



Time-resolved studies on the photoisomerization of a phenylene–silylene–vinylene type compound in its first singlet excited state

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ARTICLE INFO

Article history:

Received 17 June 2010

Received in revised form

19 October 2010

Accepted 26 October 2010

Available online 3 November 2010

Keywords:

Trans–cis photoisomerization

Transient absorption

Triplet sensitization

The first singlet excited state

2-dimethylphenylsilylethenylbenzene

ABSTRACT

In femtosecond laser-flash photolysis experiments, the first singlet excited state of *trans*-ST, ((*E,E*)-[1,4-bis(2-dimethylphenylsilyl)ethenyl]benzene) showed a strong S₁(π,π^*)-Sn absorption band at 540 nm in acetonitrile and at 550 nm in hexane. The lifetime of this state was determined to be 13.2 ± 2.0 and 11.1 ± 1.5 ps, respectively. Intersystem crossing was shown not to be a principal route for the deactivation of this S₁ state of *trans*-ST. Evidence for this conclusion involved two complementary nanosecond laser-flash photolysis experiments. In one experiment involving direct excitation, no transient absorption spectrum was detected in the 350–650 nm spectral range. Yet, in the second experiment, on triplet sensitization, using xanthone, a transient absorption at 400 nm was tentatively assigned to the triplet state absorption of *trans*-ST. Photoisomerization was monitored in nanosecond time-resolved bleaching experiments. From these experiments the *trans–cis* photoisomerization quantum yield was determined to be 0.23 on direct *trans*-ST excitation. In a xanthone-sensitized stationary-state excitation experiment, the *trans–cis* isomerization quantum yield was determined to be 0.32. The main deactivation route of *trans*-ST in its S₁ state is repopulation of the ground state directly through internal conversion or with the intermediacy of conformers with twisted geometry.

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1. Introduction

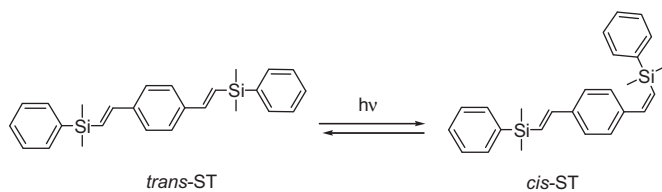
Organosilicon polymers have received increasing attention in potential applications as photo- and electroluminescent materials [1–4]. However, these luminescence quantum efficiencies can be limited by the presence of nonradiative pathways such as internal conversion S₁ → S₀ and/or intersystem crossing from the singlet to the triplet manifolds [5]. Photophysical and photochemical properties such as UV–vis absorption, emission, *cis–trans* and *trans–cis* isomerization have been recently studied for compounds containing silylene–vinylene–phenylene moieties [6–10]. Comparative studies on a silylene–vinylene–*p*-phenylene polymer and a model compound *trans*-ST ((*E,E*)-[1,4-bis(2-dimethylphenylsilyl)ethenyl]benzene) (see structure in Scheme 1) indicate that the 2-dimethylphenylsilylethenylbenzene chromophore is responsible for their photophysical properties and reactivities of their first singlet S₁ excited states [6]. Photoexcited *trans*-ST produces fluorescence with a quantum yield $\Phi_F=0.008$ and undergoes *trans–cis* isomerization with a quantum yield $\Phi_{\text{trans} \rightarrow \text{cis}}=0.23 \pm 0.02$ in dichloromethane. The *cis* isomer, *cis*-ST, was isolated as a

photoproduct (see Scheme 1) and was found to be a nonfluorescent species ($\Phi_F < 1 \times 10^{-4}$).

Photodegradation of *trans*-ST in dichloromethane was found to be a minor process in the deactivation of its S₁ state ($\Phi \leq 1 \times 10^{-2}$) [6]. Lack of an oxygen effect on the photoisomerization quantum yield led to the conclusion that the triplet excited state is not involved in the photodegradation reaction [6]. However, there remained the open question of whether intersystem crossing is a significant deactivation pathway for the S₁ state of *trans*-ST.

