Photochromism of styryl cyanine dyes in solution

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Abstract

The photochemical and spectral behavior of two styryl cyanine dyes were studied in different solvents. The experimental results indicate that in solution the compounds exist in two forms—closed and open. The equilibrium is strongly shifted toward the closed form. From the absorption and luminescence properties, the conclusion can be made that absorbed energy can be lost through different channels: photochemical closed–open form and cis–trans isomerization and through photophysical processes such as fluorescence. The quantum yield of the process, closed–open form is measured. The reasons for the photochromic behavior of these compounds are discussed.   © 1998 Elsevier Science S.A.

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1. Introduction

Due to their large change of the electronic spectrum, which can be induced upon irradiation, photochromic compounds are attractive candidates for incorporation in materials for optical memory media, photochromic decorations, optical switches and optical filters [1]. Styryl cyanine dyes (derivatives of 3H-indole), which possess 2-hydroxyethyl group on the nitrogen atom, are a comparatively new class of structure offering possible photo-, electro-, thermo-, halo- and radiochromic properties. The potential to extend the oxazine cycle, lengthen the conjugated system and change the structural fragments at the end of the molecule, are important available options when making modifications with a view to obtain special combinations of the properties just mentioned.

2. Experimental

The compounds-3,3-dimethyl-2-(4-dimethylaminostyryl)indolino[1,2-b]oxazoline (1) and 3,3-dimethyl-2-[4(4-dimethylaminophenyl)1,3-butadienyl]indolino[1,2-b]oxazoline (2) were synthesized and purified by the procedure described in Ref. [2]. Ethanol, acetonitrile, chlorobenzene and cyclohexane were used as solvents. All were of spectral grade and used without further purification. Typical concen-

trations employed were around 1×10^{-3} mol/l. Absorption spectra were recorded on a Perkin–Elmer 19 UV/VIS spectrophotometer. Fluorescence measurements were carried out on a Hitachi 4500 Fluorescence Spectrophotometer. The laser experiments were carried out with Ar-laser ($\lambda = 514$ nm). The laser beam was focused by a cylindrical lens into a rectangular quartz cell with 2 mm pathlength along the excitation axis. A mercury lamp ($\lambda = 254$ nm) was the source of the photoactivating radiation for the photochemistry studied here. The energy absorbed by the sample was determined by measuring the UV light intensity with a power meter in front of quartz cell with.

The differential quantum yield is found:

$$\phi = \frac{d[x]/dt}{n}$$

where $d[x]/dt$ is the rate of change of a measurable quantity and n the amount of photons absorbed per unit time.

Table 1
The spectral data for the compounds

| Solvent	Compound 1 λ(nm), ε(dm^3 mol^{-1} cm^{-1})	Compound 2 λ(nm), ε(dm^3 mol^{-1} cm^{-1})
EtOH	295(29629), 546(40987)	312(42758), 555(108823)
CH$_3$CN	297(27931), 538(30000)	325(16095), 550(12352)
C$_6$H$_5$Cl	303(21208), 559(147500)	317(14059), 572(29297), 629
Cyclohexane	298	320

ε = molar extinction coefficient.

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Photodiode is used for determining the number of photons per unit time.

3. Results and discussion

Compound 1

closed form   open form

Compound 2
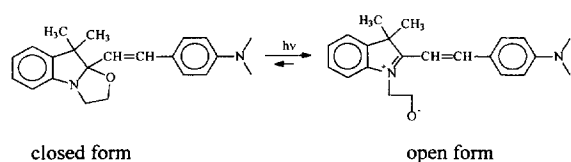
closed form   open form
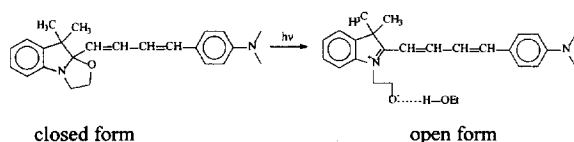
The analysis of the spectral data indicates that the open form of these molecules can be identified with an absorption maxima at 550–620 nm and the closed form with an absorption maxima at 295–325 nm (Table 1).

