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Invited paper

Spectral properties and photoreactivity of sydnonyl-stilbenes

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ABSTRACT

This work follows an earlier one where some sydnone derivatives, interesting for their biological and biomedical applications, were synthesized and the effect of substituents on their photoreactivity was studied in irradiation conditions of high intensity and high substrate concentrations. The aim of the present work is to investigate the deactivation pathways of the excited states of three of these compounds, bearing a stilbene moiety, and to determine the quantum yield of the competitive fluorescence/photoreactions in soft irradiation conditions. Flash photolysis measurements with nanosecond resolution were also carried out to obtain information on the transient intermediates responsible for the photoproducts found in the previous work. The oxygen effect on the photoproducts and the energy transfer from triplet donors were also investigated. The experimental results, supported by quantum chemical calculations, showed that different substituents at the sydnone ring can drive the photoreactivity towards different products, thus confirming the results of the previous work. In particular, phenyl-substitution favours the formation of benzodiazepine derivatives.

1. Introduction

A wide interest can be found in the literature in the physico-chemical and photochemical properties of sydnone and its derivatives [1]. In fact, this 5-term heterocycle ring with dipolar (mesoionic) character forms various derivatives with interesting biological and pharmaceutical properties [2,3]. In previous papers the synthesis, NMR characterization and photochemical properties of some sydnone derivatives bearing a stilbene moiety were described [4–6]. Since these compounds can lead to photoproducts with interesting heteropolycyclic structures, the main aim of the previous work was to find a synthetic route to obtain benzodiazepine derivatives, namely psychoactive drugs with various biomedical properties [7]. The previous paper[5] reported an important effect of the substituent at the position 4 of the sydnone moiety on the nature of the photoproducts. The work was based on the idea that 1H-1,2-benzodiazepine (BD) derivatives could be obtained by cyclization of the nitril-immine intermediate, produced by photolysis of the 4-(H/Me/Ph)-3-stilbenylsydnone [5]. Concentrated (10^{-3} M) solutions of three compounds (Scheme 1) in benzene and/or acetonitrile were irradiated in anaerobic conditions in a Rayonet reactor (λ_{exc} = 300 nm for A and B and 350 nm for C) up to complete conversion (60 min for A and B and 20 min per C).

The following photoproducts (Scheme 2) were identified after chromatographic separation: from A, only a quinoline derivative (Q) and *trans*-o-aminostilbene were obtained; from B, benzodiazepine (BD) and Q derivatives in a 4:1 ratio were formed with modest chemical yields; from C, only a BD derivative was obtained with good yield. It is interesting to note that the study of the antiproliferative activity of these compounds indicated that better results were found when the stilbene moiety was in the cis configuration [6].

The present work aims to further investigate the photobehaviour of the three compounds of Scheme 1 in mild conditions (low irradiation intensity, low concentration) and in the first stage of irradiation to measure the quantum yields of the competitive reactive/radiative channels in the primary decay steps, to investigate the possible role of the triplet state and other transient species by laser flash photolysis, and to compare these results with those described by irradiation in preparative conditions.

2. Experimental

The three compounds investigated (Scheme 1) were synthesized as described in the previous paper [5]. The present measurements were carried out in acetonitrile (CH_3CN). In order

