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Photochemistry of *o*-Pyrrolylstilbenes and Formation of Spiro-2*H*-pyrroles and Their Rearrangement to Dihydroindoles

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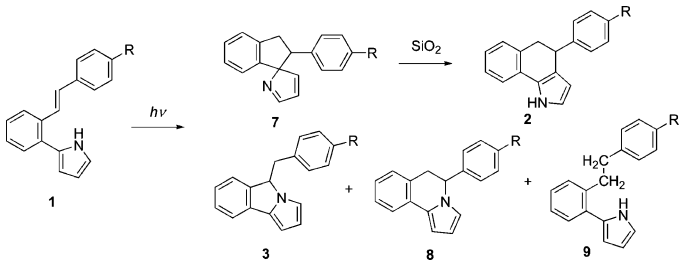

Excited states of stilbenylpyrroles **1a**−**1c** deactivate by two photochemical processes: cis−trans-isomerization and hydrogen transfer of NH to the stilbene double bond. NH-transfer results in the formation of two quinone dimethane intermediates, **10** and **11**, and biradicals **12**. Intramolecular cyclization of intermediates **10**−**12** gives rise to polycyclic compounds spiro-2*H*-pyrroles **7**, pyrroloisoindoles **3**, and pyrroloisoquinolines **8**. Spiro-2*H*-pyrroles **7** rearrange on silica gel, giving dihydroindoles **2**.

Introduction

Synthesis of polycyclic compounds that contain pyrrole or indole subunits has attracted considerable attention, mainly because of the interesting biological properties of these compounds.[1] Besides numerous reports on the synthesis of porfirines, quite significant progress has been documented in previous decades on the synthesis of pyrroloisoindoles,[2] pyrroloisoquinolines,[3] and benzoindoles.[4]

In continuation of our research on the synthesis and photochemistry of furan[5] and pyrrole[6] derivatives of *o*-divinylbenzenes, we discovered a convenient photochemical method for the transformation of stilbenylpyrroles to indole and isoindole derivatives.[7] It was revealed that, after photolysis of stilbenylpyrrole (SP) **1a** both dihydroindole (DHI) **2a** and pyrroloisoindole (PI) **3a** were isolated. We proposed a mechanism for

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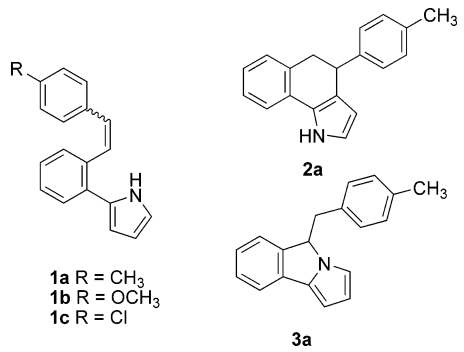
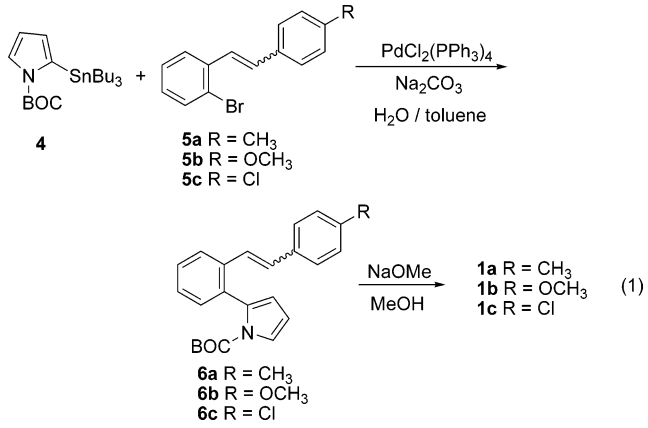


the photochemical transformation that included an intramolecular electron transfer followed by an intramolecular NH hydrogen transfer. A similar mechanism has also been proposed for the other examples of intramolecular[6] and intermolecular[8] addition of pyrrole and amines to double bonds. Whereas the thorough investigation of the mechanism of the photochemical addition of amines has been carried out,[9] photochemical addition of pyrrole to double bonds is still under investigation, especially the intramolecular version.

In this paper we explore in greater detail the intramolecular photochemical addition of pyrrole to the stilbene double bond by changing substituents on the para position of the stilbene moiety. It was anticipated that the change of substituents may lead to improved regioselectivity of the reaction and applicability for the synthesis of DHI or PI. Moreover, an investigation of the mechanism of intramolecular photochemical addition of pyrrole to the stilbene double bond by product analysis and spectroscopic methods is presented.

Results and Discussion

Synthesis. The *N*-Boc-protected stilbenylpyrroles (**6a**−**c**) were prepared by a Stille reaction following the procedure described in the literature[10] from *N*-Boc tin derivative **4**[7] and the corresponding *o*-bromostilbenes **5**[11] (eq 1). The removal of



the Boc group and preparation of SPs was accomplished by treatment of **6** with a solution of NaOMe in MeOH. In that way mixtures of *cis*- and *trans*-SPs (**1a**−**c**) were obtained, which were separated by column chromatography on silica gel.

Preparative Irradiations. The prepared SPs **1a**−**c** were characterized by absorption bands between 280 and 350 nm, which allowed for preparative photolyses by irradiating compounds at 300 nm, in Ar-purged benzene or acetonitrile solutions ($\sim 1 \times 10^{-3}$ M). Besides preparative irradiations, in the case of **1a**, the course of the photochemical reaction was followed by irradiating a C_6D_6 solution in a NMR tube and by recording the NMR spectra after each irradiation. Short irradiations (a few minutes in a NMR tube) resulted only in cis−trans-isomerizations. After 10 min of photolysis, the conversion of the cis- to the trans-isomer and vice versa was the same, at approximately ∼20%. Since the rate of isomerization the cis-isomer to trans and vice versa is the same, this indicates that the reaction does not depend on the starting material. On prolonged irradiation, there is also a competing formation of spiro-2*H*-pyrroles **7a** (SI), the rate of which also did not depend on the starting material (*cis*- or *trans*-**1a**). Thus, irradiation of **1a** does not result in the formation of a photostationary state. The formation of products **7** is in competition with the observed isomerization.

