

# Absorption, Fluorescence, Photochemical and Thermal cis/trans Isomerization Reactivity of 1-Methyl-4-(4'-aminostyryl)pyridinium Iodide

FARAG M A ALTALBAWY\* and EL-SAYED A M AL-SHERBINI

Department of Measurements and Environmental Applications, National Institute of Laser Enhanced Sciences (NILES), University of Cairo, Giza, 12613, Egypt

*f\_altalbawy@yahoo.com*

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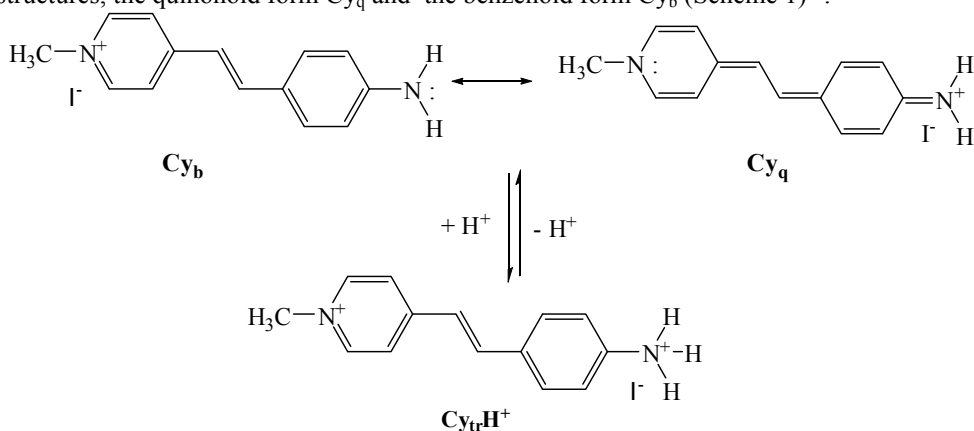
**Abstract:** The photo and thermal cis/trans isomerization reactions are studied for 1-methyl-4-(4'-aminostyryl)pyridinium iodide, Cy, which is prepared in the trans form. In a basic solution the trans form, Cy<sub>tr</sub>, cannot isomerise directly to the cis form. Its protonated form, Cy<sub>c</sub>H<sup>+</sup>, is active and reacts photochemically from trans to cis configuration, Cy<sub>c</sub>H<sup>+</sup>. The quantum yields  $\Phi_{tc}$  and  $\Phi_{ct}$  are determined in water. Deprotonation process of Cy<sub>c</sub>H<sup>+</sup> yields the cis isomer, Cy<sub>c</sub>, which can thermally back to the stable trans form. The rate constants and the activated parameters of the thermal reaction are determined. Due to irreversibility of the thermal reaction, a complete molecular reaction cycle is performed in one direction. To get more information on the spectral characteristics of protonated form, the photochromic of the title compound is studied in different fourteen solvents. The linear relationships between absorption energy with hydrogen bond acceptor ability of the solvents and fluorescence energy of CyH<sup>+</sup> with free energy for transferring the proton to the solvent,  $DG_t^0$  were determined.

**Keywords:** Styryl pyridinium cyanine dye, Photochemical and thermal trans/cis isomerization, Photochromism

## Introduction

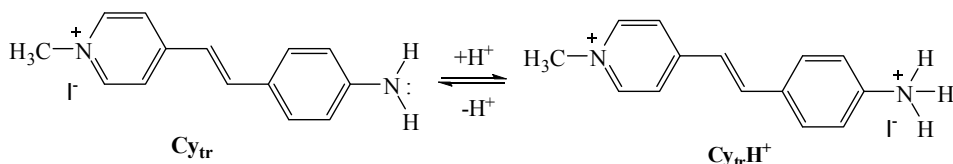
Styryl dyes are known as heterocyclic organic molecules of the general formula R-Het<sup>+</sup>-CH=CH-ArX<sup>-</sup> can undergo E-Z photo-isomerization, electrocyclization and [2+2] Cycloaddition photoreactions owing to the presence of ethylene bonds in the dye molecules<sup>1-5</sup>. The photochemical properties of styryl dyes have been extensively studied<sup>6-12</sup>, owing to their applications in several areas. These compounds were originally utilized as sensitizing additives to photographic emulsions and other additives in photographic industry, but their unique structural and photophysical characteristics have since proven useful for a wide variety of other applications requiring photosensitive materials, such as optical recording media and solar cells<sup>13-16</sup>. These materials also represent an important group of

biologically active compounds and are widely applied in the pharmaceutical industry<sup>17</sup>. In recent years, interest in the application of styrylcyanines as novel and successful fluorescent probes in numerous bioanalytical methods has grown especially in RNA and DNA analyses<sup>18-22</sup>. On the other hand cyanine dyes are well known as solvatochromic and photoreactive compounds<sup>23</sup>. Due to these properties they are potentially useful in many areas such as solar energy<sup>24,25</sup>, photodynamic therapy<sup>26</sup>, photosensitizers<sup>27</sup>, in laser doublers<sup>28</sup>. Merocyanine dyes are also used as an electrochromic molecular probe to measure the membrane potentials with high voltage sensitivity<sup>29,30</sup>. The molecular structure of a typical styrylcyanine dye, 1-methyl-4-(4'-aminostyryl)pyridinium iodide (Cy), has two mesomeric structures, the quinonoid form  $Cy_q$  and the benzenoid form  $Cy_b$  (Scheme 1)<sup>31</sup>.



