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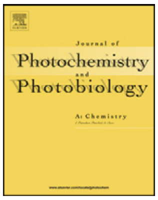

Charge transfer fluorescence of *trans*-stryrylpyridinium iodides

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ABSTRACT

The photoprocesses of *trans*-1-methyl-4-[4-R-styryl]pyridinium iodide (R = H, P1) and derivatives with a cyano, a nitro and a methoxy group at the phenyl moiety, P2–P4, respectively, were studied in solution. In solvents of relatively low polarity, e.g. tetrahydrofuran, where contact ion pairs are present, the fluorescence spectrum of the styrylpyridinium is significantly red-shifted and the quantum yield is strongly enhanced. These findings are due to photoinduced electron transfer from I^- to the excited singlet state of the cation. The features of complementary *trans*-styrylquinolinium iodides are in good accordance.

1. Introduction

The photophysical and photochemical properties of quaternary azastilbenes (also denoted as stilbazolium salts) in solution are the subject of various studies [1–9]. Several iodides of the structural type *trans*-1-methyl-4-[4-R-styryl]pyridinium ($+A_t$-R) with R: H, cyano, nitro, methoxy (P1, P2, P3, P4, respectively) have been investigated [4–7]. Quaternary dialkylaminoazastilbenes, such as *trans*-1-methyl-4-[4-dimethylaminostyryl]pyridinium iodide (P-NMe_2), have frequently been applied as fluorescence sensors [10–18]. UV irradiation of the *trans*-isomer of parent P1 yields the *cis* isomer, but this does not take place for P-NMe_2 [9]. The quantum yield (Φ_c) of *trans* → *cis* isomerization of the iodides P1–P4 as well as the perchlorates (P′1–P′4) in a polar solvent, such as acetonitrile or water, is $\Phi_c = 0.4–0.5$ [4–7]. A similar mechanism has been reported for styrylquinolinium salts [4–9].

Other photochemical studies deal with related betaines, e.g. *trans*-1-methyl-4-[4-R-styryl]pyridinium, R = OH, for which, in aqueous solution, an equilibrium between the hydroxide and the deprotonated forms with $pK_a = 8.5$ has to be considered [19–21]. Characteristic spectroscopic properties of styrylaromatic salts have been reviewed [1,2]. Photodimerization is another photoprocess of quaternary azastilbenes [22]. The non-linear optical properties of styrylpyridinium ions are the subject of various studies [23,24]. The properties of photochromic molecules and materials and the ion-pair charge transfer (CT) complexes have been summarized [24]. Photoinduced electron transfer can play a decisive role when the anion is iodide, in contrast to perchlorates or other innocent anions [2,5]. The spectroscopy of specific pyridinium iodides is of special interest, because these salts exhibit an intermolecular CT absorption band [25–30]. The CT interaction is also the subject of various studies concerning salts with aromatic cations [31–33]. The intermolecular CT fluorescence is a rare phenomenon in the literature [34].

Here, the photophysical CT properties of iodides of *trans*-1-methyl-4-[4-R-styryl]pyridinium with R: H, CN, NO_2 and OMe, P1–P4, respectively, and *trans*-1-methyl-4-[4-R-styryl]quinolinium iodides with R: H, NO_2 and OMe (Q1, Q3, Q4) were studied. The fluorescence maxima of most iodides in solvents of low polarity are strongly red-shifted, especially for P3 and Q3. The corresponding perchlorates (P′1–P′4) and (Q′1, Q′3, Q′4) show no CT effects and were used for the purpose of comparison, Chart 1.

2. Experimental

The salts were the same as used previously [3–9]. The molar absorption coefficients in methanol solution are $\varepsilon_{348} = 2.5 \times 10^4$ and $\varepsilon_{370} = 2.4 \times 10^4\ M^{-1}\,cm^{-1}$ for P1 and P4, respectively [7]. The solvents (Aldrich, Merck) were of the purest spectroscopic quality, methyltetrahydrofuran (MTHF); dioxane, tetrahydrofuran (THF), dichloromethane, dimethyl sulfoxide (DMSO) and acetonitrile were Uvasol quality. The absorption spectra were monitored on a diode array spectrophotometer (HP, 8453). The iodides were dissolved in THF either by using a DMSO stock solution (<1%) or with ultrasound. In the former case, the absorption spectra change

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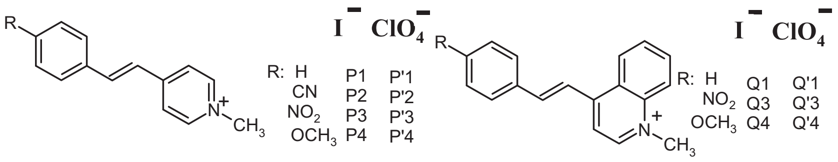

Chart 1.

with time (in the 1–200 min. range) in the manner that the CT absorption bands (A_{CT}) at 280–300 and ca. 450 nm became maximum. On the other hand, a too long storage (>1 d) was found to decrease both A_{CT} and the fluorescence intensity markedly. A spectrofluorimeter (Varian Cary, eclipse) was employed to measure the fluorescence spectra. The quantum yield of fluorescence was obtained using 9,10-diphenylanthracene in air-saturated cyclohexane ($\Phi_f = 0.6$) and rhodamine 101 in ethanol ($\Phi_f = 0.9$) as references. The quantum yield Φ_c of *trans* → *cis* isomerization was obtained using P1 in argon-saturated acetonitrile as reference, $\Phi_c = 0.5$ [7]. The ratio of absorption coefficients $\varepsilon_t/\varepsilon_c$ and the quantum yields of *cis* → *trans* and *trans* → *cis* photoisomerization are:

$$\left(\frac{cis}{trans}\right)_0 = \frac{\varepsilon_t \times \Phi_c}{\varepsilon_c \times \Phi_t} \qquad \text{(I)}$$

Electrochemical measurements were performed in an air-tight cell under an argon atmosphere in anhydrous acetonitrile with Bu_4NPF_6 as the supporting electrolyte, using a potentiostat (EG&G, 273A) with a 0.01 N $AgNO_3/Ag$ in acetonitrile as reference electrode. Glassy carbon disk electrodes served as working and counter electrodes. The potentials are given as peak potentials of square wave voltammograms vs. ferrocene/ferrocenium values: $-E^{\circ\prime} = 1.34$, 1.19, 1.14 and 1.40 V for P1–P4, respectively. The measurements refer to 24 °C.

