293K,(.....) 273K, (——) 260K, (-- --) 224K and (--.--) 203K.

In figure 6 the rise times of the ICT formation in a series of alcohols are plotted versus the longitudinal relaxation time of the solvent, and it can be seen that the rise times are longer than the solvent relaxation time. In table VII, the rise times of the time-resolved experiments of 4COB in 1-butanol in a temperature region of 183K to 353K are shown. The observed rise times are somewhat longer than the longitudinal relaxation times of the solvent especially for the short chain alcohols but within experimental error. A good correlation between the longitudinal relaxation time and the rise time of the solvent, however, can be observed for experiments with a better time resolution (streak camera) performed on other compounds[31-33].

Table VII: Experimental rise times for 4COB in 1-butanol at different temperatures.

Temp.	τ_r (ps)	Temp.	τ_r (ps)	Temp.	τ_r (ps)
353K	90	293K	217	233K	365
343K	100	283K	229	223K	373
333K	121	273K	270	213K	407
323K	144	263K	312	203K	466
313K	157	253K	333	193K	486
300K	180	243K	354	183K	502

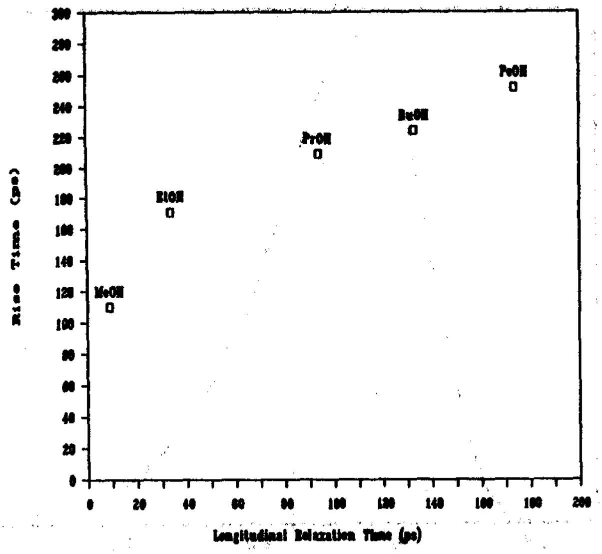

Figure 6: Experimental rise time versus the longitudinal relaxation time of the solvent in a series of alcohols at room temperature.

3.3. Importance of hydrogen bonded clusters in the ICT stabilization

In order to study the role of hydrogen bonded clusters in the stabilization of the intramolecular charge transfer of 4COB, the emission dynamics in polar solvent mixtures of 1-butanol/butyronitrile were examined. This solvent system was chosen because the components possess almost the same solvent polarity parameter ($(f(\varepsilon,n)_{1\text{-butanol}} = 0.263$ and $f(\varepsilon,n)_{\text{butyronitrile}} = 0.274)$) and ICT formation occurs in both solvents. If the internal rotation and charge separation is faster than the solvent relaxation, the emission dynamics as a function of the alcohol concentration will reflect the importance of the alcohol structure in the stabilization of the ICT state.

Steady state fluorescence

In figure 7, the fluorescence spectra for 4COB in 1-butanol and butyronitrile are shown. Their emission spectra at room temperature are nearly identical, as expected from the similarity of the solvent polarity parameters. The fluorescence spectra for 1-butanol/butyronitrile mixtures are also similar to those observed for the neat solvents.

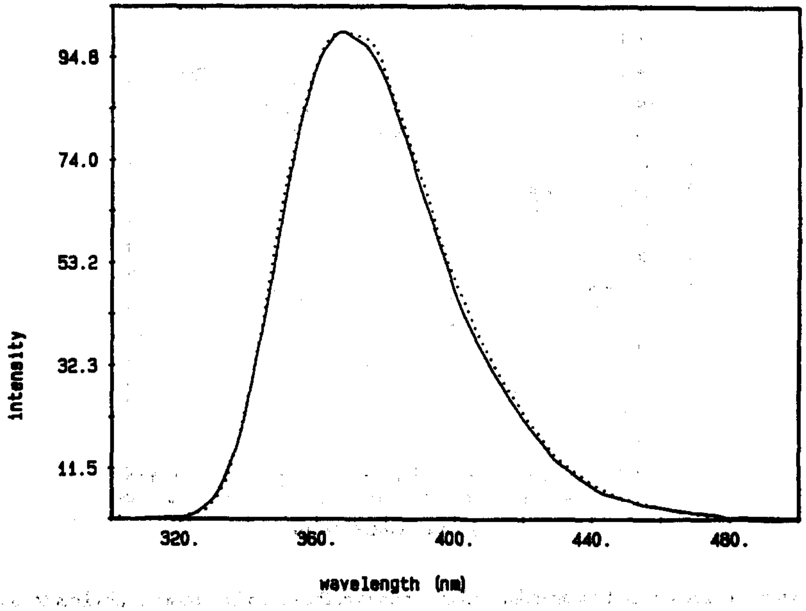

Figure 7: Fluorescence spectrum of 4COB in (——) butyronitrile and (.....) 1-butanol.(R.T.)

