On the TICT Mechanism of 9,9′-Biaryl Compounds

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The UV/Vis absorption and fluorescence spectra for 9,9′-biacridinyl (BAC) and 9-(9′-acridyl)carbazole (C9AC) were recorded in approximately 50 different solvents. The analysis of the solvatochromic behaviour of the two chromophores, in terms of both polarity and polarizability (SPP), revealed that TICT emission in C9AC prevails only in solvents with SPP ≥ 0.63, while that in BAC predominates throughout the solvent range studied [from 2-methylbutane (SPP = 0.479) to DMSO (SPP = 1.0)]. The peculiar behaviour of BAC suggests that the chromophore requires no cooperation from the solvent to trigger its TICT mechanism. Various hypotheses usually employed in analysing the TICT mechanism of biaryl compounds, including model emissions used to deconvolute spectra, the variation of TICT emission with the difference in redox potential between the chromophores involved, etc., are discussed.

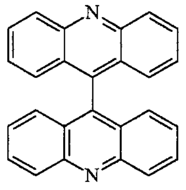
Aromatic compounds that possess two identical fluorophores and exhibit dual fluorescence are especially interesting[1][2][3][4][5] because the additional fluorescence is produced by a molecular structure resulting from an electron transfer between the two fluorophores, a process that takes place in some highly significant and naturally occurring mechanisms such as vision and photosynthesis[6]. Whether or not the two fluorophores are identical, this type of process is of potential interest with a view to producing laser light[7] and storing solar energy[8].

This novel type of structure with strongly separated charges is usually assigned to a twisted intramolecular charge transfer (TICT) mechanism; its feasibility is increased by appropriate redox potentials in the chromophores, and by increased polarity of the medium, which helps stabilize the polar structures. The fluorescence is produced by different electron states (one of which is much more polar than the other) that will exhibit a differential solvatochromic behaviour. The earliest analysis of the solvatochromism of a compound of this type, viz. 9,9′-bianthryl (BA), was reported in 1968 in the pioneering paper by Schneider and Lippert[9]. These authors demonstrated a bilinear variation of the solvatochromism of this compound with the solvent polarity, $f(\varepsilon,n)$, in 22 solvents. Recently, we reinvestigated the behaviour of this compound in a total of 60 solvents and found its solvatochromism to vary bilinearly with our solvent polarity/polarizability parameter, SPP[10]; however, against what was previously postulated by Schneider and Lippert[9], the emission maximum of this compound does not become solvent independent in low polarity solvents. A similar study of *N*,*N*′-bicarbazyl (BC) led us to conclude that this compound produces no dual fluorescence; this seemingly anomalous behaviour can be ascribed to the fact that the carbazole function possesses an inappropriate redox potential, so that it exhibits a linear solvatochromism throughout the polarity range spanned by the solvents studied[10]. The characterization of solvent polarity using the SPP scale is more desirable than other empirical polarity scales on the following basis: 1) the SPP scale describes more purely than any other scale the polarity contribution of a solvent[10], and 2) the SPP scale allows us to adequately isolate, with the aid of the SA and SB scales, the solvatochromic shifts due to non-specific solvent effects. These solvatochromic shifts, as demonstrated in our outcoming paper[12], parallel the dipole moment changes undergone in an electronic transition.

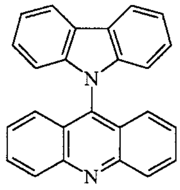
In this work, we examined the solvatochromic behaviour of 9,9′-biacridinyl (BAC), the chromophore of which (acridine) theoretically possesses more favourable redox potentials for an electron transfer. We also studied 9-(9′-acridyl)-carbazole (C9AC), which includes a carbazole and an acridine chromophore and should thus be even more prone to an electron transfer. In the light of the results for these compounds (relevant photophysical data for which are seemingly unavailable) and of others previously obtained for BA, C9A, and BC, we discuss the validity of the hypotheses traditionally employed to explain the photophysical behaviour of biaryl compounds.

Results and Discussion

As can be seen from Figure 1, the envelope of the absorption spectrum for BAC in the region from 300 to 410 nm changes very little with solvent. Especially prominent in this region is a peak at 385 nm in 2-methylbutane that is slightly shifted with increasing polarizability (to 387.3 nm in *cis*-decalin, for example); the peak is also scarcely sensitive to the solvent polarity (it appears at 391 nm in as polar a solvent as DMSO). This first absorption peak can in prin-



BAC



C9AC

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ciple be ascribed to the 0−0 spectral component, and will be used to quantify the Stokes shift for the compound in the different solvents studied. Table 1 gives the wavelengths for the first absorption and fluorescence emission maximum for BAC in the different solvents. In contrast to its absorption spectra, the emission spectra for BAC exhibit a strong bathochromic shift as the solvent polarity is raised; as can be seen from Table 2, the corresponding Stokes shifts range from 1667 cm^{-1} in 2-methylbutane to 3743 cm^{-1} in DMSO. Also, the emission spectra are structureless (includ-

Figure 1. Normalized absorption spectra for BAC in (a) 2-methylbutane, (b) toluene, (c) ethanol, and (d) DMSO