There has been a long tradition in the *cis–trans* photoisomerization of olefins where phantom states (“perpendicular” excited states in the mechanism as intermediates, formed by rotation about the axis of the C=C bond), in addition to triplet states, have been implicated in the reaction mechanisms [11–13]. Using time-resolved spectroscopy techniques of observing transients in alkenes photoexcited to the S₁ state [14–17] it is possible to probe directly the *cis–trans* photoisomerization mechanisms elaborated from classical stationary-state photochemistry [12]. Photophysical and photochemical properties of the parent hydrocarbon, the *E,E* isomer of 1,4-distyrylbenzene (side 2-methylphenylsilyl groups in *trans*-ST substituted with phenyls), have been recently described [18,19]. The S₁ state of 1,4-distyrylbenzene is mainly deactivated by fluorescence ($\Phi_F=0.84$, $\tau_{S_1}=1.7$ ns in methylcyclohexane/3-methylpentane), with some contribution from S₁ → S₀ internal conversion, while *trans–cis* photoisomerization ($\Phi < 0.001$) and S₁ → T₁ intersystem

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Scheme 1. *Trans*–*cis* photoisomerization.

crossing can be neglected [18]. The current paper will show that *trans*-ST exhibits an extremely short lifetime in the S_1 state (~ 12 ps in hexane or acetonitrile), mainly due to a radiationless process repopulating *trans*-ST in the ground state. We will apply transient absorption spectroscopy (including femtosecond) with UV–vis detection to describe the properties of the *trans*-ST compound in its S_1 state (lifetime, absorption spectrum) and its deactivation pathways. Similarities to the classical works on *trans*-stilbene will be mentioned.

2. Experimental

Trans-ST was synthesized and purified by the methods described elsewhere [6]. The solvents for ultrafast studies were of spectrophotometric grade from Aldrich and used as received. The femtosecond transient absorption system has been described elsewhere [20]. The excitation wavelength was set to 322 nm, corresponding to the low-energy edge of the *trans*-ST absorption band (transition $S_0 \rightarrow S_1(\pi, \pi^*)$, Fig. 2 in Ref. [6]). The molar absorption coefficient at 322 nm in hexane is $13,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, higher than that of the isomerization product *cis*-ST ($6300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The sample concentration was adjusted to an absorbance of 0.75 at the excitation wavelength in a 1 mm flow cell, and the sample volume was 50 ml. The pump pulse energy was about 6 μJ in the sample. To avoid rotational-diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°) [21]. The entire set of pump–probe delay positions (cycle) was repeated at least three times, to determine data reproducibility from cycle to cycle. Transient absorption spectra were corrected for chirp in the probe continuum [22]. Kinetic analysis was performed by global fitting of traces, at selected probe wavelengths, to the sum of a single exponential and a constant offset. Convolution with a Gaussian response function was included in the global fitting procedure. The instrumental response was approximately 300 fs (FWHM).

Triplet-sensitized experiments were performed with a nanosecond transient absorption spectrometer described previously [23]. Pump pulses (355 nm) with energies of about 1 mJ in the sample, 8 ns (FWHM), were generated at a repetition rate of 0.5 Hz by a Q-switched Nd:YAG laser (Continuum Surelite II). The probing light source was a 150 W xenon arc lamp (Applied Photophysics), used in the pulsed mode with a 1 Hz repetition rate. The transmitted probe light was dispersed by a monochromator (6 nm spectral resolution, Acton Research SpectraPro 300i) and detected by a photomultiplier (R928 Hamamatsu) coupled to a digital oscilloscope (Tektronix TDS 680 C). A home-made program written in the LabView 4.1 environment was used for the ΔA calculations, data fitting, and the dialog between the PC and the oscilloscope. An input output card (PCI-MIO-16XE-10) was used for time-control of TTL signals to trigger the laser, lamp pulser, and shutters. Experiments were performed on 4 ml solution samples contained in a quartz cell (1 cm \times 1 cm cross-section). All solutions were deaerated for about 15 min prior to each experiment with an argon gas flow to remove traces of O_2 . For monitoring of the *trans*-ST bleaching kinetics, another nanosecond laser-flash photolysis setup was used [24].

