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Analysis of the Solvatochromism of 9,9'-Biaryl Compounds Using a Pure Solvent Dipolarity Scale

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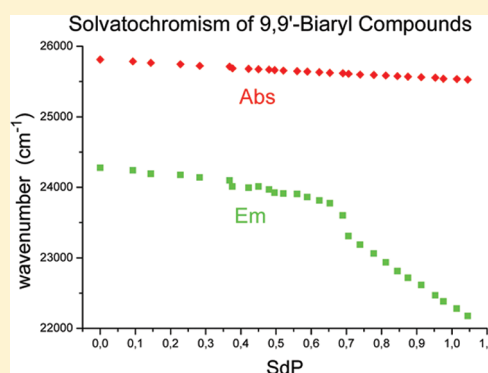
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S Supporting Information

ABSTRACT: The UV/vis absorption and fluorescence spectra of 9,9'-bisanthracenyl (BA), 9,9'-bisacridinyl (BAC), 9,9'-bicarbazyl (BC), and 9-(9'-anthracenyl)carbazole (C9A) were precisely recorded in solvents that change their solvent dipolarity scale (*SdP*) values from 0.000 (in 2-methylbutane at 293 K) to 1.294 (in 1-chlorobutane at 77 K). An analysis based (i) on the solvatochromic behavior of the four 9,9'-biaryl compounds in terms of the dipolarity of the solvents used, quantified by means of their *SdP* values, and (ii) on the behavior of the emission band profiles, allows the conclusion that, whereas the apolar 9,9'-biaryl compounds BA, BAC, and BC need solvents with *SdP* values larger than 0.74 to give a twisted intramolecular charge-transfer (TICT) process after excitation, for dipolar C9A the TICT mechanism is predominant already at solvent *SdP* values smaller than 0.23, i.e., near a solvent dipolarity of 0. The accuracy and simplicity achieved by application of the *SdP* scale in analyzing the solvatochromic behavior of the four 9,9'-biaryl compounds studied make evident the advantages of this solvent scale in comparison to other empirical solvent scales, which not only include the solvent's dipolarity but also consist of a more limited numerical range of values only.



INTRODUCTION

The dual emission from solutions of certain chromophores, observed when the solvent's dipolarity changes, has received great interest in the last sixty years,^{1–6} because the new emission band generated was ascribed to a second electronic excited state with a zwitterionic molecular structure exhibiting a large charge separation, a process that is involved in many important, naturally occurring photochemical mechanisms such as vision and photosynthesis.⁷ This type of process is also of potential interest for producing laser light,^{8,9} storing solar energy,⁹ developing transistors,¹⁰ and organic conductors or even superconductors.¹¹

In this connection two phenomena are of importance: (i) the solvent-induced inverted solvatochromism of meropolymethine dyes, discovered by Kiprianov et al.¹² and Brooker et al.,¹³ which was recently studied also by our research group,¹⁴ and (ii) the twisted intramolecular charge transfer (TICT) of so-called tictoid compounds, discovered by Schneider and Lippert.¹⁵ In this work, the TICT mechanism¹⁶ is studied with four representative 9,9'-biaryl compounds (Scheme 1), i.e., 9,9'-bisanthracenyl (BA), 9,9'-bicarbazyl (BC), 9,9'-bisacridinyl (BAC), and 9-(9'-anthracenyl)carbazole (C9A) within the full range of solvent dipolarity, using as its measure the empirical solvent dipolarity (*SdP*) scale, obtained in 2009 by splitting the formerly introduced solvent polarizability/dipolarity (*SPP*)

values into *SdP* (solvent dipolarity) and *SP* (solvent polarizability) values by means of a substituted polyene chromophore (ttbP9).¹⁷

The solvatochromism of the four 9,9'-biaryl compounds involved in the TICT process should exhibit a bilinear behavior as indicated by Schneider and Lippert,¹⁵ i.e., with one range of solvent dipolarity dominated by the locally excited (LE) fluorescence emission, and another range of solvent dipolarity showing the TICT emission.

In this work a wide solvent dipolarity scale will be employed for the first time, ranging in the liquid phase from *SdP* = 0.000–1.045, using for it pure 2-methylbutane and 1-chlorobutane as limiting solvents. For instance, dipolar solvents such as formamide, dimethyl sulfoxide, water, and *N,N*-dimethylformamide have *SdP* values of 1.006, 1.000, 0.997, and 0.977, respectively, whereas *SdP* values of apolar solvents such as 2-methylbutane and *n*-hexane amount to 0.000.¹⁷ The TICT process is studied for three molecules with *D*_{2d} symmetry (BA, BAC, and BC) and one with *C*₁ symmetry (C9A) in the electronic ground state (Scheme 1). The first three molecules exhibit a zero dipole moment and the fourth a nonzero dipole

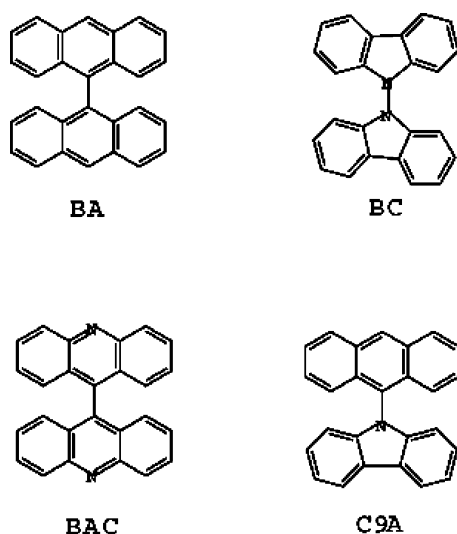
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Scheme 1. Molecular Structures of the Four 9,9'-Biaryl Compounds Studied



moment (estimated to $\mu \approx 2 \text{ D}^{18}$) in their electronic ground state. The TICT mechanism assumes that these four molecules adopt an almost orthogonal conformation with respect to the two rings in the electronic ground state. On photoexcitation, these molecules dissolved in not very polar solvents, exhibit structured UV/vis absorption and emission spectra, with a rotation of the two aryl rings toward a more coplanar conformation in the excited state with increasing solvent polarity, from which they emit fluorescence bands without vibronic structure.

The pioneering work of Schneider and Lippert^{15,19} deals with the solvatochromism of 9,9'-bisanthracenyl (**BA**), measured in 30 solvents of different polarity, and the results were interpreted with the famous Lippert $\Delta f(\epsilon_r, n)$ equation. This study shows that 20 of the 30 solvents exhibit a bilinear behavior of the corresponding correlation lines, whereas for 9 solvents of lowest polarity a linear relationship with a slope of 0 was observed.

