

PHOTOREACTIVITY OF 5-[E]-2-PHENYLETHENYL-3-METHYL-4-NITROISOXAZOLE

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Abstract

The photobehaviour of 5-[E]-2-phenylethenyl-3-methyl-4-nitroisoxazole (**1a**) was reinvestigated in solid state, solution and adsorbed on silica gel cyclohexane slurry. Evidence from UV-Vis absorption and Raman spectra for the presence of the E-Z photoisomerization of **1a** either in solid state or solution and adsorbed on silica are observed. The low frequency UV-Vis absorption band of **1a** was assigned to the $\pi\pi^*$ transition. The λ_{\max} of the corresponding band ranges from 347 nm (cyclohexane) to 360 nm (benzene, silica slurry, solid state). The interaction between compound **1a** and silica was also evidenced by Raman Spectra. Fluorescence emission of compound **1a** ($\lambda_{\max} \cong 414$ nm) and of the corresponding excimer ($\lambda_{\max} = 460-497$ nm) are registered. Picosecond fluorescence decay time of the excimer was measured using the single photon counting technique.

1. Introduction

The photoisomerization and photodimerization of olefines are still the subject of many investigations in organic and physical chemistry.

Stilbene covers the role of parent compound in this kind of reactions because of its ability to give photoisomers and photodimers [1].

In addition the study of photoreactions of substances adsorbed on silica or other substrates is an interesting field owing to the interactions between the adsorbing systems and the adsorbed molecules.

Under these conditions the course of reactions may become mainly stereospecific [2].

The photodimerization of stilbene-like molecules belongs to the family of pericyclic reactions named $[2\pi_s+2\pi_s]$ photoadditions which are stereospecific and concerted being the new bonds formed in concert.

It has been found that in the photochemical reaction of stilbene and of most of its derivatives, the reactive excited state is the lowest singlet state being the fluorescence and the trans-cis isomerization processes in competition with bimolecular photoreactions.

Mechanistic studies have established that singlet excimers and exciplexes are intermediates in these cycloaddition processes where a very important role is played by the pericyclic minimum which is postulated when the two molecules are so close to react [1].

Recently Bernardi et al. on the basis of their calculations assume for the pericyclic complex a distorted asymmetric rectangular geometry stabilised by diagonal interaction which gives a pericyclic funnel rather than a discrete state and allows a rapid disactivation of S_1 to S_0 [3].

The straight evidence of the pericyclic state in the experimental measurement is at the moment absent.

A direct observation of the presence of the excimer states has been established only in the high viscosity media [4 - 6] or in the solid state [7, 8].

5-[E]-2-phenylethenyl-3-methyl-4-nitroisoxazole (**1a**) under exposure to ultraviolet light reacts to give photodimers as shown in fig. 1

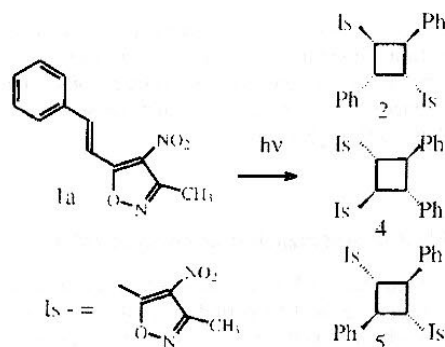


Fig.1 The most important photodimers obtained from irradiation of compound **1a** in solution (photodimer **3** of ref 9 is not reported)

The photoreaction take place either in solution, in the solid state or on adsorbed molecules on silica gel giving a different ratio of products [9] as reported in Table 1.

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	Reaction time	Compound			% total yields
		% relative yields			
		2	4	5	
Solid state	90 min.	99			90%
Benzene solution	30 days	35.7	44.0	15.7	58%
Silica gel (cyclohexane slurry)	30 hours	83.5	6.7	8.6	61%

TABLE I

Photoreaction products of compound **1a**.

