trans-Stilbene Photochemistry Beyond 500 nm

M. Seydack[1] and J. Bendig[1]

trans-Stilbene and its derivatives have been widely investigated over the past decades in terms of both photophysics and photochemistry. This study presents an intramolecular energy transfer within a triple chromophore from an optically excited fluorescein onto an extremely low-lying *trans*-stilbene T_1 state. As in many stilbenes an isomerization along the triplet pathway was sufficiently effective to be monitored by a decrease in the *trans*- and a concomitant increase in the *cis*-stilbene absorption bands. Semiempirical calculations and sensitizing experiments were performed to obtain a good estimate of the S_0–T_1 energy difference, which was found to be about 142 kJ/mol. This uncommonly low value enables a long-wavelength photochemistry of *trans*-stilbene at exciting light wavelengths ranging from 500 nm (fluorescein) up to at least 680 nm (applying an external triplet sensitizer such as methylene blue).

INTRODUCTION

Both *trans*-stilbene and its 4,4′-substituted derivatives have long been observed to isomerize to the thermodynamically less stable *cis*-stilbene when exposed to UV light, i.e., when its S_1 state is populated. In most cases several competing processes, e.g., intersystem crossing, fluorescence, photocyclization of the generated cis-compound, etc., could be observed as well [1]. Many of these *trans*-stilbenes, however, are also capable of following a triplet route of isomerization. Here, the T_1 state may be populated either by an efficient intersystem crossing from the initially excited S_1 state or artificially by inter- or intramolecular sensitizing [2,3] according to the exchange mechanism described by Dexter [4]. The triplet energy of these 4,4′-substituted *trans*-stilbenes ranges from 189 to 218 kJ/mol [1].

In our study we coupled *trans*-stilbene in the 4-4′-position to two chromophores, e.g., fluorescein (Fig. 1a). The participating π-electron systems were spacially separated by introducing thioureanyl bridges. Thus we obtained a triple chromophoric dye according to the common definition given in Ref. 5. On this basis it can be assumed that the properties of the overall molecule are to be understood in terms of a linear combination of the individual chromophores DPS and PFT (Figs. 1b and c). As for the absorbance, this assumption is clearly confirmed (Fig. 2), with some deviations below 320 nm originating from twice as much thioureanyl in the sum of one DPS and two PFT absorption spectra than in the DFS triple chromophore. Comparison of steady-state fluorescence spectra yields no difference in band shape or peak wavelengths, either. Also, the fluorescence decay times of the fluorescein chromophore, measured by time-correlated single-photon counting, for fluorescein, PFT, and DFS are in very good aggreement (3.9–4.0 ns).

Exciting *trans*-DFS at UV wavelengths invariably excites all chromophores including the stilbene (DPS) moity itself, which in turn leads to an isomerization to *cis*-DFS. Correspondingly, a gradual decrease in the *trans*-DPS A-band (centered at 349 nm) could be observed, with a concomitant increase in the major *cis*-DPS absorption around 254 nm. If irradiated at 514 nm,