Later on,²⁰ the same solvatochromic data for **BA** were drawn against the solvent dipolarity/polarizability *SPP* values. The relationship observed was also bilinear, except for 9 low-polar solvents, which gave a correlation line with a nonzero slope meeting the gas-phase value.²¹ On the other hand, Acree et al.²² studied the behavior of **BA** in 45 solvents: for 42 solvents, for which Lippert's²³ or Bilot-Kawski's²⁴ $f(\epsilon_r, n)$ function were available, they obtained such highly dispersive results that the bilinear relationship suggested by Schneider and Lippert^{15,19} was only observed clearly when 8 values were omitted. After this work, our group²⁵ analyzed the solvatochromism of **BA**, measured in 60 solvents, by correlation with the *SPP* scale: a bilinear relationship was observed, however, with a significantly large standard deviation. Durocher et al.^{26,27} studied the solvatochromism of **BC** in a small number of solvents and they concluded that, contrary to the behavior of **BA**, **BC** does not show a TICT mechanism.

Thereafter, our group²⁵ analyzed the solvatochromism of **BC**, measured in 54 solvents, by correlation with the *SPP* values, confirming the absence of a bilinear relationship. It is important to point out that **BAC**, studied in 48 solvents, does not show any bilinear response in the correlation with the *SPP* values.²⁸

Rettig et al.²⁹ studied the solvatochromism of the asymmetric 9,9'-biaryl compound **C9A** in diethyl ether, tetrahydrofuran, 1-chlorobutane, 1,2-dichloroethane, *n*-butyronitrile, acetonitrile, and they found a linear relationship in the correlation with the corresponding $\Delta f(\epsilon_r, n)$ values. On the other hand, our research group²⁸ found for **C9A** in 60 solvents also a linear relationship with *SPP*, however, without the data obtained for perfluoro-*n*-alkanes; although the standard deviation is quite large, a linear relationship is clearly seen.

Based on the evidence from the solvatochromism of these 9,9'-biaryl compounds, the conclusion could be drawn that an adequate description of their solvatochromic behavior has not yet been achieved. Their controversial behavior found for the same range of solvents is still not well understood. For instance, from 2-methylbutane to dimethyl sulfoxide as solvents, the solvatochromism of **BA** yields a bilinear relationship, whereas it is linear for **BAC** and **BC**; all these molecules exhibit D_{2d} symmetry and are apolar (i.e., without dipole moment).

If the two aryl rings of these molecules in the electronic ground state are rotated out-of-plane to avoid steric hydrogen/hydrogen repulsions at the peri-ring positions and the TICT mechanism consists of rotating both rings toward a coplanar structure, then the question can be raised, how is it feasible that **BC** presents a peri-H/H repulsion that is significantly smaller than the corresponding peri-H/H repulsion for **BAC**, which does not exhibit TICT, or for **BAC**, which does exhibit TICT? In our opinion, this controversy can be due to the lack of sufficient solvatochromic data, which should depend only on the solvent's dipolarity. Therefore, the until now available solvatochromic data seem to be contaminated with specific solute/solvent interactions. This interpretation can possibly explain the large standard deviations found in the correlations studied. On the other hand, there is a lack of an adequate solvent parameter which can describe the solvent's dipolarity only.

In this work, both factors are minimized by using a pure solvent dipolarity parameter, i.e., the recently introduced, solvatochromically derived solvent dipolarity scale *SdP*,³⁰ and by measuring *SdP* values larger than 0.39 by means of the pure solvent 1-chlorobutane, and *SdP* values smaller than 0.37 by means of binary 2-methylbutane/1-chlorobutane mixtures.

■ EXPERIMENTAL SECTION

The 1-chlorobutane used was of Chromasolv grade (purity 99.8%; bp 77–78 °C) with a moisture content equal to or less than 0.001%, and 2-methylbutane was of Merck-Uvasol grade (purity $\geq 99.5\%$; bp 30 °C). Samples of the four biaryl compounds studied were synthesized following procedures given in the literature:^{31–33} 9-(9'-anthracenyl)anthracene (9,9'-bisanthracenyl, **BA**) was obtained by reduction of anthrone with zinc;³¹ 9-(9'-carbazyl)carbazole (9,9'-bicarbazyl, **BC**) was synthesized by oxidation of carbazole with potassium permanganate³² and was purified by column chromatography using *n*-hexane/trichloromethane (90:10% v/v) as eluent; 9-(9'-acridinyl)acridine (9,9'-bisacridinyl, **BAC**) was prepared by reduction of 9-chloroacridine with zinc³³ and was purified by column chromatography using *n*-hexane/ethyl acetate (50:50% v/v) as eluent; 9-(9'-anthracenyl)-9H-carbazole (**C9A**) was obtained by fusion of carbazole with 9-bromoanthracene at 300 °C for 2.5 h³³ and was purified by column chromatography using *n*-hexane/trichloromethane (60:40% v/v) as eluent. All compounds were colorless crystals with melting points corresponding to the literature values.

The temperature of solutions of the four biaryl compounds in the range 77–293 K were controlled with an Oxford DN1704 cryostat, purged with dried nitrogen of 99.99% purity, and equipped with an ITC4 controller interfaced to the spectrometers. Sample temperatures in the range 293–343 K were controlled within ± 0.1 °C with a Fisons-Haake D8 GH thermostat.

All UV/vis absorption spectra were recorded with a Cary-5 spectrophotometer at variable temperatures from 77 to 293 K, using Suprasil quartz cells of 1 cm path length that were fixed to the cryostat and to a cell holder thermostatted between 293 and 343 K.

Corrected fluorescence spectra were obtained with a calibrated Aminco-Bowman AB2 spectrofluorometer. The sensitivity factors for the emission channel, which include not only those depending on the detector but also those related to the emission monochromator and the optical arrangement (channel emission included), were obtained by using the correction kit FP-123 from SLM Instruments. This required mounting a standard lamp in a channel at right angles to the emission channel in an OL 254 M spectra irradiance lamp from Optronic Laboratories. The lamp was operated at a constant voltage supplied by an SP-270 power source. Its light output was driven into an integrating sphere with a pinhole leading to the fluorometer emission channel. The conversion factors thus obtained allowed us to convert the measured spectra into absolute spectra, which are independent of the instrument used.

RESULTS AND DISCUSSION

To complete the recently introduced solvent dipolarity scale *SdP* for 1-chlorobutane,³⁰ we start by using a solvent that is structurally similar to that of 1-chlorobutane, i.e., 2-methylbutane with *SdP* = 0.000 (apolar), to *SdP* = 0.399 (dipolar), the latter value corresponding to that of 1-chlorobutane at 343 K, the lowest *SdP* value measurable with this solvent.³⁰ That is, we use 2-methylbutane for *SdP* = 0.000 and binary 2-methylbutane/1-chlorobutane mixtures at 293 K for *SdP* values between 0.000 and 0.399. Thereafter, the photophysics of the 9,9'-biaryl compounds is analyzed between 293 and 143 K (a temperature at which 1-chlorobutane is still a liquid), with emphasis on the photophysics of **BA**. Subsequently, the solvatochromism of the symmetrical biaryl compounds **BA**, **BC**, and **BAC** is explained, as well as the photophysical behavior of nonsymmetrical **C9A**. Finally, all data observed are assessed in terms of the TICT mechanism.