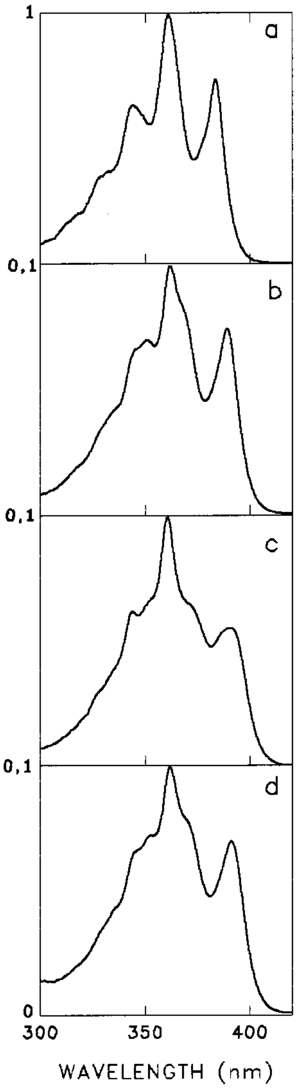


Table 1. Wavelength for the absorption and fluorescence emission maximum for BAC and C9AC in the solvents studied

solvent	BAC λ_{abs}^{0-0} [nm]	 λ_{em}^{max} [nm]	C9AC $\lambda_{abs}^{3rd\ peak}$ [nm]	 λ_{abs}^{0-0} [nm]	 λ_{em}^{max} [nm]
2-methylbutane	383.5	409.7	360.2	406.3	421.1
n-pentane	383.6	411.6	360.5	406.2	421.9
n-hexane	384.5	415.8	360.5	407.7	424.2
n-heptane	384.7	413.1	360.6	407.4	424.8
cyclohexane	385.9	409.7	361.2	409.5	426.8
methylcyclohexane	385.6	412.6	361.0	409.6	424.8
n-hexadecane	386.0	416.6	361.1	409.5	426.5
cis-decalin	387.3	417.6	361.6	411.3	429.0
p-xylene	388.7	421.0	362.0		470.2
tri-*n*-butylamine			360.8		459.2
tetrachloromethane	388.2	424.1	361.7		443.9
o-xylene	389.1	422.1	361.9		471.1
ethylbenzene[a]	389.3	419.9	361.9		472.3
di-*n*-butyl ether	386.2	418.6	361.0		464.2
toluene	388.9	421.7	361.6		471.9
benzene	389.9	433.9	362.1		478.1
tetralin			362.5		469.9
diethyl ether	385.7	425.4	359.8		473.1
1,4-dioxane	388.3	421.5	361.0		481.2
2-methyltetrahydrofuran			360.8		489.4
isoamyl acetate			360.8		485.4
fluorobenzene	388.7	424.9	361.7		493.5
chloroform	390.8	426.4	361.9		506.6
ethyl acetate	386.7	434.8	360.6		511.8
1-hexanol	392.0	431.4	361.2		512.4
1-pentanol	391.9	432.8	360.9		522.1
tert-butyl alcohol	389.6	426.1	360.6		511.0
butanol	391.8	432.4	361.1		526.9
1-propanol	391.5	432.0	360.6		532.4
2-propanol	391.2	430.6	360.5		523.0
ethanol	390.2	441.2	360.8		542.1
methanol	391.2	442.3	360.3		557.7
n-propyl formate	386.9	425.4	360.6		509.6
chlorobenzene	390.0	425.9	362.4		498.8
ethyl benzoate	389.5	436.3	361.6		501.8
methyl benzoate	390.0	429.2	362.0		508.8
1-chlorobutane	386.9	425.0	360.6		482.8
tetrahydrofuran			361.3		499.7
acetonitrile	386.4	439.7	360.8		532.2
propionitrile	386.8	433.2	360.4		524.5
butyronitrile	387.1	422.2	360.6		512.8
benzonitrile	390.6	435.6	362.2		513.5
dichloromethane	389.7	434.4	361.3		515.8
1,2-dichlorobenzene	390.6	429.8	362.9		507.0
propylene carbonate	388.5	442.0	360.7		535.6
N,N-diethylacetamide	388.8	433.4	361.4		511.2
N,N-diethylformamide	389.0	433.8	361.5		519.4
N-methylimidazole	391.7	451.2	362.4		538.7
tetramethylurea			362.0		515.7
N,N-dimethylformamide	389.1	440.1	361.7		529.8
N,N-dimethylacetamide	389.2	434.7	361.8		522.1
γ-butyrolactone	389.3	442.9	361.5		529.5
sulfolane	390.6	444.7	361.9		531.3
dimethyl sulfoxide	391.0	458.0	361.8		545.0

[a] In a previous paper[10], we showed that, surprisingly, the spectrum of BA in this solvent is structured, whereas those in benzene and toluene are not. In this work, we found that the spectra in propylbenzene and butylbenzene are also structureless. The structured envelope obtained in ethylbenzene was due to an impurity in the 99% pure anhydrous ethylbenzene supplied by Aldrich. The purified solvent produced structureless BA fluorescence.

ing those in the scarcely polar solvents, as can be seen from Figure 2). These photophysical features suggest that BAC requires no assistance from the solvent to reach its TICT state, which is thus responsible for the emission of this compound throughout the solvent range studied[13]. This behaviour can be explained in principle on the basis of the redox potentials of acridine (Table 3); in fact, the redox potential difference, $E_D^{ox} - E_A^{red}$ = 2.62 V, is much smaller than that for BA (3.37 V), so the formation of its TICT state must be extremely favourable.