Prolonged irradiation of all SPs **1a**−**c**, leading to the total conversion of the starting material, gave similar results, ir-

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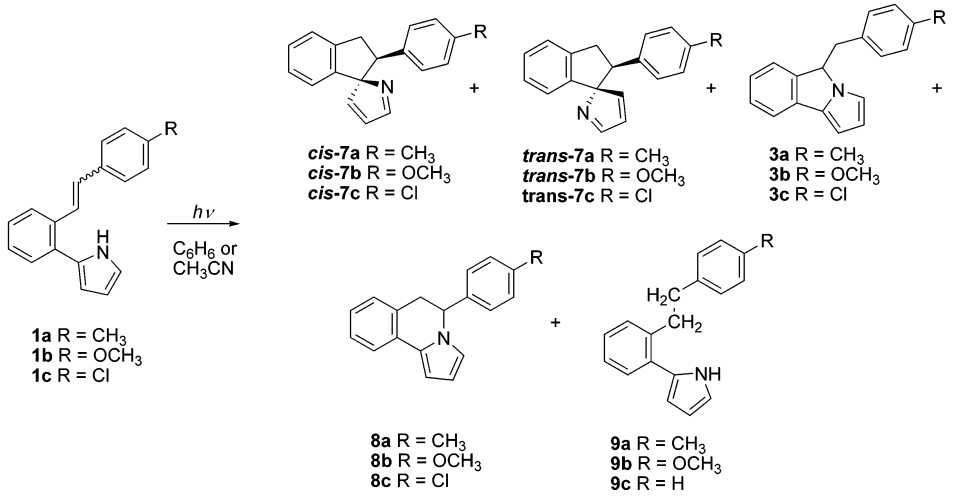
SCHEME 1



respective of the substituent on the stilbene moiety. ^{1}H NMR spectra of the crude photolysis mixtures revealed formation of two major compounds, spiro-isomers **7** (∼50−70%), which were formed in a ratio of 2:1. Besides **7**, some smaller amounts of **3** (∼3−10%), **8** (<5%), and **9** (∼3−10%) (Scheme 1) were also formed. We were especially interested in spiro-2*H*-pyrroles **7**, hitherto not observed, because of the occurrence of similar compounds in nature and due to their biological activity.[12] For an example, derivatives of spiro-2*H*-pyrroles have been found in *Horsfieldia superba*, a woody species that grows in South East Asia,[13] while the derivatives of spirotryprostatins have been found in the fungus *Aspergillus fumigatus*. The later showed inhibitory activity on the cell cycle progression, which is a useful property for the potential application for cancer treatment.[14] Moreover, spiro-2*H* pyrroles are intermediates in the biosynthesis of uroporphyrogen III, the important precursor in the biosynthesis of heme, chlorophyll, and vitamin B_{12}.[12f−h,15]

Even though spiro compounds **7** were formed as major products, we were not able to isolate them. Any attempt to isolate **7** by column chromatography resulted in their rearrangement, giving DHI derivatives **2** in 30−60% yield. The yields of the isolated products after photolyses and chromatographic separations are presented in Table 1. Besides isolated compounds and high molecular weight material that remained on chromatography columns, some smaller amounts (<1%) of unidentified products were detected, but no attempt was made to isolate and characterize them. The instability of **7a**−**c** on silica and their transformation to DHIs can be explained by their basicity, where **7** is protonated on the silica, giving **7aH**$^+$−**7cH**$^+$ (Scheme 2).

TABLE 1. Isolated Yields of the Products after Photolysis of 1a−c (in CH_3CN or C_6H_6) and Column Chromatography

	2	3	8	9
1a[a]	32.5	4.5	−[d]	9.5
1b[b]	27.8	9.8	3.8	−[d]
1c[c]	58.4	2.0	traces	6.7[e]

[a] Irradiation for 30 min at 300 nm. [b] After 2 h of irradiation at 300 nm, 10.9% of **1b** was recovered by column chromatography. [c] Irradiation for 15 min at 300 nm. [d] Compound was not detected. [e] The isolated reduction product did not contain Cl.

The protonated forms then undergo rearrangement (1,2-alkyl shift), resulting in the more stable, tertiary benzylic carbonium ions **2aH**$^+$−**2cH**$^+$. The loss of a proton yields DHIs **2a**−**c**, which were isolated in moderate to good yields.

Even though we were not able to isolate isomers **7a**−**c**, their structure was undoubtedly assigned according to ^{1}H and ^{13}C NMR spectra of the crude mixtures after photolyses. The aliphatic regions of the ^{1}H NMR spectra of the major spiro isomers were characterized by the presence of a doublet of doublets corresponding to the vicinal H at δ ∼3.6 ppm, and two doublets of doublets at 3.75 and 2.95 ppm corresponding to geminal H. On the other hand, protons of the minor isomers appear in the aliphatic region at δ 4.20 (vicinal H) and 3.10 ppm (corresponding to 2 geminal H). The important characteristic of the aromatic regions of the ^{1}H NMR of **7a**−**c** (major isomers) is the presence of three signals corresponding to the protons of cycloimines: doublets at 5.8 (J = 4.9 Hz), doublets of doublets at 6.9 ppm (J = 4.9 Hz, J = 0.9 Hz), and broad singlets at 7.3 ppm. The carbon signals of the cycloimine are present at δ ∼162, 156, 130 (doublets), and ∼90 (singlet) ppm, while the aliphatic region of ^{13}C spectra shows the presence of doublets at δ ∼38 and triplets at 54 ppm. The values of the chemical shifts of the cycloimine carbons and protons are also in accord with the values found in the literature for similar molecules.[12f−h] Additional support to the assigned spiro structure of compounds **7** and their acid-catalyzed rearrangement was obtained by filtration of the crude photochemical mixture after photolysis of **1c** through a column filled with neutral aluminum oxide. The filtration furnished a very small quantity of the separated major stereoisomer of **7c**, indicating that spiro compounds are stable unless exposed to acidic condition or silica. However, since we were not able to isolate pure isomers

