HAMMETT TYPE CORRELATIONS FOR INTRAMOLECULAR CHARGE TRANSFER (ICT) DIPOLE MOMENTS OF 4'-SUBSTITUTED 9-STYRYLACRIDINES IN THE GROUND STATE AND IN THE EXCITED STATE

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Abstract - 9-Styrylacridine(**1a**) and a series of 4'-substituted 9-styrylacridines (**1b-f**) (substituent : Me, OMe, NMe_2, Cl, NO_2) have been prepared to study their spectroscopic properties in several solvents of different dipolarity. They show strong Stokes shifts from the ground state to the S_1 excited state ($\Delta\bar{\nu} \approx$ - 5400 to – 8700 cm^{-1}) which denotes an important change of conformation in the fluorescing state. AM1 calculations suggest that the coplanarity increases in the S_1 state. The fluorescence spectra exhibit a positive solvatochromism, allowing the determination of excited state dipole moment (μ_E). Hammett correlations between σp and μ_G (ground state dipole moments) and μ_E respectively, show that the electronic influence of substituent on the internal charge transfer (ICT) is *ca.* 3 times stronger in the S_1 excited state than in the ground state.

INTRODUCTION

There has been a sustained interest in the study of 9-styrylacridines, especially their 4'- substituted derivatives[1] for applications as photoinitiators for photopolymerizable copying materials,[1] UV stabilizers in polymers,[2] charge transfer agents in electrophotography,[3] electric insulator components,[4] and as additives for electrets in polymers.[5] They also have been used for the determination of water content in solvents,[6] as optical sensors (optodes) in PVC membranes for continuous monitoring of silver ion[7] and pH indicators for the near IR region.[8] Such compounds were proposed also for solar energy storage in the visible region on account of an unusual enthalpy of Z / E conversion.[9]

Recently, Grummt and coworkers have prepared and studied a series of 9-(4'-dialkylaminostyryl)acridines as pH sensitive sensitizers for the photodynamic therapy of cancer[10] and performed an extensive spectroscopic and photochemical investigation of 4'-diethylamino-9 styrylacridines and four of their derivatives.[11] The charge transfer intensity is reflected in the value of the dipole moment which, for this family of compounds, is known to increase in the excited state. To our knowledge, no other extensive study of this sort has been devoted to other substituted 9-styrylacridines. Because of the widespread interest of these compounds, we set out to investigate the influence of substituents in 4' position of **1b-f** (substituent : Me, OMe, NMe$_2$, Cl, NO$_2$) (Scheme 1) on the spectroscopic properties.

In this paper, we report the electronic absorption and fluorescence spectra of **1a-g** in solvents of different polarity in order to study their solvatochromic properties and, given that the substituents in *para* positions are devoid of significant steric influence, establish quantitative relations between the dipole moments and the electronic properties of the substituents.

1	X	R
a	H	H
b	Me	H
c	OMe	H
d	NMe$_2$	H
e	Cl	H
f	NO$_2$	H
g	OMe	OMe
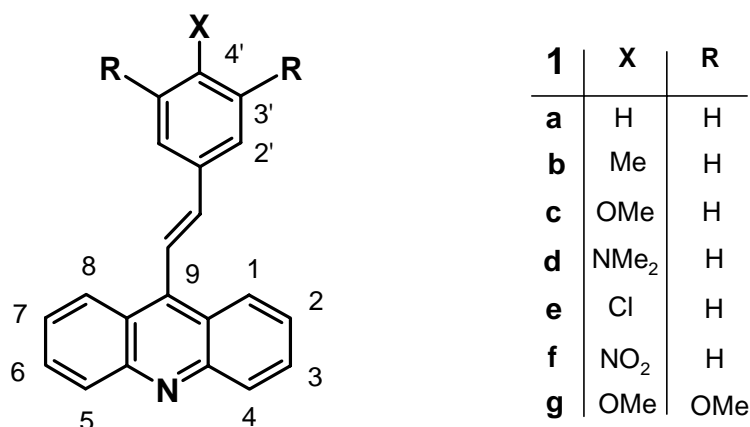
Scheme 1

SYNTHESIS AND STRUCTURE

Compounds (**1a-f**) were prepared using a known method, described by Ogata *et al.*[12] It consists of refluxing a mixture of 9-methylacridine and the relevant *para*-substituted benzaldehyde in the presence of acetic anhydride and acetic acid (Scheme 2). The present procedure has been found to be very convenient but the yields have not been optimised (see EXPERIMENTAL).
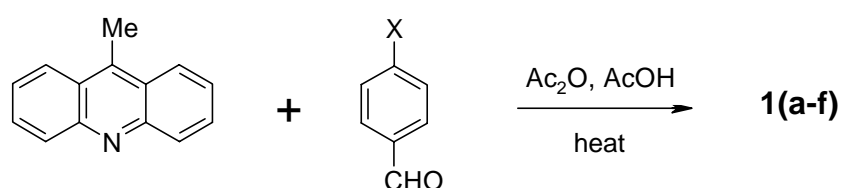
Scheme 2: Synthetic pathway for the preparation of 4'-substituted 9-styrylacridines