Enlarging the *SdP* Scale for Completeness. By employing only one dipolar solvent, i.e., 1-chlorobutane, at different temperatures, we established a comprehensive solvent dipolarity scale, ranging from *SdP* = 0.399 (1-chlorobutane at 343 K) up to *SdP* = 1.294 (1-chlorobutane at 77 K).³⁰ For the sake of completeness, we have now enlarged the *SdP* scale from 0.000 (2-methylbutane; μ = 0 D) to 0.399 by adding dipolar 1-chlorobutane (μ = 1.90 D at 20 °C in CCl_4 ³⁰) to apolar 2-methylbutane. Table 1 compiles the long-wavelength UV/vis absorption maxima of 3,20-di-*tert*-butyl-2,2,21,21-tetramethyl-5,7,9,11,13,15,17,19-docosanonaene (ttbP9; 0 \rightarrow 0 component) and 2-(dimethylamino)-7-nitrofluorene (DMANF) for the binary mixtures mentioned above as well as the corresponding *SdP* values derived from the equations reported in ref 17. As can be seen, it is sufficient to use a 50:50% (v/v) 2-methylbutane/1-chlorobutane mixture for completing the *SdP* scale adequately.

Table 1. Wavenumbers $\tilde{\nu}$ (cm^{-1}) of the Maxima of the Long-Wavelength UV/Vis Absorption Band of the Reference Compounds ttbP9 (0 \rightarrow 0 Component) and DMANF, Measured in Five 2-Methylbutane (2-MB)/1-Chlorobutane (1ClB) Mixtures at 293 K, and the Corresponding *SdP* Values¹⁷

mixtures 2-MB/1ClB (%, v/v)	ttbP9 (0 \rightarrow 0) $\tilde{\nu}/\text{cm}^{-1}$	DMANF $\tilde{\nu}/\text{cm}^{-1}$	<i>SdP</i> values
90:10	21872	25171	0.093
80:20	21825	25004	0.144
70:30	21795	24734	0.228
60:40	21745	24707	0.283
50:50	21715	24472	0.368

Photophysics of the 9,9'-Biaryl Compounds. On the UV/Vis Absorption and Emission of **BA**, **BC**, and **BAC**. Figure 1 brings into focus the UV/vis spectral pattern of these 9,9'-

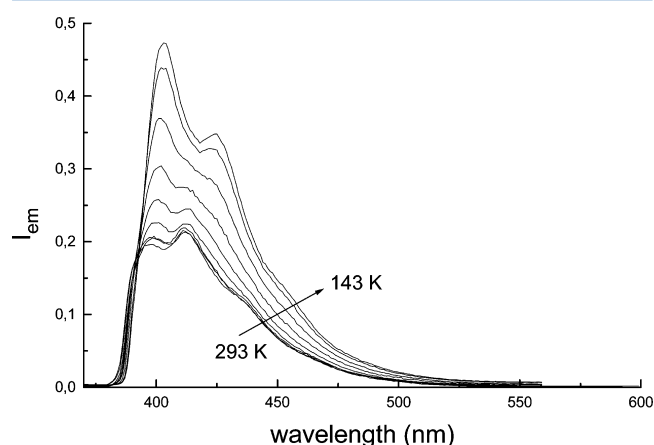


Figure 1. Emission spectra (λ_{exc} = 350 nm) of **BA**, dissolved in 2-methylbutane ($c = 2 \times 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

biaryl compounds. It shows the emission band of **BA**, measured in 2-methylbutane at different temperatures, with a vibronic structure at room temperature, which increases significantly in structure and intensity with decreasing temperature, particularly the 0 \rightarrow 0 component. It is important to point out that the vibronic structure of the emission band of **BA** (Figure 3) is significantly smaller than that exhibited by its UV/vis absorption spectra, measured in 1-chlorobutane at different temperatures (Figure 2).

This observation indicates that, on photoexcitation of **BA**, its molecules relax in this solvent their molecular structure by decreasing the interplanar angle between the two rings to such an extent that fosters a significant loss of vibronic structure in its emission spectrum, accompanied by a small band shift.

The corresponding emission spectra of **BA**, measured in 1-chlorobutane at different temperatures (Figure 3), exhibit a vibronic structure at room temperature, which diminishes with decreasing temperature, leading eventually to an absence of vibronic structure at 253 K. When the solution temperature increases from room temperature (293 K) to 343 K, the emission band gains in vibronic structure; the same observation is made with solutions of **BA** in 2-methylbutane/1-chlorobutane mixtures rich in 2-methylbutane.

To sum up, we found two kinds of fluorescence behavior for solutions of these three 9,9'-biaryl compounds: (i) one with an

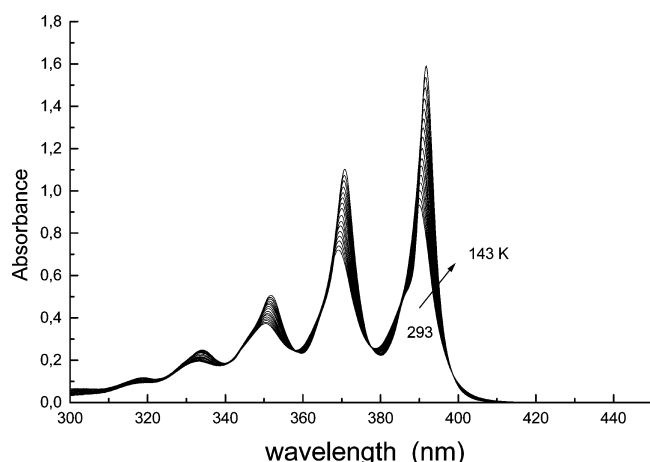


Figure 2. UV/vis absorption spectra of BA, dissolved in 1-chlorobutane ($c = 2 \times 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

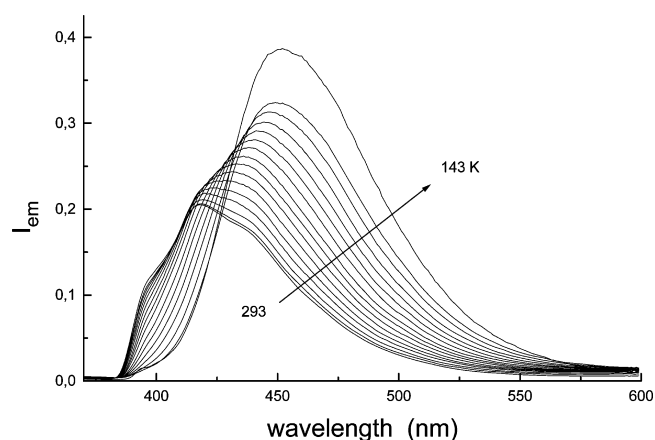


Figure 3. Emission spectra ($\lambda_{\text{exc}} = 350$ nm) of BA, dissolved in 1-chlorobutane ($c = 2 \times 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

emission band possessing vibronic structure similar to that shown by BA solutions in 2-methylbutane (Figure 1), which can be ascribed to the relaxed molecular structure to be generated by the Franck–Condon photoexcitation, and (ii) another emission below 253 K, generated from a new molecular structure formed in the excited state from the relaxed excited-state structure, presenting a spectral band envelope without vibronic structure (Figure 3).