A XeCl excimer laser was operated at 308 nm, 8 mJ pulse energy with a 20 ns pulse width. Transients were monitored with a pulsed 1 kW xenon lamp, with the monitoring beam perpendicular to the laser beam. All experiments were carried out in rectangular quartz cells (0.5 cm \times 1 cm). The monitoring light pathlength was 0.5 cm. All transient absorption experiments were performed at room temperature.

Xanthone was used as a triplet sensitizer, along with stationary-state excitation ($\lambda_{\text{irr}} = 351$ nm, argon laser), in order to investigate the *trans*–*cis* photoisomerization of triplet *trans*-ST in acetonitrile. The experiments were carried out in a 1 cm \times 1 cm rectangular cuvette equipped with a tube for the solution containing $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ of *trans*-ST and $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ of xanthone in acetonitrile. The solution was bubbled with argon (15 min) before the experiment and stirred during the irradiations. The power of the argon laser was lowered to 15 mW in order to decrease the light intensity sufficiently to be able to observe the reaction's progress within a convenient time interval. The progress of the reaction was monitored by GC. The quantum yield of *trans*–*cis* isomerization was obtained by extrapolation to zero irradiation time.

The phosphorescence spectrum of *trans*-ST was measured on a Perkin–Elmer MPF3 spectrofluorimeter. The sample was frozen, and argon was circulated around the cell holder to avoid condensing moisture on the walls of the cell.

3. Results and discussion

Ultrafast photolysis (322 nm) of *trans*-ST in hexane produced the transient UV–vis spectra presented in Fig. 1. Initially, a broad positive transient absorption band was formed instantaneously (< 300 fs) in the probe range 380–625 nm, and a negative band was formed in the spectral range 350–380 nm. The initial negative band was spectrally located in the range of the *trans*-ST fluorescence spectrum peaking at about 350 nm. Thus it can be ascribed to the $S_1 \rightarrow S_0$ stimulated emission. At later delay times, within a 0.3–50 ps time window, the absolute magnitude of both bands decayed to zero. An isosbestic point was observed at 380 nm between the negative band and the positive band. This indicates that both of these spectral components were decaying with the same kinetics (lifetime, see below). Hence, the two spectral bands are likely to characterize the same species. Thus the initial band peaking at 550 nm is assigned to the $S_1 \rightarrow S_n$ *trans*-ST absorption. Kinetic traces at selected probe wavelengths (550 and 360 nm) are shown in Fig. 1b. Based on a global fitting analysis, the S_1 state lifetime of *trans*-ST is 11.1 ± 1.5 ps in hexane. Changing the solvent from hexane to acetonitrile resulted in a 10 nm blue-shift of the S_1 absorption band (Fig. 1c), and the S_1 lifetime was determined to be the same as in hexane, within experimental error, (13.2 ± 2.0 ps). At longer delay times, from 50 ps to 2 ns, only a weak absorption band at 460 nm was observed in hexane, but in acetonitrile a relatively strong band was still present at 445 nm (Fig. 1c).

These bands cannot be assigned to the triplet excited state based on the following evidence from nanosecond laser-flash photolysis spectroscopy. No positive absorption bands in the 400–500 nm spectral region were observed on direct *trans*-ST excitation with $\lambda = 266$ nm in acetonitrile. However, evidence for the location of the *trans*-ST triplet–triplet absorption band was obtained from a triplet sensitization experiment. Using xanthone as the triplet sensitizer, a new band appeared at 400 nm (see Fig. 2), which is tentatively assigned to the triplet–triplet absorption of *trans*-ST (however by analogy to stilbene contribution from twisted conformer in the triplet state cannot be ruled out of consideration [13]). The lifetime of this *trans*-ST triplet state was determined to be 25 ± 5 ns (see also Figs. S1 and S2). The absence of triplet formation, following the direct excitation of the S_1 state of *trans*-ST,

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