An additional photodimer (dimer **3** in ref. 9) of **1a** derived from cycloaddition of the styryl double bond on the 4,5-isosazole positions of a second molecule was also reported [9]. Because dimers obtained from 5-[Z]-2-phenylethenyl-3-methyl-4-nitroisoxazole (**1b**) isomer are not found, this behaviour could be due to the absence of E-Z photoisomerization or, as observed for some stilbene derivatives [1], to the photodimerization of the E-isomer alone.

We now report additional spectroscopic results of compound **1a** in different solvents with or without silica. Different behaviour is observed in relation with the interaction energy between the solute and the solvent or solute and the silica substrate.

2. E-Z Photoisomerization of compound **1a**

It was observed that the UV-Vis absorption spectrum of **1a** decreased during the first period of irradiation (about 15 minutes) which is sufficient to reach the stationary state for the isomerization but is too short to initiate the dimerization process.

This behaviour correlated to the E-Z isomerization as observed for stilbene or other stilbene derivatives.

Fig.2 shows the absorption spectrum of **1a** in cyclohexane solution about 10^{-4} molar before (curve A) and after (curve B) irradiation with a Hg vapour lamp filtered with a Rolling Optics 65:1005 (0.86 mW/cm^2).

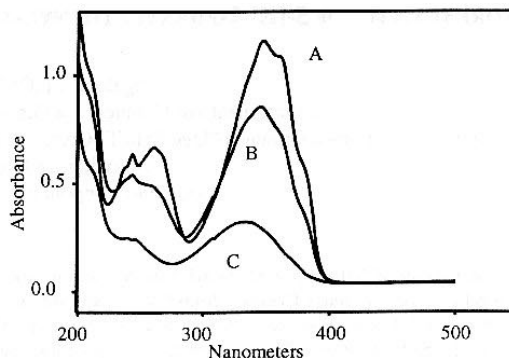


Fig.2 Changes of absorption spectra of compound **1a** in cyclohexane solution:

- A) not irradiated
- B) after 15 minutes of irradiation at 347 nm
- C) curve obtained from curve B after subtraction of half intensity of curve A (see text)

The two bands observed at $\lambda_{\text{max}} = 347 \text{ nm}$ ($\epsilon \cong 10^4$) and $\lambda_{\text{max}} = 260 \text{ nm}$ (curve A) decrease their intensity after irradiation and partially lose the vibronic structure observed as shoulders at 333 nm, 360 nm, 380 nm.

However it is interesting to notice the radiation effect on the shoulder near 333 nm which decreases at less extent than the two others shoulders suggesting the occurrence of a new band in this region.

If we assume that, as for the stilbene molecule, the photoisomerization proceeds up to 50% of the reactant, we can subtract from the curve B the half intensity of the curve A giving the curve C which we can thus attribute to the spectrum of the Z form.

This spectrum which, as expected, shows a maximum at higher energy than that of E form and does not show vibronic structure is very similar to the spectrum of Z stilbene[10].

While the separation of Z isomer was possible for the irradiated 5-[E]-2-p-Cl-phenylethenyl-3-methyl-4-nitroisoxazole [11], due to the very low difference of the polarity of the two isomers, we were not able at the moment to separate **1b** from **1a** with the usual chromatographic methods.

From the curve C we have estimated for **1b** a molar extinction coefficient (ϵ) of about 10^4 .

The above deductions are supported also by the Raman spectra registered on the solid sample of pure **1a** (fig 3 curve A)

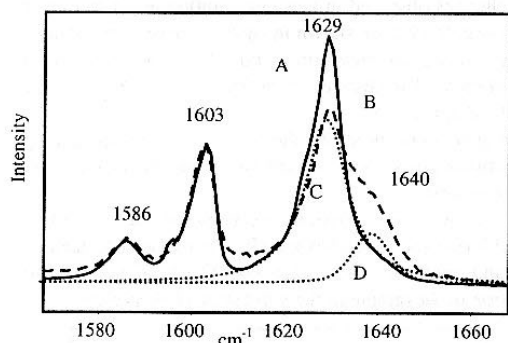


Fig.3 Raman spectra of powders obtained from cyclohexane solution of **1a** before (curve A) and after 15 minutes of irradiation (curve B). Curves C and D are obtained from deconvolution of curve B.

and on powders obtained by evaporating the cyclohexane solution previously irradiated for 15 minutes (fig.3 curve B).