The corresponding UV/vis excitation spectra for the aforementioned emission spectra match the spectral behavior shown by the respective UV/vis absorption spectra, either for the 2-methylbutane or for the 1-chlorobutane solutions, which exhibit bands with a significant vibronic structure.

Figures 4 and 5 show the UV absorption and emission spectra of BC, measured in 1-chlorobutane at different temperatures. The temperature-dependent spectral absorption behavior of BC resembles that shown by solutions of BA (Figure 2). Therefore, the comments given for the BA spectra are also valid for the BC spectra.

Figures 6 and 7 show the UV absorption and emission spectra of BAC, measured in 1-chlorobutane at different temperatures. Its spectral absorption behavior is equivalent to that of BA and BC, but the emission behavior of BAC shows large differences. For instance, the emission spectra of BAC,

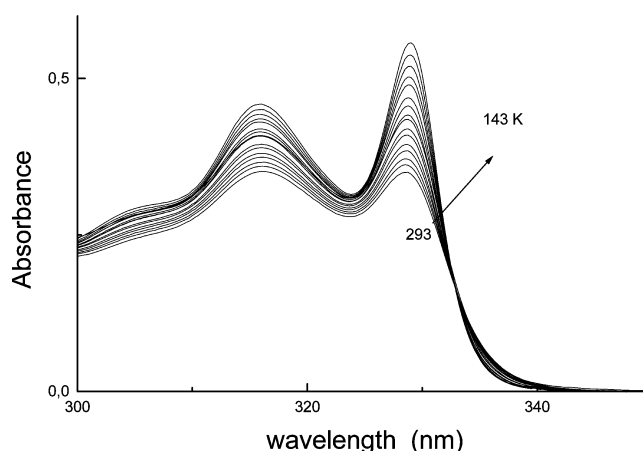


Figure 4. UV absorption spectra of BC, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

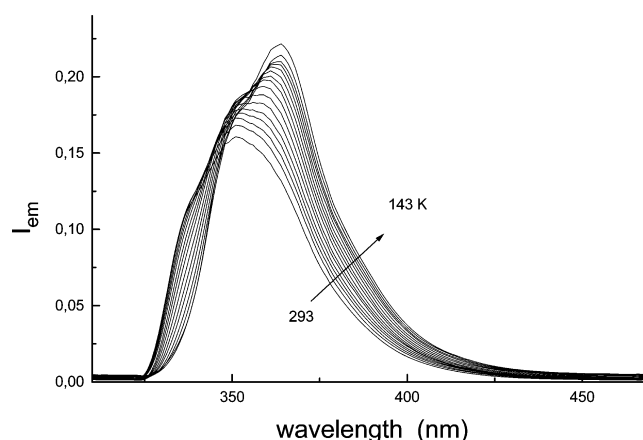


Figure 5. Emission spectra ($\lambda_{\text{exc}} = 290$ nm) of BC, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

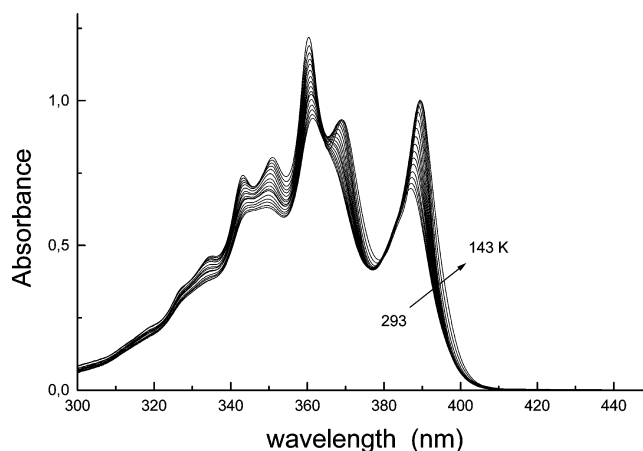


Figure 6. UV/vis absorption spectra of BAC, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

measured from 343 to 143 K, do not exhibit vibronic structure in 1-chlorobutane, as well as its emission spectra measured in 2-methylbutane/1-chlorobutane mixtures and in pure 2-methylbutane. This unique loss of vibronic structure for BAC as

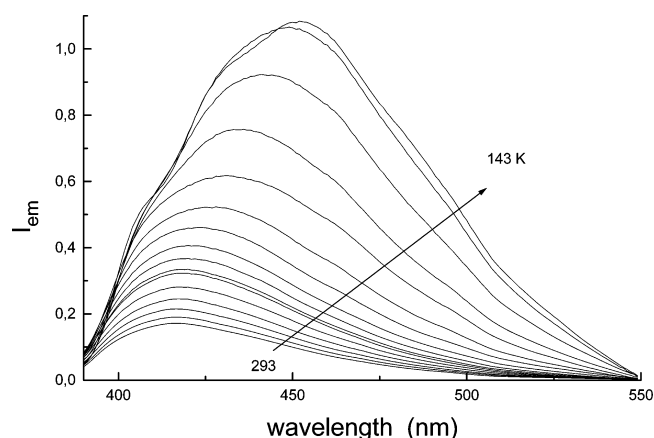


Figure 7. Emission spectra ($\lambda_{\text{exc}} = 345$ nm) of **BAC**, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at solution temperatures between 293 and 143 K.

compared to the significant vibronic structure found for the **BA** and **BC** emission spectra, provides the following information: (i) the structural relaxation in the electronic excited state of **BAC** is larger than that for **BA** and **BC**, which makes at first sight no sense because all three compounds are symmetrical 9,9'-biaryl compounds, whereas their absorption behavior is similar with a significant vibronic structure in all three cases; (ii) the emission band of the acridine chromophore of **BAC** might be much less structured than that of the other chromophores anthracene and carbazole, and on photo-excitation **BAC** gets relaxed, and their emission spectra do not show vibronic structure.

To test the last proposition, the emission spectra of anthracene, carbazole, and acridine were measured in 1-chlorobutane at 293 K (Figure 8). It can easily be seen that the emission spectrum of acridine exhibits a much less vibronic structure than those of anthracene and carbazole.