The compounds are stable in their closed-ring isomeric forms and give colorless solutions. The equilibrium between the closed and open forms is strongly shifted to the closed form in the dark. In fresh solutions the open form of the compounds is detectable only in EtOH. One month after the preparation of solutions of these compounds, there were no changes in the equilibrium between the closed and open forms (Table 2).

The spectra of the colored forms of compounds were obtained by irradiating the solution at 254 nm and subsequently recording the UV/VIS absorbance (Figs. 1 and 2). This was repeated until spectral changes were no longer evi-
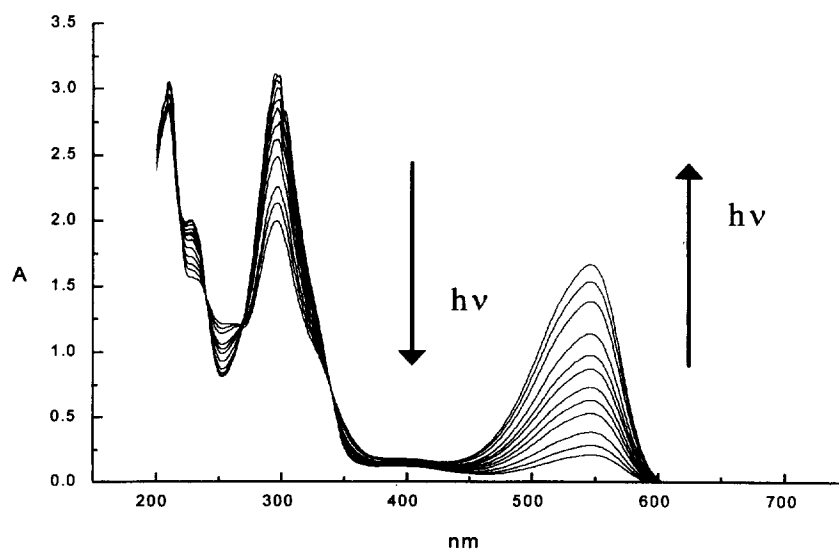
Table 2
The correlation between the closed and open forms as percentages

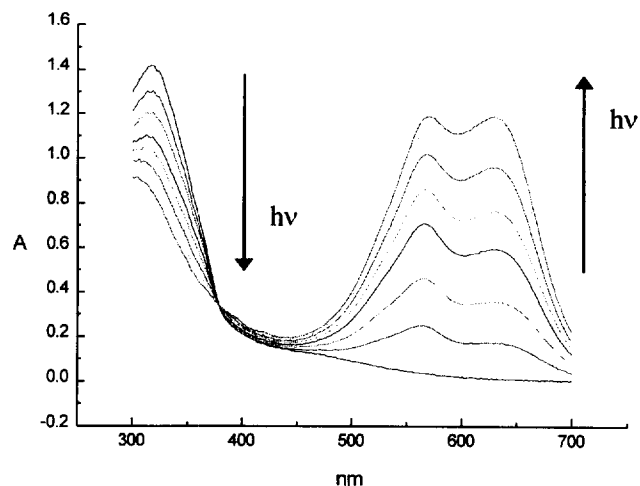| Solution | Compound 1 | | | | Compound 2 | | | |
| | Unirradiated | | Irradiated | | Unirradiated | | Irradiated | |
	Closed	Open	Closed	Open	Closed	Open	Closed	Open
EtOH	95.3	4.7	62.5	37.5	91.04	8.96	88.3	11.7
CH_3CN	100	0	88.8	11.2	91.1	8.9	88.4	11.6
C_6H_5Cl	100	0	83.9	16.1	98.8	1.2	59.4	40.6

Fig. 2. The spectral changes of compound **2** in C_6H_5Cl ($c = 1.10-3$ mol/l) due to UV irradiation.