[1] Institute of Chemistry, Humboldt University, Hessische Str. 1-2, 10115 Berlin, Germany.
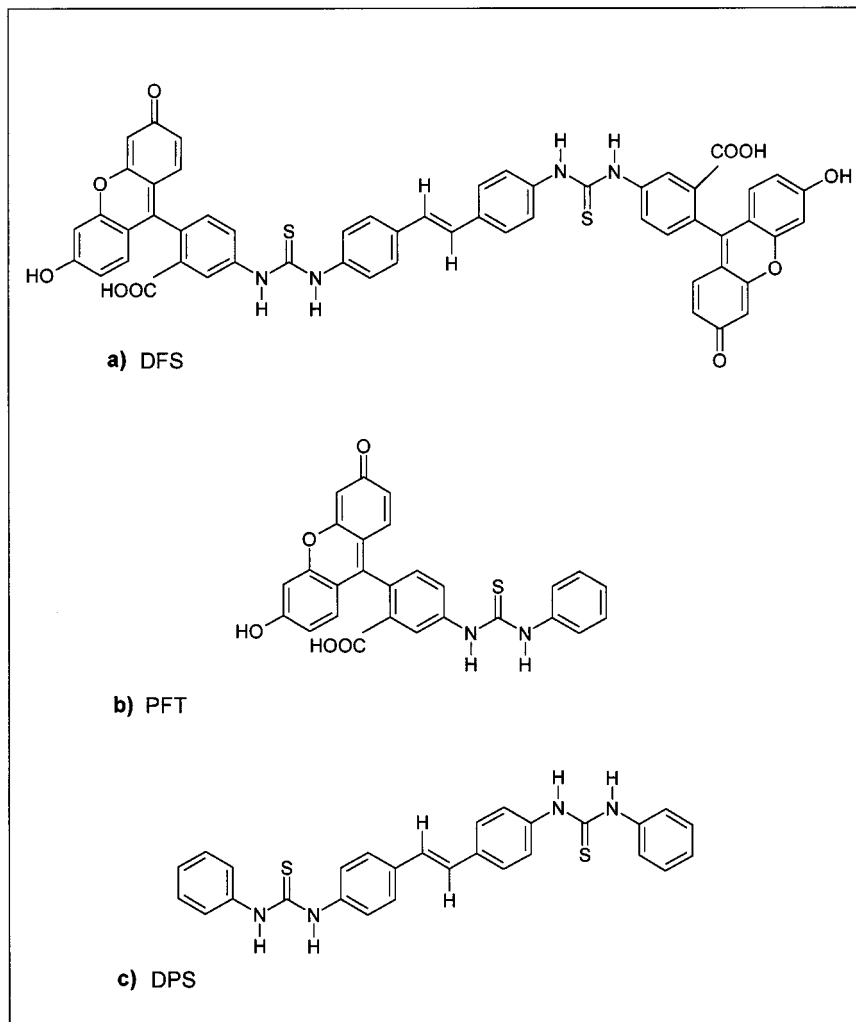
Fig. 1. (a) *trans*-4,4′-Di(fluorescein-5″-yl-thioureanyl)-stilbene (DFS). (b) *N*-Phenyl-*N*′-(fluorescein-5″-yl)-thiourea (PFT). (c) *trans*-4,4′-Di(phenyl-ureanyl)-stilbene (DPS).

however, only the fluorescein may absorb. Unexpectedly, though, in this case the same changes in the absorption spectra were found (Fig. 3) and both DFS isomers could be seperated chromatographically by Nickoleit [6]. Preliminary investigations [6,7] suggested that a simultanous excitation of both fluorescein chromophores followed by an ISC process and a subsequent triplet–triplet annihilation accounts for this finding. In the present study we critically reviewed this two-photon model and found clear evidence for a different reaction pathway.

EXPERIMENTAL

All experiments were performed both in deaerated and in aerated solutions of methanol (Uvasol; Merck).

No marked differences between these two cases could be detected. At the measured pH 6.3 the monoanionic form of fluorescein is dominant, which is confirmed by the form of the absorption spectra [12]. All spectra were recorded on an Hitachi U-3410 spectrophotometer. Irradiations at 514.5 nm were carried out using a Lexel 3500 Ar⁺-Laser. A long-pass edge filter was used to block spontaneous UV emission from the laser resonator. An HBO 500 high-pressure mercury lamp (Oriel) combined with 254/313/333-nm interference filters (Carl Zeiss Jena) served as the UV source. Solutions were contained in air-sealed 1 cm quartz cuvettes at all times and a magnetic stirrer was used during irradiation.

