Media Effect upon the Fluorescence Ability of Differently Substituted α-Cyanostilbenes

Peter Nikolov, Irina Petkova, and Stefan Stoyanov[a]

Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

[a] Department of Chemistry, Sofia University, 1164 Sofia, Bulgaria

Reprint requests to Dr. I. P.; Fax: 003592-70225; E-mail: iripet@orgchm.bas.bg

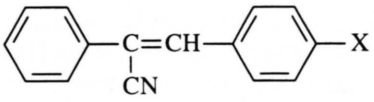
Z. Naturforsch. **56 a,** 447–451 (2001); received January 23, 2001

The steady state and dynamic photophysical characteristics of α-cyanostilbene derivatives have been investigated in solution and in polyvinylchloride (PVC) film at 300 K as well as in a frozen matrix at 77 K. While no emission is observed in solution, a significant fluorescence ability is registered both in PVC and frozen media. This fact is attributed to the matrix effect, which lessens the possible intramolecular motions around the central double bond. No phosphorescence at 77 K is observed. The fluorescence lifetimes at 77 K are compared with literature data for similar chemically fixed structures.

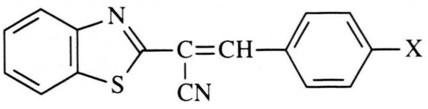
Key words: α-Cyanostilbene Derivatives; Fluorescence; Matrix Effect.

Introduction

Differently substituted stilbenes and α-cyanostilbenes have often been investigated because of their structural features [1] and biological activities [2 - 4]. Literature data concerning the spectra of stilbene and α-substituted stilbene-like structures do exist [5 - 8], but we could not find results on their fluorescence in dependence of the α-substitution.



1: X = N$(CH_3)_2$; **2**: X = OCH_3; **3**: X = CH_3; **4**: X = H; **5**: X = Cl; **6**: X = NO_2.



Model compounds. **7**: X = N$(CH_3)_2$; **8**: X = H.

Scheme 1. Structure and substituents of the investigated compounds.

The structure of the investigated compounds and the corresponding substituents is presented in Scheme 1. Compounds **7** and **8** were used as model compounds for showing the effect of replacement of the benzothiazole fragment by a phenyl ring. Spectral data of **7** and **8** are presented and discussed in [9].

In the present paper, the effect of CN-group substitution at the α-position of the ethenyl chain of stilbene on the radiative and non-radiative deactivation processes of the fluorescence $S_1(\pi\pi^*)$ state is studied. For that purpose, differently substituted α-cyanostilbenes in solution and polyvinylchloride (PVC) film at 300 K as well as in a frozen matrix at 77 K were investigated and the results were compared with the literature data on similar structures.

Experimental

Different substituted α-cyanostilbenes **1 - 6** are synthesized as described in [10 - 12]. The PVC films are prepared according to the following procedure: 3 g PVC are dissolved in 50 ml dichloromethane, and 5 ml of this solution are added to 3 ml 10^{-4}M dichloromethane solutions of the investigated compounds. The final solutions are plated in horizontal glasses and left for 24 hours to evaporate the solvent. The films obtained have uniform width (40 - 50 mμ), and the concentration of the investigated compounds is about 0.300 - 0.500 weight %.

The absorption spectra are recorded on a Specord UV-VIS spectrophotometer (Carl Zeiss Jena). The corrected fluorescent spectra as well as corrected excitation spectra are recorded on a Perkin-Elmer MPF 44 spectrofluorimeter. The fluorescent quantum yields (Q_{fl}) are measured relating to p-methoxy-benzylidenphtalide (Q_{fl} = 0.14 in ethanol) [13]. The emission of the compounds in solid phase is measured at an angle of 30°/60° between the normal to the surface and the exciting emitted light. The low temperature luminescence measurements are performed at 77 K in the standard phosphorescence accessory to MPF 44 in quartz tubes of 4 mm diameter. Fluorescence grade solvents are used. The fluorescence decay curves (10,000 counts in the maximum, 512 channels, 0.1 ns/chan) are collected at 77 K on a nanosecond Single Photon Counting spectrofluorimeter System PRA 2000, using a nitrogen filling flash lamp with λ_{ex} 337 nm or 354 nm – depending on the absorption of the different compounds, and emission wavelength corresponding to the maxima of the emission bands. The natural lifetime τ is estimated by a standard deconvolution procedure, the accuracy of the fit is controlled by the weight residuals, the autocorrelation function of the residuals and the reduced χ^2. The quantum-chemical calculations are carried out with AM1 approximation, taking into consideration all single and double excited configurations among 10 molecular orbitals and simulating solvent effects in the ground and excited state.