Time resolved fluorescence

The time resolved emission data for 4COB in 1-butanol, butyronitrile and the 1-butanol/butyronitrile mixtures are shown in table VIII. In butyronitrile and in 1-butanol/butyronitrile mixtures with a ratio less than 1, the emission rise times are ≤ 110 ps and depend only weakly on solvent composition. For larger alcohol contents, the rise times lengthen considerably.

Table VIII: Statistical parameters and decay parameters for the two-exponential decay for 4COB in 1-butanol/butyronitrile mixtures analyzed globally for each solvent composition. The χ^2 and $Z(\chi^2)$ are also given.

1-butanol/butyronitrile	τ_r (ps)	τ_d (ns)	χ^2_{glob}	$Z(\chi^2)_{glob}$
1-butanol	217	1.371	1.066	1.478
10/1	194	1.393	1.015	0.366
5/1	180	1.397	1.105	2.640
2/1	128	1.415	1.113	2.848
1/1	114	1.422	1.116	2.919
1/2	101	1.425	1.086	2.151
1/5	100	1.414	1.131	3.133
1/10	81	1.417	1.117	2.948
butyronitrile	89	1.408	1.133	2.877

For a better understanding of the origin of the rise times observed in 1-butanol and 1-butanol/butyronitrile mixtures, infrared spectra were recorded of the 4COB solutions. The O-H stretch region is shown in figure 8. At low alcohol concentrations a single peak is observed, this peak is characteristic for monomer alcohol in solution. No remarkable changes in the band shape or its position are observed until the 1-butanol/butyronitrile ratio is 1/2. Increasing the alcohol concentration broadens the absorption band and the maximum shifts to lower energy. The spectral broadening corresponds to the formation of hydrogen bonded aggregates. These hydrogen bonded clusters decrease the mobility of the alcohol molecules and slow down the relaxation. These results show that there is a good correlation between the emission rise times observed in the ICT-formation of 4COB in 1-butanol/butyronitrile mixtures and their respective relaxation times.

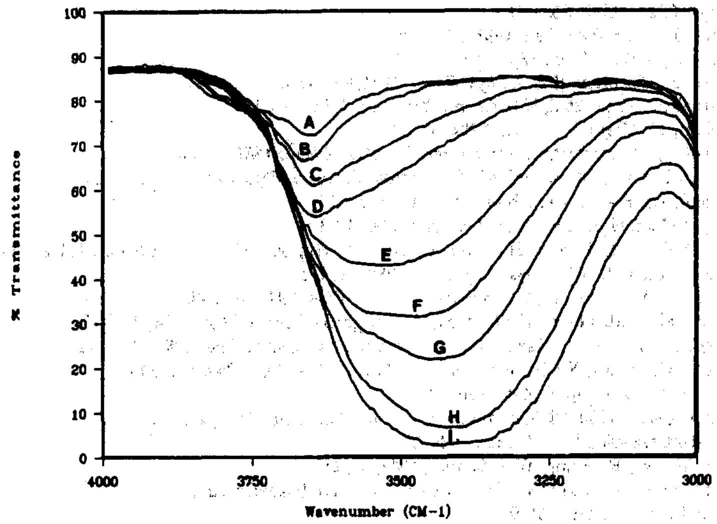

Figure 8: Infrared spectra of the O-H stretching region 1-butanol/butyronitrile solutions of 4COB : 1:40 (A), 1:20 (B), 1:10 (C), 1:5 (D), 1:2 (E), 1:1 (F), 2:1 (G), 5:1 (H) and 10:1 (I). With increasing alcohol concentration the band gradually broadens and shifts to lower energy, characteristic for the formation of hydrogen bonded aggregates.

4. Conclusion.

The photophysical properties of 4COB have been examined in a range of solvents. A solvatochromic shift was observed. Together with a large rise time component observed over the whole emission range, this is an indication that the emission originates from an ICT state. Even in nonpolar solvents (alkanes), rise times were observed indicating the fast rotational relaxation toward the planar ICT state. The ICT formation studied in 1-butanol and in diethylether shows that there the stabilization of the ICT state is governed by solvent dynamics. Furthermore, the importance of hydrogen bonded clusters in the stabilization of the ICT state is demonstrated. The rise times observed in 1-butanol/butyronitrile mixtures reflect the influence of the alcohol structure.