Some of these compounds have been prepared by other authors who proposed different methods.[2,13a,b] The spectral characteristics have been found to be in agreement with the structure. Of particular interest is the coupling constant J_{HH} for the ethylenic hydrogen atoms found to be $\approx$ 17 Hz for all derivatives which points to an *E* configuration. A deeper insight into the molecular geometry is provided by the X-Ray structure analysis of **1a** (*vide infra*) but it was not possible to obtain single crystals suitable for structure determination of **1b-f**.

The trimethoxy derivative (**1g**) was prepared using the same method (see EXPERIMENTAL) with the purpose of increasing the ICT intensity in increasing the number of donating substituents (and not merely by changing their nature) but **1g** was excluded from the Hammett correlation because of the steric interference between the adjacent substituents.

UV-VIS ABSORPTION SPECTROSCOPY

Electronic absorption transitions of acridines have been assigned by several authors[14,15] who showed that they resemble those of anthracenes and are situated in the 250-390 nm spectral region.

The *E*-9-styrylacridines (**1a-f**) present similar UV absorption bands which are structured and, in addition, an unstructured intramolecular charge transfer (ICT) in the VIS spectral region. Some of the compounds investigated in this work have been examined by others but not with the purpose of comparing the influence of the *para* substituents on the absorption and on the emission properties. This is illustrated in Figure 1 where the absorption spectra of **1a** are displayed in several solvents of different polarity {methylcyclohexane (MCH), acetonitrile (AN) and methanol}; the solvents properties have no *significant*

effect on the ICT transition whose $\lambda_{max} \approx 380$ nm. The spectra were recorded at a concentration (10^{-5} M) where Beer's law is obeyed.[11] In the presence of carboxylic acid, the acridine nitrogen is protonated and the absorption spectrum is known to be shifted to long wavelengths,[10a,11] a phenomenon called "acidichromism". For **1a**, the ICT band is shown to undergo a sizable bathochromic shift (λ_{max} 380 to 445 nm: $\Delta\bar{v} \approx -3800$ cm^{-1}). Bathochromic shifts are expected to be enhanced by an increased conjugation between the donating styryl part (with X = OMe and NMe$_2$) and the acridyl electron accepting moiety, as shown in Figure 2. Similar effects were noticed for **1g**.
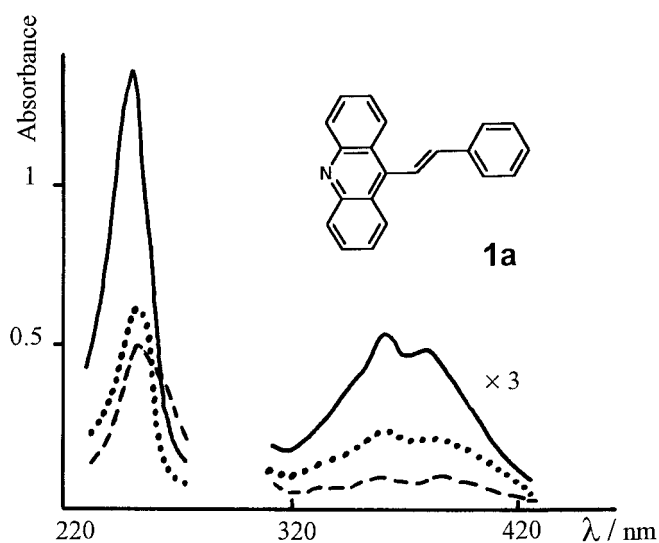