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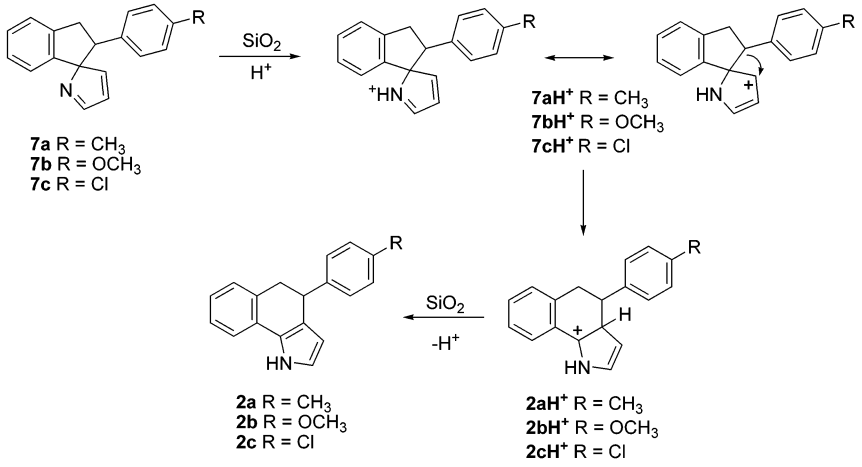
SCHEME 2



7, the stereochemistry on the spiro carbons was not unambiguously assigned.

The structures of the isolated products **2**, **3**, **8**, and **9** were assigned according to ^{1}H and ^{13}C NMR and MS. DHIs **2a**−**c** are characterized by the presence of three signals in the aliphatic region of ^{1}H NMR which appear as ABX systems at δ ∼4.1, 3.0, and 2.9−3.0 ppm. On the other hand, in the aromatic region only two pyrrole C−H multiplets are present at 6.3 and 6.0 ppm. In the ^{13}C NMR spectra, in the aliphatic region the doublets and the triplets are present (∼40 and 39 ppm), while the aromatic region clearly indicates the presence of only two pyrrole doublets at δ ∼118 and 108 ppm. The DHI structures **2a**−**c** were additionally indicated by MS, where the characteristic basic signal (m/z = 168) after the loss of tolyl, methoxyphenyl, or chlorophenyl group, respectively, was present.

The PIs **3a**−**c** are characterized by the presence of three signals in the aliphatic region of the ^{1}H NMR spectrum at δ ∼4.8, 2.9, and 2.6−2.8 ppm, while three pyrrole protons appear as very narrow multiplets at δ ∼6.3−6.5 ppm. However, ^{13}C NMR spectra clearly showed the pyrrole doublets at δ ∼116, 112, and 98 ppm. In the aliphatic region the doublets at δ ∼62 and the triplets at 41 ppm indicate the addition to the stilbene double bond. The final evidence that pointed to the assigned structure was obtained from MS, where the characteristic basic signal (m/z = 154) after cleavage of *p*-methylbenzyl, *p*-methoxybenzyl, and *p*-chlorobenzyl was present.

The pyrroloisoquinolines (PIQ) **8** were formed only in minor quantities. The highest yield of PIQ was observed on irradiation of methoxy-SP (**1b**) (∼4%). The PIQ derivatives were characterized by the presence of three signals in the aliphatic region of ^{1}H NMR at δ ∼4.6, 2.8, and 2.6 ppm. The most important evidence that points to the presence of the PIQ structure is the characteristic fragmentation in MS, namely the cleavage of the chlorophenyl or methoxyphenyl group.

The reduction products **9a** and **9c** were characterized by the presence of multiplets in ^{1}H NMR at δ ∼2.9 and 2.7 ppm and the triplets in ^{13}C NMR at ∼37 and 35 ppm. The structure of the reduction products was additionaly indicated by their MS. It should be mentioned that photolysis of SP **1c** furnished reduction product without a chlorine atom. The cleavage of chlorine in the formation of the reduction product is not surprising when taking into account the radical mechanism of the reaction (vide infra) and the relatively low dissociation energy of the C−Cl bond.

The photolysis of SPs was further investigated by changing the polarity of the solvent. We have not observed any difference in the formation of polycyclic compounds (no effort was made to investigate the influence of solvent polarity on cis−trans-isomerization) of SPs in solvents of different polarity (acetonitrile or benzene). On the other hand, differently substituted SPs showed pronounced differences in reactivity when irradiated under the same conditions. It was found that the chloro-substituted SPs (**1c**) were clearly the most reactive, ∼2 times more reactive than **1a** and ∼8 times more than **1b**, based on the conversion of the starting material over the same irradiation time. This finding indicates that electron-withdrawing substituents on the stilbene moiety facilitates an intramolecular photochemical reaction giving **3**, **7**, and **8**. Quantum yields for the product formation were not determined due to the competitive cis−trans-isomerization and the formation of high molecular weight material.

Absorption and Fluorescence Measurements. In order to get some further insight into the mechanism of the photochemcial transformation of SPs to polycyclic compounds **3**, **7**, and **8**, some preliminary photophysical investigations were performed. We recorded absorption and emission spectra of SPs in several solvents. In the absorption spectra of the trans-isomers, the maximum appeared at ∼280 nm with shoulders at 300 and 340 nm, whereas cis-isomers showed the presence of two maxima at 280 and 300 nm. Similar spectra have also been observed for *cis*- and *trans*-*o*-aminostilbene.[16]The position of the maxima in the absorption spectra of *trans*-**1a**−**c** and *cis*-**1c** are presented in Table 2.

Whereas solvent polarity did not display any influence on the absorption spectra of SPs **1a**−**c**, solvatochromic effects were observed in their emission spectra. For example, the emission spectra of *trans*-**1a** obtained by recording fluorescence in four aprotic solvents of different polarity are presented in Figure 1. All the fluorescence spectra were broad and lacked any vibronic structure, regardless of solvent polarity. The same behavior was also observed for *trans*-SPs **1b** and **1c**. The biggest solvatochromic effects were observed for the chloro-substituted SPs *cis*- and *trans*-**1c** and the smallest for methoxy-SP **1b**. Stokes shifts were not determined due to the difficulties caused by

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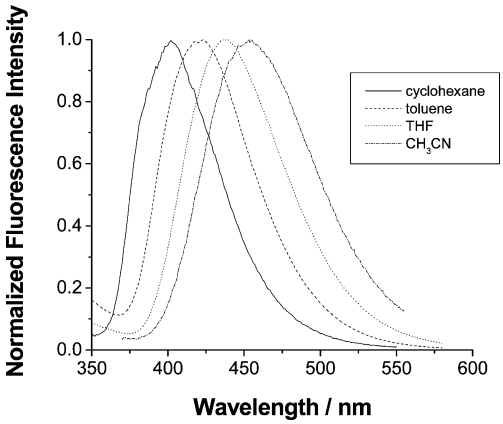

FIGURE 1. Normalized fluorescence spectra of SP **1a** recorded in four solvents: cyclohexane, toluene, THF, and acetonitrile ($\lambda_{ex} = 300$ nm).

overlapping of the lowest energy absorption transition with those of higher energy.