**Scheme 1.** The tautomerism of 1-methyl-4-(4'-aminostyryl)pyridinium iodide

Photochromic studies were carried out on Cy in different solvents<sup>31,32</sup>. The hypsochromic band shift of the longest absorption band is indicative of the dipole moment decreasing up on electronic excitation and this shift was found to be greater than the bathochromic shift of the fluorescence band, which was observed concomitant with a decrease of the Stokes shift as the solvent polarity decreases. Also, absence of the effect of hydrogen bonding on the absorption and fluorescence shifts of Cy strengthens the effect of the intramolecular charge transfer on its spectral shifts<sup>31</sup>. Protonation process of  $Cy_{tr}H^+$  represents a limiting case of the quinonoid and benzenoid resonance, with a predominant benzenoid contribution, (Scheme 2). The photochemically trans/cis isomerization is one of the most important processes in photochemical and photobiological reactions. On the other hand, no information has concerned the chemical reactivity of the  $Cy_{tr}H^+$  structure and its absorption and fluorescence spectra. Also, not enough studies have been reported for the activity of cis form in the literatures, except for the papers of Williams et al., who reported spectroscopic detection of cis and trans isomers on the bishydrochlorides and methiodidehydrochlorides of some 4'-amino-2-styrylpyridines by UV irradiation in aqueous and 50% (v/v) MeOH-H<sub>2</sub>O solutions<sup>32,33</sup>. Behera et al. synthesized the cis isomer of the hemicyanine dye by a novel method using Ag<sub>2</sub>O as a catalyst<sup>34,35</sup>. In view of these observations and in continuation of our previous work directed to the synthesis of novel heterocyclic compounds and study its isomerization and tautomerism<sup>12,31,36-43</sup>, we reported here a facile methods for the applied the physical constraints approach on the photochemical and thermal isomerization reactivity for the protonated and unprotonated forms, which hitherto unreported in cis form and have been known only in the trans form.



**Scheme 2.** Protolytic forms of 1-methyl-4-(4'-aminostyryl)pyridinium iodide

## Experimental

1-Methyl-4-(4'-aminostyryl)pyridinium iodide was synthesized according to procedures described in literature<sup>31,43</sup> as follows: *p*-amino benzaldehyde (1.21 g, 10 mmol) dissolved in a minimum amount of absolute ethanol, was added drop wise to (2.35 g, 10 mmol) of 1-methylpicolinium iodide dissolved in 25 mL of absolute ethanol was added piperidine (1.5 mL, 10 mmol). The reaction mixture was stirred for 20 h at room temperature and then refluxed for 30 min. The resulting solution was cooled to room temperature and the light brown precipitate was filtered off, washed with cold water, dried and recrystallized several times from distilled water. The melting points was determined and founded to be 278-280 °C, of 1-methyl-4-(4'-aminostyryl)pyridinium iodide, (Cy) (Scheme 1).

### Apparatus and experimental conditions

The electronic absorption spectra were recorded on a Perkin-Elmer lambda 17 spectrophotometer by using a cuvette of 1 cm path length and a cuvette holder equipped for variable temperatures thermostated by using Julbo Thermo-Bath-U3. The fluorescence spectra measurements were recorded on a Shimadzu RF-5000 spectrofluorometer by using a cell of 1 cm path length and a cuvette holder equipped for variable temperatures thermostated by using thermobath TB-85. Fluorescence intensity was measured at right angle to the exciting light. A 5 mmol dm<sup>-3</sup> stock solution of the dye in methanol was prepared and diluted to 30 μmol dm<sup>-3</sup>. Acidic solution was prepared by adding 10 mmol dm<sup>-3</sup> HCl. Basic solution was prepared by adding 1 mmol dm<sup>-3</sup> NaOH. Fluorescence quantum yield was determined by comparing the fluorescence intensity of the solution with a reference solution. Narrow excitation slits were used in order to maintain the photo-isomerization reaction at a low rate. Quinine sulphate dissolved in (1 N) H<sub>2</sub>SO<sub>4</sub> was an appropriate solution as spectral and fluorescence reference with of  $\Phi_f^r = 0.55$ ,  $\lambda_{ex} = 366$  nm. Also, fluorescein dye dissolved in 0.1 mol dm<sup>-3</sup> NaOH was selected as spectral and fluorescence reference for the basic structure with  $\Phi_f^r = 0.9$  at  $\lambda_{ex} = 450$  nm<sup>44</sup>. The  $\Phi_f^s$  value was calculated by using the equation (1):

$$\Phi_f^s = \Phi_f^r \left( \int I_s(d\nu) A_r n_s^2 \right) / \left( \int I_r(d\nu) A_s n_r^2 \right) \quad (1)$$

Where  $\Phi_f^s$  and  $\Phi_f^r$  are the fluorescence quantum yields for the substance under investigation and the reference, respectively. Integrals over  $I_s$  and  $I_r$  are the areas under the corrected emission spectra.  $A_s$  and  $A_r$  are the absorbance values for the substance and the reference.  $n_s$  and  $n_r$  are the refractive index for solvent used and for the solvent of the reference.