Table 2. Stokes shifts for BAC and C9AC in the solvents studied and SPP values for the solvents

solvent	SPP	Stokes shift BAC	Stokes shift C9AC[a]
2-methylbutane	0.479	1667	4017 (867)
n-pentane	0.507	1776	4036 (915)
n-hexane	0.519	1956	4163 (952)
n-heptane	0.526	1785	4190 (1002)
cyclohexane	0.557	1506	4254 (989)
methylcyclohexane	0.563	1696	4161 (873)
n-hexadecane	0.578	1901	4249 (978)
cis-decalin	0.601	1871	4345 (1004)
p-xylene	0.617	1975	6355
tri-*n*-butylamine	0.624		5938
tetrachloromethane	0.632	2182	5122
o-xylene	0.641	2011	6405
ethylbenzene	0.650	1871	6459
di-*n*-butyl ether	0.652	2007	6157
toluene	0.655	2002	6466
benzene	0.667	2600	6702
tetralin	0.668		6305
diethyl ether	0.694	2419	6656
1,4-dioxane	0.701	2027	6920
2-methyltetrahydrofuran	0.717		7282
isoamyl acetate	0.752		7113
fluorobenzene	0.769	2193	7323
chloroform	0.786	2134	7894
ethyl acetate	0.795	2861	8192
1-hexanol	0.810	2331	8169
1-pentanol	0.817	2412	8554
tert-butyl alcohol	0.829	2200	8163
1-butanol	0.837	2397	8713
1-propanol	0.847	2394	8948
2-propanol	0.848	2340	8620
ethanol	0.853	2962	9270
methanol	0.857	2955	9824
n-propyl formate	0.815	2340	8109
chlorobenzene	0.824	2164	7547
ethyl benzoate	0.835	2752	7729
methyl benzoate	0.836	2345	7971
1-chlorobutane	0.837	2317	7021
tetrahydrofuran	0.838		7666
acetonitrile	0.895	3140	8928
propionitrile	0.875	2769	8682
butyronitrile	0.915	2148	8230
benzonitrile	0.960	2645	8135
dichloromethane	0.876	2641	8290
1,2-dichlorobenzene	0.911	2336	7833
propylene carbonate	0.930	3118	9054
N,N-diethylacetamide	0.930	2650	8108
N,N-diethylformamide	0.939	2653	8410
N-methylimidazole	0.950	3368	9030
tetramethylurea	0.952		8232
N,N-dimethylformamide	0.954	2978	8774
N,N-dimethylacetamide	0.970	2689	8486
γ-butyrolactone	0.987	3109	8776
sulfolane	1.003	3117	8809
dimethyl sulfoxide	1.000	3743	9291

[a] Data in brackets are evaluated from the 0−0 absorption band.

Figure 2. Normalized emission spectra for BAC in 2-methylbutane (—), toluene (- - -), ethanol (···) and DMSO (−··−)

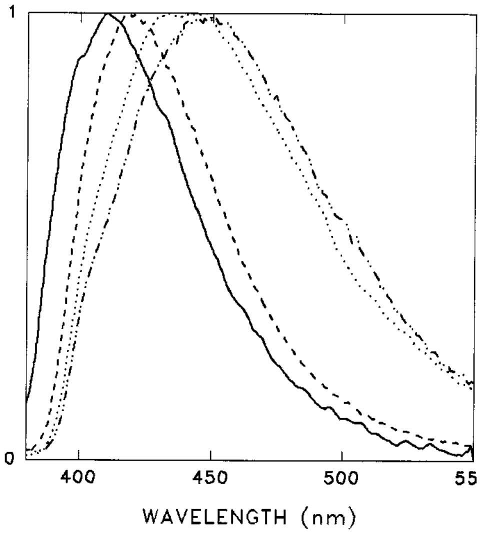


Table 3. Redox potentials and TICT transition energy of biaryls derivatives (all data in V)

biaryl[a]	E_D^{ox} ACN	E_A^{red} ACN	E_A^{red} DMF	$E_D^{ox} - E_A^{red}$	$h\nu_{TICT}$ ACN
BC	1.16[e]		−2.68[f]	3.84	([j])
DCBA	1.74[g]	−1.70[g]		3.44	2.39[k]
BA	1.45[g]	−1.96[g]	−1.92	3.37	2.64[j]
BAC	1.58[h]		−1.04[i]	2.62	2.82[l]
CBA[b]	1.45[g]	−1.70[g]		3.15	2.14[k]
C9AC[c]	1.16[e]		−1.04[i]	2.20	2.33[l]
C9A[d]	1.16[e]		−1.92[f]	3.08	2.63[j]

[a] BC: 9,9′-bicarbazyl; DCBA: 10,10′-dicyano-9,9′-bianthryl; BA: 9,9′-bianthryl; BAC: 9,9′-biacridinyl; CBA: 10-cyano-9,9′-bianthryl; C9AC: 9-(9-acridyl)carbazole; C9A: *N*-(9-anthryl)carbazole. − [b] The donor is the anthryl moiety. − [c] and [d] The donor is the carbazol moiety. − [e] Ref.[14]. − [f] Ref.[15]. − [g] Ref.[16]. − [h] Ref.[17]. − [i] Ref.[18]. − [j] Ref.[10]. − [k] Ref.[19]. − [e] This work.