SPs **1a**−**c** are characterized by a mezomeric electron-donating pyrrole unit and an electron-withdrawing stilbene moiety, revealing that this excitation probably possesses pyrrole→stilbene charge-transfer character. Therefore substitution of the stilbene moiety by an electron-withdrawing (chloro) substituent would further enhance the charge-transfer character of the excited state, while an electron-donating substituent (OMe) would decrease this effect. It is interesting to note that the higher polarity of the excited state (as it is the case with chloro substituent) coincides with the higher reactivity of SP toward intramolecular reaction, giving polycyclic compounds **7**, **3**, and **8**.

Contrary to the usual emission properties of the stilbene derivatives, which can undergo cis−trans-isomerization, SPs were characterized by quite strong emissions of trans-isomers with quantum yields of fluorescence of 0.20−0.60 and somewhat lower quantum yields of fluorescence for the cis-isomers. Moreover, to our surprise, quantum yields of fluorescence increased in solvents of higher polarity, which appears to be in contradiction with the observed solvatochromic effects in the emission spectra. However, such a behavior was seen in some systems such as push−pull 2,6-disubstituted anthracenes[18] or 3,5-dimethoxystilbenes.[19] Higher fluorescence quantum yields in more polar solvents might be explained by relatively small solvent reorganization due to charge-transfer stabilization. In that way some other nonradiative processes (such as cis−trans-isomerization or intersystem crossing that may take place with lower quantum yields in solvents of higher polarity) might compensate for the loss in energy due to solvent reorganization, resulting in an overall increase of the quantum yield of fluorescence. Since shifting of the maxima in the emission spectra of SPs (by increasing polarity) is not that big, there is no extra stabilization of the emissive state via large amplitude nuclear motion. The similar solvatochromic behavior was seen for *trans*-*o*-aminostilbene, where the position of the maximum in the fluorescence spectrum shifted from 407 nm in cyclohexane to 445 nm in CH_3CN. However, the quantum yield of fluorescence of *o*-aminiostilbene decreased from 0.88 to 0.69 by going from cyclohexane to acetonitrile.[16] In addition, the lower quantum yield of SPs fluorescence in cyclohexane might be attributed to a lower solubility of SPs in that solvent. Although we have not observed the influence concentration on the quantum yield of fluorescence, fluorescence quenching due to the aggregation in nonpolar solvent cannot be totally disregarded. The position of the maxima in the emission spectra of SPs, as well as the associated quantum yields of fluorescence, are presented in Table 2.

TABLE 2. Photophysical Properties of SPs 1a−c

compd	solvent	λ_{abs} (max/nm)[a]	λ_{em} (max/nm)[b]	ϕ_f[c]
trans-**1a**	cyclohexane	277	404	0.27
	CH_3CN	277	453	0.42
	CH_3OH	277	451	0.54
trans-**1b**	cyclohexane	280	402	0.22
	CH_3CN	281	444	0.37
	CH_3OH	281	445	0.48
trans-**1c**	cyclohexane	278	408	0.30
	CH_3CN	277	474	0.38
	CH_3OH	277	468	0.50
cis-**1c**	cyclohexane	277	411	0.07
	CH_3CN	277	469	0.14
	CH_3OH	278, 298	475	0.16

[a] Maxima in the absorption spectra. [b] Maxima in the emission spectra. [c] Quantum yield of fluorescence is measured by using quinine sulfate as a reference ($\Phi = 0.55$ in 1.0 N H_2SO_4).[17] Estimated error is ±0.05.

TABLE 3. Decay Times of SPs Measured by Using the Single Photon Timing Technique

compd	solvent	τ_1/ns	τ_2/ns
1a	cyclohexane	0.5 ± 0.2	4.3 ± 0.1
	CH_3CN	3.3 ± 0.2	7.9 ± 0.1
1b	cyclohexane	0.5 ± 0.1	1.7 ± 0.1
	CH_3CN	3.0 ± 0.2	6.6 ± 0.1
1c	cyclohexane	0.3 ± 0.1	4.4 ± 0.1
	CH_3CN[a]	0.3 ± 0.1 and 5 ± 1	8.9 ± 0.2

[a] The fluorescence decay was fitted using a three-exponential function.

To further investigate the photophysics of SPs, we measured singlet lifetimes in nonpolar (cyclohexane) and polar solvent (CH_3CN). Fluorescence decays were measured by a single photon counting technique and analyzed by global analysis (fitting for the decay times and associated preexponential factors). Since we were able to perform measurements on a setup with nanosecond time resolution, we could not get information about the solvation effects taking place on picosecond and subpicosecond time scales. However, measured lifetimes in combination with quantum yields of fluorescence could provide the values of the rate constants of radiative and nonradiative deactivation pathway. Analysis of the SPs fluorescence decays revealed that none could be fitted by a one-exponential function (giving one lifetime), so a second exponent was needed to be introduced (as judged by χ_g^2 and plots of the weighted residuals and autocorrelation functions). For **1c** in CH_3CN, a third decay time was necessary. The decay times of SPs obtained by global analysis are presented in Table 3.