Semiempirical calculations were performed using the ZINDO/S implementation of the Hyperchem 5.1 Professional software package. Configuration interaction
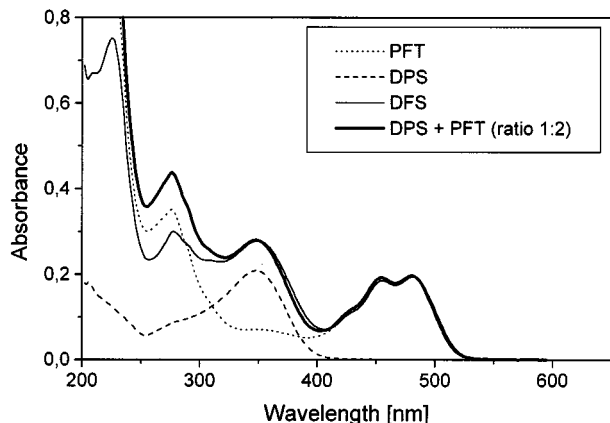
Fig. 2. Absorbance of DFS compared to DPS, PFT, and the sum of DPS and PFT (ratio, 1:2).

was always included. Prior to the quantum chemical calculations the molecular geometries were optimized by applying the MM+ forcefield method.

RESULTS AND DISCUSSION

Investigating the intensity dependence of the 514 nm-induced isomerization of DFS revealed a linear correlation between the laser power (and thus the photon flux) and the decrease in the *trans*-stilbene A-band at 349 nm. Preliminary investigations showed that the proportion of *cis*-stilbene contributing to the overall absorbance at this wavelength is minimal. Therefore a two-photon absorption as the primary proccess can be *excluded*, as in that case a square law holds [8]. This result is corroborated by experiments with the photon number fixed for all intensities and by varying the focus of the exciting light.
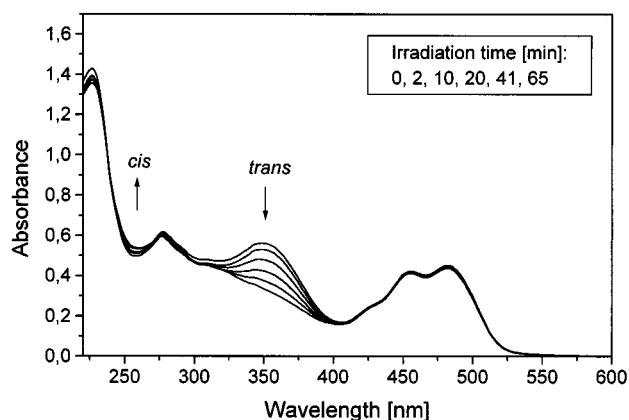
Since a simple singlet energy transfer (radiative or nonradiative) from fluorescein to *trans*-stilbene is energetically not feasible, the positions of the triplets involved were given a closer look: fluorescein in polar solvents has a triplet energy of 189.2 kJ/mol [9], which corresponds to the phosphorescence spectra taken. Triplet energies of 4,4′-substituted *trans*-stilbenes vary between 189 and 218 kJ/mol [1]. Allowing for nonvertical energy transfer, which was found in all isomerizations around ethylene bonds [1], it is impossible to judge from this point whether a triplet energy transfer is possible. For that reason, sensitizing experiments with compound DPS were performed. DPS can be expected to be identical to DFS in terms of its spectroscopic properties as far as the substituted stilbene is concerned (compare Fig. 2). It was shown that a solution of DPS can be isomerized when fluorescein is added and the mixture is irradiated at 514 nm, meaning that the process described is effective at both an intra- and an intermolecular level. Going one step farther, it appeared that DPS was even isomerized by irradiating added sensitizers such as erythrosin, rhodamine B, perylene, and, finally, methylene blue (Fig. 4).

As, e.g., $E_T = 146$ kJ/mol for methylene blue, this implies an *unusually low-lying T_1 state* of *trans*-DPS and also by that of the stilbene chromophore in *trans*-DFS.