Figure 1: UV-VIS absorption spectra of *E*-9-styrylacridine (**1a**) in methylcyclohexane (MCH) (- - - -), MeOH (•••••) and MeCN (——), conc.$\approx 10^{-5}$M at ambient temperature.
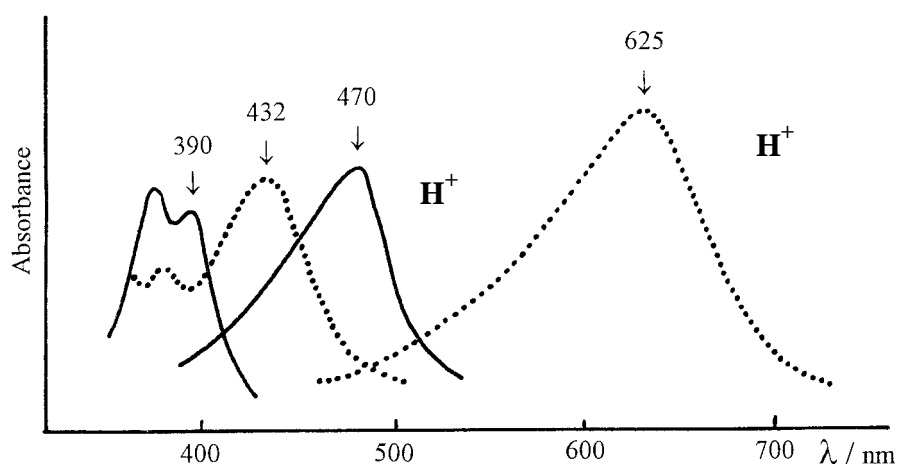

Figure 2: absorption spectra of **1c** (X = OMe)(—) and **1d** (X = NMe$_2$) (•••••), conc.$\approx 10^{-5}$M at ambient temperature in neutral and acidic (CF$_3$CO$_2$H) acetonitrile, respectively; the acidic form being redshifted: $\Delta\bar{v}$ (**1c**) ≈ -4400 cm^{-1}; $\Delta\bar{v}$ (**1d**) ≈ -7100 cm^{-1}.

However no change was noticed for the nitro derivative (**1f**) where λ_{max} (CT) was observed at 380 nm in neutral or acidic acetonitrile. The sensitivity to solvent polarity, although not marked for the other compounds of the series, is nevertheless clearly noticeable for the dimethylamino derivative (**1d**) as shown in Figure 3.
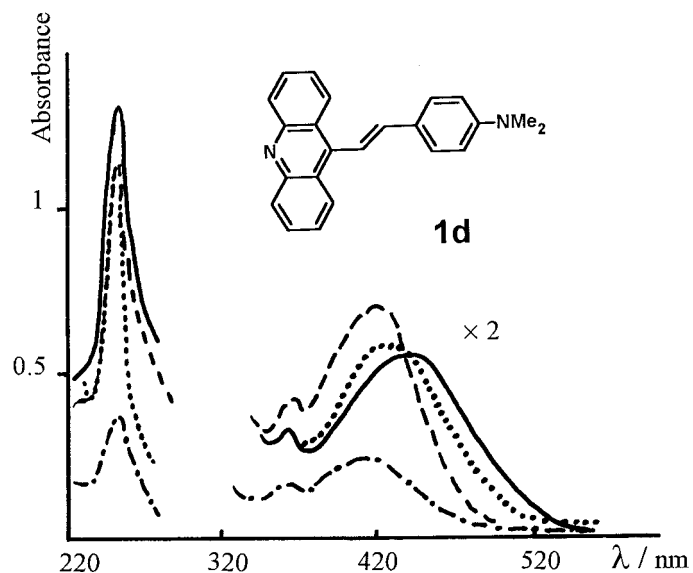

Figure 3: Absorption spectra of **1d**, conc.≈ 10^{-5}M at ambient temperature in different solvents.

λ_{max}(nm) in methylcyclohexane (MCH) (— · — ·): 411, in Et$_2$O (—   —   —) : 413,

in MeOH (•••••): 422 and in MeCN (——) : 432.

GROUND STATE STRUCTURE AND DIPOLAR MOMENTS

The X-Ray structure analysis of **1a** (*E* configuration) has been published.[16] A salient feature is the non coplanarity between the double bond and the acridine nucleus; the dihedral angle ϕ_1 (see Scheme 3) was found to be 55°5. Grummt found an angle of *ca.* 60° as a result of AM1 calculation[11] on the para NEt$_2$ derivative of **1** (X = NEt$_2$) which is closely related to **1d**.

We have applied the semi-empirical method AM1[17a] to determine the angles ϕ_1 and ϕ_2, the calculation of ground state dipole moments μ_G (See Table 1). The ZINDO program[17b] was used to calculate the first electronic transition of the UV absorption spectra. The results indicate that the latter is essentially of HOMO-LUMO nature except for X = NO$_2$ where it was found to be partly HOMO-LUMO (40%) and partly HOMO-LUMO + 1 (48%) in character.
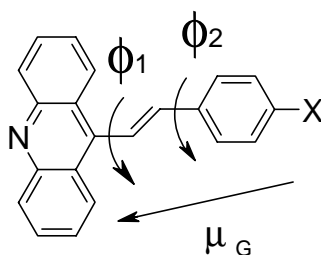
Scheme 3: Ground state structure of **1**. ϕ_1 denotes the rotation of the acridine nucleus (considered to be planar) around the single bond to the central ethylene group; ϕ_2 denotes the rotation of the *para*-substituted benzene ring around the single bond to the central ethylene group. ϕ_1: 55.5° and ϕ_2 : 169.2° were found by X-Ray structure analysis for X = H.