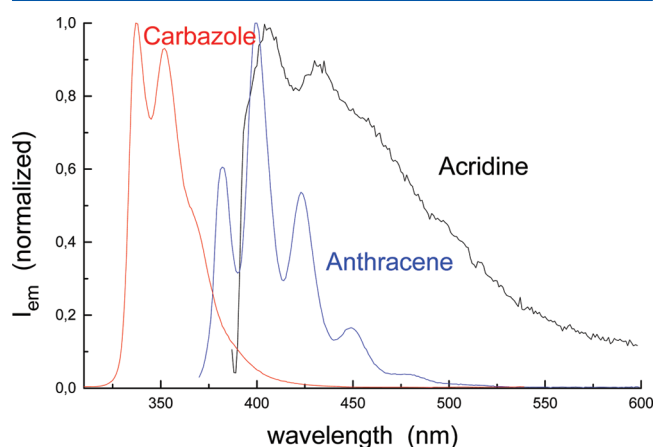


Figure 8. Normalized emission spectra of anthracene ($\lambda_{\text{exc}} = 325$ nm), carbazole ($\lambda_{\text{exc}} = 280$ nm), and acridine ($\lambda_{\text{exc}} = 325$ nm), dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at 293 K.

On the UV/Vis Absorption and Emission of C9A. The UV/vis absorption and emission spectra of **C9A**, measured in 1-chlorobutane at different temperatures, are shown in Figures 9 and 10. In Figure 9, at longer wavelengths one can see the absorption peaks due to the anthracene chromophore (see also

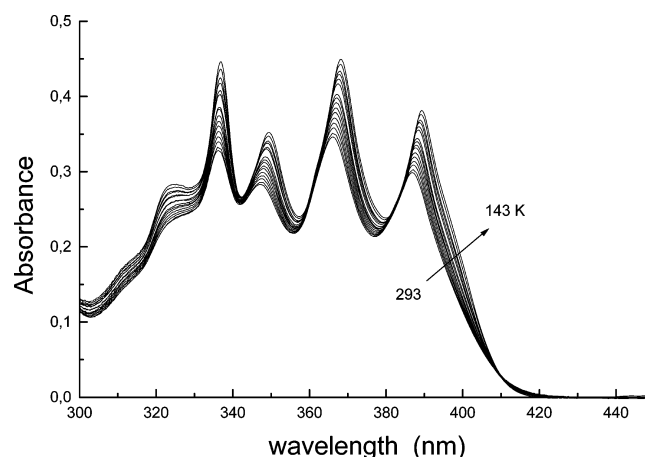


Figure 9. UV/vis absorption spectra of **C9A**, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at temperatures between 293 and 143 K.

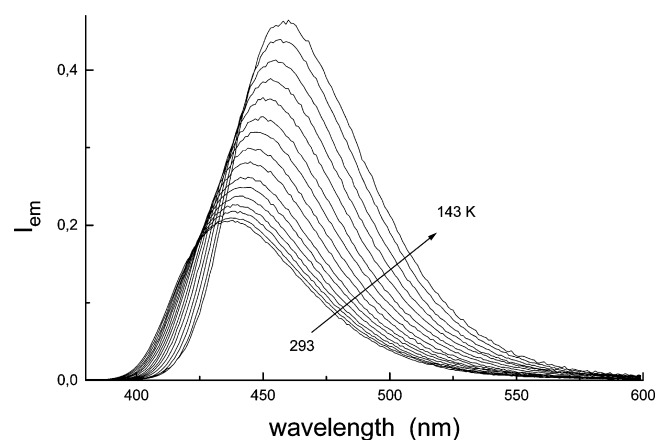


Figure 10. Emission spectra ($\lambda_{\text{exc}} = 325$ nm) of **C9A**, dissolved in 1-chlorobutane ($c \approx 10^{-6}$ mol/L), measured at temperatures between 293 and 143 K.

Figure 2), and at shorter wavelengths the peaks corresponding to the carbazole chromophore (see also Figure 4).

The emission spectra of **C9A**, measured in 1-chlorobutane from 343 to 143 K, show no vibronic structure. However, for solutions of **C9A** in 2-methylbutane and 2-methylbutane/1-chlorobutane mixtures from 90:10 to 70:30% (v/v), the emission spectra exhibit a vibronic structure (Figure 11). One should keep in mind that the emission spectra of anthracene and carbazole, in particular that of anthracene, show a neat vibronic structure (Figure 8).

Solvatochromism of the 9,9'-Biaryl Compounds.

Figures 12–15 compile the solvatochromic results obtained from the UV/vis absorption and emission spectra of **BA**, **BC**, **BAC**, and **C9A**, dissolved in media with a wide range of solvent dipolarity, that is, from $SdP = 0.000$ to 1.045.^{17,30} From these results the following conclusions can be drawn:

- The large standard deviations reported in previous studies^{15,25} for analogous correlations of solvatochromic data (obtained at 25 °C for a wide range of solvents characterized by means of the polarity function $\Delta f(\epsilon_r n)$,¹⁵ and of the dipolarity/polarizability parameters SPP^{25}) with the SdP scale are absent in Figures 12–15. The correlations are now statistically much improved.

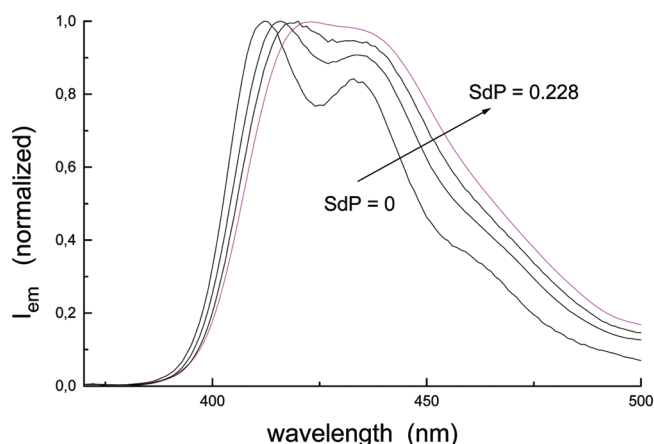


Figure 11. Emission spectra ($\lambda_{\text{exc}} = 335$ nm) of C9A, dissolved in 2-methylbutane ($SdP = 0.000$) and 2-methylbutane/1-chlorobutane mixtures up to 70:30% (v/v) ($SdP = 0.228$), measured at 293 K.