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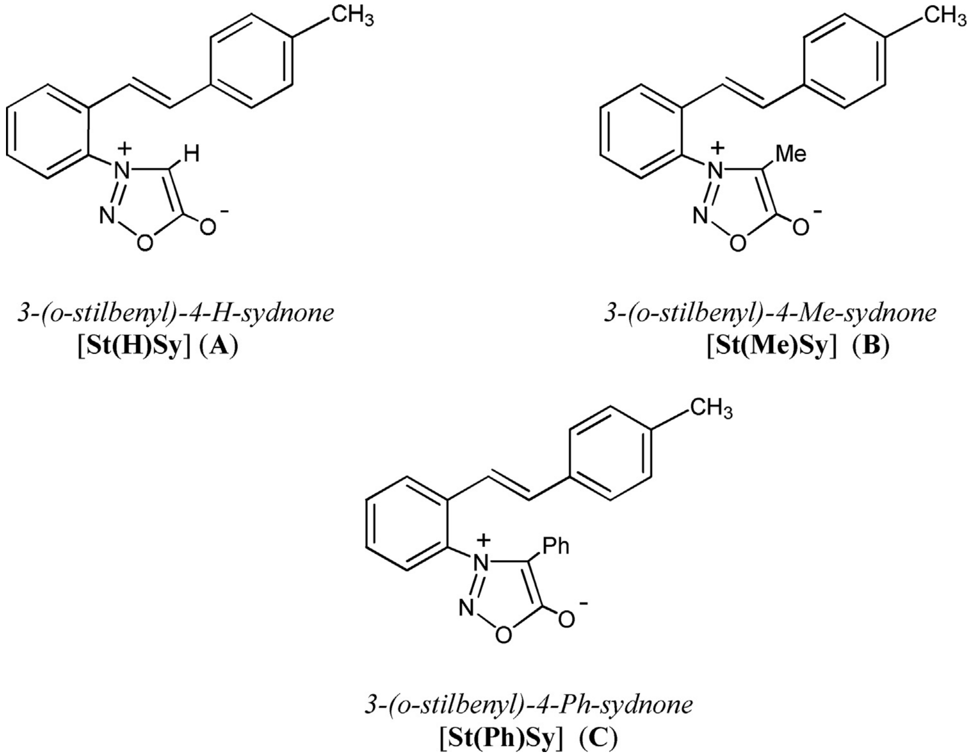
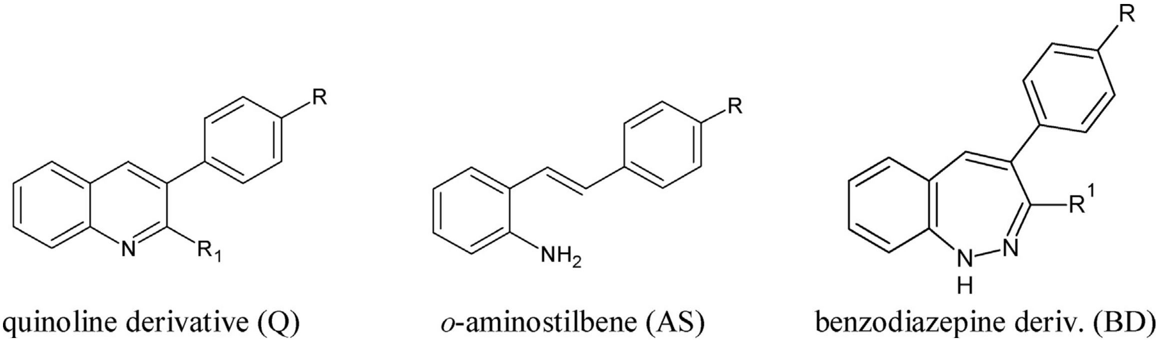


3-(o-stilbenyl)-4-H-sydnone
[St(H)Sy] (A)

3-(o-stilbenyl)-4-Me-sydnone
[St(Me)Sy] (B)

3-(o-stilbenyl)-4-Ph-sydnone
[St(Ph)Sy] (C)

Scheme 1. Compounds investigated.



quinoline derivative (Q)

o-aminostilbene (AS)

benzodiazepine deriv. (BD)

Scheme 2. Main photoproducts obtained under drastic irradiation.

to evaluate the solvent effect, the fluorescence quantum yields were measured also in cyclohexane (CH).

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra were measured with a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance < 0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric measurements. The fluorescence quantum yields (ϕ_F) were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}). 2-(1-naphthyl)-5-phenyl-3,4-oxadiazole (α-NPD) in CH was used as fluorimetric standard ($\phi_F = 0.70$ in deaerated solvent) [8].

For photochemical measurements (potassium ferrioxalate in water as actinometer) a 150 W high pressure xenon lamp coupled with a monochromator and a 500 W mercury lamp with an interference filter at 313 nm were used. The photoreaction (solute concentrations $\sim 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with analytical Gemini C18 (4.6×250 mm; 5 μm) column and an UV diode-array detector. Mixtures of water and CH_3CN were used as eluent. The error for the very small quantum yields of the radiative and reactive processes is of the order of 15%. Biacetyl in CH_3CN was used in the sensitized photoreactions by selective excitation at 435 nm.

For time-resolved laser flash photolysis measurements on the nanosecond time scale, the third harmonic ($\lambda_{exc} = 355$ nm) from a Continuum Surelite Nd:YAG laser was used with the energy less than 1 mJ per pulse [9]. Spectrophotometric analysis was performed by using a 150 W Xenon source, a Baird-Tatlock monochomator, a Hamamatsu R29 photomultiplier and a Tektronix DSA 602 digital analyzer. The transient spectra were obtained by monitoring the change of absorbance over the 300–800 nm range and averaging at least 10 decays at each wavelength. The experimental setup was calibrated by an optically matched solution of benzophenone in CH_3CN [10]. Dithienylketone (DTK) and tioxanthone (TX) in CH_3CN were used as triplet sensitizers [10].

The quantum-mechanical calculations were performed by using semi-empirical programs (PM3 and ZINDO/S from the Hyperchem 7.5 packet). The computed transition energies and oscillator strengths were obtained by the ZINDO/S program at the geometries optimized with a PM3 software, using a 9 × 9 configuration interaction.

3. Results and discussion

3.1. Absorption and emission spectra

The absorption, fluorescence and excitation spectra of the three compounds of Scheme 1 were measured in CH_3CN. The spectra of the phenyl substituted compound C are shown in Fig. 1 as an example. All compounds display an intense, bell-shaped, absorption band with a maximum in the range 300–310 nm and a weaker band at lower wavelengths in the range 200–210 nm (Table 1). They emit weakly, particularly B and C, with bell-shaped bands much red-shifted with respect to the absorption. The weak emission can be due to a process originating from a low-energy forbidden state, non reached by absorption, that could explain the very large Stokes shift observed.