The linear variation of the solvatochromism of this compound with SPP throughout the solvent polarity range studied (Figure 3) supports the previous conclusion. Also, the relationship between these two variables allows one to conclude that the Stokes shift for BAC in the gas phase must be very small, since the intercept of the fitted curve was only 285 cm^{-1}.

The insolubility of this compound in perfluorinated compounds precluded determining whether it produces LE emission in them. Figure 4 shows the absorption and emission spectra for BAC in 3:1 decalin/methylcyclohexane at 77 K; from the figure it follows that the decalin/methylcyclohexane matrix hinders the formation of the TICT state of BAC at 77 K. The figure includes the excitation and emission spectra for BAC in DMSO at 77 K; the structure of the spectrum supports the previous conclusion.

The absorption spectrum for C9AC between 300 and 340 nm only allows the precise location of the 0−0 component in inert solvents; the corresponding values are listed in

Figure 3. Plot of the Stokes shifts of BAC in different solvents against the SPP values of the solvents (slope: 2711 cm^{-1})

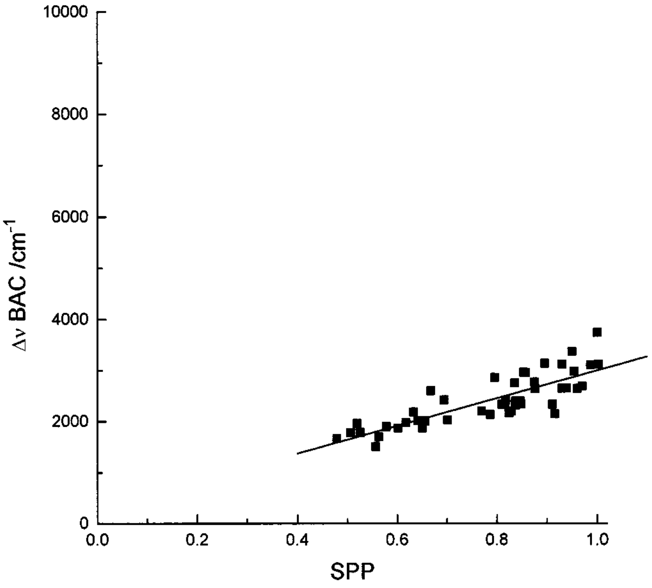


Figure 4. (a) Normalized absorption and emission spectra for BAC at 77K in 3:1 decalin/methylcyclohexane and (b) normalized emission and fluorescence excitation of BAC at 77K in DMSO

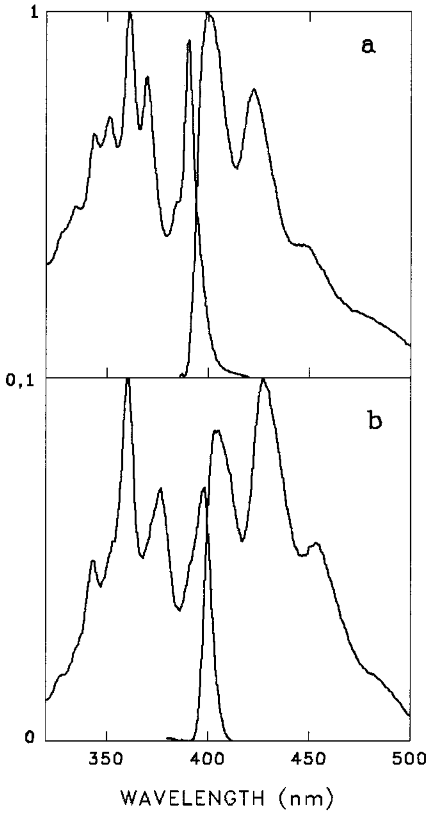


Figure 5. Normalized absorption spectra for C9AC in (a) 2-methylbutane, (b) toluene, (c) ethanol, and (d) DMSO

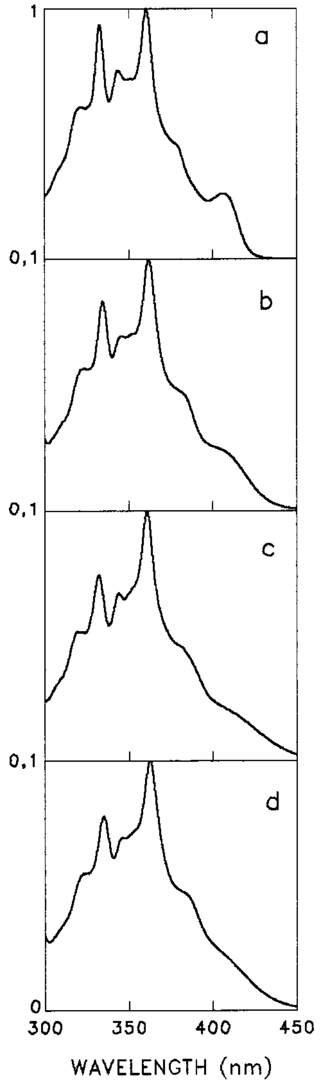


Table 1. In the other solvents, the peak broadens to a small shoulder (see Figure 5). As in BAC, the peak at about 360 nm is very strong and sharp in all the solvents studied (see Figure 5); the position of the peak is also given in Table 1. We thus used this peak to determine the corresponding Stokes shifts.