These spectra are normalized to the bands at 1586 and 1603 cm^{-1} which are to be assigned to the phenyl and heterocyclic rings vibrations and do not change appreciably under the photoisomerization process.

The Raman band at 1629 cm^{-1} relative to the central double bond decreases in intensity in the spectrum B with respect to the pure compound. The new band which appear as a shoulder at 1640 cm^{-1} is assigned to the central double bond of **1b** and lies at higher frequency being less conjugated.

The same effect is observed on samples irradiated in the solid state whose Raman spectra are reported in fig 4 .

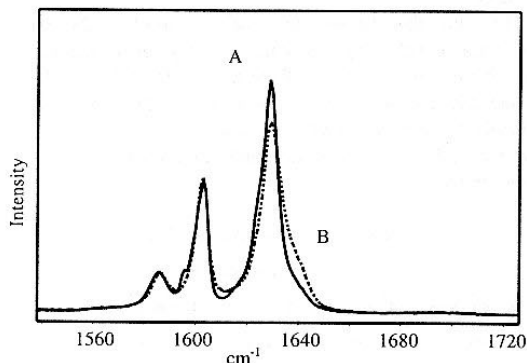


Fig.4 Raman spectra of solid samples of compound **1a** before (spectrum A) and after short time of irradiation in the solid state (spectrum B).

The **1a/1b** ratio in the irradiated stationary solid state is greater than that observed in solution. Actually by keeping a sample of mixture irradiated in the solid state before the complete transformation to the dimer **2** and irradiating this sample in cyclohexane solution with the filtered Hg lamp we observed a further isomerization from the E to Z form.

The presence of the **1b** is supported also by the analysis of the $^1\text{H-NMR}$ spectrum of the photoreaction mixture

obtained by the irradiation of **1a** in cyclohexane solution using the Hg lamp without filter for long-time.

In this spectrum we observed the presence of the signals of the **1a** (olefinic doublets centered at $\delta=7.83$ and 7.69 ppm), of the already reported dimers **2**, **4** and **5** [9] (multiplets of cyclobutanic hydrogens centered at $\delta=5.23$ ppm, 4.635 ppm and 4.58 ppm respectively) and in addition the appearance of two doublets centered at $\delta=7.035$ ppm and 7.326 ppm ($J=12.8$ Hz) and a singlet at $\delta=2.61$ ppm which can be assigned to the methyl group of the **1b**.

The signal integrations allow to estimate that the relative amounts of dimers **2**, **4** and **5** (which together represent the 17% of the reactants) are similar to those observed for the photoreaction in benzene solution [9] and that the signal of **1a** is 1.36 times with respect to **1b**.

The isomers **4** and **5** presents in the reaction mixture are due surely to the photodimerization of **1a** whereas the isomer **2** could also be due to the **1b**.

However the absence in the mixture of other isomers due to the photocyclization of **1b**, strongly suggests that the photodimerization occurs only between two molecules of **1a**.

Following these hypothesis we evaporate the solvent from the reaction mixture containing **1a** and **1b** and irradiate the powder obtained in order to dimerize all the E isomer and isolate the Z form.

The powder irradiated for long-time was completely transformed in the dimer **2** as shown by the $^1\text{H-NMR}$ spectrum where signals due to **1b** and **1a** isomers are absent, meaning that **1b** photoisomerizes in the solid state to give **1a**.

3. Absorption and fluorescence spectra.

The UV-Vis absorption spectra of **1a** in various solvents are reported in fig.5.