For all compounds the fluorescence excitation spectrum satisfactorily overlaps the absorption spectrum. Very small differences (slight shifts towards the red with respect to the absorption spectrum are caused by the decrease in the lamp intensity in this spectral region. The spectral properties of the three compounds in two solvents (CH_3CN and CH) are summarized in Table 1. They are in very good agreement with the values in EtOH [5], also reported in Table 1 for comparison. A clear, even rather modest, blue shift of the absorption spectrum on increasing the solvent polarity indicates that the excited state reached by absorption is less polar than the ground state. In Table 1 also the weak emission quantum yields are reported.

3.2. Quantum-mechanical calculations

The quantum-mechanical calculations performed on the three compounds allowed to evaluate the spectral properties (energy and oscillator strength) and physical properties (formation enthalpy and dipole moment) reported in Table 2.

For all three compounds the highest oscillator strength (f) is associated to a H → L + 1 transition to the S_4 excited state corresponding to absorption around 300 nm (293, 308 and 310 nm for A, B and C, respectively). These values are in reasonable agreement with the experimental values of Table 1 assigned to the transition of the stilbene moiety. The f value for the transition to S_1 (H → L) is very small for A and B ($f = 0.02$ and 0.04 at $\lambda = 362$ and 356 nm, respectively), indicating that the emission originates from a forbidden state which could involve the sydnone group (see below). For C, $f = 0.24$ was calculated at $\lambda = 372$ nm. The quite higher f value indicates that a larger excitation energy is localized on the sydnone group. The transition to S_3 (H − 1 → L) has a similar f value of ~0.44 for the three compounds and $\lambda = 325$, 334 and 356 nm for A, B and C, respectively.

Table 1
Spectral properties and fluorescence quantum yields of A, B and C in different solvents.

Compound	Solvent	λ^{abs}_{max} (nm)	ε_{max} (10^4 $cm^{-1}M^{-1}$)	λ^{em}_{max} (nm)	Stokes shift (cm^{-1})	$\Phi_F \times 10^3$
St(H)Sy	CH_3CN	304	3.60	504	13200	17
	CH	310		400		0.7
St(Me)Sy	EtOH[a]	312	2.82			
	CH_3CN	310		450	10570	1.9
	CH	314		348		1.9
St(Ph)Sy	EtOH[a]	315	2.30			
	CH_3CN	313		506	12260	4.8
	CH	316		400		1.8

[a] from ref. [5].

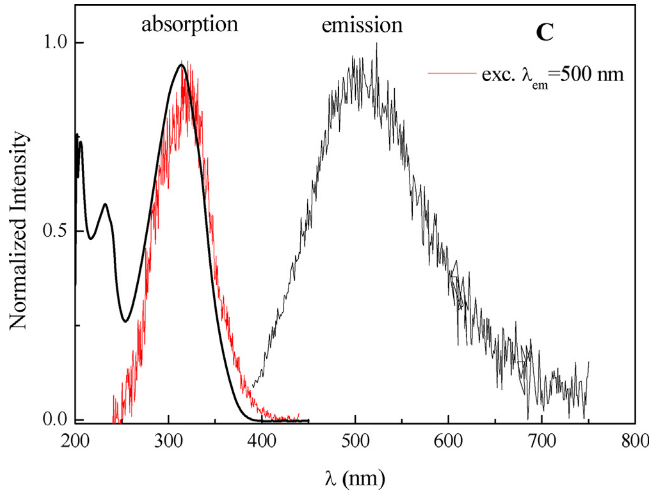


Fig. 1. Normalized absorption, fluorescence and excitation spectra of C in CH_3CN.

The presence of excited states with low f values (S_1–S_3) and an energy lower than that of the state observed in the absorption spectrum, explains the larger Stokes-shifts in Table 1.

Three possible transitions of different nature are evidenced by the calculated molecular orbitals (MOs) reported in Fig. 2.

The main configuration involved in the first transition (H → L in Fig. 2(1)) has a charge transfer (CT) character since the electron density of the ground state is delocalized on the entire molecule while in the excited state it is localized on the sydnone ring. In the prevalent configuration of the second transition (H-1 → L in Fig. 2(2)) the density is localized on the sydnone group in both the ground and excited state (the nature of this transition can be related to what reported in the previous paper where the sydnone group was described as the most photoreactive moiety) [5]. The transition with the highest oscillator strength has a $\pi \rightarrow \pi^*$ character, typical of stilbene-like molecules (Fig. 2(3)), where the excitation leads to a weakening of the double bond and then favours the formation of the cis isomer. On the other hand, the presence of low energy excited states with transitions totally localized on the sydnone moiety, can explain the photoreactivity of this ring leading to quinoline and benzodiazepine derivatives [5].