Unlike those for BAC, the emission spectra for C9AC can be divided into two groups; thus, the spectra in scarcely polar solvents (SPP $\leq$ 0.62) are structured, whereas those in the more polar solvents (SPP $\geq$ 0.62) are structureless (see Figure 6). As with C9A[10], the former can tentatively be assigned to LE emission and the latter to TICT emission. A plot of the Stokes shifts given in Table 2 against the corresponding SPP values for the solvents (Figure 7) demonstrates a bilinear relationship, similar to that previously observed in C9A[10].

The chromophore in C9AC that acts as the electron donor is the carbazole unit, with an oxidation potential of 1.18 V (Table 3), and that which acts as the acceptor is the acridine unit, with a reduction potential of −1.04 V. The resulting potential difference, 2.30 V, is even smaller than that of BAC; accordingly, C9AC should exhibit TICT emis-

Figure 6. Normalized emission spectra for C9AC in 2-methylbutane (—), toluene (- - -), ethanol (···) and DMSO (— ·· —)

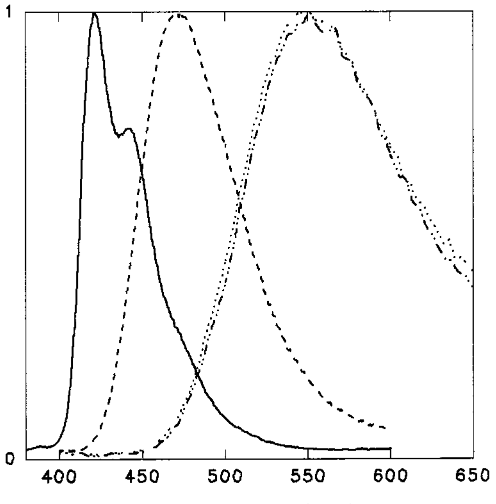
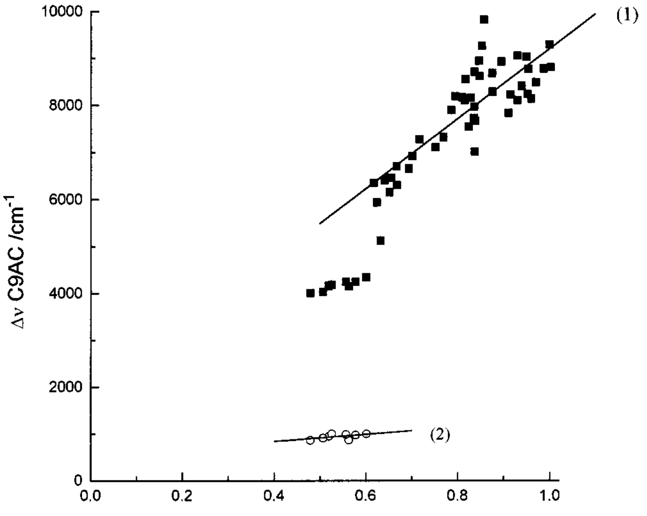


Figure 7. Plot of the Stokes Shifts of C9AC in different solvents against the SPP values of the solvents [slopes: (1) 7425 cm^{-1}, (2) 764 cm^{-1}]



sion throughout the solvent range studied, which, as shown above, is not the case.

It should be noted that the Stokes shifts for C9AC used in Figure 7 were exaggerated by about 3200 cm^{-1} as a result of calculating them from the absorption peak at 360 nm. If we re-evaluate the corresponding Stokes shifts in those solvents whose 0−0 component could be precisely located, and reconstruct Figure 7, the behaviour of these solvents suggests that the shift in the LE emission of C9AC in the gas phase must be close to zero (the intercept of the fitted curve is only 534 cm^{-1}).

Figure 8 shows the absorption spectra for acridine in 2-methylbutane, toluene, ethanol, and DMSO. The spectra reveal that the first excited singlet of BAC and C9AC can be assigned to the acridine unit, perturbed by the acridine and carbazole residue, respectively. The strong bathochromic shift in the 0−0 component from BAC to C9AC can in principle be ascribed to the higher electron-donor power of the carbazole group (E^{ox} = 1.16 V) relative to the acridine group (E^{red} = 1.58 V) (see Table 3).