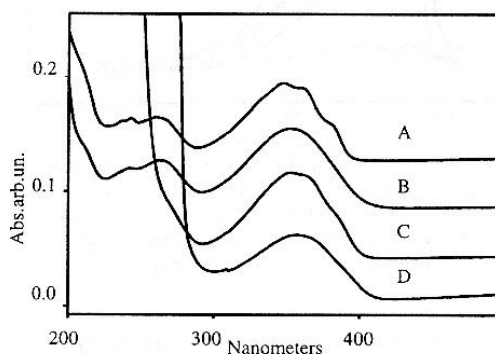


Fig 5 Absorption spectra of compound **1a** in cyclohexane (curve A), methanol (curve B), carbon tetrachloride (curve C) and benzene (curve D) solutions .

As already reported the spectrum in cyclohexane solution (curve A) is characterised by two prominent groups of bands; the group at lower energy is constituted by a broad

band with maximum at 347 nm showing a well pronounced vibronic structure at the lower frequency (360 nm sh and 380 nm sh).

The system at higher energy shows maxima at 260 nm and 243 nm and a shoulder at 237 nm.

The band observed at 347 nm is very similar to that found for E-stilbene in the cyclohexane solution which occurs at 297 nm and is due to the conjugated system of two phenyl rings[12].

The spectrum is sensitive to the change of the solvent which causes either the loss of the vibronic structure either the shift toward lower energy of the absorption bands.

In methanol solution (curve B) the maximum of the low energy band is shifted at 354 nm being the band completely unresolved. This band seems lightly structured in carbon tetrachloride solution where its maximum is also detected at 354 nm (curve C) and is shifted at 360 nm in benzene solution where the structure is also missed (curve D).

The UV-Vis absorption spectrum of solid **1a** in KBr pellet (not reported in fig. 5) shows a very broad band at low energy with maximum again at 360 nm.

The fluorescence spectra (fig. 6) of **1a** are characterised by two bands whose intensity and λ_{\max} strongly depend on the nature of the solvent; the former is found in the range of 412-420 nm and is assigned to the emission from the lower singlet $\pi-\pi^*$ state of the **1a**, the latter ranges from 460-480 nm and is assigned to the emission of the excimer.

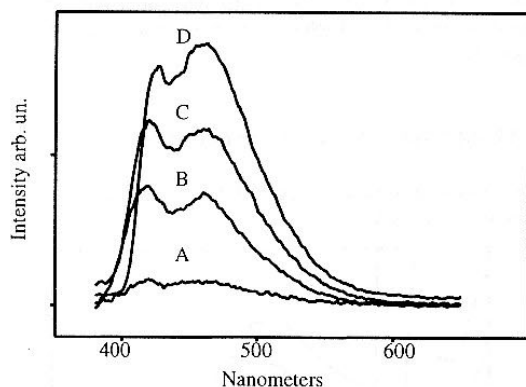


Fig.6 Fluorescence emission of compound **1a** in benzene solution. Curve A (conc. $\cong 3.2 \cdot 10^{-6}$), B (conc. $\cong 2.7 \cdot 10^{-5}$), C (conc. $\cong 8 \cdot 10^{-5}$) are obtained by subtracting the benzene fluorescence band. The concentration of curve D (conc. $\cong 5.1 \cdot 10^{-4}$) is estimated from the corresponding absorption spectrum

The assignment of the low energy band is proposed on the basis of the frequency (which is close to that of the excimer band of E-stilbene and of other similar molecules) and on the basis of the behaviour of its intensity upon the change of the concentration.

Actually, even if these bands are very weak, we have found that the extinction coefficient of the band at higher energy decreases if we increase the concentration whereas the band at 460-480 nm shows an opposite behaviour.

The changes observed in benzene solution as a function of the concentration are shown in fig 6. Curves are obtained by subtracting the emission of pure benzene from that of the solution. The changes in the intensity of the bands are small but appreciable.

At higher concentration the onset of the quenching phenomena gives a kind of saturation and the changes are not detectable.

Fig 7 shows the emission spectrum of **1a** in carbon tetrachloride (A), cyclohexane (B), benzene (C), acetone (D) and methanol (E) solutions. Curve F refers to emission of **1a** sample in the solid state (KBr pellet).