3.3. Photoreactivity

The evolvement of the UV–vis spectra under irradiation was followed also by HPLC. The monitoring wavelengths used for the HPLC measurements were chosen as those where the absorbance is practically constant during the irradiation ($\lambda = 267$, 264, 265 nm per A, B and C, respectively). This allowed to evaluate approximately the relative quantity of the main photoproducts from the area of their chromatographic peaks. The trans isomers of A, B and C were irradiated at $\lambda_{exc} = 313$ nm. A second main photoproduct of A (Fig. 3A), absorbing at 256 nm with weaker bands at 285 and 325 nm, was assigned to Q with an yield of 0.4%. A third product with two bands of similar intensity at 288 and 340 nm and a yield of 0.8% remained unidentified.

The same measurements carried out for B gave the results shown in Fig. 3B. The spectrum with $\lambda_{max} = 233$ nm and 319 nm was assigned to the Q derivative, the second detectable product with maxima at 236 and 275 nm was assigned to BD.

The absorption spectra of the main photoproducts of C, obtained from net photoreactions, are shown in Fig. 3C. The red one shows two maxima at $\lambda_{max} = 229$ and 296 nm, assigned to the

Table 2

Calculated spectral properties (energy, λ, and oscillator strength, f) and physical properties (formation enthalpy, ΔH_f^0, and dipole moment, μ) of A, B and C.

Compound	μ (D)	ΔH_f^0 (kcal/mol)	λ (nm)	f	Configuration (coefficient)
St(H)Sy (A)	7.82	74.33	362	0.02	$H \rightarrow L\ (0.47) + H-5 \rightarrow L\ (-0.37)$
			349	0.03	$H \rightarrow L\ (0.45) + H-5 \rightarrow L\ (0.43)$
			325	0.44	$H-1 \rightarrow L\ (0.69)$
			293	1.02	$H \rightarrow L+1\ (0.67)$
			224	0.17	$H \rightarrow L+2\ (-0.40)$
			220	0.22	$H-1 \rightarrow L+5\ (-0.62)$
St(Me)Sy (B)	7.73	65.17	356	0.04	$H \rightarrow L\ (0.48) + H\text{-}5 \rightarrow L\ (0.38)$
			346	0.06	$H \rightarrow L\ (0.45) + H\text{-}5 \rightarrow L\ (-0.42)$
			334	0.41	$H-1 \rightarrow L\ (0.67)$
			308	1.26	$H \rightarrow L+1\ (-0.67)$
			231	0.27	$H-1 \rightarrow L+5\ (0.62)$
St(Ph)Sy (C)	7.48	99.84	372	0.24	$H \rightarrow L\ (0.67)$
			356	0.44	$H-1 \rightarrow L\ (0.62)$
			345	0.08	$H-7 \rightarrow L\ (0.44)$
			310	1.20	$H \rightarrow L+1\ (0.61)$
			268	0.21	$H-1 \rightarrow L+3\ (0.45)$
			223	0.23	$H \rightarrow L+2\ (0.37) + H-3 \rightarrow L+1\ (0.42)$