Some Comments on LE Emission and the Relationship of hν_{TICT} to ΔE_{redox} in Biaryls

While the currently accepted mechanism for dual fluorescence of biaryls is the TICT mechanism[5], various alternative interpretations specific to DMABN, ranging from those involving emissions from the ^1L_a and ^1L_b states (proposed by Lippert et al.[9]), solvent exciplexes[20][21][22] or the formation of dimers or excimers[23][24], to those based on a proton phototransfer mechanism[25][26] or the more recent involving the so-called "pseudo Jahn-Teller coupling effect"[27][28], rehybridization of the amino nitrogen atom[29] or twisting of cyano groups[30], have also been put forward. In any case, it is widely accepted that the dual fluorescence of biaryls is the result of a TICT mechanism involving a dramatic change in the torsional angle between rings that produces a new, structureless fluorescence that opposes the normal, locally excited (LE) structured fluorescence.

There is general consensus that in some solvents both fluorescences of BA are so similar that they are rather difficult to resolve. Two working hypotheses based on deconvoluting the fluorescences, and on identifying the nature of the TICT emission, have been developed.

The emissions of BA were deconvoluted into its LE and TICT components by Rettig and Zander[31], based on the hypothesis of Schneider and Lippert[9] that the LE emission is not influenced by the solvent, so that any solvent can be used as a model for all; they adopted the emission of di-*n*-butyl ether (which they did not show) as their model. Subsequently, Zachariasse et al.[19] adopted the emission of BA in *n*-nonane (which they did not show either) as their model, and Schutz and Schmidt[32] adopted the fluorescence in perfluorodecalin (which is scarcely structured, see Figure 1 from ref.[32]) as theirs. Figure 9 shows the three emissions as observed by us; note the more structured fluorescence spectrum for BA obtained in perfluorodecalin. The vibronic structure exhibited by the BA fluorescence in these solvents cannot be accounted for due to an artifact since the emission envelope of BA, composed of two peaks, does not change in the solvents used: 1) when varying the BA concentration (OD_{368} = 0.004, 0.015, 0.04, and 0.08); 2) upon excitation at the whole range of wavelengths (λ_{exc} = 366, 347, 330, 280, and 250 nm); and 3) with further purification of the solvents. Nor the appearance of vibronic structure can be atributed to an inappropriate correction for the instrumental sensivity vs. the emission wavelength, for the reason that we have calibrated our spectrophotometer using a standard lamp of spectral irradiance (Optronic Laboratories, Inc., OL 245M). The figure also shows the emissions of BA in perfluorohexane and 2-methylbutane. An obvious question arises: how could the above-mentioned authors possibly subtract the LE emission in 2-methylbutane or per-

Figure 8. Absorption spectra of acridine in (a) 2-methylbutane, (b) toluene, (c) ethanol, and (d) DMSO

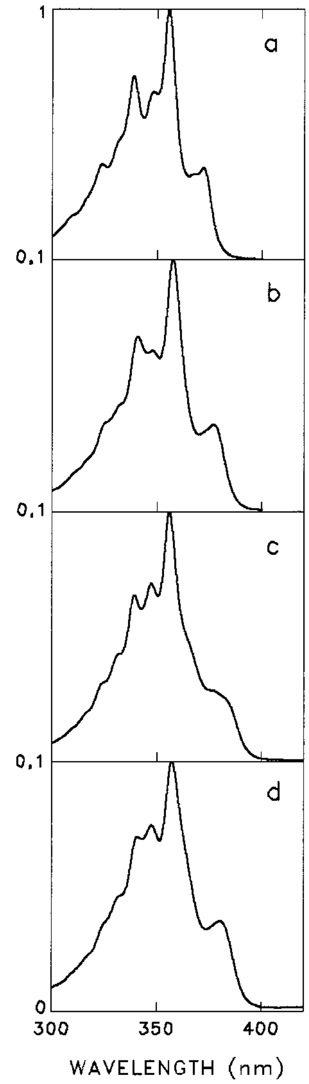
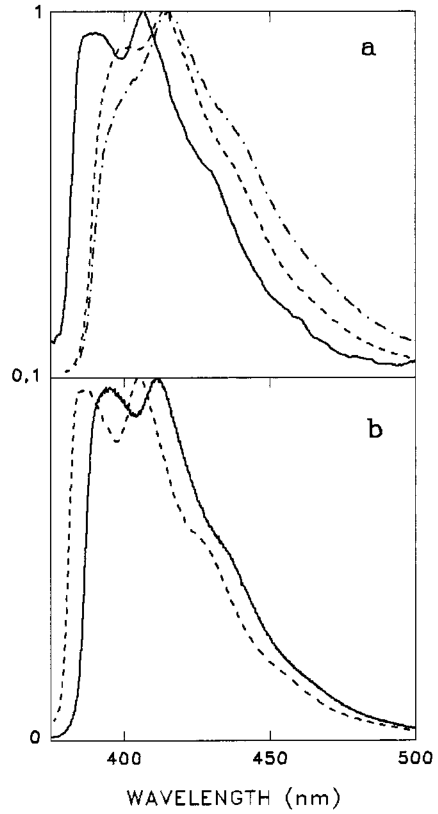


Figure 9. Normalized emission spectra of BA in (a) perfluorodecaline (—), *n*-nonane (- - -), di-*n*-butyl ether (— · —), (b) perfluorohexane (- - -) and 2-methylbutane (—)



fluorohexane in their models if the spectra were structureless?