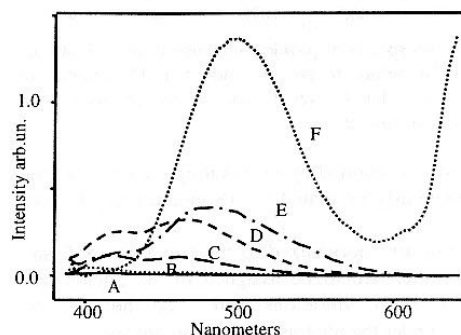


Fig.7 Normalized emission (see text) spectra of compound **1a** in carbon tetrachloride (A), cyclohexane (B), benzene (C), acetone (D) and methanol (E) solutions. Curve F refers to emission of solid state (KBr pellet) sample.

The spectra are registered in solutions with absorbance at λ_{\max} in the range 0.1-0.5 and are normalized by dividing the intensity by the corresponding values of the absorbance.

It can be seen that the emissions of cyclohexane (B) and carbon tetrachloride (A) solutions are very weak and the excimer band is nearly absent. Both the bands of the low S_1 state and the excimer state are evident in the spectra E (methanol), D (acetone) and C (benzene).

The wavelength of the absorption and emission bands are reported in table 2.

	absorption	monomer emission	excimer emission
Cyclohexane	347 nm	412 nm	485 nm
Methanol	354 nm	414 nm	485 nm
Acetone	354 nm	414 nm	470 nm
CCl ₄	354 nm	414 nm	
Benzene	360 nm	415 nm	460 nm
Solid	360 nm		495 nm

TABLE 2

UV-Vis. absorption and emission maxima of compound **1a** under different experimental conditions

From the results reported on the table it can be seen that solutions where the absorption band is found at higher

frequency give rise to an excimer emission band at lower energy, see cyclohexane with respect to benzene. Very strong excimer emission is observed in the solid state spectrum (F) where the monomer emission is nearly absent

4. Compound **1a** adsorbed on silica dispersed in organic solvents.

Strong changes in the electronic structure and energies are observed when organic molecules are adsorbed on silica. Usually interaction causes a red-shift of the electronic absorption bands and the loss of the vibronic structure. Two different mechanism of interaction are supposed for non polar and polar organic molecules[13]; the former interacts weakly with the activate silanol groups via dispersive forces giving small shifts and causing the absence of vibronic structure in the UV-Vis absorption spectra. In this case few molecules parallel to the silicon surface are adsorbed. In the second case a lot of polar molecules interact via their functional groups and are disposed perpendicular to the solid surface. As a consequence the effects on the absorption electronic spectra are much more evident. The two mechanism causes a different restriction of the molecular motion [14].

The interaction of the molecules with the substrate strongly affects also its photochemical behaviour opening a large field of investigation in the heterogeneous catalysis.

In the case of **1a** the highly symmetric photodimer **2** is obtained predominantly under ultraviolet irradiation of the substance adsorbed on silica in cyclohexane environment (slurry).

In this section we report the results of our investigation on the interaction mechanism between substance and substrate which gives this highly stereospecific reaction throughout the analysis of the photophysical properties of **1a** adsorbed on silica.

As expected, the addition of silica to a solution of **1a** in cyclohexane causes a red-shift of the λ_{max} of the UV-Vis absorption bands together with the loss of the vibronic structure (fig 8).

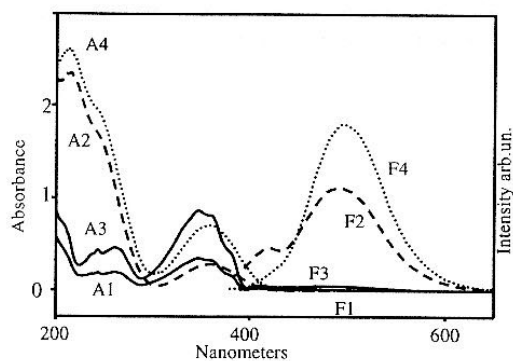


Fig.8 Absorption (A1, A2, A3, A4) and emission(F1, F2, F3, F4) spectra of compound **1a** in cyclohexane solution (A1, A3, F1, F3,) and in silica gel cyclohexane slurry (A2, A4, F2, F4) at concentration of $7 \cdot 10^{-5}$ M. (A1,A2,F1,F2) and of $1.74 \cdot 10^{-4}$ M. (A3,A4,F3,F4)

The red-shift is of about 1050 cm^{-1} for the band at 347 nm (spectrum A3) which moves to 360 nm (spectrum A4) and for the band at 260 nm in the spectrum A3 which occurs at 270 nm in slurry (curve A4).