As can be seen, SPs **1a**−**c** are characterized by relatively long decay times, which is not usual for the stilbenes characterized by double bonds that can undergo cis−trans-isomerization. However, it coincides with high quantum yields of fluorescence and is in accord with similarly long lifetimes that were measured for ortho- or meta-substituted amino- and methoxystilbenes[16,19]

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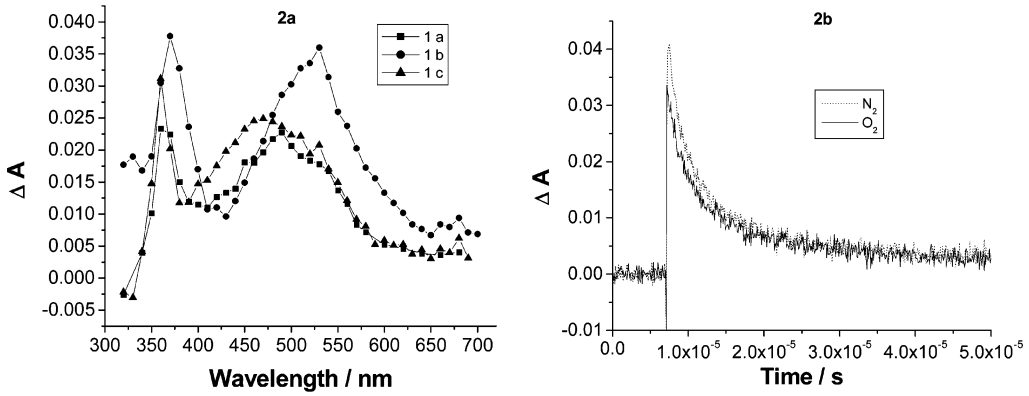

FIGURE 2. (a) Transient absorption spectra of SPs **1a**−**c** recorded in O_2-purged CH_3CN, immediately after the laser excitation. (b) Decay of transient absorbance at 520 nm recorded for SP **1b** in the presence of N_2 and O_2.

and sterically hindered stilbenes.[20] The existence of more than one decay time in the fluorescence decay may be explained by the existence of more than one emissive tautomer. Such conformational equilibria and the existence of more than one emissive tautomer are quite common in unsymmetrical stilbenes.[21] Hence, the thorough investigation of the dependence of decay times and quantum yields of fluorescence on temperature, viscosity, and excitation wavelengths was not in the scope of this manuscript.

Laser Flash Photolysis (LFP). Nanosecond LFP was used to probe for intermediates formed on photolyses of SPs **1a**−**c**, with the transient absorption spectra recorded in N_2 and O_2 purged CH_3CN solutions. The obtained spectra, recorded immediately after the laser pulses, were characterized by the presence of strong transient absorptions in the whole visible range with the broad maxima between 450 and 550 nm (Figure 2) and additional bands at wavelengths shorter than 375 nm. The intensity of the observed bands at shorter wavelengths was reduced, due to the reversible bleaching caused by the absorption of the laser flash by the substrate. In order to decrease the probability of two-photon excitation resulting in the formation of stilbene radical cations,[22] laser pulses were kept at low power (<30 mJ per pulse). However, two-photon excitation could not be totally suppressed and to some extent contributed to the transient absorption intensity.

Transient absorption spectra of SP **1a** and decay of the transient absorbance were not affected by the presence of O_2. The observed transient absorption was fitted to the sum of three exponential functions giving the following rate constants $k_1 = (7.3 \pm 0.2) \times 10^5\ s^{-1}$ ($\tau \sim 1.4\ \mu s$), $k_2 = (1.5 \pm 0.1) \times 10^5\ s^{-1}$ ($\tau \sim 6.6\ \mu s$), and $k_3 \sim 4 \times 10^4\ s^{-1}$ ($\tau \sim 20-30\ \mu s$). The position of the maximum at 483 nm and the associated lifetime of ~6−7 μs is in accord with the formation of stilbene radical-cation.[22,23] However, transient absorption spectra were much broader than reported for the radical cation, and the decay could not be fitted to a one-exponential function. Therefore, it was evident that the observed transient absorption corresponded to several species. Since we have not observed shortening of the decay in the presence of oxygen, we may tentatively assign the transient absorption to the presence of quinone dimethanes **10a** and **11a** (Scheme 3) and not to the presence of biradicals or triplets. Moreover, the similarity of the observed transient absorptions to those corresponding to *cis*- and *trans*-enoles obtained by H-abstraction reaction in the derivatives of 2-methylbenzophenones[24] encouraged us to tentatively assign the shorter lifetime (1.4 μs) to **10a** and the longer one (20−30 μs) to **11a**.

Transients obtained by LFP (in N_2 purged CH_3CN) of **1b** were more complex than those of **1a**. They were characterized by the decays that were fitted to the sum of minimally four exponential functions characterized by the rate constants $k_1 = (2.0 \pm 0.3) \times 10^6\ s^{-1}$ ($\tau \sim 510$ ns), $k_2 = (7.5 \pm 0.4) \times 10^5\ s^{-1}$ ($\tau \sim 1.3\ \mu s$), $k_3 = (9 \pm 1) \times 10^4\ s^{-1}$ ($\tau \sim 11\ \mu s$), and $k_4 \sim 3 \times 10^3\ s^{-1}$ ($\tau \sim 330\ \mu s$). Contrary to the other SPs, transients obtained from **1b** were affected by O_2. Namely, the shortest-living transient species was not detected when the solution was purged with O_2 (Figure 2b). The following rate constants were obtained for the decay of the transient absorbance in O_2-purged CH_3CN solution: $k_1 = (8.0 \pm 0.3) \times 10^5\ s^{-1}$ ($\tau \sim 1.2\ \mu s$), $k_2 = (7.8 \pm 0.4) \times 10^4\ s^{-1}$ ($\tau \sim 13\ \mu s$), and $k_3 \sim 5 \times 10^3\ s^{-1}$ ($\tau \sim 200\ \mu s$). The disappearance of the short-lived transient in the presence of O_2 encouraged us to tentatively assign it to the presence of biradical **12b**, while the other three transients were tentatively assigned to the presence of intermediates **10b** (1.2 μs), stilbene radical-cation (13 μs),[22] and **11b** (~200 μs). Substitution of the stilbene moiety by an electron-donating substituent partly stabilizes the formed biradical **12b**, and therefore, this biradical has a longer lifetime than **12a** and **12c**.