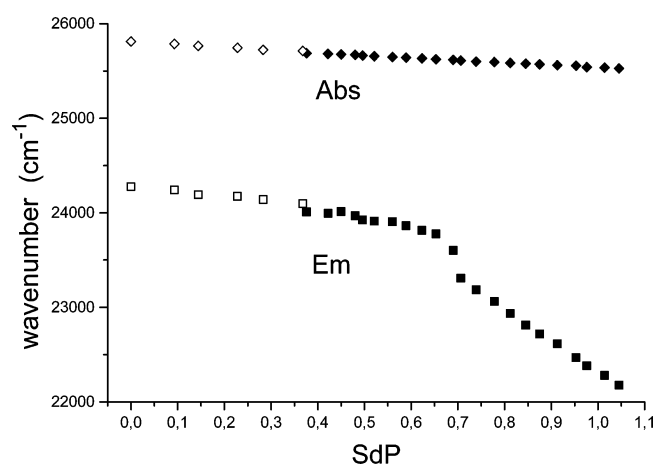


Figure 12. Correlation between the absorption and emission wavenumbers of BA and the 1-chlorobutane dipolarity parameter SdP .³⁰

- (ii) The absorption and emission data values corresponding to 2-methylbutane and its mixtures with 1-chlorobutane are drawn with empty diamonds and empty squares to

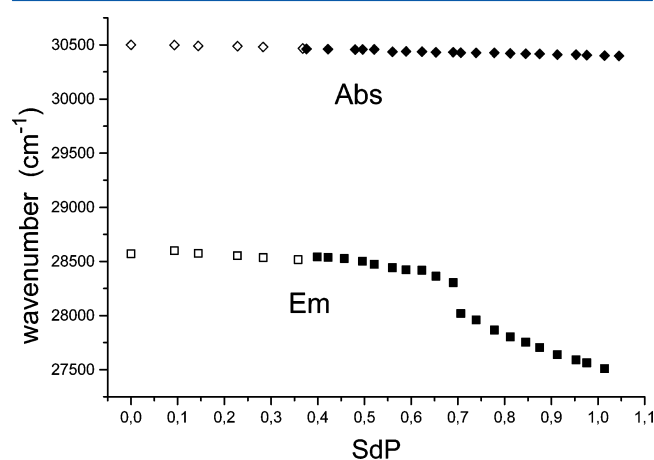


Figure 13. Correlation between the absorption and emission wavenumbers of BC and the 1-chlorobutane dipolarity parameter SdP .³⁰

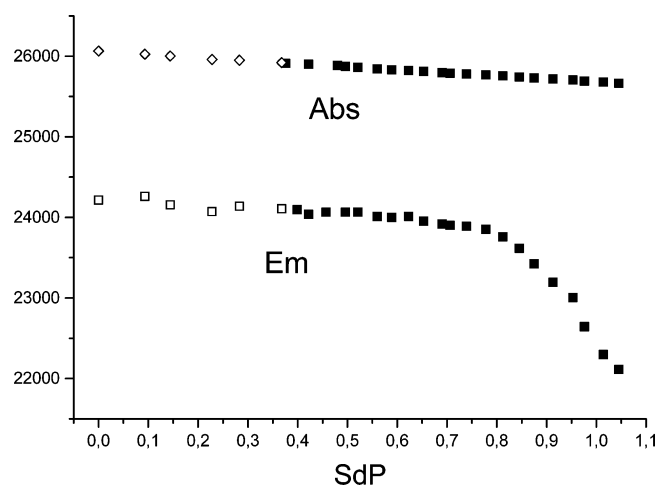


Figure 14. Correlation between the absorption and emission wavenumbers of BAC and the 1-chlorobutane dipolarity parameter SdP .³⁰

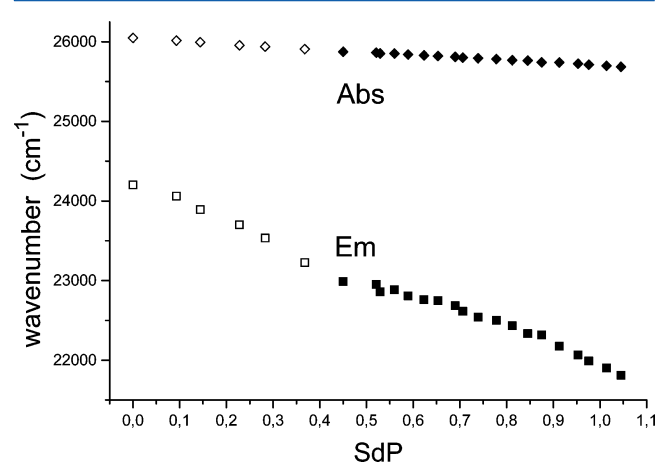


Figure 15. Correlation between the absorption and emission wavenumbers of C9A and the 1-chlorobutane dipolarity parameter SdP .³⁰

- demonstrate that they fit adequately into the remaining data of the SdP scale.³⁰
- (iii) The data values derived from the absorption-band maxima indicate that there is only one solvatochromic pattern throughout the whole SdP scale applied. The absorption-band maxima shift to the red (to lower wavenumbers \rightarrow bathochromic band shift) as the solvent's dipolarity increases, leading to correlation lines with small negative slopes: -267 ± 4 for BA (Figure 12), -103 ± 3 for BC (Figure 13), -374 ± 3 for BAC (Figure 14), and -349 ± 4 for C9A (Figure 15).
- (iv) The emission data allow the conclusion that, for low solvent-dipolarity ranges where these molecules do not undergo a TICT mechanism, the solvatochromic slopes indicate that the bathochromic band shift is significantly larger than that observed for the absorption data, showing the following negative slopes: -770 ± 41 for BA (Figure 12), -318 ± 33 for BC (Figure 13), and -435 ± 39 for BAC (Figure 14).
- (v) When at larger SdP values the TICT mechanism comes into play, the bathochromic shift of the emission bands increases significantly with the solvent's dipolarity,

leading to the following solvatochromic negative slopes: -3332 ± 35 for **BA** (Figure 12), -1643 ± 58 for **BC** (Figure 13), -7300 ± 447 for **BAC** (Figure 14), and -2207 ± 48 for **C9A** (Figure 15).

The data values given in (iv) and (v) foster the existence of an excited-state relaxation process, implemented in the analysis of the spectral informations observed, which involves a significant loss of vibronic structure of the emission bands of the four compounds studied, in which the basic chromophores anthracene, carbazole, and acridine are coupled to give the respective biaryl molecular structure. These results confirm the conclusions drawn from femtosecond pulse studies,^{34,35} which read as follows: "... in nonpolar solvents, the original mutually orthogonal anthracenyl units relax by torsional motions to a twist angle of about 70° , and the emitting state does not involve appreciable CT character".

The solvatochromic slopes m of the TICT process for the three symmetrical 9,9'-biaryl compounds **BA**, **BC**, and **BAC** are quite different from each other; however, they follow a linear relationship with the difference of the redox potentials ($\Delta E = E_D^{\text{ox}} - E_A^{\text{red}}$, with E_D^{ox} = oxidation potential of the electron donor, and E_A^{red} = reduction potential of the electron acceptor) for the electron donor/acceptor chromophores involved (Table 3 in ref 28), with the following correlation equation: $m = (4697 \pm 456) \cdot (E_D^{\text{ox}} - E_A^{\text{red}}) - 19483$ (with $n = 3$, $r = 0.9953$, and a standard deviation of $sd = 397$). The unsymmetrical 9,9'-biaryl compound **C9A** does not follow this equation because of its dipolar character, which is essential for the TICT mechanism, and that distinguishes its behavior from that of the other three 9,9'-biaryl compounds which are apolar.