This high shift is not attributed to the polarity effect since the maximum of the low lying band is located at 354 nm in methanolic solution (Table 2).

The above shift is not due to protonation effect, in fact the spectrum of the methanolic solution is unaffected by addition of acids.

This is than in agreement with the interaction between **1a** and silanol groups.

The same absorption bands are observed in the spectra of the slurry in carbon tetrachloride and in benzene.

Very high changes are also observed in the emission spectra of **1a** adsorbed on silica in the cyclohexane medium.

The curves A1 and F1 are the absorption and the emission spectra of the **1a** in cyclohexane solution at the concentration of $7 \cdot 10^{-5}$ M.. The spectra A2 and F2 are taken on the same solution after the addition of silica into the cell.

It can be seen that the interaction with silica causes a very high emission observed in the range of the excimer fluorescence whereas a well pronounced shoulder is present in the range of the monomer emission.

The curves A3 and F3 are the absorption and the emission spectra registered on a solution of $1.74 \cdot 10^{-4}$ M. and A4 and F4 are the absorption and the emission registered on the same samples containing silica.

It is evident that at higher concentration the emission of the monomer nearly completely disappears and the emission of the excimer (λ_{max} 497 nm) increases. The intensity of this band increases less than the augment of the concentration indicating the onset of other competitive processes like quenching or photochemical reactions.

Whereas a very similar behaviour is observed for the solution of **1a** in carbon tetrachloride added with silica, a general decrease of the fluorescence emission was observed when the silica was added to the acetone or methanol, in the range of concentration of 10^{-4} molar .

The addition of the silica to the benzene solution causes, in the low concentration ($\cong 4 \cdot 10^{-5}$ M.), a small increment of the fluorescence emission for both the bands, at higher concentration ($\cong 4 \cdot 10^{-4}$ M.) the growth of the excimer band predominates.

As the photoisomerization process of **1a** is concerned, we have found for molecules adsorbed on silica a behaviour similar to that observed in cyclohexane solution.

Actually we observed a lowering of the intensity and a little blue-shift of the low lying absorption band in the UV-Vis. spectrum of the compound after irradiation which is ascribed to the formation of the Z isomer (fig.9). In this case the lack of the vibronic structure cannot be used to

infer the formation of the Z isomer which remain the faster process under ultraviolet light irradiation.

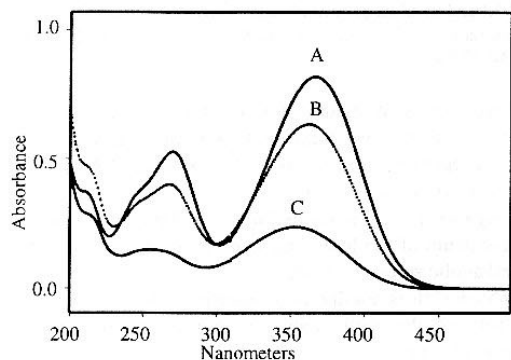


Fig.9 Absorption of compound **1a** in silica gel cyclohexane slurry before (curve A) and after (curve B) short time of irradiation. Curve C is obtained from curve B after subtraction of half intensity of curve A .

The presence of the strong fluorescence band of the excimer allows to monitor the photoisomerization process in cyclohexane slurry for concentration lower than the 10^{-7} moles/gr of silica where are absent phenomena of self quenching and for short time when photodimerization is still absent.

Fig. 10 shows the intensity (curve A) of the fluorescence band at 480 nm [band which is drawn in the inset before the irradiation (curve B) and in the stationary state (curve C)] as function of time when the solution was irradiated with the 365 nm light of the spectrofluorimeter lamp.