The quantum yields of the photochemical trans/cis and cis/trans isomerization reactions ( $\Phi_{tc}$  and  $\Phi_{ct}$ ) were carried out in the quantum yield reactor OYR-20 from applied photophysics limited at 366 nm. The samples were irradiated in cuvette of 1 cm path length and 3 cm<sup>3</sup> volume, connected to a thermostat. The absorption spectrophotometer was used

for recording the absorption spectra at different stages of photoreaction. The intensity of the absorbed light,  $I_0$ , was measured by using a potassium ferrioxalate actinometer and the Hatchard and Parker method<sup>45,46</sup>. Gauglitz's method was applied for determining the quantum<sup>47-50</sup> yields  $\Phi_{tc}$  and  $\Phi_{ct}$ . Equation (2) was used by Gauglitz to determine the pseudo total quantum yield  $Q$  by measuring the absorbance  $E$  at time  $t$  in the presence of light flux  $I_0$ .

$$I_0 = \frac{1}{-Q(t_1 - t_2)} \left( \left[ \frac{F(E_1)(E_2 - E_\infty) - F(E_2)(E_1 - E_\infty)}{E_2 - E_1} \ln \frac{E_1 - E_\infty}{E_2 - E_\infty} \right] + F(E_1) - F(E_2) \right) \quad (2)$$

Where  $E_N$  is the absorbance of the photo-stationary state at time  $N$  and also  $E_1$  and  $E_2$  are at  $t_1$  and  $t_2$ , respectively.  $F(E)$  is the photo kinetic factor, equation (3):

$$F(E) = \frac{1}{-Q(t_1 - t_2)} E / (1 - 10^{-E}) \quad (3)$$

The pseudo total quantum yield  $Q$ , which is independent of time and concentration, was determined using several absorbance values at different times of irradiation, yielding the corresponding values of  $\Phi_{tc}$  and  $\Phi_{ct}$ , equation (4):

$$Q = 1000 (\Phi_{tc}\epsilon_{tr} + \Phi_{ct}\epsilon_c) \quad (4)$$

Where  $\epsilon_{tr}$  and  $\epsilon_c$  are the molar extinction coefficients for pure trans and cis forms, respectively. The Blanc and Ross method<sup>51</sup> was used after modification to calculate the molar extinction coefficient of the cis,  $\epsilon_c$ . This method can be applied to a mixture of two isomers, only one of which exhibits fluorescence and allows one to determine the absolute absorption spectrum of the non-fluorescing isomer by comparing the fluorescence intensities of two solutions different in their optical densities. Since the geometrical factor is different for the two samples, which have different optical densities, in the developed method the fluorescence intensities of the two samples with different total concentrations of the isomers, but with equal optical densities  $D$  at the excitation wave length, are compared. Equation (5) was used for determining the molar extinction coefficient of cis isomer at the excitation wave length,  $\epsilon_c$ .

$$\epsilon_c = \frac{I_{f1} - I_{f2}}{C_2 I_{f1} - C_1 I_{f2}} \times \frac{D}{d} \quad (5)$$

Where  $I_{f1}$  and  $I_{f2}$  are fluorescence intensities of  $c_1$  and  $c_2$  concentrations and  $d$  is the optical path length of the cuvette. In this work 5 mmol dm<sup>-3</sup> stock solution of the dye in methanol was diluted to 30  $\mu$ mol dm<sup>-3</sup> by using the solvent.

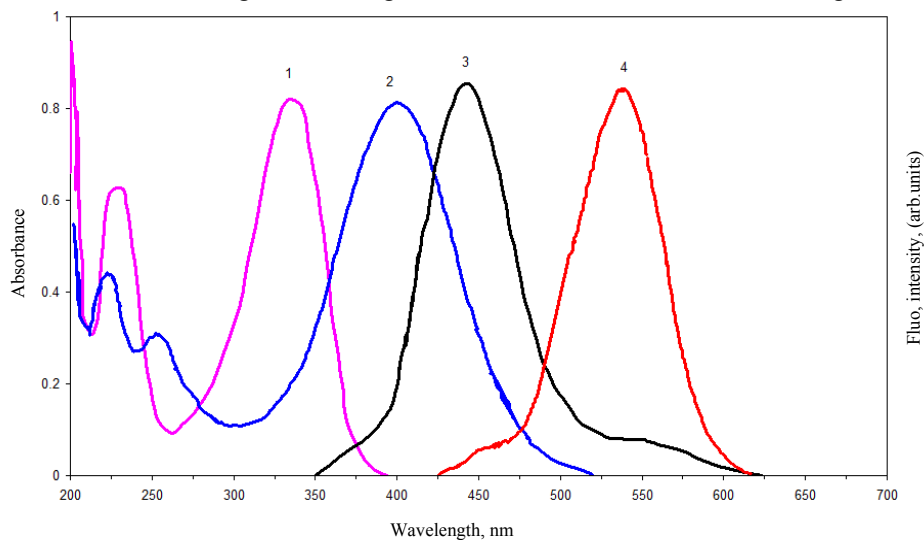
Thermally cis/trans isomerization was studied as; the concentration of the (Cy) was 30  $\mu$ mol dm<sup>-3</sup> was prepared in 50% ethanol solution which is very slightly acidified using 10 mmol dm<sup>-3</sup> HCl, this was found to be enough for the (Cy) to react photochemically under the effect of irradiation at 366 nm to give the protonated cis form. The cuvette was irradiated for 30 minutes. The thermal reaction was followed immediately spectrophotometrically at 449 nm after addition of one drop of 1.0 N NaOH (pH=10). The first order rate constant of cis/trans isomerization was measured at different temperatures to determine the activation parameters.