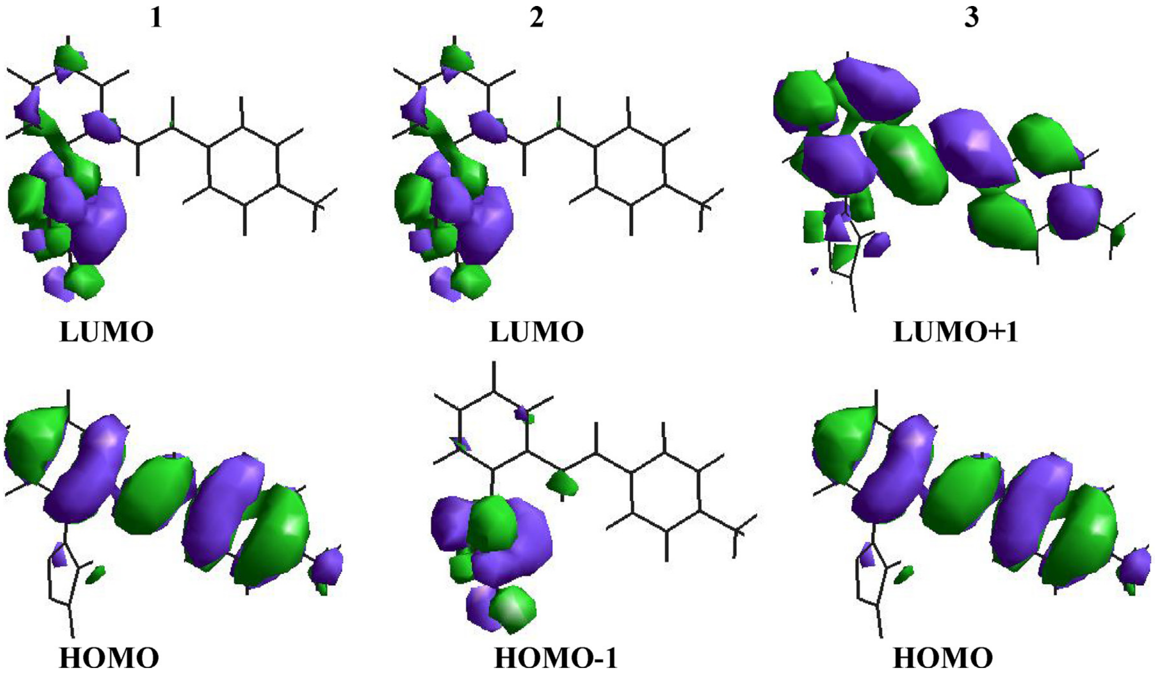


Fig. 2. Different main configurations (1, 2 and 3) involved in the first four electronic transitions of St(H)Sy.

cis isomer, while the blue one shows two maxima at $\lambda_{max} = 245$ and 288 nm, assigned to BD.

The quantum yields of the main photoreactions thus detected are reported in Table 3.

The very low quantum yields obtained for both fluorescence and photoreactions indicate that the largest part of decay occurs by radiationless pathways, $S_1 \rightarrow S_0$ internal conversion or $S_1 \rightarrow T_1$ intersystem crossing.

3.4. Transient absorption

In order to evaluate the role of the transient intermediates in the photoreactivity of the three compounds, flash photolysis measurements with a resolution time of 0.3 μs were performed.

The compound A (Fig. 4A) shows two absorption bands: a broad one in the region around 450 nm and a sharp one with maximum at 520 nm. They decay by the same kinetic parameter and then pertain to the same transient species (T). Irradiation in aerated and deaerated (by bubbling N_2) solutions led to decay kinetics scarcely affected by oxygen. This behaviour excludes a triplet nature of T that is then assigned to a neutral or cationic radical that is expected to decay by recombination. The decay was then processed by a second order kinetics [11] and the results are reported in Table 4.

Fitting of the data gives a kinetic constant k (Eq. (1)) corresponding to the ratio between the second order constant (k_2) and the absorption coefficient (ε_T) of T at the wavelength of analysis (optical path = 1 cm).

$$k = k_2/l\varepsilon_T(\lambda) \qquad (1)$$

Since $\varepsilon_T(\lambda)$ of the transients is unknown, k was multiplied by ΔA at different wavelengths to check that the two bands decay