At this point it should be emphasized that the results reached in this work on changing the temperature from 345 to 77 K of a biaryl solution in 1-chlorobutane (with the corresponding variation in medium dipolarity) are physically consistent with those obtained for biaryl solutions in pure solvents of different dipolarity at a constant temperature of 298 K. To prove this, the solvatochromism of **BA** and **C9A** (both measured in a wide range of pure solvents at 298 K²⁵) has been checked, taking into account that **BA** shows a clear-cut bilinear behavior (Figure 12) and, on the other hand, **C9A** a linear solvatochromic behavior (Figure 15).

Among the 60 solvents employed to study the normal solvatochromism of **BA** (the so-called a emission in ref 25), we have chosen 19 solvents with solvent dipolarity values SdP lower than 0.4 (i.e., perfluoro-*n*-hexane, 2-methylbutane, *n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, methylcyclohexane, *n*-hexadecane, *cis*-decalin, triethylamine, *p*-xylene, *o*-xylene, tri-*n*-butylamine, di-*n*-butyl ether, toluene, benzene, tetralin, diethyl ether, and 1,4-dioxane). To describe the TICT solvatochromism of **BA** (the so-called b emission in ref 25), 22 solvents with SdP values larger than 0.7 have been selected (i.e., *tert*-butanol, 1-propanol, 2-propanol, ethanol, methanol, acetonitrile, propionitrile, *n*-butyronitrile, benzonitrile, dichloromethane, pyridine, propylene carbonate, *N,N*-diethylacetamide, ethylene glycol, *N,N*-diethylformamide, *N*-methylimidazole, tetramethylurea, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, γ -butyrolactone, sulfolane, and dimethyl sulfoxide).

The normal solvatochromism of **BA** follows eq 1:

$$\tilde{\nu}_a = -(1782 \pm 167)SP - (651 \pm 139)SdP + (25354 \pm 108) \quad (1)$$

with $n = 19$, $r = 0.967$, and $sd = 70 \text{ cm}^{-1}$.

The TICT solvatochromism of **BA**, however, follows eq 2:

$$\begin{aligned} \tilde{\nu}_b = & -(2308 \pm 964)SP - (6560 \pm 848)SdP \\ & - (1211 \pm 363)SA + (951 \pm 361)SB \\ & + (29090 \pm 980) \end{aligned} \quad (2)$$

with $n = 22$, $r = 0.925$, and $sd = 302 \text{ cm}^{-1}$.

Equations 1 and 2 allow us to discount those solute/solvent interactions which are distinct from solute/solvent dipolarity interactions. Therefore, the normal emission solvatochromism for each solvent appears to be equal to $(\tilde{\nu}_a + 1782 \times SP)$, whereas the TICT solvatochromism yields $(\tilde{\nu}_b + 2308 \times SP + 1211 \times SA - 951 \times SB)$, thus enabling us to plot these solvatochromic variations against the corresponding SdP values of these solvents, as shown in Figure 16. By comparing Figure

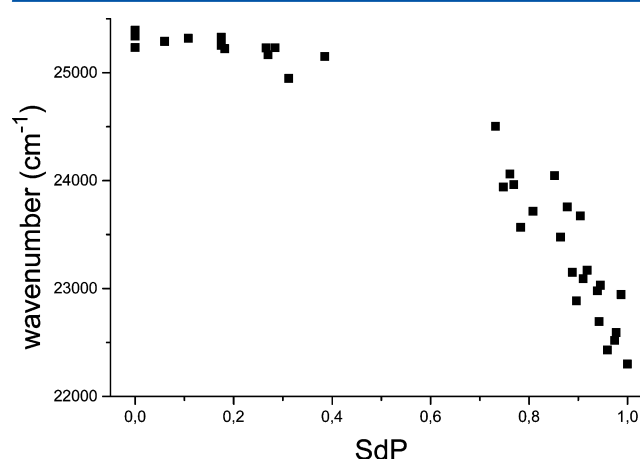


Figure 16. Bilinear correlation between the emission wavenumbers of **BA**, measured at 298 K and corrected as described in the text, and the solvent dipolarity parameter SdP .³⁰

12 (observed for 1-chlorobutane at different temperatures) with Figure 16 (obtained for different solvents at 298 K), one can draw the conclusion that both analyses are consistent, both showing a bilinear solvatochromic behavior of **BA** as the solvent dipolarity changes.

In addition, it should be mentioned that eqs 1 and 2 indicate that (i) the polarizability influence on the emission from the TICT excited structure of **BA** is significantly larger than that on the emission from the normal excited structure of **BA**, according to -2308 ± 964 (eq 2) vs 1782 ± 167 (eq 1), respectively, and (ii) the dipolarity influence on the TICT emission (at 298 K) is about 10 times larger than that of the normal emission, according to -6560 ± 848 (eq 2) vs -651 ± 139 (at 298 K; eq 1) or -770 ± 41 (by changing the temperature of a **BA** solution in 1-chlorobutane; Figure 12), and about twice than that of the TICT emission recorded by changing the temperature of a **BA** solution in 1-chlorobutane, corresponding to -3332 ± 35 (Figure 12).

The solvatochromic analysis of the **C9A** emission, measured in 55 solvents (i.e., 41 solvents as used for the analysis of the **BA** solvatochromism plus fluorobenzene, trichloromethane, ethyl acetate, 1-hexanol, 1-pentanol, 1-butanol, 1-propyl formate, dibenzyl ether, anisole, chlorobenzene, methyl benzoate, 1-chlorobutane, tetrahydrofuran, and 1,2-dichlorobenzene; extracted from ref 25) leads to eq 3:

$$\tilde{\nu} = -(2370 \pm 340)SP - (2393 \pm 91)SdP + (25563 \pm 236) \quad (3)$$

with $n = 55$, $r = 0.974$, and $sd = 224 \text{ cm}^{-1}$.

Equation 3 again allows one to subtract for **C9A** those solute/solvent interactions that are distinct from solute/solvent dipolarity interactions. As a result, the solvatochromism for each solvent corresponds to $(\tilde{\nu} + 2370 \times SP)$; a plot of this solvatochromism against the solvent dipolarity values SdP is shown in Figure 17. As can be seen, the correlation lines of Figures 15 and 17 show a consistent linear behavior on changing the solvent dipolarity.