## Results and Discussion

### *Spectroscopic and protolytic properties*

In aqueous basic solution the absorption spectrum of 30  $\mu$ mol dm<sup>-3</sup> of unprotonated (Cy<sub>tr</sub>), exhibits the longest intramolecular charge transfer band at 400 nm with molar extinction

coefficient,  $\epsilon_{\max}=26.6$  ( $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). The fluorescence spectrum of  $\text{Cy}_{\text{tr}}$  exhibits a fluorescence band at 537 nm when the solution is excited at  $\lambda_{\text{ex}}=400$  nm. Absorption and fluorescence band maxima change up on protonation from 400 and 537 to 325 and 430 nm, respectively, (Figure 1). Also, this process changes the fluorescence yield,  $\Phi_{\text{f}}$ , from 0.070 to 0.043. In pure basic solution, the absorbance of unprotonated  $\text{Cy}_{\text{tr}}$  did not change after irradiation for 15 min. Therefore,  $\text{Cy}_{\text{tr}}$  could be considered as a photochemical inactive dye. On the other hand, absorption spectrum of the protonated structure,  $\text{Cy}_{\text{tr}}\text{H}^+$ , was unstable and the absorbance of the longest wave length band decreases even under the room light.



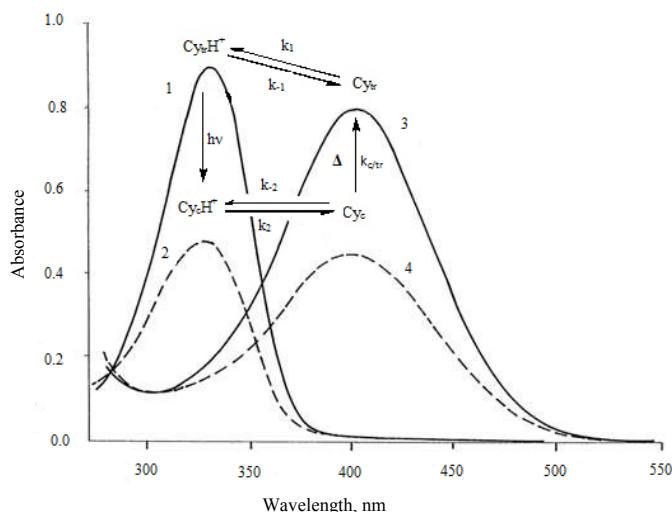
**Figure 1.** Excitation and emission spectra of  $30 \mu\text{mol dm}^{-3}$  aqueous solution for 1-methyl-4-(4-aminostyryl)pyridinium iodide in both acidic and basic forms. (1) Absorption spectrum of  $\text{CyH}^+$ , (2) absorption spectrum of  $\text{Cy}$ , (3) fluorescence spectrum of  $\text{CyH}^+$ ,  $\lambda_{\text{ex}}=325$  nm and (4) fluorescence spectrum of  $\text{Cy}$ ,  $\lambda_{\text{ex}}=400$  nm

Therefore the absorption spectrum was recorded in the dark to avoid its photoreactivity. Absorption spectra of pure protonated  $\text{trans Cy}_{\text{tr}}\text{H}^+$  and its photostationary state are shown in Figure 2.

The  $\text{pK}_{\text{a}}$  of the dye was determined spectrophotometrically by measuring the absorption spectrum in different buffer solutions. Due to the presence of simple protolytic equilibrium between  $\text{Cy}_{\text{tr}}\text{H}^+$  and  $\text{Cy}_{\text{tr}}$  forms, sharp isosbestic points could be obtained after measuring the solutions only in the dark. The  $\text{pK}_{\text{a}}$  and  $\text{pK}_{\text{a}}^*$  values in ground and excited state were calculated as 3.35 and 0.62, respectively at  $25^\circ\text{C}$ .