Results and Discussions

Absorption in Solution and PVC Film at 300 K

UV-VIS absorption and fluorescence characteristics of differently substituted α-cyanostilbenes in cyclohexane, methanol and PVC matrix at 300 K are presented in Table 1. The absorption spectra of compounds **1**, **4** and **7** in methanol at 300 K are shown in Fig. 1a, where the vertical lines indicate the calculated electron transitions. The polarization degrees P_0 in frozen ethanol solution at 77 K calculated from the polarized fluorescence excitation spectra of **1**, **4** and **7** according to [14], are given in Figure 1b.

The absorption spectra of compounds **2** - **6** in solution at 300K are in the region 260 - 360 nm in cyclohexane as well as in methanol and consist of one wide absorption band (Fig. 1a, compound **4**) with molar absorptivities ε = 14,000 - 22,000 $\mathrm{l mol^{-1} cm^{-1}}$ in methanol (Table 1). The absorption characteristics (energy of the maxima and shape of the absorption bands) of **2** - **6** do not indicate any significant effect of the substituents OCH_3, CH_3, Cl, NO_2 at p-position in the phenyl ring of the investigated structure, while in the absorption spectrum of **1** ($X = N(CH_3)_2$) a new absorption band (ε =27,000 $\mathrm{l mol^{-1} cm^{-1}}$ in methanol), red shifted with about 5,000 $\mathrm{cm^{-1}}$ against the absorption band of **4** (X = H), is observed. This new band should be attributed to a CT-transition between the strongest electron-donating substituent $N(CH_3)_2$ in the phenyl ring and the electron accepting CN-group at α-position in ethylene chain. A similar effect of the $N(CH_3)_2$ group at the same position is observed in α-cyanostyrylbenzothiazoles (compound **7**) [9] where the longest wavelength absorption band (Fig. 1a) is also shifted bathochromically compared to the longest wavelength absorption band of the corresponding non-substituted compound **8** (X = H).

Table 1. Spectral characteristics of the investigated compounds (**1** - **6**) in cyclohexane, methanol and PVC at 300 K [a].

Comp. No	Cyclohexane λ_{abs}	Methanol λ_{abs}	Methanol ε	PVC λ_{abs}	PVC λ_{fl}
1	380	400	27,870	390	470
2	330	330	19,200	340	400
3	320	330	22,000	320	390
4	320	330	15,000	320	390
5	320	330	27,740	330	400
6	330	330	14,200	330	–

[a] λ_{abs} and λ_{fl}: absorption and fluorescence Franck-Condon transitions in [nm], ε: molar extinction coefficient in [$\mathrm{l\ mol^{-1}\ cm^{-1}}$], – : no fluorescence is observed.

Our quantum-chemical calculations of α-cyanostilbenes as well as the literature data for stilbene [12] also support the assumption that the wide absorption bands of **2** - **6** are due only to one electronic transition. In the case of compound **1** ($X = N(CH_3)_2$) the calculations identify two different electronic transitions which are in fair agreement with the experimental results for the absorption maxima and polarization degrees P_0.

As is shown on Fig. 1b, the P_0 remains constant over the whole absorption band of compound **4** and is at about 0.2, the angle β between the absorption and the emission transition moments calculated from P_0 is ±40°. The polarization results for compounds **1** and **7** show two different values of P_0 corresponding to two different bands in their absorption spectra. The polarization degrees of the longest wavelength absorption bands are 0.5 ($\beta = \pm 15°$) and 0.12 ($\beta = \pm 45°$), respectively, to **1** and **7**. These values decrease