3. Results

3.1. Absorption

The absorption spectra of *trans*-styrylpyridinium salts in polar solvents, e.g. acetonitrile or ethanol, have maxima (λ_t) at 340–380 nm. The peak at $\lambda_t = 344$ nm is the same for either P′1 or P1, but the iodide absorbs weekly at 450 nm, in contrast to the perchlorate. An example of the thermal absorption changes in THF is shown in the inset of Fig. 1. The absorption at 280 and 450 nm increases with time and at λ_t decreases. These changes become minor after a few h. As a measure of this CT absorption, the relative contribution A_{450}/A_{max} is given in Table 1; this ratio is 0.002–0.1 in THF and much smaller in dichloromethane. An example of the concentration effects is shown in the inset of Fig. 2, indicating the absence of aggregation.

Table 1
Maximum of *trans* isomer, isosbestic point, relative CT absorption and quantum yield of *trans* → *cis* isomerization.[a]

Comp.	Solvent	λ_t (nm)	λ_i (nm)	A_{450}/A_{max}	Φ_c[b]
P′1	THF	344	305	<0.001	0.5
P1	THF	344	310	0.10	0.03
	Dichloromethane	357	302	0.002	0.012
	Acetonitrile	343	290	<0.001	0.5
P′2	THF	344	310	<0.001	0.5
P2	THF	344	310	0.09	0.03
P3	THF	343	303	0.10	0.02
	Dichloromethane	345	310	0.002	0.07
	Acetonitrile	338	300	<0.001	0.4
P4	THF	360		0.09	0.4
Q1	THF	375		0.10	0.4
Q3	THF	374	313	0.09	0.005
	Acetonitrile	372	314	<0.001	0.4

[a] In air-saturated solution.
[b] Under argon using $\lambda_{irr} = 366$ nm.

Photolysis of a *trans* isomer leads to the *cis* isomer and eventually a photostationary state, the latter of which results from a further decay pathway, i.e. of the singlet-excited *cis* isomer leading to the *trans* and *cis* isomers. For a given *trans*-styrylpyridinium iodide Φ_c is substantial in acetonitrile but smaller in dichloromethane and very small in THF. The time dependence of A_{350} indicates the efficient *trans* → *cis* photoisomerization of the perchlorate in contrast to the iodide (Fig. 3, inset). Examples of the absorption changes vs. time of irradiation at 366 nm are shown in Fig. 3. The absorption spectra of P′1 in THF upon irradiation at 366 nm show an isosbestic point at $\lambda_i = 300$ nm.

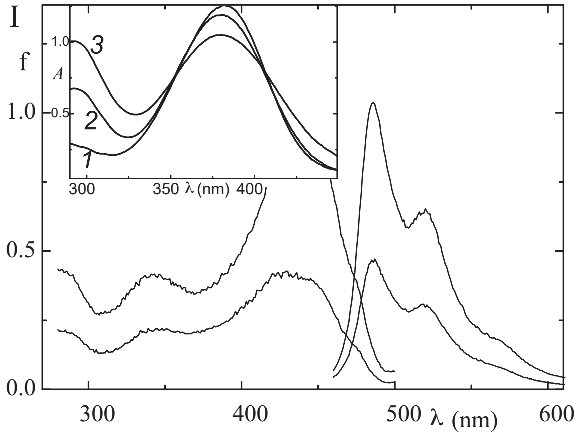

Fig. 1. Fluorescence emission ($\lambda_{ex} = 450$ nm) and excitation ($\lambda_f = 530$ nm) spectra in THF at 10 and 100 min after mixing of 0.5% P4 in DMSO; inset: absorption spectra at 1, 10 and 100 min (1–3), respectively.

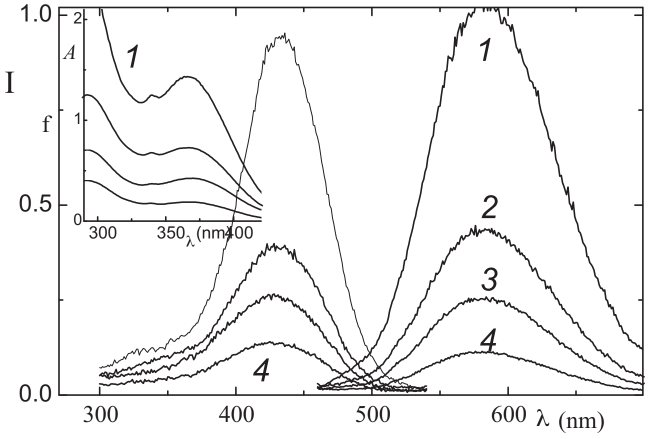

Fig. 2. Fluorescence emission ($\lambda_{ex} = 450$ nm) and excitation ($\lambda_f = 600$ nm) spectra of Q3 in THF-DMSO (100:1) upon each 50% dilution by THF (1–4, respectively); inset: corresponding absorption spectra.