Table 1: Calculated ground state dipole moments (Debye units) of **1a-f** using
the semi-empirical AM1 method[17a]

X	H	Me	OMe	NMe$_2$	Cl	NO$_2$
μ_G	2.44	2.82	3.00	4.51	0.95	-3.86

The calculated ground state dipole moments seem in reasonable agreements with literature data for pyridine[18a] or stilbene[18b] derivatives observed dipole moments except that the dipole moment of **1c** (X = OMe) appears to be underestimated.

FLUORESCENCE SPECTROSCOPY

The fluorescence spectra of **1a-g** recorded in MCH, Et$_2$O, MeOH and AN display an important stokes shift ($\Delta \bar{v} \approx$ - 5400 to - 8700 cm^{-1}) and positive solvatochromism. The latter is illustrated for **1a**, **1d** and **1f** in Figures 4, 5 and 6, respectively.

There is no distinct dual fluorescence observed and, in agreement with Grummt, who did not find a rise time in the fluorescence kinetics for X = NEt$_2$, there is no necessity to interpret the emission in terms of a twisted intramolecular charge transfer (TICT).[11,20]
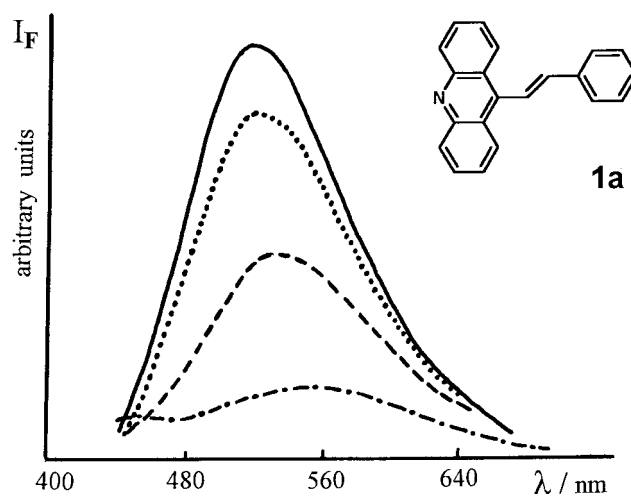
Figure 4: Fluorescence spectra (not scaled) of **1a**, conc. $\approx 10^{-5}$M at ambient temperature, $\lambda_{exc.}$ 390 nm, in MCH (——), Et$_2$O (•••••), MeOH (— — —), and MeCN (— · — ·)
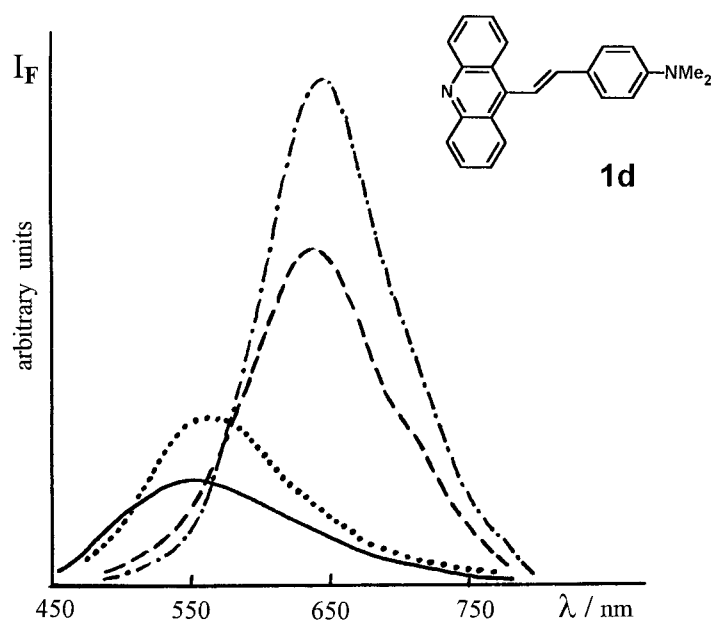

Figure 5: Fluorescence spectra (not scaled) of **1d**, conc. $\approx 10^{-5}$M at ambient temperature, $\lambda_{exc.}$ 390 nm, in MCH (——), Et$_2$O (•••••), MeOH (— — —), and MeCN (— · — ·)