One immediate consequence of the emission spectra of Figure 9 is that they invalidate the hypothesis that the LE emission of BA is solvent independent; it is obvious that the spectral envelope and position change between solvents, so there can be no such thing as an LE emission prototype that one can use to deconvolute the emission of BA in any solvent. In future work, we shall test a working hypothesis which, to our minds, could solve the problem posed by the simultaneous occurrence of two strongly overlapped, mutually masked emissions in BA[33]. The aim is to find a compound acting as an appropriate homomorph for the LE emission of BA in any solvent, so that the fluorescence spectrum for the homomorph in a given solvent can be used to subtract the potential contribution of LE to the spectrum for BA in that solvent and hence to explain the coexistence of fluorescences and determine their respective contributions to BA emission.

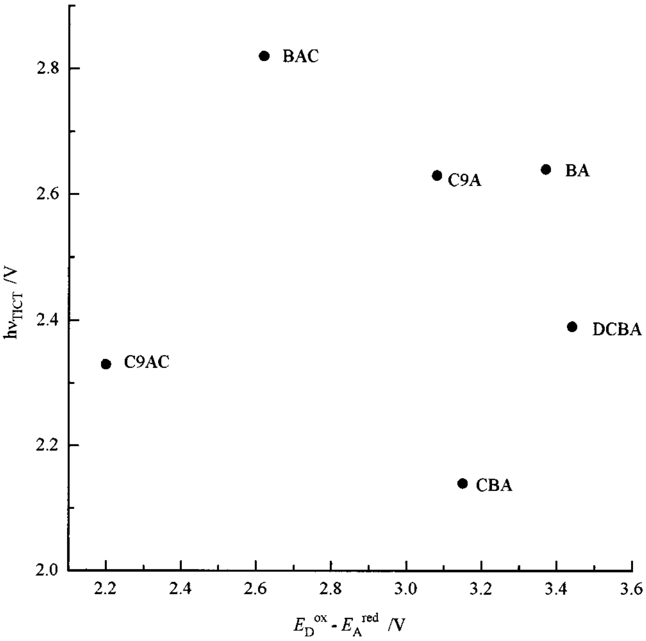
On the other hand, there is the linear relationship between the redox potential of the chromophores and the TICT transition energy for biaryls proposed by Zachariasse et al.[19] based on the excimer formation of model of Weller[34]. Figure 10 shows that, contrary to the predictions of Zachariasse et al.[19] for these compounds, such a relationship does not exist in acetonitrile. In any case, the model is clearly useful to, for example, understand why BC exhibits no TICT mechanism whereas BAC does throughout the solvent polarity range and BA only above a given solvent polarity level. However, it cannot explain why C9AC seemingly requires the cooperation of the solvent polarity in order to produce the TICT emission whereas BAC does not.

Conclusions

BAC at room temp. seems to require no cooperation from the solvent to produce TICT emission in any of the solvents tested. This exceptional behaviour for a biaryl compound is consistent with both its structureless fluorescence and with the linear variation of its solvatochromism with the solvent polarity.

By contrast, C9AC exhibits structured emission in scarcely polar solvents, structureless emission in the more polar solvents and bilinear solvatochromism towards the solvent polarity.

Figure 10. TICT transition energy for a serie of biaryls plotted against the redox potential difference



While the behaviour of BC, BA, and BAC can be explained in the light of the redox potentials of their chromophores, the differential behaviour of BAC and C9AC cannot. Also, contrary to the assumption of Zachariasse et al., the difference in redox potentials , and the TICT emission energy for biaryl compounds in polar solvents, are not linearly related, being a possible explanation for this unexpected behavior the fact that these compounds possess very different Coulomb terms.

The above findings suggest a need to revise existing LE emission models for analysing BA emission.

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Experimental Section

Absorption spectra were recorded with a Shimadzu 2100 UV/Vis spectrophotometer. The monochromator was calibrated in terms of wavelength by using the 486.0 and 656.1 nm lines from a deuterium lamp. A Cary 5 spectrophotometer was used in those cases where a chromophore was scarcely soluble in any of the solvents, and also in recording absorption spectra at 77 K (with the aid of an Oxford DN 1704 cryostat). Both instruments were routinely checked for wavelength accuracy by using holmium oxide and didymium filters. All spectral measurements were made at 25°C, using a matched pair of quartz cells of 1 cm path length. The maximum wavelength in each case was determined from the corresponding derivative function.

Fluorescence spectra at 25°C and 77 K were recorded on an Aminco Bowman Series 2 spectrofluorimeter with its excitation and emission polarizers arranged at the magic angle. The emission monochromator was calibrated in wavelength by using an Oriel 6035 Hg (Ar) spectral calibration lamp. Both emission and excitation spectra were duly corrected. All solutions used were diluted to a sufficient extent in order to avoid significant inner-filtering effects. As with absorption spectra, the maximum wavelength was determined from the derivative function in each case.

The chromophores were synthesized according to reported procedures[35]. Thus, BAC was prepared by reducing 9-chloroacridine with zinc and C9AC was obtained by fusion of carbazole and 9-chloroacridine through heating at 300°C for 3 h. Both products were purified by column chromatography, using 50:50 ethyl acetate/*n*-hexane as eluent. All solvents used were of the highest available purity and supplied by Aldrich or Fluka; some were redistilled in an inert atmosphere prior to use (decalin and perfluorodecalin were purified by passage through a neutral alumina column).