dent. It can be seen from these spectra that absorption in the closed form region decreases and that absorption in the open form region increases during this process. Strong evidence for the existence of only two forms and the presence only of the process 'closed ⇌ open' form is found in the isosbestic points (at 340 nm and 380 nm). The photoinduced color changes can be explained by the large change in extent of the
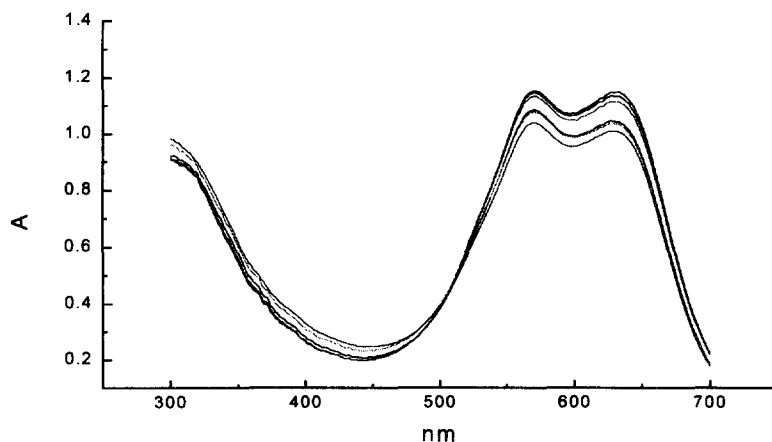

Fig. 1. The spectral changes of compound **1** in EtOH ($c = 1.10-3$ mol/l) due to UV irradiation.

Fig. 3. The spectral changes of compound 2 in C_6H_5Cl ($c = 1.10-3$ mol/l) due to Ar-laser irradiation.

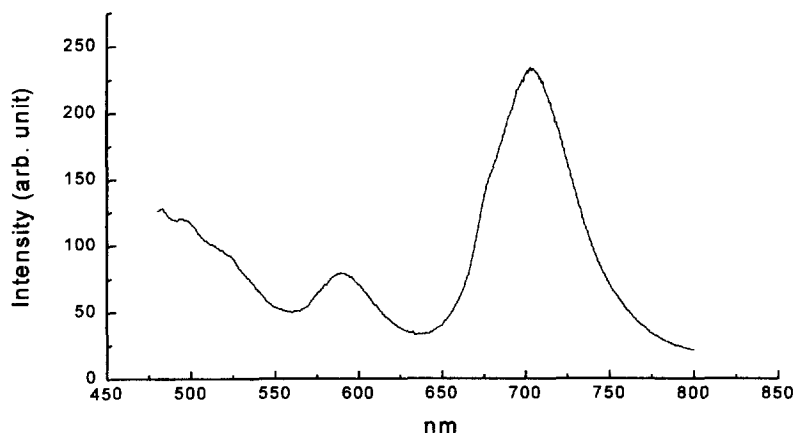Fig. 4. The emission spectra of compound 2 in C_6H_5Cl. Closed form $\lambda_{ex} = 300$ nm; Open form $\lambda_{ex} = 450$ nm.

conjugated system in going from the open form to the closed form. This photochromic behavior was observed for both compounds 1 and 2 in the used solvents.

The colored species seemed stable in the dark at ambient temperatures as no changes in the color and in the absorbance were detected. Reversible color changes were promoted by visible light irradiation ($\lambda = 514$ nm) only for compound 2 (Fig. 3). Prolonged irradiation caused deviation of the isosbestic points and saturation of the increase in the absorbance at 420 nm, which suggests the probability of decomposition of the two forms.

The quantum yields for the 'closed form–open form' reaction were estimated to be 0.58 (compound 1) and 0.48 (compound 2) in chlorobenzene. In this solvent (at room temperature), only weak emission could be detected (Table 3, Fig. 4) from these compounds thus, the quantum yield for fluorescence must below.

Photochromism, as a characteristic property of compounds 1 and 2 in solution, is well documented from these results. With high quantum yields of ≈ 0.5, the dominant photochemical process is the formation of the open form. This is a simple reaction as illustrated by the presence of the isosbestic points.