The strong experimental bathochromic shift is likely to be due to an increase of the degree of conjugation between the benzene and the acridine nuclei through the double bond. This is supported by the results of AM1 calculations.[17a] They show that the ϕ_1 dihedral angle decreases from $\approx 54°$ (in the ground state) to $\approx 23°$ (in the S$_1$ excited state); in parallel the ϕ_2 angle increases from $\approx 154°$ to $\approx 176°$ (for **1a-f**, the

calculated ϕ_1 angles were found to be in the range 53.7-55.5° and ϕ_2 angles between 146-153.7°, respectively). Even if the method is somewhat crude to describe accurately the excited states, the results point to an increased degree of coplanarity for **1a-f**.
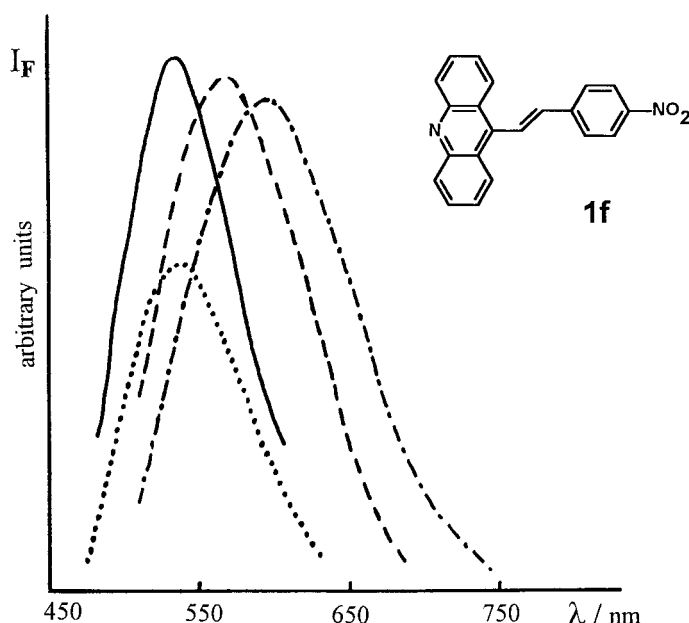

Figure 6: Fluorescence spectra (not scaled) of **1f**, conc. $\approx 10^{-5}$M at ambient temperature, $\lambda_{exc.}$ 390 nm, in methylcyclohexane (——), Et$_2$O (•••••), MeOH (— — —), and MeCN (— · — ·)

The fluorescence quantum yields (Table 2) were found to be low ($\phi_F \approx 0.01$ - 0.09) as expected for ethylenic compounds that are known to undergo radiationless relaxation to S_0 and *E / Z* isomerization. The ϕ_F values for **1a** are of the same order of magnitude as those found by Mazzucato and coworkers.[24]
In acidic media (in the presence of CF_3CO_2H), the quantum yields were found to be still lower (*ca.* 2 to 5 fold) than in neutral media and no fluorescence was detected for **1d**.

Table 2: Fluorescence quantum yields ϕ_F of **1a,c,d,f,g** at ambient temperature (non degassed samples)

	MCH	Et$_2$O	MeOH	AN
1a	0.03_5	0.05_6	0.01	0.01_1
1c	0.01_2	0.01_8	0.01	0.02_8
1d	0.03_4	0.09_6	0.02_1	0.05_4
1f	0.02_4	0.02_7	0.01_8	0.01
1g	0.03_9	0.05_9	0.01_6	0.01_4

EXCITED SINGLET STATE DIPOLE MOMENTS DETERMINATION AND HAMMETT CORRELATIONS

Lippert[21] and Mataga[22] derived equations, based on Onsager's theory,[23] allowing the determination of excited singlet state dipole moment (μ_E) from fluorescence solvatochromism. We have selected Mataga's equation (1) which takes into account the reorganization of the solvent molecules in the fluorescent state :

$$\bar{v} = -2\mu_E (\mu_E - \mu_G) \Delta f'/hca^3 + \text{constant} \qquad (1)$$

where $\bar{v}$ = maximum fluorescence wavenumbers, h = Planck constant, c = light rate and a = radius of the molecule considered as spherical by Onsager.[23]

$$\Delta f' \text{ (polarity parameter)} = (\varepsilon-1)/(2\varepsilon +1) - \tfrac{1}{2} (n^2-1)/(2n^2 + 1)$$

The experimental maximum fluorescence wavenumbers and the calculated 'a' values are tabulated in the experimental section (Table 4). From the slope of the straight line obtained in plotting $\bar{v}$ *vs* $\Delta f'$, and using the calculated ground state dipole moments (μ_G, Table 1), the μ_E values were derived. They are listed in Table 3 together with the σp Hammett constants.[25]

Table 3: Singlet excited state dipole moments determined from fluorescence solvatochromism of **1a-f** in Debye (D) and σp Hammett constants of the X groups[25]