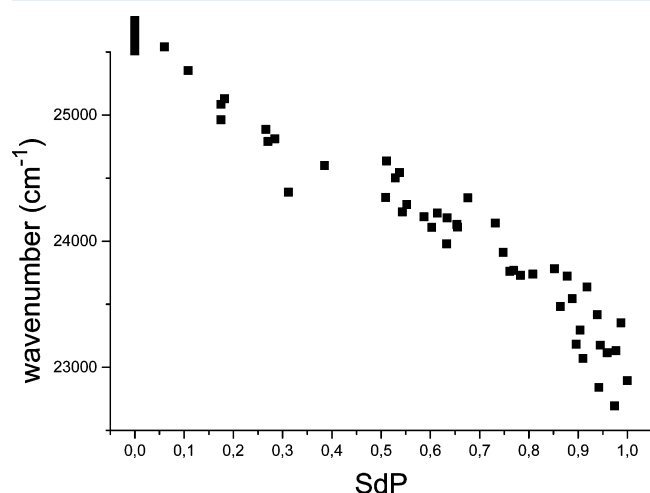


Figure 17. Linear correlation between the emission wavenumbers of **C9A**, measured at 298 K and corrected as described in the text, and the solvent dipolarity parameter SdP .³⁰

Although solvent polarizability and dipolarity perturb significantly the TICT emissions of **BA** and **C9A**, the TICT processes generate, in addition, cavity effects that may differ for solvents such as 1-chlorobutane as compared to solvents of different molecular structure. These contributions may shift the TICT emission to the red due to the instability caused by the solvation of the Franck–Condon ground state as function of the molecular structure of the solvents employed, which may help to discriminate both solvatochromic treatments.

On the Inter-ring Torsional Nature of the TICT Mechanism. The TICT mechanism was originally conceived as a torsional process which triggers an electronic charge-transfer between two chromophore fragments of the same molecule in the excited state, which is modulated by the polarity of the surrounding medium. However, frequently it was tried to analyze these mechanisms as generated by an electronic charge-transfer (CT) process between two chromophore fragments of the molecule which are not involved in any torsional rotation process.

To shed some light on this point, the emission spectrum of **BA** was measured in 1-chlorobutane at 293, 143, and 123 K (Figure 18). The spectrum at 143 K does not exhibit any vibronic structure and the emission band is significantly shifted to the red as compared to the spectrum measured at 293 K. Therefore, the emission spectrum measured at 143 K should come from a TICT or CT state. However, by lowering the sample temperature down to 123 K, the emission spectrum shows now a significant vibronic structure and sharp peaks

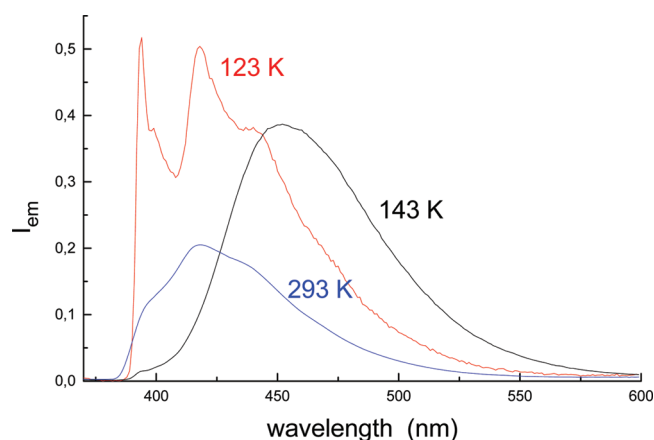


Figure 18. Emission spectrum ($\lambda_{\text{exc}} = 350 \text{ nm}$) of **BA**, dissolved in 1-chlorobutane ($c \approx 10^{-6} \text{ mol/L}$), measured at solution temperatures of 293, 143, and 123 K.

almost at the same wavelength positions as observed in the emission spectrum of **BA** measured at 293 K. A careful analysis of the emission spectra of Figure 18 allows the conclusion that, by decreasing the temperature of the 1-chlorobutane solution of **BA** from 293 to 143 K, the dipolarity of the medium increases significantly from $SdP = 0.560$ to 1.045 ,³⁰ and consequently, the TICT process is now switched on. Although by decreasing the sample temperature further from 143 to 123 K, the dipolarity of the medium is also further increased from $SdP = 1.045$ to 1.162 ,³⁰ the TICT process is stopped, and the emission band is hypsochromically shifted to the blue, now being located at the peak-maxima positions of the emission spectrum measured at 293 K (Figure 18). In other words, the process occurring in the excited state in the temperature range 293 to 143 K, yielding an emission band without vibronic structure and a bathochromic band shift, involves a distortion of the molecular structure which is unreachable at 123 K, a temperature at which the surrounding solvent matrix is so rigid that this distortion is obviously hindered. The dramatic increase in vibronic structure in the emission band of **BA** at 123 K, as compared to its emission spectrum at 293 K, should be emphasized, which supports the idea of a relaxation process experienced by **BA** in its first electronic excited state before emitting fluorescence.

From the three emission spectra of **BA** shown in Figure 18, that at 143 K can be taken as prototype for a TICT process, that at 293 K as prototype for a locally excited (LE) fluorescence emission, and that recorded at 123 K as pattern for a Franck–Condon state emission.

Taking into account the evidence mentioned before, a tentative photophysical diagram can be proposed for all four 9,9'-biaryl compounds studied in this paper (Figure 19).

CONCLUSIONS

The application of the solvent dipolarity scale SdP ^{17,30} is an excellent tool for the study of solution processes depending on the medium dipolarity, as demonstrated in this paper by the analysis of the solvent- and temperature-dependent photophysical behavior of the four 9,9'-biaryl compounds **BA**, **BC**, **BAC**, and **C9A**.

The loss of vibronic structure in the emission bands of these 9,9'-biaryl compounds can be ascribed to a TICT process if their emission bands exhibit a large bathochromic band shift. This allows to distinguish between the loss of vibronic structure

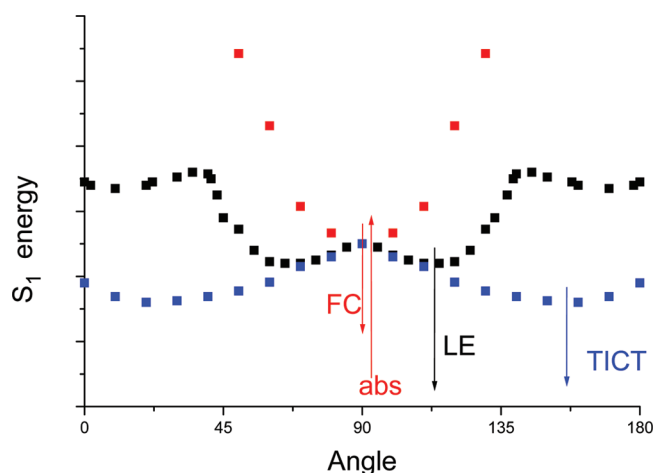


Figure 19. Tentative photophysical diagram for the angle dependence of the S_1 energy of the four 9,9'-biaryl compounds studied (angle = interplanar angle between the two aryl rings).

found for BAC: (i) as not caused by a TICT process below solvent dipolarity values of $SdP = 0.74$ and (ii) due to a TICT process for solvent dipolarity values of $SdP > 0.74$.

■ ASSOCIATED CONTENT

■ Supporting Information

Table S1 with all solvent SdP values available at present. This information is available free of charge via the Internet at <http://pubs.acs.org>

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