Table 3
The emission spectral data for the compounds 1 and 2

Compound	Closed form		Open form	
	λ_{ex} (nm)	λ_{fl} (nm)	λ_{ex} (nm)	λ_{fl} (nm)
1	300	373, 730	300 [a], 500 [b]	376 [a], 605 [b]
2	300	378, 735	450	590, 705

[a] $- \lambda_{ex} = 300$ nm; $\lambda_{fl} = 376$ nm.
[b] $\lambda_{ex} = 500$; $\lambda_{fl} = 605$ nm.

The fact that these compounds are also photochromic in dilute solutions and in solid polymer matrices demonstrates the molecular character of the process. From Figs. 1–3, it can be seen that the photochromic species are not formed as rapidly in acetonitrile as in ethanol and chlorobenzene. This strongly suggests that the formation of the open form is through the cleavage of the C(spiro)–O bond of the oxazoline ring, since this process is known to be very sensitive to the type of solvent—especially proton donors (e.g., EtOH) and aromatic solvents (e.g., C_6H_5Cl) [1].
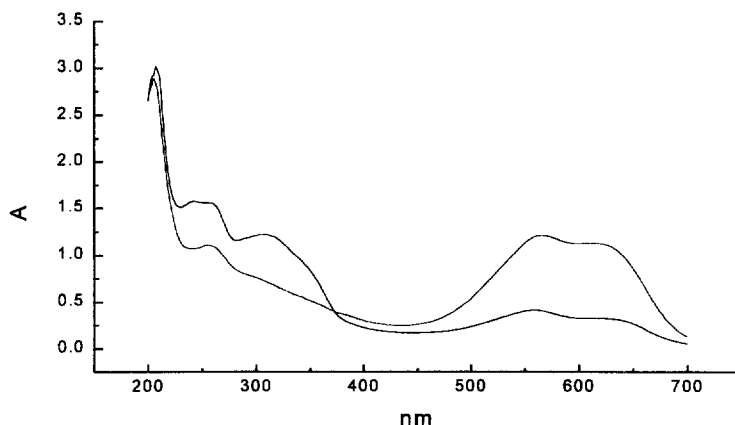
Fig. 5. The spectral changes of compound 2 in EtOH in presence of HCl. (a) without HCl; (b) with HCl.

Table 4
The number of formation molecules of the open form for 1 min

Solution	Compound 1	Compound 2
EtOH	6.9×10^{17}	7.7×10^{15}
CH$_3$CN	2.5×10^{17}	1.09×10^{17}
C$_6$H$_5$Cl	2×10^{19}	2.13×10^{19}

The solvent-dependent formation of the molecules in their open forms reveals some interesting conclusions (Table 4).

First, there is the influence of the character of the solvent (for example EtOH and CH$_3$CN). The possibilities of the formation of the hydrogen bond in ethanol make easier the opening of the closed form. The result in chlorobenzene can be explained only on the basis of chlorobenzene as a sensitizer [3]. The high values of the quantum yields are in accordance with the conclusion that the photoinitiated reaction of the opening will take place through a triplet state T$_1$. The higher number of molecules of the open form, obtained during the irradiation show that the structural factor (longer conjugate system for compound 2) play an important role in the process.

The presence of HCl, in ethanolic solutions of compound leads to the fast process of opening of the closed form. (Fig. 5). In this respect, the stability of the open form to visible light (Ar-laser, in ethanol) can be explained with the formation of associates on the base of intermolecular hydrogen bond.
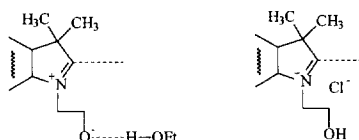
In chlorobenzene, where the interaction between solvent and compound (open form) has another character (π-electronic system), there is a formation process of the closed form under the influence of the visible light. Such effect is absent for compound 1 in C$_6$H$_5$Cl. The reason for this is most likely the shorter conjugate system than that of compound 2. Compounds 1 and 2 possess the possibility for *cis–trans* isomerization as well as closed to open form [4]. The difference of the conjugate system of the two compounds is the reason for the lower quantum yield of the photochromic process for compound 2. That fact, and the presence of the fluorescence, show that in these compounds take place and other processes, which are connected with the spending of the absorbed light.

References

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