X	NMe$_2$	OMe	Me	H	Cl	NO$_2$
μ_E (D)	17.5	7.8	9.9	6.1	7.9	-12.5
σp	-0.83	-0.27	-0.17	0.00	+0.23	+0.78

Finally, the Hammett plots for the ground state (μ_G) and the excited state (μ_E) were derived. Hammett constants σ rather than Brown constants (σ^+) or (σ^-) were selected because the charge transfer is partial due to the compounds not being planar. One can speculate that for X = NMe$_2$, the nitrogen to nitrogen distance being 10-11 Å, for a complete electron transfer, the expected dipole moment would be $10.5 \times 4.8 = 50.4$ Debye. The value obtained (Table 3) is 17.5D, *ca.* $\tfrac{1}{3}$ of the theoretical value. The plots are shown in Figures 7 and 8.
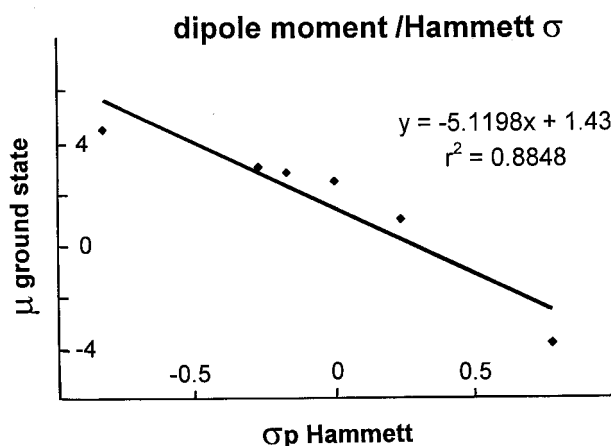
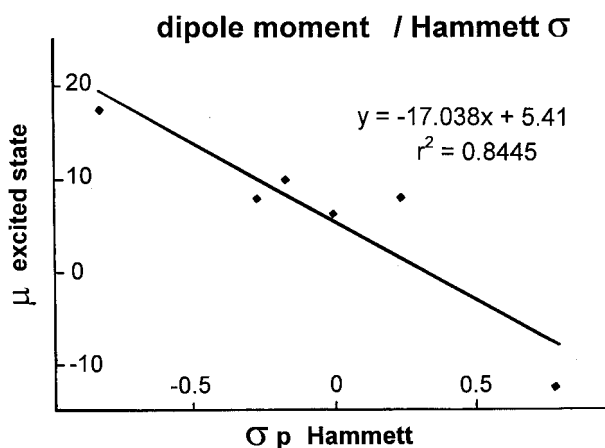Figure 7: Graph of the ground state dipole moment *vs* Hammett constant

Figure 8: Graph of the excited state dipole moment *vs* Hammett constant

The correlation coefficients seem satisfactory, given the difficulty to determine the ICT maximum wavelengths with accuracy and the theoretical approximations (μ_G calculation, Onsager's theory) especially in the fluorescent state. The polarity parameter ($\Delta f'$) does not always fit very well as making no difference between MeCN and MeOH (H-bonding is not taken into account).

The main result emerging from these correlations is the clear influence of the electronic properties of the *para*-substituents on the spectroscopic response, and this, about 3 times more in the excited than in the ground state (ratio of the two slopes: (μ_E *vs* σp) / (μ_G *vs* σp) = 17.04/5.12 = 3.33). This is due to an increase (conjugation) electronic delocalisation in the S_1 state which is the result of a more planar geometry as reflected in the decreased Stokes shift.

Related to our work, one may cite a report on the fluorescence of 9-arylacridinium by Verhoeven and coworkers,[26] a study by Darling and coworkers[27] on the effect of temperature and viscosity on the fluorescence of 4-p-dimethylaminostyrylpyridinium salts as well as the investigation in depth of the

solvent influence on the photophysical properties of styrylcyanine dyes by Abdel-Mottaleb *et al.*[28] But these studies concern molecular cations and not neutral molecules and none of these has addressed a systematic comparison of the electronic influence of the para substituents.

CONCLUSION

Despite experimental uncertainties and the approximations of the Lippert-Mataga formula based on the electrostatic theory of Onsager, it has been shown that the fluorescence solvatochromism of a series of 4'-substituted 9-styrylacridines strongly depends on the electronic properties of the substituents; quantitative relations based on plots between excited state and ground state dipole moments, respectively *vs* Hammett σp indicate that the excited state sensitivity to electronic effects is about three fold that of the ground state.