Transient absorption spectra of chloro SP **1c** were also characterized by the presence of decays that were fitted to a sum of minimally three exponential functions, giving three rate constants (or lifetimes). The following rate constants were revealed: $k_1 = (1.0 \pm 0.1) \times 10^6\ s^{-1}$ ($\tau \sim 1.0\ \mu s$), $k_2 = (8.4 \pm 0.5) \times 10^4\ s^{-1}$ ($\tau \sim 12\ \mu s$), and $k_3 \sim 5 \times 10^3\ s^{-1}$ ($\tau \sim 200\ \mu s$). In the presence of O_2, neither of the transients showed

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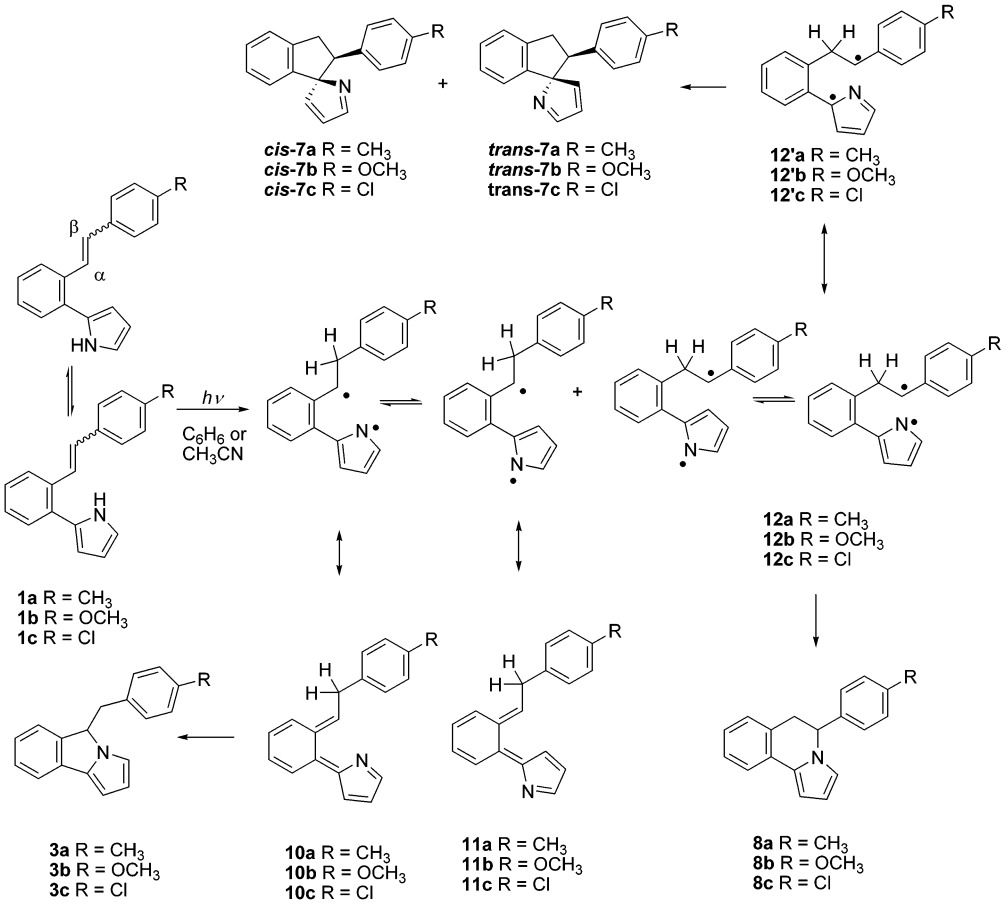
SCHEME 3



significant shortening of their lifetime. Thus, we tentatively assigned the transient absorptions to the presence of **10c** (1 μs), stilbene radical cation (12 μs), and **11c** (200 μs). However, with the data at hand, we can only tentatively assign the observed transients to **10a**−**c**, **11a**−**c**, and **12b**, with the data from LFP consistent with the proposed mechanism (vide infra). In order to verify assignments of transients, quenching experiments should be performed, which is difficult due to the concomitant formation of stilbene radical cations.

Reaction Mechanism. From the present product study, fluorescence, and LFP measurements we may propose a reaction mechanism for the photochemical transformation of SPs **1a**−**c**, which is presented in Scheme 3. Electronic excitation of SPs results in the population of singlet states that have substantial charge-transfer character. Polar singlet excited states of **1a**−**c** can deactivate by photophysical processes and by two competing photochemical pathways: cis−trans-isomerization and NH-hydrogen transfer. Due to the existence of at least two conformers in the ground state, excitation leads to the formation of more than one excited-state conformer, the presence of which was indicated by the biexponential decay of fluorescence. One of the conformers with the pyrrole NH oriented toward the stilbene double bond has a shorter singlet lifetime, possibly attributed to the higher efficiency of intramolecular hydrogen transfer of NH to the stilbene double bond. Hydrogen transfer is not specific and results in formation of the three intermediates **10**−**12**.

In the case of H-transfer to the β-C-atom of the stilbene double bond, reaction from the singlet state gives rise to two conjugated neutral intermediate molecules, **10a**−**c** and **11a**−**c**. However, formation of intermediates **10** and **11** may also be explained by a [1,9]-hydrogen shift, especially in the case of **11a**−**c**, where the H-atom transfer is less probable due to the longer distance. The intermediates **10a**−**c** decay by two processes: by intramolecular cyclization, giving **3a**−**c**, and reverse [1,9]-hydrogen shift (giving starting material). Due to the steric hindrance caused by the two hydrogens, intramolecular cyclization from **11** to pyrroloindenes is less favored and probably does not take place. Thus, **11a**−**c** probably decay only by the [1,9]-hydrogen shift, thereby yielding the longer lifetime. Besides isolation of products **3a**−**c**, formation of **10** and **11** was also indicated by LFP experiments, where we saw the presence of the short-lived transients tentatively assigned to **10** and longer-living transients tentatively assigned to **11** (vide supra).