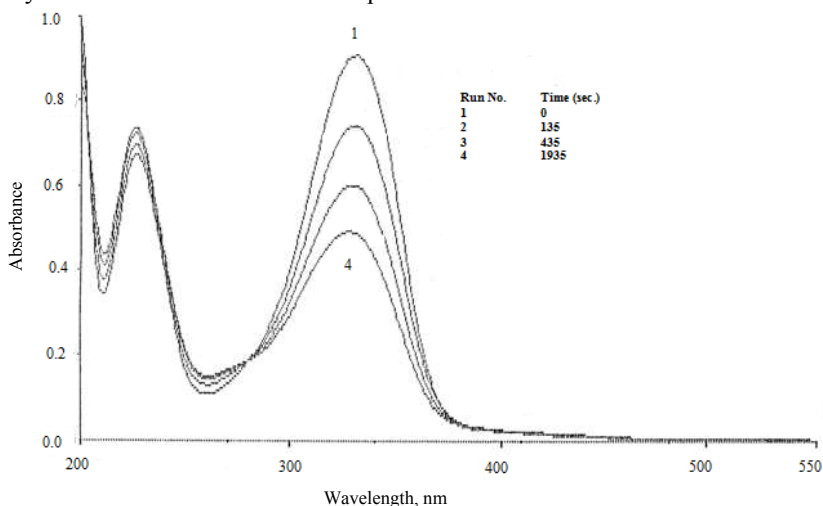
### Molecular reaction cycle

The dipolar properties of unprotonated  $\text{Cy}_{\text{tr}}$  and protonated  $\text{Cy}_{\text{tr}}\text{H}^+$  structures are different in their positive charges and it is interesting to compare their physical and chemical reactivity. The whole skeleton of protonated  $\text{Cy}_{\text{tr}}\text{H}^+$  in the ground state shows that the total charges equal  $+2.0e$  and the distribution of the added charges as a result of protonation is mostly distributed over the aniline and the bridge moieties with a little extent over the pyridinium moiety. The molecular structure of  $\text{Cy}_{\text{tr}}\text{H}^+$  represents an essentially stilbene-analogous structure, with two benzenoid rings and an ethylenic  $\text{C}=\text{C}$  double bond, offering the possibility of *cis/trans* isomerism known for many stilbene derivatives.

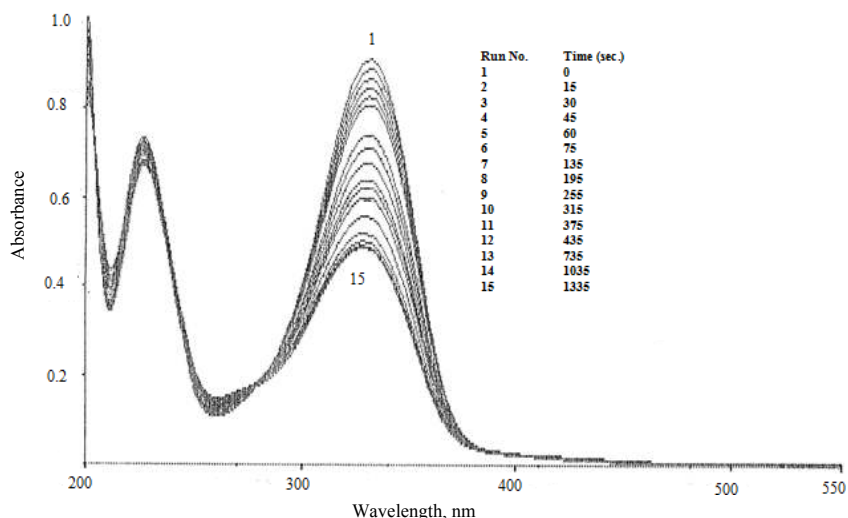


**Figure 2.** Absorption spectra representing the four stages of the reaction cycle (1) Absorption spectra of  $30 \mu\text{mol dm}^{-3}$  of pure protonated trans isomer (100%  $\text{CyH}^+_{\text{tr}}$ ) in aqueous solution, (2) photo-stationary state ( $\text{CyH}^+_{\text{c}} + \text{CyH}^+_{\text{tr}}$ , 64:36) mixture obtained after irradiation of  $\text{CyH}^+_{\text{tr}}$  at 366 nm and (3) Absorption spectra of  $30 \mu\text{mol dm}^{-3}$  of pure trans isomer (100%  $\text{Cy}_{\text{tr}}$ ) in aqueous solution and (4) spectrum of a 64:36  $\text{Cy}_{\text{c}}/\text{Cy}_{\text{t}}$  mixture obtained after addition of 1 drop of conc. NaOH on the photo-stationary state mixture solution

A  $30 \mu\text{mol dm}^{-3}$  aqueous solution of  $\text{Cy}_{\text{tr}}$ , prepared in the dark, was protonated by adding  $1\text{mmol dm}^{-3}$  HCl. Irradiation of  $\text{Cy}_{\text{tr}}\text{H}^+$  with 366 nm was performed and the progress of the reaction was followed by measuring the absorbance at different stages of the radiation until reaching the photo-stationary state (Figures 3 and 4).  $\text{Cy}_{\text{c}}\text{H}^+$  could not be achieved thermally as cis/trans isomerization in aqueous solution.