EXPERIMENTAL

Equipment and General Procedure: Melting points were measured using capillary tubes (Büchi). Thin layer chromatography was effected on silica gel 60 F254 spread on alumina foils. Column chromatography was performed with silica gel 60 70/230 mesh. NMR spectra were recorded with Varian EM 360 (60 MHz) and Bruker Spectrospin AC 200 (200 MHz); δ is in ppm from TMS using the residual solvent signal as an internal reference. IR spectra (KBr pellets 1%) were taken with Pye-Unicam SP3-300 and 1600. MS spectra were recorded with a NERMAG R10-LOC [electronic impact (EI), chemical ionisation (Cl, NH_3) or fast atom bombardment (FAB)]. UV-VIS spectra were recorded on a Hitachi U-3300 Spectrophotometer and emission spectra on a Hitachi F-4500 Fluorescence Spectrofluorometer corrected for emission and excitation, respectively. The samples used for fluorescence studies were purified by HPLC (HP 1100 fitted with a Chromasil C18 column, eluant water-acetonitrile gradient). The maximum wavenumbers were plotted *versus* Δf' and the slope of the linear plots are listed in Table 4. A microbalance (Mettler UM3, sensitivity 0.1 μg) was used to weigh the sample to be dissolved in spectroscopic grade solvents for spectroscopic measurements. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest. The *fluorescence quantum yields* were determined by comparison with quinine sulfate in $1N-H_2SO_4$ (ϕ_F = 0.55 at $\lambda_{exc.}$ 370 nm) as the standard[29,30] and a refraction index correction was effected.[30] For each case the *excitation spectrum* was found to be similar to the absorption spectrum at room temperature.

Table 4 : Fluorescence maxima wavenumbers in MCH, Et$_2$O, AN and MeOH for **1a-f**, slope and correlation coefficient (r^2) of the linear plot of $\bar{v}$ *vs* Δf^i. The "radius" "a" = 0.4 × ρ; ρ is the calculated length of molecules (**1**) along the highest conjugated path (for ellipsoidal molecules, Lippert[21] recommends to take 40% ρ).

compound	Fluorescence $\bar{v}$ max (cm^{-1})				Slope $\bar{v}$ /Δf'(cm^{-1}) (r^2)	a(Å)
	MCH	Et$_2$O	AN	MeOH		
1a	19267	19193	18867	18867	-1342 (0.89)	5.6
1b	18083	17992	17129	16683	-4008 (0.77)	5.7
1c	18552	18348	17762	18050	-2129 (0.84)	5.7
1d	18182	17575	15385	15576	-9018 (0.90)	6.4
1e	18369	18315	17787	17212	-2969 (0.67)	5.8
1f	18657	18518	16611	17606	-5253 (0.68)	6.0

$^i\Delta f$' = 0.08 (MCH); 0.25 (Et$_2$O) ; 0.392 (AN) ; 0.393 (MeOH)

Semi-empirical calculations: Due to the size of the molecular systems studied, the semi-empirical AM1 Hamiltonian proposed by Dewar *et al.*[17a] was selected to calculate the ground state dipole moment as well as the optimized equilibrium geometries in the ground state and in the singlet excited state. The standard parameter set available in MOPAC was used for the calculations, with the exception of the electronic transition moments which were calculated using INDO/S-SCF/CI as parametrized by Ridley and Zerner.[17b] Uncertainties in the calculated excited state geometries and long calculation times prevented direct calculation of the excited state dipole moment for all the compounds investigated.

Syntheses: 9-methylacridine and the *para*-substituted benzaldehydes used in this study are commercially available.

General procedure: 9-Methylacridine (1.5 g, 7.8 mmol), acetic anhydride (1.63 g, 16 mmol) and acetic acid (0.96 g, 16 mmol) were stirred and heated in a round bottom flask equipped with a reflux condenser

and a dropping funnel; when the temperature reached *ca.* 50°C, the benzaldehyde (4-XC$_6$H$_5$CHO, x mmol) was added dropwise; then the mixture was refluxed under stirring for 5 h. After cooling, the medium was neutralized with sodium carbonate and extracted with dichloromethane; the organic solution was dried with sodium sulfate and evaporated in *vacuo*. The solid was chromatographed on silica gel.

9-Styrylacridine (**1a**)

From benzaldehyde (0.83 g, 7.8 mmol) a yellow solid, mp 186-188°C (lit.,[13a] 184-186°C, lit.,[13b] 184-185°C), 1.2 g (55%) was obtained after chromatography (eluant: hexane/dichloromethane 1/1). ^{1}H NMR (200 MHz; CDCl$_3$) δ 6.96-8.30 (m, 15 H); IR (KBr) 2990, 1564, 1245, 970, 757. MS (EI) m/z 281 M$^+$, 100%, (IC/NH$_3$) 282 (M + H$^+$), 100%. Anal.Calcd for C$_{21}$H$_{15}$N: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.82; H, 5.40; N, 5,00.