Semiempirical calculations confirm this assumption, with values of $E_T = 150$ kJ/mol for 4,4′-thiourea-substituted *trans*-stilbenes, including DPS. According to these calculations only a twofold symmetrical substitution is capable of lowering the triplet energy levels to such an extent, while the S_1–S_0 energy difference remains practically unchanged. Obviously, the twofold substitution in combination with the overall molecular symmetry

Fig. 3. Absorbance of DFS before and after irradiation at 514 nm in deaerated methanol (3.0-ml solution; light power, $P = 390$ mW).
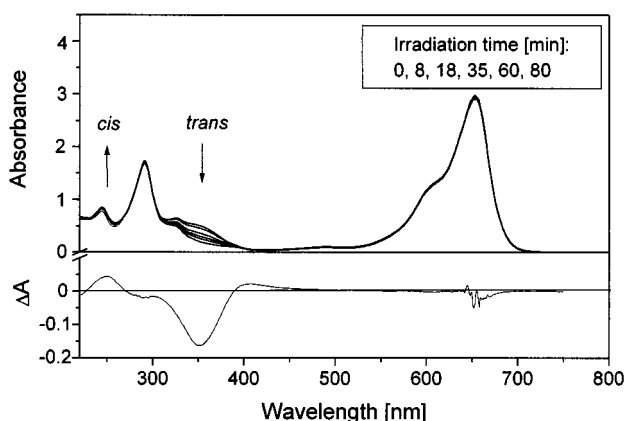

Fig. 4. Top: Absorbance of a mixture of methylene blue ($c = 3.75 \times 10^{-5}$ M) and DPS ($c = 1.24 \times 10^{-5}$ M) before and after irradiation at 514 nm in deaerated methanol (3.0-ml solution; light power, $P = 250$ mW). Bottom: Corresponding difference spectrum: absorbance after 60 min of irradiation subtracted from the initial spectrum.

increases the exchange integral, which in turn determines the singlet–triplet splitting. An induced break of the C_i symmetry, e.g., by rotating only one substituent, resulted in a lowering of the triplet energy by 35 kJ/mol. This rotation is feasible at ambient temperatures since the seperating energy barrier is of the order of only 12 kJ/mol [10].

Given the fact that chlorophyll b ($E_T = 136$ kJ/mol) proved unable to sensitize the DPS triplet and taking into account that sensitizers with triplet energies a few kilojoules per mole below that of DPS/DFS can be expected to be effective to some degree (due to nonvertical energy transfer), we assume the triplet energy of *trans*-DPS and *trans*-DFS to be at $E_T = 142 \pm 4$ kJ/mol.

Photocyclization of an excited cis-compound (*cis*-DPS/DFS) as in unsubstituted *cis*-stilbene could not be detected, even after prolonged excitation of the photoproduct at UV wavelengths. Also, a back reaction from *cis*-DPS/DFS to *trans*-DPS/DFS was not found when exposing the product to 254 or 313 nm irradiation, where the cis-compounds show a stronger absorption than the trans-educts.

Although stilbenes, once excited, are known for quite a number of competing reactions, these are extremely unlikely to account for the presented results: an electron transfer reaction between the chromophores would always result in a ground-state stilbene-anion/cation, from which an isomerization is impossible unless a second photon is absorbed [11]. This process, again, should have the characteristics of two-photon absorption, which was excluded (see above). Moreover, there was no indication of a polarity dependence of the isomerization of DFS. Due to the high pK_B value of thiourea and the pH of the solvent (typically 6.3), proton transfer reactions between those centers can be eliminated, too.

CONCLUSION

Optical excitation of DFS at wavelengths above approximately 430 nm means exciting solely the fluorescein. Among the resulting deactivation processes, intersystem crossing to the fluorescein T_1 state is the key step. Once the vibrationally relaxed T_1 state is populated, the thioureanyl-substituted *trans*-stilbene T_1 state presents an efficient, low-lying intramolecular energy acceptor. The close spacing between the chromophores enables a triplet–triplet energy transfer onto this localized T_1 state, whence the triplet route of isomerization is taken. A vital precondition for this effect is the extreme lowering of the *trans*-stilbene triplet states down to 142 ± 4 kJ/mol by introducing *two* thiourea-subtituents in the 4,4'-position.

Obviously, in DFS this mechanism is highly competitive. Phosphorescence from the excited fluorescein chromophore was hardly measurable, whereas no phosphorescence could be detected from the *trans*-stilbene subchromophore at 77 K in various solvents.

ACKNOWLEDGMENTS

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