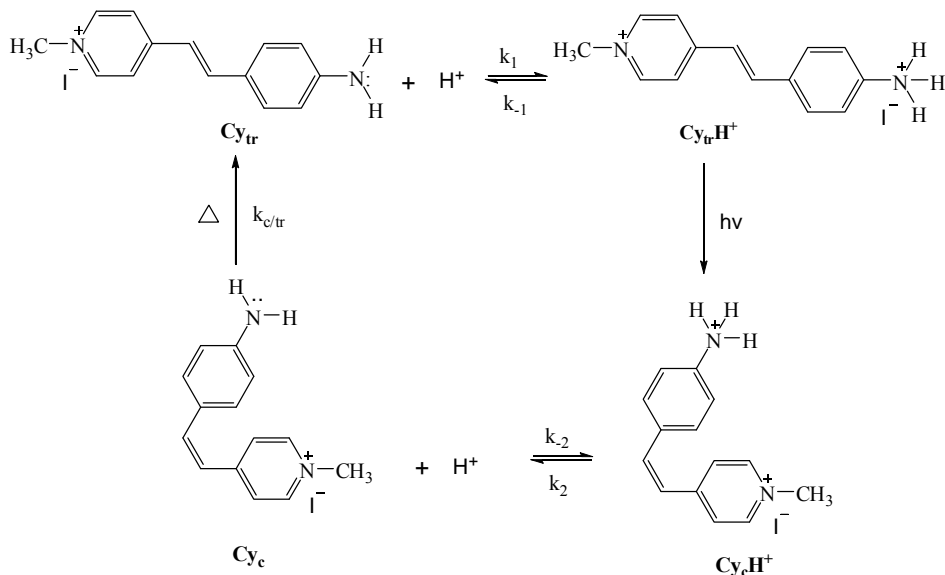
**Figure 3.** Absorption spectra of  $30 \mu\text{mol dm}^{-3}$  of pure protonated trans isomer (100%  $\text{CyH}^+_{\text{tr}}$ ) in aqueous solution at different irradiation times ( $\lambda_{\text{irr}} = 366 \text{ nm}$ )



**Figure 4.** Absorption spectra of  $30 \mu\text{mol dm}^{-3}$  of pure protonated trans isomer (100%  $\text{CyH}_{\text{tr}}^{+}$ ) in aqueous medium at different irradiation times ( $\lambda_{\text{irr}} = 366 \text{ nm}$ )

Addition of 1 drop of 1 N NaOH to the cuvette of the solution at photo-stationary state converts the irradiated molecules  $\text{Cy}_c\text{H}^{+}$  to the basic cis structure,  $\text{Cy}_c$ , which completely reverts thermally to the initial trans isomer form,  $\text{Cy}_{\text{tr}}$ , Figure 2. The spontaneous thermal reaction proceeds as a first order reaction and the progress of the reaction was followed and measured spectrophotometrically.

The protolytic, photochemical and thermal reactions represent a complete molecular reaction cycle (Scheme 3).



**Scheme 3.** The possible isomeric and protolytic forms 1-methyl-4-(4'-aminostyryl)pyridinium iodide

To get information on the photoreaction, the quantum yields of both trans→cis and cis→trans reactions are determined. For this, the spectra of pure trans and at photo-stationary state are recorded. The fraction of cis compound at photo-stationary state was calculated ( $\alpha=0.64$ ) by comparing its fluorescence intensity with a pure trans form. The modified Blanc and Ross method was used to determine the molar extinction coefficient value of the pure cis structure,  $\epsilon_c$  ( $20.47 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), and used to calculate the spectrum of pure cis form, (Figure 2). The intensity of the absorbed light,  $I_0$ , was measured ( $5.3 \times 10^{-10} \text{ E/cm}^2\text{s}$ ). By measuring the absorbance at different times of irradiation, the individual quantum yields  $\Phi_{tc}$  and  $\Phi_{ct}$  were determined as 0.61 and 0.49, respectively<sup>31</sup>.

The photochemical behavior of  $\text{CyH}^+$  as it is in good agreement with those reported for similar and with other structurally related compounds like stilbene, 1,2-diphenylpropene, 4-stilbazole and Brooker's merocyanine dye, 1-methyl-4-(4'-hydroxystyryl)pyridinium betaine,  $\text{MH}^+$  (Table 1).

**Table 1.** The photochemical and photophysical data for  $\text{CyH}^+$  and its similar compounds

Compounds	$\Phi_{tc}$	$\Phi_{ct}$	$\Phi_f$
Stilbene <sup>52</sup>	0.50	0.35	0.039
1,2-Diphenylpropene <sup>53</sup>	0.54	0.44	
4-Stilbazole <sup>54</sup>	0.44	0.25	0.003
$\text{CyH}^+$	0.61	0.49	
$\text{MH}^+$ <sup>55</sup>	0.33	0.57	0.015
1-Methyl-4'-( <i>p</i> - <i>N,N</i> -dimethyl-aminostyryl)pyridinium iodide <sup>56</sup>	0.255	0.47	0.007
4-Nitro-4'-methoxy stilbene <sup>57</sup>	0.07	0.48	

The comparison suggests that stilbene, stilbene like-structures and  $\text{CyH}^+$  have nearly the same behavior, where the  $\Phi_{tc}$  value is higher than  $\Phi_{ct}$ . By suggesting that there is analogy between 1,2-diphenylpropene, stilbene dyes and our compound cyanine dye, the photo-isomerization of  $\text{Cy}_{tr}\text{H}^+$  to  $\text{Cy}_c\text{H}^+$  and *vice versa* may proceed *via* a phantom state X, which is a common intermediate in the radiationless deactivation of both trans and the cis excited singlet states<sup>58</sup>.  $\Phi_{tX}$  can be determined by equation (6)<sup>59</sup>:

$$\Phi_{tX} = \Phi_{tc} / (1 - \Phi_{ct}) \quad (6)$$

$\Phi_{tX}$  values for  $\text{Cy}_{tr}\text{H}^+$ , 1,2-diphenylpropene and Stilbene are 1.19, 0.96 and 0.77, respectively. In other words the  $\text{Cy}_{tr}\text{H}^+$  and 0.23% of 1,2-diphenylpropene  $_{tr}\text{H}^+$  disappear through isomerization. This means that the isomerization process of  $^*\text{Cy}_{tr}\text{H}^+$  represents the main channel of deactivation processes in water. At the photostationary state the proportion of cis to trans was found to be 64:36, also Steiner<sup>58</sup> has noticed that there is an analogy in the structure of the protonated merocyanine dye and stilbene in their photochemical trans→cis isomerization reaction and in quantum yield. It was suggested that a phantom state X, which is present in the protonated form at a 90° twisted conformation of the excited state by which the deactivation process can occur to either trans or cis ground state.