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[1] Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, W. Baumann, *New J. Chem.* **1979**, *3*, 443–454.
[2] W. Rettig, *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971–988.
[3] E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, J. A. Miehe, *Adv. Chem. Phys.* **1987**, *68*, 1–173.
[4] W. Rettig, W. Baumann, *Progress in Photochemistry and Photophysics* (Ed.: J. F. Rabek), CRC Press, Boca Raton, FL, **1992**, chapter 3.
[5] W. Rettig, *Top. Curr. Chem.* **1994**, *169*, 254–299.
[6] H. Lueck, M. W. Windsor, W. Rettig, *J. Phys. Chem.* **1990**, *94*, 4550–4559.
[7] A. Wiessner, G. Hütmann, W. Kühnle, H. Staerk, *J. Phys. Chem.* **1995**, *99*, 14923–14930.
[8] W. Rettig, *Angew. Chem.* **1986**, *98*, 969–986; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 971.
[9] F. Schneider, E. Lippert, *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 1155–1160.
[10] J. Catalan, C. Dıaz, V. Lopez, P. Perez, R. M. Claramunt, *J. Phys. Chem.* **1996**, *100*, 18392–18398.
[11] J. Catalan, *J. Org. Chem.* **1997**, *62*, 8231-8234
[12] J. Catalan, J. C. del Valle, C. Dıaz, J. Palomar, J.-L. G. de Paz, M. Kasha, to be published.
[13] Actually, as suggested by a referee, the possibility of inhomogeneous line broadening cannot be excluded as a reason to account for the loss of vibronic structure exhibited by the BAC emission in non-polar solvents. The inhomogeneous line broadening would arise from, for example, torsional motion of the rings (i. e. the twist) and hence a varying degree of charge transfer resonance.
[14] J. F. Ambrose, R. F. Nelson, *J. Electrochem. Soc.* **1968**, *15*, 1159–1164.
[15] H. Bock, U. Lechner-Knoblanch, *Z. Naturforsch.* **1985**, *40b*, 1463–1475.
[16] C. K. Mann, K. K. Barnes, *Electrochemical Reactions in Nonaqueous System*, Decker, New York, **1970**.
[17] L. Marcoux, R. N. Adams, *J. Electroanal. Chem.* **1974**, *49*, 111–119.
[18] G. Anthoine, G. Coppens, J. Nasielski, E. van der Douckt, *Bull. Soc. Chim. Belg.* **1964**, *73*, 65–71.
[19] T. von der Haar, A. Hebecker, Y. Il′chev, Y. B. Jiang, W. Kühnle, K. A. Zachariasse, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430–442 and references therein.
[20] E. A. Chandross, H. T. Thomas, *Chem. Phys. Lett.* **1971**, *9*, 397–406.
[21] P. C. Weisenborn, A. H. Huizer, C. A. G. O. Varma, *Chem. Phys.* **1989**, *133*, 437–452.
[22] U. Leinhos, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem.* **1991**, *95*, 2013–2021.
[23] O.S. Khalil, R. H. Hofeldt, S. P. McGlynn, *Chem. Phys. Lett.* **1972**, *17*, 479–481; *J. Luminescence* **1973**, *6*, 229–244; *Spectrosc. Lett.* **1973**, *6*, 147–151.
[24] O. S. Khalil, *Chem. Phys. Lett.* **1975**, *35*, 172–174.
[25] H. Dodiuk, E. M. Kosower, *Chem. Phys. Lett.* **1975**, *34*, 253–257.
[26] E. M. Kosower, H. Dodiuk, *J. Am. Chem. Soc.* **1976**, *98*, 924–929.
[27] K. A. Zachariasee, Th. von der Haar, U. Leinhos, A. Hebecker, W. Kühnle, *Pure Appl. Chem.* **1993**, *65*, 1745–1750.
[28] K. A. Zachariasse, Th. von der Haar, U. Leinhos, W. Kühnle, *J. Inf. Rec. Mater.* **1994**, *21*, 501–506.

[29] W. Schuddebom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem.* **1992**, *96*, 10809–10819.

[30] A. L. Sobolowski, W. Domcke, *Chem. Phys. Lett.* **1996**, *250*, 428–436.

[31] W. Rettig, M. Zander, *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1143–1149.

[32] M. Schütz, R. Schmidt, *J. Phys. Chem.* **1996**, *100*, 2012–2018.

[33] J. Catalán, C. Díaz, work in progress.

[34] A. Weller, *Z. Phys. Chem.* **1982**, *130*, 129; *ibid.* **1982**, *133*, 93–98; and in *The Exciplex* (Eds.: M. Gordon, W. R. Ware); Academic Press, New York, **1975**, p. 23.

[35] G. Boyer, R. M. Claramunt, J. Elguero, M. Fathalla, C. Foces-Foces, C. Jaime, A. Llamas-Saiz, *J. Chem. Soc., Perkin Trans. 2* **1993**, 757–766.

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