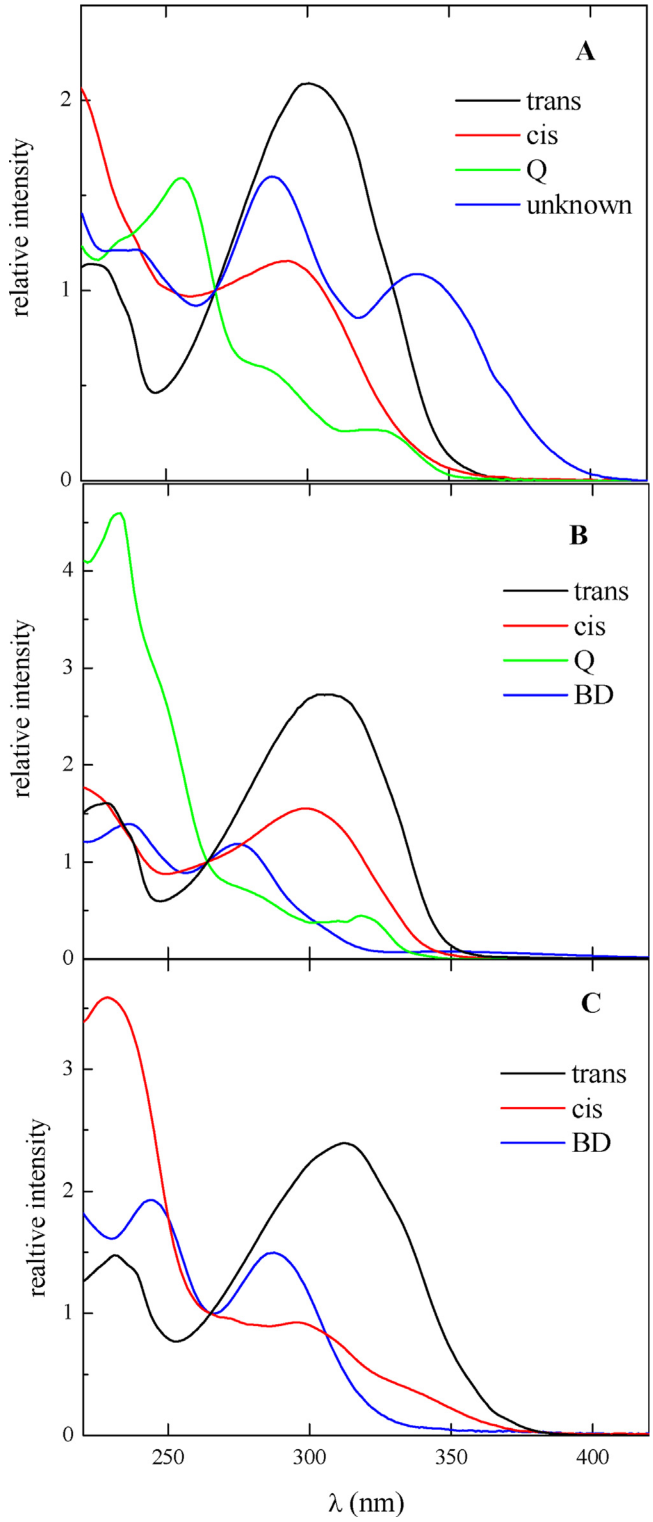


Fig. 3. Spectra of the photoproducts obtained by direct irradiation of A, B and C (λ_{exc} = 313 nm) in CH_3CN.

with the same kinetics and then pertain to the same transient species (T).

The transient spectrum of B (Fig. 4B) shows two bands analogues to those of A but also a third band at 370 nm, not well detectable because very close to the λ_{exc} of 355 nm. This third band displays a different (slower) decay kinetics and then it pertains to a different transient T'. With a bi-exponential decay treatment, it shows a fast increase of the signal followed by a slower decay. This behaviour is typical of a precursor/successor process indicating that T' is formed, at least partially, from a precursor transient, probably a short living triplet (see Section 3.5).

The transient spectrum of C (Fig. 4C) shows a band centred at 380 nm, similar to that observed at 370 nm for B, and a broad absorption in the range 450–560 nm where two transients are present decaying with faster and slower kinetics. On the basis of the previous work [5] and of the results of Section 3.3, which indicate a preferred formation of BD by irradiation of C, one can assume that the band at 370 nm is due to a transient leading to BD.

3.5. Effect of triplet sensitizers

In order to get information on the role of triplets in the photoreactions, the compounds were irradiated by flash photolysis in the presence of two triplet donor sensitizers, dithienylketone (DTK) and tioxantone (TX) in CH_3CN. The choice of the second sensitizer (TX) was justified by the fact that the $T_1 \rightarrow T_n$ absorption of DTK covers the wavelengths region around 370 nm, useful for our analysis. The triplet lifetime of both sensitizers is efficiently quenched (Table 5) by the presence of A, B and C thus proving the formation of the triplet state of the acceptor. However, the absorption ratio between the two transient bands of our compounds at 410 and 520 nm (Fig. 4) as well as their decay kinetics remain the same in the absence and the presence of the sensitizers. Therefore, the T transient is the same in the direct and sensitized experiments. Since T was tentatively assigned to a radical, one can reasonably deduce that the latter is formed by the triplet through a fast process which does not allow to detect the triplet with the resolution time of our apparatus.

The ratio of the signal intensity at 370 and 520 nm, measured for B in the presence of sensitizers, is not comparable with that obtained by direct excitation. In the specific case of TX, the small ΔA value at 370 nm can be assigned to the transient formed by direct excitation. Then, it seems that the triplet of B produced by the sensitizer TX (efficiently quenched by B) does not originate the transient at 370 nm. The species observed at 520 nm follows a kinetics longer than that found by direct excitation.

A similar behaviour was observed for compound C where the band at 370 nm is not formed by TX sensitization. Therefore one can conclude that this band, which is responsible for production of BD, is involved in a process occurring in the singlet manifold. A confirmation came from stationary experiments in the presence of a triplet sensitizer (biacetyl in CH_3CN) by exciting at 420 nm where the investigated sydnones do not absorb. In fact, no sign of the chromatographic peaks at 16.2 and 21.3 min, assigned to BD produced by compound B and C, respectively, were observed in the HPLC measurements. The disappearance quantum yield in the sensitized experiments was high (roughly around unitary value) pointing to a degradation of the starting material not leading to the cis isomer or the Q derivative. The production quantum yields of the latter are similar and roughly one order of magnitude smaller than the disappearance yield for A and B (0.04 and 0.09, respectively). The $\phi_{t\rightarrow c}^{sens}$ for C is $\cong$0.02. All these findings indicate that the photoisomerization under direct excitation proceeds mainly in the singlet manifold and that the triplet population is expected to be not very efficient.

The proposed mechanism that leads to the formation of benzodiazepine and quinoline derivatives is shown in Scheme 3. This mechanism has been hypotised both on the basis of a previous work (ref.5) and the new results on the primary decay stages after excitation by ns flash photolysis.

Table 3
Quantum yields of the main photoreactions measured in CH_3CN for the three stilbenylsydnones.