#### Thermal isomerization

The kinetics of thermal cis→trans isomerization was investigated at different temperatures. The rate of disappearance of the cis form is described by a first order reaction with strong temperature dependence, equation (7):

$$-\frac{d[M]_c}{dt} = k_{ct}[M]_c \quad (7)$$



The rate constant of the thermal reaction  $k_{ct}$  was determined and evaluated in an Arrhenius plot to yield the activation energy,  $E$  and frequency factor,  $k_0$ . The Eyring theory was applied<sup>60</sup> to calculate the activation parameters, enthalpy and entropy of activation. The following values were obtained:

$$k_{ct} = 1.00 \times 10^{-5} \text{ s}^{-1}, E_a = 28.15 \text{ kcal/mol}, k_0 = 6.0 \times 10^{-15} \text{ s}^{-1}, \Delta H^\ddagger_{298} = 27.56 \text{ kcal/mol}, \Delta G^\ddagger_{298} = 24.07 \text{ kcal/mol}, \Delta S^\ddagger_{298} = 11.66 \text{ eu/mol}$$

From the foregoing results, as it is in good agreement with those reported for similar compounds. By comparing the molecular activity of  $Cy_c$  with 1-methyl-4'-(*p*-*N,N*-dimethylaminostyryl)pyridiniumiodid ( $M_c$ ) in aqueous solution, one can notice that the rate constant of  $M_c$  reaction ( $2.2 \times 10^{-4} \text{ s}^{-1}$ ) is higher than the case of  $Cy_c$ . Also, the activation energy (26.12 kcal/mol) and the positive value of entropy of activation (10.39 eu/mol) for  $M_c$  reaction are slower than those for  $Cy_c$  reaction<sup>56</sup>. The interaction of  $Cy_c$  with water molecules is stronger than  $M_c$  because its benzenoid structure has high stability as a result of its high ground state dipole moment and due to the formation hydrogen bonding by its phenoxy moiety with water molecules<sup>61-63</sup>.

#### *Effect of solvent on absorption and fluorescence spectra of $CyH^+$*

To get information about the  $CyH^+$  structure, its absorption band was measured in fourteen solvents of variable polarity. The band position changes according to the type of solvent (Table 2). Only a linear correlation was found between absorption energies and solvent hydrogen bond acceptor ability,  $\beta$ <sup>64,65</sup>, as shown in Figure 5.

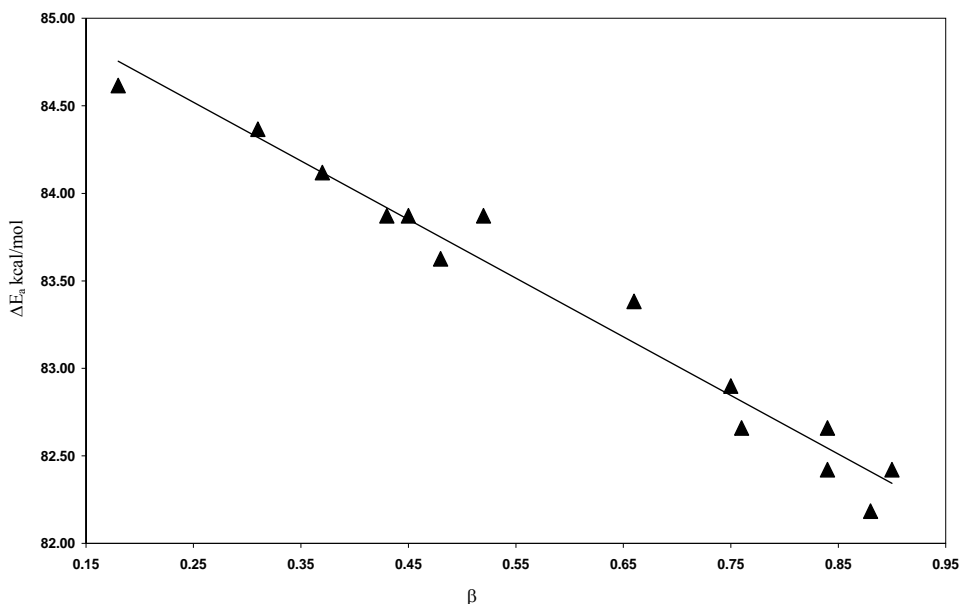
**Table 2.** Absorption band maximum  $\lambda_{max}^a$ (nm) of  $CyH^+$  and solvent hydrogen bond acceptor ability,  $\beta$ , for different polar solvents