Proton transfer to the α-position of the stilbene double bond and formation of biradicals **12** was highly indicated by the isolation of PIQ compounds **8**. On the other hand, formation of spiro products **7** seems somewhat surprising at first, but it is well-supported by the resonant stabilization of **12**. Thus, benzylic radical form **12′** probably has higher contribution in the resonance than its N-radical form **12**. Therefore, recombination of **12** and **12′** gives a higher yield of spiro comound **7** than PIQ **8**. Moreover, radical cyclization in the similar system described by Jones et al. also resulted primarily in the formation of five-membered rings and spiro compounds, rather than six-membered rings.[12c] Additional indication for the presence of biradical **12** was obtained from the LFP data of **1b**. Namely, we saw the

presence of a very short-lived transient in N_2-purged CH_3CN, which was tentatively assigned to **12b** and which disappeared upon exposure to O_2. Since **12a**−**c** are true biradicals (unlike **10** and **11**) in a singlet state, they should react with O_2 at a rate that is diffusion controlled.[25] The very short lifetime of these biradicals (**12a**−**c**) is not surprising, since they can probably react very efficiently in an intramolecular process, giving *cis*- and *trans*-**7**. Only stabilization with an electron-donating group (as in the case of **12b**) is expected to induce a longer lifetime of these species. Besides formation of cyclic products **7** and **8**, biradicals **12** probably also undergo intermolecular hydrogen abstraction or C−Cl bond cleavage (in the case of **12c**), giving reduction products **9a** and **9c**, respectively.

Substitution of the stilbene moiety has significant influence on the degree of SP photochemical reactivity. Even though photolyses furnish the same type of products, the photochemical reaction is more efficient (vide supra) and selective with electron-withdrawing substituents on the stilbene moiety. Thus, photolysis of **1c** is the most selective giving products **7c** and **3c** in a ratio of ∼30:1. On the other hand, methoxy-substituted SP **1b** gave photoproducts **7b** and **3b** in a ratio of ∼3:1. The reason for the higher efficiency and selectivity with electron-withdrawing groups probably lies with the formation of a more polar excited state (which was indicated by fluorescence measurements). The driving force for the NH hydrogen transfer is probably more in such a polar excited state, explaining the higher efficiency of the reaction. On the other hand, selectivity of the H-transfer to the α or β position is explained by the competing substituent effects of the pyrrole unit and the stilbene moiety. Thus, the more polar excited-state of **1c** (as compared to **1a** or **1b**) is probably characterized by a bigger difference in electron density on the α- and β-position of the stilbene double bond, resulting in a more selective hydrogen transfer to the α-position.

Conclusion

Excitation of SPs **1a**−**c** to the singlet state gives rise to more polar species, which can deactivate by photophysical processes and two competing photochemical pathways: cis−trans-isomerization and intramolecular NH hydrogen transfer. The NH hydrogen transfer results in formation of biradicals and quinone dimethane intermediates, which cyclize to spiro-2*H*-pyrroles **7**, PIs **3**, and PIQ **8**. The reaction of NH transfer is more efficient and more selective (toward formation of **7**) if the stilbene moiety is substituted with an electron-withdrawing group. The major photochemical products, spiro-2*H*-pyrroles **7**, easily rearrange on silica, giving DHI derivatives **2**.

Experimental Section

Synthesis of 4-Substituted 2-{2-[2-Phenylethenyl]phenyl}-pyrroles. Stille Reaction, General Procedure.[10] *N*-Boc-pyrrolylstannane (**4**)[7] (0.01 mol) and 4′-substituted 2-bromostilbene (**5a**−**c**)[11] (0.01 mol) were dissolved in toluene (15 mL). To the mixture was added a 1 M aqueous solution of Na_2CO_3 (15 mL) and the solution was purged with argon. A spatula-point of $Pd(PPh_3)_4$ was added and the reaction mixture heated under argon at reflux temperature for 1 day. The layers were separated, and the water layer was extracted three times with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$. The solution was filtered, the solvent was evaporated, and the brown residue was chromatographed on a column with silica gel using CH_2Cl_2/petroleum ether (1:4) as eluent. In the first fraction, unreacted stilbene derivatives were isolated, followed by the isolation of the mixture of *cis*- and *trans*-*N*-*tert*-butoxycarbonyl-2-{2-[2-(4-substituted phenyl)ethenyl]-phenyl}pyrrole.

A mixture of 2.47 g (98%) of *cis*- and *trans*-*N*-*tert*-butoxycarbonyl-2-{2-[2-(4-methylphenyl)ethenyl]phenyl}pyrrole (**6a**) was obtained. *cis*-**6a**: colorless oil; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.55 (m, 1H), 7.54 (d, 1H, J = 7.8 Hz), 7.39 (d, 2H, J = 8.1 Hz), 7.33 (d, 1H, J = 7.5 Hz), 7.05 (dd, 1H, J = 7.5 Hz, J = 7.8 Hz), 6.98 (dd, 1H, J = 7.5 Hz, J = 7.8 Hz), 6.92 (d, 2H, J = 8.1 Hz), 6.53 (d, 1H, J = 12.6 Hz), 6.45 (d, 1H, J = 12.6 Hz), 6.25 (m, 1H), 6.22 (dd, 1H, J = 3.3 Hz, J = 3.6 Hz), 2.09 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 149.6 (s), 138.5 (s), 137.3 (s), 135.5 (s), 135.0 (s), 134.2 (s), 131.2 (d), 130.9 (d), 129.9 (d), 129.6 (d), 129.5 (d), 129.3 (d), 127.8 (d), 127.3 (d), 122.5 (d), 115.4 (d), 111.4 (d), 83.1 (s), 27.9 (q), 21.6 (q); IR (oil) ν_{max}/cm^{-1} 1752 (CO), 1739 (CO). *trans*-**6a**: colorless oil; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.71 (dd, 1H, J = 2.4 Hz, J = 2.7 Hz), 7.62 (d, 1H, J = 7.8 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.31 (d, 1H, J = 6.9 Hz), 7.28 (d, 1H, J = 16.5 Hz), 7.20 (dd, 1H, J = 7.8 Hz, J = 7.5 Hz), 7.10 (dd, 1H, J = 6.9 Hz, J = 7.5 Hz), 7.05 (d, 1H, J = 16.5 Hz), 6.93 (d, 2H, J = 8.1 Hz), 6.23 (d, 2H, J = 2.7 Hz), 2.09 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 149.8 (s), 138.4 (s), 137.9 (s), 135.5 (s), 135.1 (s), 133.5 (s), 131.5 (d), 130.5 (d), 130.1 (d), 127.23 (d), 127.18 (d), 126.6 (d), 125.2 (d), 122.6 (d), 115.8 (d), 111.5 (d), 83.3 (s), 27.6 (q), 21.5 (q); IR (oil) ν_{max}/cm^{-1} 1738 (CO); MS *m*/*z* (%) 359 (30, M^+), 303 (35), 258 (45), 167 (50), 57 (100). Anal. Calcd for $C_{24}H_{25}NO_2$: C 80.19, H 7.01, N 3.90. Found: C 80.36, H 6.76, N 4.15.