Trans isomer	$\phi_{t\rightarrow BD}$	$\phi_{t\rightarrow Q}$	$\phi_{t\rightarrow c}$
A		0.004	0.010
B	0.022	0.004	0.048
C	0.048		0.002

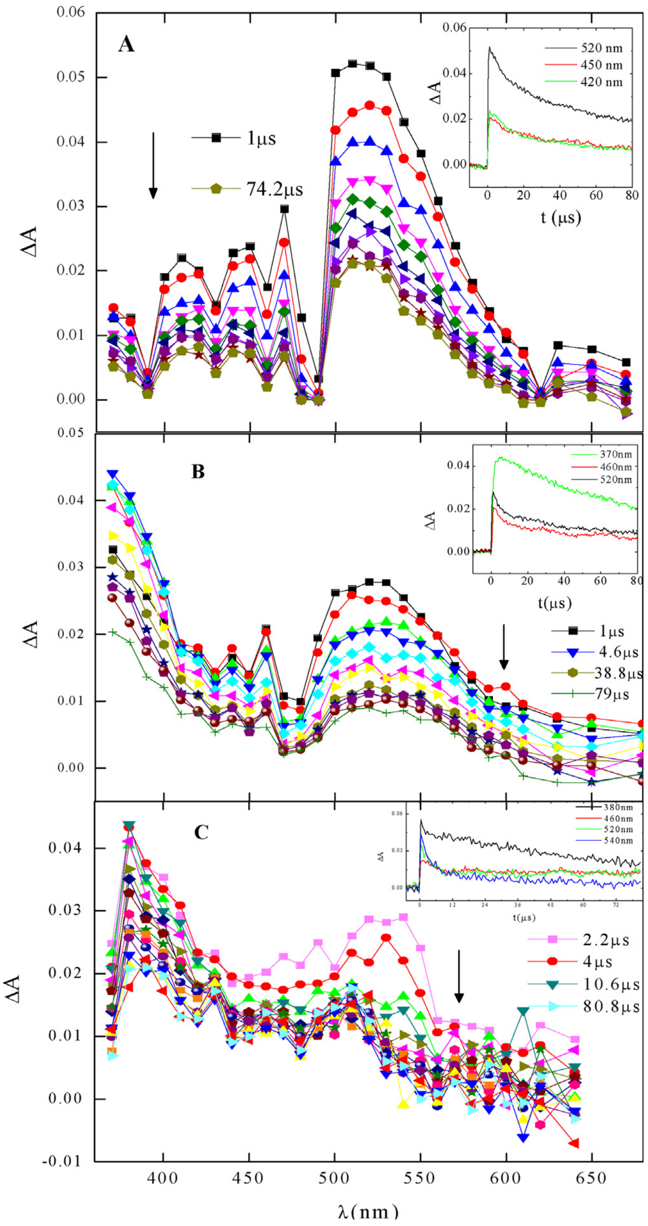


Fig. 4. Transient absorption spectrum under direct excitation of A, B and C (λ_{ecc} = 355 nm) in CH_3CN. Insert: decay kinetics at different monitoring wavelengths.

4. Conclusions

This work on the primary decay stages after excitation of three compounds bearing the stilbene and sydnone groups provided interesting information on their properties.

The absorption spectra of the three compounds were described with the help of theoretical calculations that allowed to evidence the role of very weak bathochromic transitions, not detected in the experimental spectra, in addition to the main bands of ethylenic character.

Table 4
Properties of the transients detected under excitation of St(Ph)Sy in deaerated CH_3CN (λ_{exc} = 355 nm).

compound	λ (nm)	ΔA	k ($10^5\ s^{-1}$)	k×ΔA ($10^4\ s^{-1}$)	Biexp ($10^4\ s^{-1}$)
St(H)Sy	520	0.052	4.0	2.0	
	450	0.024	14	3.2	
	420	0.019	9.5	1.8	
St(Me)Sy	520	0.028	9.1	2.5	
	370	0.044			90 (rise) 1.0 (decay)
St(Ph)Sy	520	0.029			11[a]
	380	0.045	3.3	1.5	

[a] monoexponential decay.