Solvent	$\lambda_{max}^a$ nm	$\Delta E_a$ kcal/mol	$\beta$	Solvent	$\lambda_{max}^a$ nm	$\Delta E_a$ kcal/mol	$\beta$
Water	338	84.615	0.18	DMSO	346	82.659	0.76
Ethylene glycol	341	83.871	0.52	DMF	342	83.623	0.48
Methanol	343	83.382	0.66	Acetone	341	83.871	0.43
Ethanol	345	82.899	0.75	Acetonitrile	339	84.366	0.31
1-Propanol	347	82.421	0.9	Ethyl acetate	341	83.871	0.45
1-Butanol	347	82.184	0.88	1,4-Dioxane	340	84.118	0.37
2-Propanol	347	82.421	0.84	Cyclohexanol	346	82.659	0.84

The equation corresponding to the straight lines obtained is:

$$\Delta E_a = 85.36 - 3.35\beta; n = 14, r = 0.98$$

Where  $r$  is the correlation coefficient and  $n$  is the number of solvents, as shown in Figure 5 Such linear equations indicating that studied compound the first electronic transition energy  $\Delta E_a$  of  $CyH^+$  is best correlates with the solvent proton acceptor ability. The electronic transition depends on the general environmental hydrogen bond effect while the environmental polarity has no effect. The negative sign of the correlation shows that the solvent ability of accepting proton decreases the absorption energy and can energetically destabilize the ground state of  $CyH^+$ . Upon excitation the protonated molecule undergoes significant enhancement in its acidity and be sufficient to transfer the amine proton to the solvent during its radiation lifetime<sup>66</sup>. After the transfer event, the fully solvated proton is formed<sup>67,68</sup> with a free energy of transfer to various solvents,  $\Delta G_t^\circ$  Table 3.



**Figure 5.** Correlation of absorption energy,  $\Delta E_a$ , of  $\text{CyH}^+$  and hydrogen bond acceptor ability, ( $\beta$ )

**Table 3.** Fluorescence band maximum,  $\lambda_{\text{max}}^f$  (nm), of  $\text{CyH}^+$  and free energy of proton transfer to various solvents,  $\Delta G_t^0$ , in  $\text{kcal mol}^{-1}$

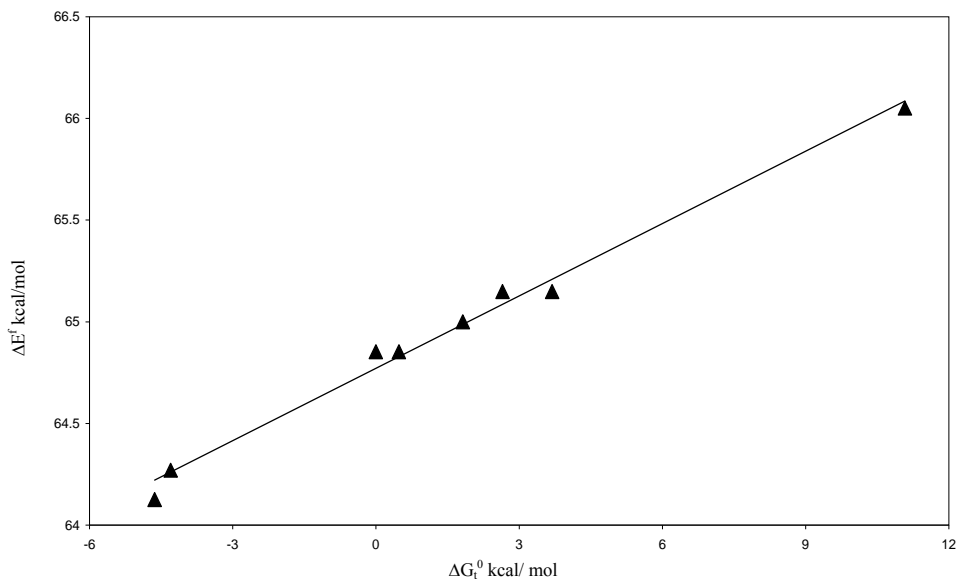
Solvent	$\lambda_{\text{max}}^f$ nm	$\Delta E_{\text{max}}^f$ kcal/mol	$\Delta G_t^0$ kcal/mol
Methanol	439	65.148	2.484
Ethanol	439	65.148	2.651
Water	441	64.853	0
Ethylene glycol	440	65.000	1.82
DMSO	446	64.126	-4.636
DMF	445	64.269	-4.299
Acetonitrile	433	66.051	11.082
1,2-Dichloethane	441	64.853	0.482

A linear relationship was found between fluorescence energy and free energy for transferring the proton to the solvent as shown in Figure 6.

The equation corresponding to the straight lines obtained is:

$$\Delta E_{\text{max}}^f (\text{kcal}) = 64.78 + 0.12\Delta G_t^0, n = 8, r = 0.98$$

Where  $r$  is the correlation coefficient and  $n$  is the number of solvents, Such linear equations indicate that aprotic solvents DMSO and DMF are better solvents for stabilizing  $S^1$  state than other solvents. In the excited state, the stability of the protonated benzenoid structure decreases with increase in the probability of the quinonoid structure by moving the negative charge from the aniline moiety to the pyridinium moiety passing through the bridge moiety. This enables aprotic solvents to be more active and effective to interact, causing more stabilization to  $S^1$  state.



**Figure 6.** Correlation of fluorescence energy,  $\Delta E^f_{\max}$ , of  $\text{CyH}^+$  and free energy of proton transfer, ( $\Delta G_T^0$ )

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