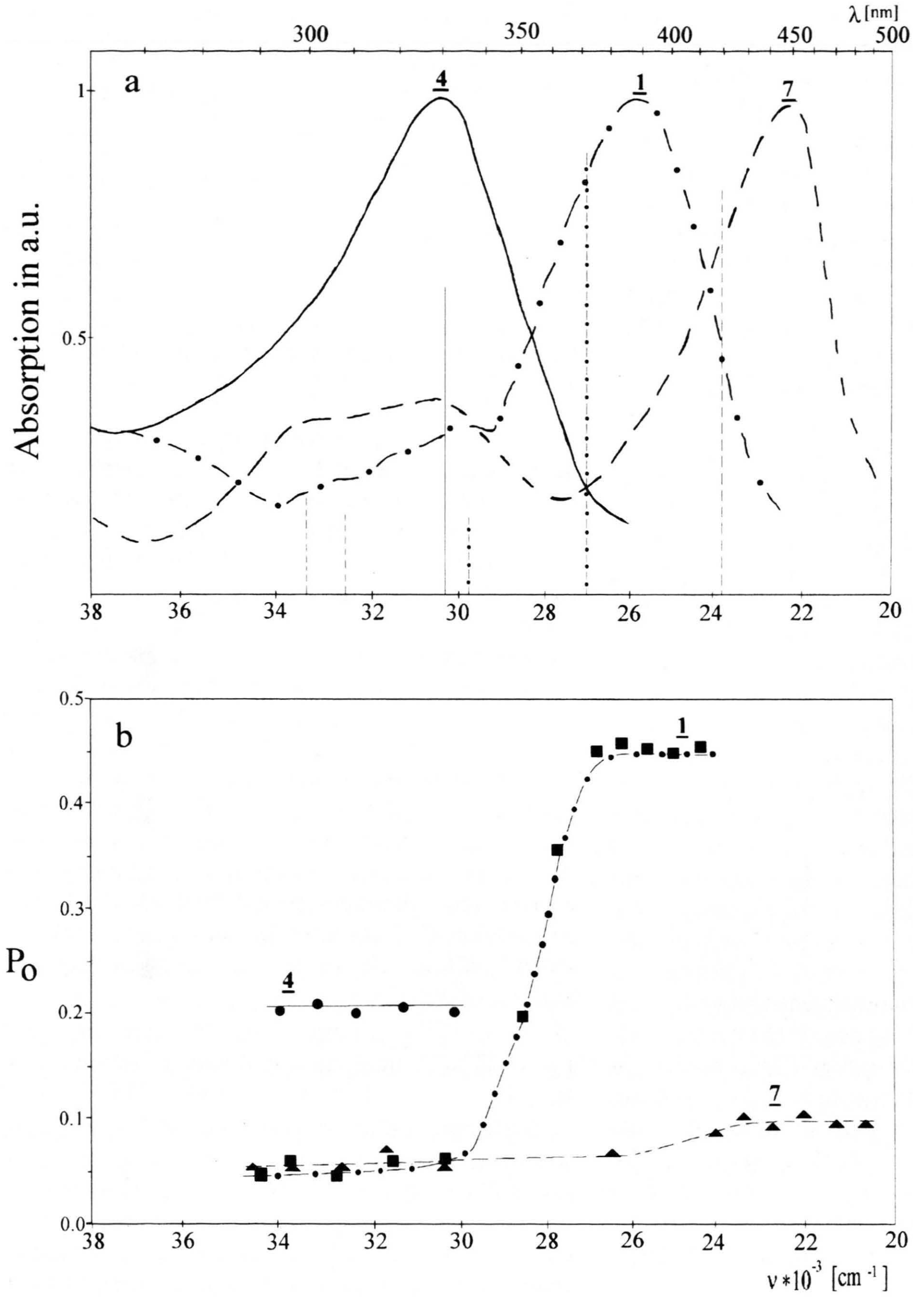


Fig. 1. a) The absorption spectra of compounds **1**, **4** and **7** in methanol at 300 K, vertical lines indicate the calculated electron transitions; b) polarization degree P_0 in frozen ethanol solution at 77 K of **1**, **4** and **7** computed from the polarized fluorescence excitation spectra according to [14].

at their shorter wavelength bands, and for both compounds are at about 0.05 with $\beta = \pm 50°$.

The experimental data for the absorption maxima of compounds **1** - **6** (Table 1) as well as for stilbene [5 - 7], styrylbenzothiazole [9] and their α-CN derivatives [5, 9] make possible a comparative discussion about the influence of the CN-group and the phenyl ring replacement with benzothiazole upon the absorption characteristics of the stilbene structure. The longest wavelength absorption band of stilbene at room temperature in cyclohexane with a maximum at 319 nm [7] corresponds to a one electronic transition

[6] and has a weak vibrational structure. In the absorption spectra of styrylbenzothiazole [9] this band is bathochromically shifted by about 4,000 cm^{-1}, and a smoothing of the vibrational structure is observed. The substitution at α-position with the CN-group shifts to the red the longest wavelength absorption maxima of α-cyanostilbene by about 3,000 cm^{-1}, while in α-cyanostyrylbenzothiazole by 800 cm^{-1}. This significant difference indicates that the influence of CN-substitution at α-position upon the energy of the S_0-S_1 ($\pi\pi^*$) transition decreases with enlarging the conjugated system due to the replacement of the phenyl ring with the benzothiazole fragment.