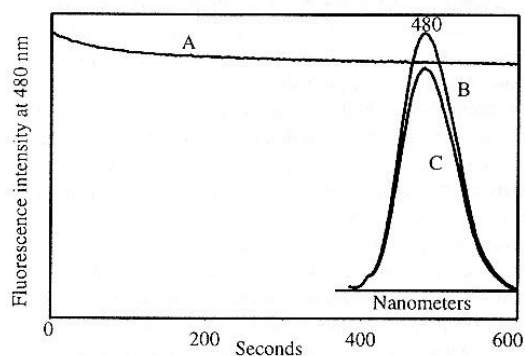


Fig 10. Fluorescence intensity of compound **1a** in silica gel cyclohexane slurry (conc. $<10^{-7}$ M./gr.of silica) at 480 nm as a function of irradiation time (curve A). Curve B and C refer to absorption before and after ten minutes of irradiation respectively.

The strong interaction of **1a** with silica is also evident in the Raman spectra of the molecule shown in fig. 11 where the spectral region relative to the stretching vibration of the central double bond of **1a** registered in the solid state, in cyclohexane solution and in slurry are reported.

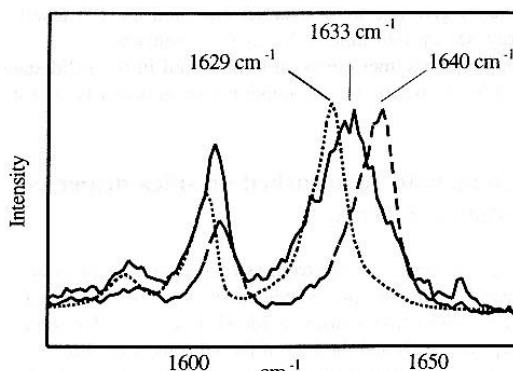


Fig. 11 Raman spectra (in the C=C stretching band region) of compound **1a** in cyclohexane solution (dashed line spectrum) in solid state (dotted line spectrum) and in silica gel cyclohexane slurry (full line spectrum).

The lower frequency (1633 cm^{-1}) observed for the C=C stretching band in slurry (full line spectrum) with respect to that observed in solution (1640 cm^{-1} in dashed line spectrum) means that the interaction with silica gives rise to a greater conjugation of the molecule (as outlined from the UV-Vis spectra) and therefore to a lowering of the strength of the central double bond.

We can therefore deduce that, under the energetic point of view, the situation of the molecule in slurry is intermediate between that observed in cyclohexane solution and that observed in the solid state where the Raman band relative to the stretching of the central double bond is located at 1629 cm^{-1} (dotted line spectrum).

The strong fluorescence emission of **1a** adsorbed on silica has allowed the measurement of the radiative decay time of this band using the single photon counting technique.

The sample in cyclohexane solution containing silica was irradiate at 297 nm with pulses of 5 ps duration and the fluorescence detected at 450 nm. The instrumental response was 300 ps due to electronic jitter of our apparatus.

The best fit of the time dependent fluorescence intensity was obtained using a biexponential decay .

The lifetime of the first exponential decay, which is the most important, was 68 ps., with a preexponential factor of 100, the lifetime of the second one was of 540 ps. and a preexponential factor of 11(fig.12).

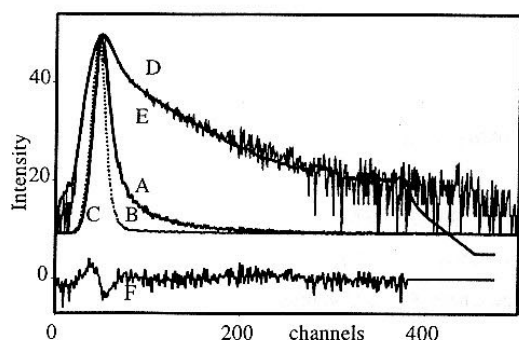


Fig. 12 Fluorescence decay time of compound **1a** in silica gel cyclohexane slurry detected at 450 nm with excitation at 297 nm in linear (curve A) and ln ordinate (curve D) scale. The best fit (curves B and E) is obtained setting $T_1=68$ ps ($A_1=100$) $T_2=540$ ps ($A_2=11$) Curves C and F are the instrumental response and the residues of the least squares fitting respectively.