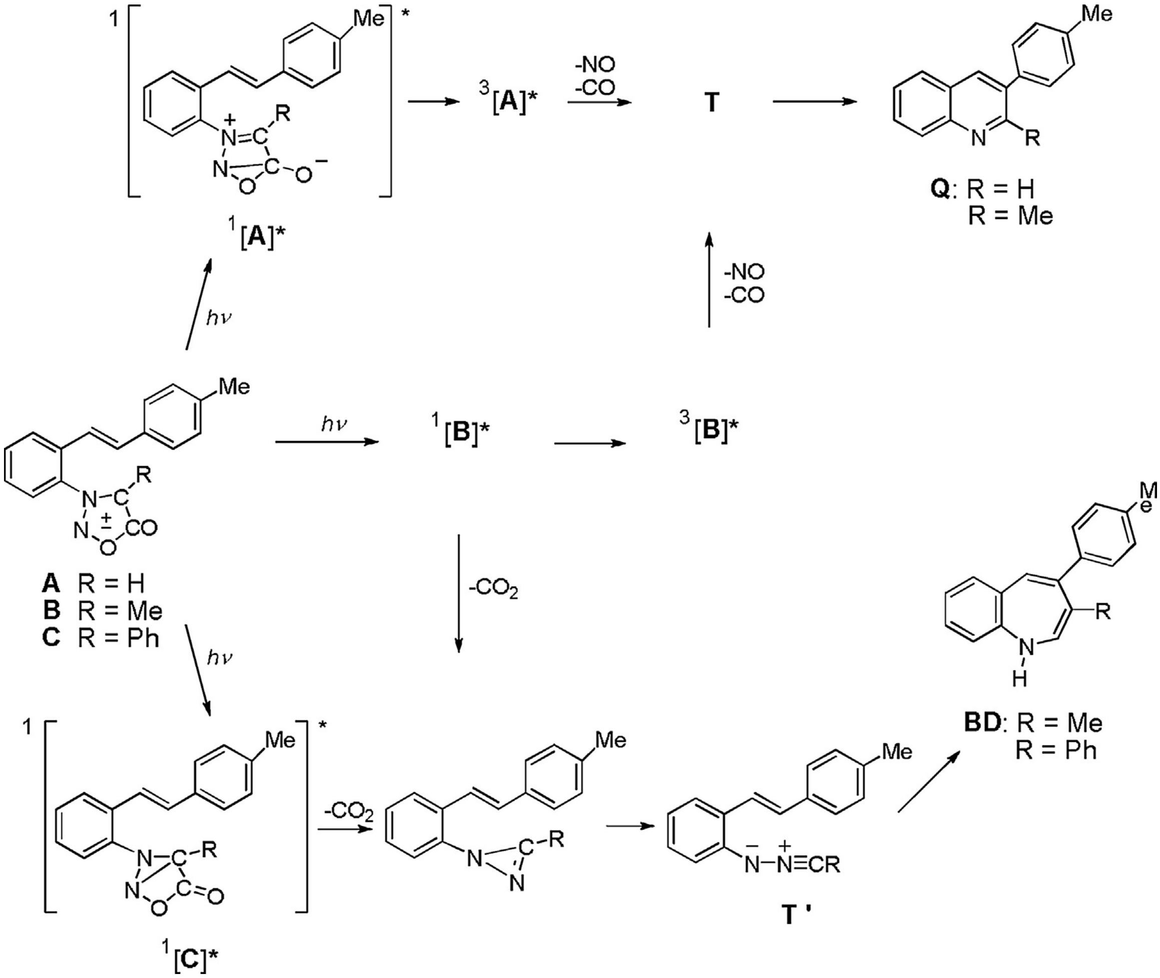
The measurements of the quantum yields of the radiative and reactive decays, both very small, evidenced the interesting effect of the substituent (H, Me and Ph) at the sydnone ring on the competition of different reactive channels. A part the presence of some trans → cis photoisomerization in all the three compounds, the yields of the competitive decay pathways showed a preference of the channel leading to the Q derivative for A, a net preference of that leading to the BD derivative for C and a small presence of both products for B. These results are in good qualitative agreement with those reported in the previous paper[5] where the photochemical study was carried out in preparative conditions.

The flash photolysis measurements showed the spectra of the intermediates leading to the Q and BD derivatives according to the substituent effect described above for the three compounds. Experiments in the presence of triplet donor sensitizers allowed to evidence a precursor role of a triplet state that fast decays to the intermediate at 520 nm leading to the Q derivative. On the other hand the absence of sensitizer effect on the transient at 370 nm, responsible for the BD formation, indicated that this last process takes place in the singlet manifold.

Table 5
Effect of the addition of the investigated compounds on the transient absorption of the triplet sensitizers in CH_3CN (λ_{exc} = 355 nm).

compound	sensitizer	λ (nm)	ΔA[a]	τ_T (μs)	τ_T[a] (μs)	k ($10^5\ s^{-1}$)
St(H)Sy (A)	DTK	680	0.067	2.5	0.83	
		520	0.044			2
		410	0.039			≅70
	TX	630	0.47	6.53	1.03	
		520	0.066			3
		410	0.051			14
St(Me)Sy (B)	DTK	680	0.20	2.5	0.58	
		520	0.09			2.5
		370	0.15[b]			
	TX	630	0.46	6.53	0.81	
		520	0.062			1.3
		370	0.005[c]			
St(Ph)Sy (C)	DTK (I)	680	0.11	2.36	0.96	
		520	0.064			40
		370	0.065[b]			
	DTK (II)	680	0.22	2.36	1.3	
		520	0.11			33
	TX	630	0.23	6.53	1.4	
		520	0.017			9
		370	undetectable			

[a] values obtained after addition of the investigated compounds.
[b] signal due to the triplet DTK absorption.
[c] too low signal, impossible to fit.



Scheme 3. The proposed mechanism that leads to the formation of benzodiazepine and quinoline derivatives is shown in Scheme 3. This mechanism has been hypotised both on the basis of a previous work (ref. [5]) and the new results on the primary decay stages after excitation by ns flash photolysis.

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