Fluorescence at 300 K

No fluorescence is observed from the non-polar (cyclohexane) and polar (methanol) solutions of the investigated α-cyanostilbenes at 300 K. Since stilbene fluoresces at 300 K ($Q_{fl} = 0.07$ in ethanol) [7] the lack of fluorescence in the investigated structures **1** - **6** is due either to the quenching effect of the substitution at α-position in the ethylene chain or to a specific influence of the electron accepting CN-group at this position. The effect of -CN, -C_6H_5 and -CH_3 at α-position on the electronic spectra of similar structures [9, 15] is investigated, and there are no indications for some specific influence. On the other hand, all these substituents cause lessening the planarity of the structure [16], decreasing the conjugation and consequently increasing the probability of twisting and out-of-plane bending around the central double bond which is decisive for the lowering of the fluorescence quantum yield. While no emission is registered in solutions of **1** - **6**, a weak fluorescence (Q_{fl} in methanol less than 0,001) is observed in solutions of **7** and **8** [9]. It could be concluded that the intramolecular motions with great amplitude in the structure of α-cyanostyrylbenzothiazoles are weaker than those in α-cyanostilbenes because of the enlarged conjugated system in the first one.

In order to verify whether the assumption that the librations and vibrations around the central double bond are responsible for the absence of fluorescence in solution at 300 K, the structures were fixed in a PVC matrix. The energy of the maxima and the shape of the absorption bands in PVC film remain practically the same as in solution, but all compounds fluoresce, and this fact strongly supports the above-proposed assumption. The only exception is **6** (X = NO_2) which does not fluoresce and, like in [17] this should be attributed to a specific quenching effect of the NO_2-group, which is connected with its strong electron accepting influence (σ_p = 0.78). The relative fluorescence intensities of **1** - **5** as well as of **7** and **8** (normalized to equal optical densities at λ_{ex}) are of the same order, indicating the similar fluorescence ability of α-cyanostilbene- and α-cyanostyrylbenzothiazole-structures in PVC matrix. The fluorescence Franck-Condon maxima of **2** - **5** in PVC are at about 390 nm, while the fluorescence maximum of compound **1** (X = $N(CH_3)_2$) is strongly shifted to the red and is at about 470 nm (Table 1). Similarly to the longest wavelength absorption bands, the fluorescence maxima of the compounds **7** (X = $N(CH_3)_2$) and **8** (X = H) in PVC film are bathochromically shifted by about 3,000 cm^{-1} in comparison to the corresponding maxima of **1** and **4**.

Table 2. Spectral characteristics in methylcyclohexane and ethanol at 77 K [a].

Comp.	Methylcyclohexane		— Ethanol —				
No	λ_{fl}	Q_{fl}	λ_{fl}	Q_{fl}	τ	K_r	K_{nr}
1	430	0.25	450	0.4	1.6	0.25	0.38
2	400	0.2	400	0.3	1.9	0.15	0.37
3	385	0.2	385	0.3	/	/	/
4	370	0.4	380	0.4	2.1	0.19	0.28
5	380	0.35	380	0.35	2.1	0.16	0.3
6	–	–	–	–	/	/	/

[a] Q_{fl}: fluorescence quantum yield, τ: natural lifetime in ns, K_r and K_{nr}: radiative and non-radiative rate constants, – : no fluorescence is observed, / : no measurements.

Luminescence Characteristics at 77 K

The luminescence measurements at 77 K in ethanol and methylcyclohexane matrix were carried out to compare the effect of a frozen matrix upon the fluorescence ability of the investigated compounds with those in PVC. Similarly to PVC, an intensive fluorescence is observed for all compounds (except **6** (X = NO_2)) with Q_{fl} of about 0.3 both in frozen non-polar and polar media (Table 2). The high fluorescence intensity both in PVC and at 77 K is evidence for the hypothesis that motions of the phenyl fragments in the ethenyl chain are responsible for the quenching of the fluorescence in solution. The fluorescence maxima of **1** - **5** both in ethanol and methylcyclohexane matrix are slightly blue shifted by about 500 cm^{-1}

against the fluorescence Franck-Condon maxima in PVC film.