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REFERENCES

[1] a) Rettig, W.; Wermuth, G.; Lippert, E. *Ber. Bunsen-Ges. Phys. Chem.* 1979, 83, 692
b) Rettig, W.; Bonacic-Koutecky, V. *Chem. Phys. Lett.* 1979, 62, 115

[2] a) Rotkiewicz, K; Grellman, H; Grabowski, Z.R., *Chem. Phys. Lett.*, 1973, 19, 315
b) Rotkiewicz, K; Grabowski, Z.R.; Krowczynski, A.; Kuhnle, W., *J. Lumin.*, 1976, 12/13, 877

[3] Rettig, W.; Lippert, E. *J. Mol. Struct.* 1980, 61, 17

[4] Rettig, W. *J. Phys. Chem.* 1982, 86, 1970

[5] Heisel, F.; Miehe, J. *Chem. Phys. Lett.* 1983, 100, 183

[6] Wang, Y.; Eisenthal, K.B. *J. Chem. Phys.* 1982, 77, 6076

[7] Wang, Y.; Novak, F.; Eisenthal, K.B. *J. Phys. Chem.* 1981, 85, 3736

[8] Hicks, J.; Babarogic, Z.; Eisenthal, K.B. *Chem. Phys. Lett.* 1985, 116, 18

[9] Rettig, W.; Zander, M. *Chem. Phys. Lett.* 1982, 87, 229

[10] Wermuth, G.; Rettig, W.; Lippert, E. *Ber. Bunsen-Ges. Phys. Chem.* 1981, 85, 64

[11] Siemiarczuk, A.; Asher, M.; Ottolenghi, M.; Grabowski, Z. *Chem. Phys. Lett.* 1977, 51, 315

[12] Rettig, W.;. Chandross, E.A. *J. Am. Chem. Soc.* 1985, 107,5617

[13] Kosower, E.M.; Dodiuk, H. *J. Am. Chem. Soc.* 1978, 100, 4173

[14] Kosower, E.M.; Dodiuk, H.; Kanety, H.; Jovin, T.; Boni, H.; Huppert, D. *J. Phys. Chem.* 1983, 87, 2479

[15] David, C.; Bayens-Volant, D. *Mol. Cryst. Liq. Cryst.* 1980, 59, 181

[16] Tamai, N.; Yamazaki, I.; Masuhara, H.; Mataga, N. *Chem. Phys.* 1984, 106, 485.

[17] Tamai, N.; Yamazaki, I.; Masuhara, H.; Mataga, N. *Springer Ser. Chem. Phys.* 1984, 38, 355.

[18] a) Van den Zegel, M.; Boens, N.; Daems, D.; De Schryver, F.C. *Chem. Phys.* 1986, 101, 311.
b) Van den Zegel, M.; Boens, N.; De Schryver, F.C., *Chem. Phys. Lett.* 1984, 111, 340.

[19] Marquardt, D. *J. Soc. Indust. Appl. Math.* 1963, 2, 431

[20] Rettig, W., *Angew. Chem.* 1986, 98, 958; *Angew. Chem. Int. Edit. Engl.* 1986, 25, 971

[21] Rotkiewicz, K.; Rubaszewska, W. *J. Lumin.* 1984, 29

[22] Swiatkowsky, G; Menzel, R.; Rapp, W, *J. Lumin.*, 1987, 37, 183

[23] Klock, A; Van Damme, M; Rettig, W.; De Schryver, F.C., unpublished results

[24] Lippert, E. *Z. Elektrochem.*, 1957, 61, 962

[25] a) Knutson, J.R.; Beechem, J.M.; Brand, L., *Chem. Phys. Lett.*, 1983, 223, 155
b) Boens, N., Janssens, L., De Schryver, F.C., *Biophys. Chem.*, 1989, 33, 77

[26] Ware, W.R.; Lee, S.K.; Brant, G.J.and P. P. Chow, *J. Chem. Phys.* 1971, 54, 4729

[27] Lessing, H.E.; Reichert, M. *Chem. Phys. Lett.* 1977, 46, 111

[28] Safarzadeh-Amiri, A. *Chem. Phys. Lett.* 1986, 125, 272

[29] Halliday, L.; Topp, M.R. *Chem. Phys. Lett.* 1977, 48, 40

[30] Okumura, T.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* 1983, 94, 339

[31] Shyh-Gang Su; Simon, J.D. *J. Phys. Chem.* 1986, 90, 6475

[32] Shyh-Gang Su; Simon, *J.D. J. Phys. Chem.* 1987, 91, 2693

[33] Declemy, A.; Rulliere, C.; Kottis, Ph. *Chem. Phys. Lett.* 1987, 133, 448