9-(4-Methylstyryl)acridine (**1b**)

4-Methylbenzaldehyde (0.95 g, 79 mmol), after chromatography (eluant: hexane/dichloromethane 1/1) led to 0.82 g (35%) of a yellow microcrystalline solid, mp 189-190°C (lit.,[13b] 191-192°C). ^{1}H NMR (200 MHz) δ 2.40 (s, 3H); 6.90-8.30 (m, 14H). IR (KBr) 3073, 2960, 1470, 1250, 1180, 1080, 980, 810, 675. MS (IC, NH$_3$) 296 (M + H$^+$, 100%). Anal.Calcd for C$_{22}$H$_{17}$N: C, 89.46; H, 5.80; N, 4.74. Found: Anal.Calcd for C, 89.08; H, 5.82; N, 4.76.

9-(4-Methoxystyryl)acridine (**1c**)

From 4-methoxybenzaldehyde (1.3 g, 9.5 mmol), after chromatography (eluant: hexane/dichloromethane 1/1), 0.6 g (25%) of a pale yellow solid was isolated, mp 174-176°C (lit.,[13b] 195-196°C). ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.00 (s, 3H); 6.75-8.40 (m, 14H); IR (KBr) 2994, 1602, 1506, 1245, 1173, 1033, 970, 751 cm^{-1}. MS (EI) m/z 311 (M$^+$, 100%), 280 (33), 267 (35), 203 (36). Anal.Calcd for C$_{22}$H$_{17}$NO: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.96; H, 5.50; N, 4.52.

9-(4-N,N-dimethylaminostyryl)acridine) (**1d**)

4-*N,N*-Dimethylbenzaldehyde (0.8 g, 5.37 mmol) provided after chromatography (eluant: hexane/dichloromethane 1/4), 0.4 g (23%) of a red powder, mp 260-262°C (lit.,[10a] 240°C). ^{1}H NMR (200 MHz, CDCl$_3$) 3.90 (s, 6H); 6.95-8.35 (m, 14H). IR (KBr) 3080, 2922, 1603, 1521, 1361, 1185, 757. MS (EI) m/z 324 (M$^+$, 100%), 309 (59), 280 (27), 204 (28). Anal.Calcd for C$_{23}$H$_{20}$N$_2$: 85.15; H, 6.21; N, 8.63. Found: C, 85.30; H, 6.22; N, 8.73.

9-(4-Chlorostyryl)acridine (**1e**)

From 4-chlorobenzaldehyde (0.73 g, 5.2 mmol) compound (**1e**), 0.62 g (38%) was isolated as a yellow solid, mp 224-226°C, after chromatography (eluant: hexane/dichloromethane 1/1). ^{1}H NMR (200 MHz) δ 7.25-8.35 (m, 14H). IR (KBr) 3070, 3000, 1560, 1440, 1040, 969, 760, 740 cm^{-1}. MS (EI) 317 (M$^+$, 33%), 315 (M$^+$, 100%), 280 (81), 204 (35). Anal.Calcd for $C_{21}H_{14}NCl$: C, 79.87; H, 4.47; N, 4.44. Found: C, 80.10; H, 4.28; N, 4.36%.

9-(4-Nitrostyryl)acridine (**1f**)

4-Nitrobenzaldehyde (1.2 g, 79 mmol) provided after chromatography (eluant: hexane/dichloromethane 1/4), 0.8 g (31%) of a yellow solid, mp 285-288°C (lit.,[13b] 291-292°C). ^{1}H NMR (200 MHz) δ 7.00-8.50 (m, 14H). IR (KBr) 3075, 2980, 1550, 1477, 1146, 1098, 996, 805, 675. MS (EI) m/z 326 (M$^+$, 100%), 278 (55), 204 (42). Anal.Calcd for $C_{21}H_{14}N_2O_2$: C, 77.28; H, 4.32; N, 8.58. Found C, 77.43; H, 4.31; N, 8.54.

9-(3,4,5-Trimethoxystyryl)acridine (**1g**)

From 3,4,5-trimethoxybenzaldehyde (0.97 g, 4.95 mmol), after chromatography (eluant: hexane/dichloromethane 1/1), 0.6 g (32%) of a yellow powder, was isolated, mp 172-174°C. ^{1}H NMR (200 MHz) δ 4.00 (s, 9H); 6.85-8.55 (m, 14H). IR (KBr) 3060, 2995, 1580, 1502, 1323, 1117, 1010, 751. MS (EI) m/z 373 (M$^+$, 100%), 356 (29); 241 (21). Anal.Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found C, 77.22; H, 6.24; N, 3.96.

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