The fluorescence decays at 77 K are monoexponential. The natural lifetimes τ of the fluorescence $S_1(\pi\pi^*)$ state, the radiative K_r and non-radiative K_{nr} rate constants for the studied compounds are presented in Table 2. The natural lifetimes τ are about 2 ns and are in line with the results obtained for several structurally rigid *trans*-stilbene derivatives [7] where the freezing effect at 77 K is simulated. The radiative and non-radiative rate constants calculated from Q_{fl} and τ are of the same order of magnitude (Table 2) and also are in agreement with the data in [7].

To our knowledge there are very few data for phosphorescence observed in stilbene-like compounds [18 - 20]. In our case no phosphorescence at 77 K of the investigated compounds in frozen solutions is registered.

Conclusions

The experimental results for the luminescence characteristics of α-cyanostilbenes in solution and in PVC film at 300 K as well as in frozen matrix at 77 K indicate that the absence of fluorescence of this structure in solution at room temperature is connected with intramolecular librations with great amplitude of the two aryl fragments at both sides of the ethenyl chain. On the other hand, the high fluorescence quantum yields in rigid matrix should be considered as a proof for the fluorescence capability of α-cyanostilbene structures.

Acknowledgements

The authors are very thankful to Dr. Ivan Binev for the kindly supplying us with differently substituted α-cyanostilbenes and to Natalia Litova for technical assistance.

[1] A. R. Gregory and D. F. Williams, J. Phys. Chem. **83**, 2652 (1979) and references cited therein.

[2] J. C. Dore, J. Chim. Phys. **71**, 1411 (1974).

[3] J. C. Dore and C. Viel, J. Chim. Phys. **71**, 1413 (1974).

[4] R. S. Shelton, M. G. Van Campen Jr., D. F. Meisner, S. M. Parmerter, E. R. Andrews, R. E. Allen, and K. K. Wyckoff, J. Amer. Chem. Soc. **75**, 5491 (1953).

[5] S. Millefiori, G. Scarlata, A. Millefiori, and D. Carbone, Z. Physik. Chemie, Neue Folge **128**, 63 (1981).

[6] M. Klein and V. Buss, Chem. Phys. Lett. **124**, 6, 509 (1986).

[7] C. Pyun, T. A. Lyle, G. H. Daub, and S. Park, Chem. Phys. Lett. **124**, 1, 48 (1986).

[8] N. Castel and E. Fischer, J. Chem. Soc. Perkin Trans. II **12**, 1969 (1985).

[9] I. Petkova, P. Nikolov, and V. Dryanska, J. Photochem. Photobiol. A: Chemistry **1-5**, 5474 (2000).

[10] C. N. R. Rao and R. Venkataraghamvan, Can. J. Chem. **39**, 1757 (1961); I. Juchnovski, Dokl. AN USSR **186**, 878 (1969).

[11] I. Binev and I. Juchnovski, Commun. Dept. Chem. Bulg. Akad. Sci. **6**, 595 (1973).

[12] I. Juchnovski, Zh. Strukt. Chimii **8**, 544 (1967).

[13] P. Nikolov, F. Fratev, and St. Minchev, Z. Naturforsch. **38a**, 200 (1983).

[14] F. Perrin, J. Phys. Radium **7**, 390 (1926).

[15] S. Sharafy and K. A. Muszkat, J. Amer. Chem. Soc. **93**, 17, 4119 (1971).

[16] F. Fratev, J. Mol. Str. **30**, 217 (1976).

[17] a) E. Lippert, Z. Phys. Chem. (N. F.) **2**, 328 (1954); b) B. M. Krasovitskii and B. M. Bolotin, Organic Luminophors (Russ.), Khimiya, Moskva, USSR 1984.

[18] H. Gorner, J. Phys. Chem. **93**, 1826 (1989).

[19] J. Saltiel, G. E. Khalil, and K. Schanze, Chem. Phys. Lett. **70**, 233 (1980); ibid. **73**, 199 (1980).

[20] T. Ikeyama and T. Azumi, J. Phys. Chem. **89**, 5332 (1985); ibid. **92**, 1383 (1988).