Nearly the same times are found for the fluorescence measured at 500 nm where a little increment of the long time emission was observed.

The above lifetimes are very different from those found for the excimer fluorescence in solution where excimer formation and decay are correlated to the diffusional processes [15].

The lifetime for the excimer of pyrene was found to be 66 ns. [16].

However it is noteworthy to observe that in the solid state at low temperature the observed decay times are in the range of tenth or hundred picoseconds [17,18].

Again this supports our findings on the nature of adsorbed molecules which show a behaviour close to that of the solid state.

5. Discussion.

The changes observed in the UV-Vis absorption and fluorescence spectra of **1a** in various solvents and on molecules adsorbed on silica gel are explained in terms of different interaction strength between solute-solvent, solute-solute and solute-silica molecules.

Compound **1a** is composed of two prominent residues with different electronic and electrostatic properties linked by the central double bond. The substitute isoxazole part has well defined polar character and is expected to interact strongly with polar or protic solvents; the phenyl residue ring on the other side will interact with non polar solvents through electronic polarizability or dispersive forces.

The lack of emission from the singlet electronic excited state of the compound **1a** or of the excimer in the cyclohexane solution means that the central double bond of two solute molecules are not so close to allow the excimer formation before the occurrence of non radiative energy decay or reactive pathway.

The solute-solute interaction in cyclohexane environment probably take place through the isoxazole residues.

In methanolic solution, where the monomer and excimer fluorescence is observed, a strong interaction of the nitro group of the molecule with the -OH group of the solvent is expected. This allows the interaction between two molecules of solute in the suprafacial position, sin head-to-tail or head-to-head, through the diffuse π electronic orbitals.

The loss of the vibronic structure and the shift to lower energy of the UV absorption band at higher wavelength are attributed to its nature of $\pi\pi^*$ for which a higher dipole moment in the excited state is expected and therefore a greater stabilization in polar solvent occurs.

Strong solute-solvent interactions are also present in benzene which has high electronic polarizability. In this case the maximum of the absorption band is found at 360 nm and emissions from monomer and excimer are detected.

The addition of silica to methanolic-like or benzene-like solutions causes only a little changes in the intensity and energy of the emission spectra since only a small amount of substance is adsorbed on the silica surface as displayed by the absorption spectra.

Compound **1a** dissolved in cyclohexane strongly interacts with the -OH groups of the added silica through the nitro group as showed by the red shift of the electronic absorption spectrum and by the lower energy, with respect to the pure solution, of the central C=C stretching mode observed in the Raman spectra.

The **1a** molecule linked to the silica surface through the silanol groups can therefore interact strongly with an other solute molecule in the sin head-to-tail position allowing the fast excimer formation under light excitation.

The photodimerization of **1a** in cyclohexane slurry leading mainly to dimer **2** derives from the behaviour of the adsorbed molecules which can be considered intermediate between solution and solid state. In fact the energies of the absorption and of the excimers fluorescence emission bands of **1a** in cyclohexane slurry are close to those observed in the solid state.

This is also in agreement with the short lifetime observed for the excimer fluorescence which is of the same order of magnitude of the excimer in the solid state.

6. Conclusions.

As observed for other stilbene derivatives the stereospecific $[2\pi_s+2\pi_s]$ photodimerization of **1a** involves the lower $\pi\pi^*$ singlet state.

The energy of the low lying absorption band and the intensity of the excimer fluorescence in different solvents are found to be closely correlated with the photochemical behaviour of the photoreaction.

The absorption of **1a** on silica causes an enhancement of the stereoselectivity due to different strength of interaction between solute-solvent, solute-solute and solute-silica surface.

E-Z photoisomerization process was found in the solid state, in solution and in slurry with different stationary

states; no evidence was found of the photodimerization process involving the Z form.

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