A mixture of 3.23 g (86.0%) of *cis*- and *trans*-*N*-*tert*-butoxycarbonyl-2-{2-[2-(4-methoxyphenyl)ethenyl]phenyl}pyrrole (**6b**) was obtained. *cis*-**6b**: yellowish oil; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.48 (dd, 1H, J = 1.5 Hz, J = 7.5 Hz), 7.47 (dd, 1H, J = 3.3 Hz, J = 3.3 Hz), 7.33 (d, 2H, J = 8.7 Hz), 7.29 (dd, 1H, J = 1.5 Hz, J = 7.5 Hz), 7.02 (ddd, 1H, J = 1.5 Hz, J = 7.5 Hz, J = 7.5 Hz), 6.95 (ddd, 1H, J = 1.5 Hz, J = 7.5 Hz, J = 7.5 Hz), 6.62 (d, 2H, J = 8.7 Hz), 6.41 (d, 1H, J = 12.3 Hz), 6.35 (d, 1H, J = 12.3 Hz), 6.19 (dd, 1H, J = 3.3 Hz, J = 3.3 Hz), 6.16 (dd, 1H, J = 3.3 Hz, J = 3.3 Hz), 3.24 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 159.1 (s), 148.9 (s), 138.1 (s), 134.8 (s), 133.7 (s), 130.6 (d), 129.9 (d), 129.6 (s), 128.9 (d), 127.6 (d), 127.2 (d), 126.6 (d), 121.8 (d), 114.7 (d), 113.6 (d), 110.7 (d), 81.2 (s), 55.0 (q), 27.9 (q); IR (oil) ν_{max}/cm^{-1} 1751 (CO); MS *m*/*z* (%) 375 (55, M^+), 319 (55), 274 (68), 168 (45), 84 (50), 57 (100). Anal. Calcd for $C_{24}H_{25}NO_3$: C 76.77, H 6.71, N 3.73. Found: C 76.71, H 7.04, N 3.94%. *trans*-**6b**: yellowish crystals; mp 88−89 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.67 (dd, 1H, J = 3.0 Hz, J = 3.0 Hz), 7.58 (d, 1H, J = 7.8 Hz), 7.26 (d, 2H, J = 7.8 Hz), 7.22−7.29 (m, 1H), 7.12−7.20 (m, 1H), 7.12 (d, 1H, J = 16.2 Hz), 7.05 (dd, 1H, J = 7.2 Hz, J = 7.5 Hz), 6.97 (d, 1H, J = 16.2 Hz), 6.63 (d, 2H, J = 7.8 Hz), 6.19−6.22 (m, 2H), 3.25 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 159.9 (s), 149.5 (s), 138.2 (s), 134.6 (s), 133.2 (s), 131.2 (d), 130.6 (s), 129.7 (d), 128.1 (d), 128.0 (d), 126.6 (d), 125.0 (d), 124.6 (d), 122.1 (d), 115.3 (d), 114.5 (d), 111.1 (d), 82.9 (s), 54.7 (q), 27.2 (q); IR (KBr) ν_{max}/cm^{-1} 1733 (CO).

A mixture of 3.21 g (84.6%) of *cis*- and *trans*-*N*-*tert*-butoxycarbonyl-2-{2-[2-(4-chlorophenyl)ethenyl]phenyl}pyrrole (**6c**) was obtained. *cis*-**6c**: yellowish oil, ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.43 (dd, 1H, J = 1.8 Hz, J = 3.0 Hz), 7.27 (d, 1H, J = 7.5 Hz), 7.26 (d, 1H, J = 7.5 Hz), 7.12 (d, 2H, J = 8.4 Hz), 6.99 (ddd, 1H, J = 7.5 Hz, J = 7.5 Hz, J = 1.5 Hz), 6.95 (d, 2H, J = 8.4 Hz), 6.89 (ddd, 1H, J = 7.5 Hz, J = 7.5 Hz, J = 1.5 Hz), 6.42 (d, 1H, J = 12.0 Hz), 6.16 (d, 1H, J = 12.0 Hz), 6.12−6.15 (m, 2H), 1.10 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 149.5 (s), 137.8 (s), 136.2 (s), 135.4 (s), 134.1 (s), 133.5 (s), 131.3 (d), 131.2 (d), 130.7 (d), 129.4 (d), 129.3 (d), 128.9 (d), 127.9 (d), 127.6 (d), 122.6 (d), 115.4 (d), 111.4 (d), 83.2 (s), 27.9 (q); IR (oil) ν_{max}/cm^{-1} 1750

(25) Miranda, M. A.; Font-Sanchis, E.; Pérez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **2001**, *66*, 2717−2721. (b) Font-Sanchis, E.; Miranda, M. A.; Pérez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **2002**, *67*, 6131−6135.

(CO). Anal. Calcd for $C_{23}H_{22}ClNO_2$: C 72.72, H 5.84, N 3.69. Found: C 72.32, H 5.99, N 4.03. *trans*-**6c:** yellowish oil; ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.62 (dd, 1H, J = 1.8 Hz, J = 3.0 Hz), 7.48 (d, 1H, J = 7.8 Hz), 7.22 (d, 1H, J = 7.8 Hz), 7.13 (dd, 1H, J = 7.2 Hz, J = 7.8 Hz), 7.08 (d, 1H, J = 16.2 Hz), 7.06 (dd, 1H, J = 7.2 Hz, J = 7.8 Hz), 6.95 (d, 2H, J = 9.0 Hz), 6.94 (d, 2H, J = 9.0 Hz), 6.75 (d, 1H, J = 16.2 Hz), 6.17 (dd, 1H, J = 3.0 Hz, J = 3.6 Hz), 6.15 (dd, 1H, J = 1.8 Hz, J = 3.6 Hz), 1.02 (s, 9H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 149.7 (s), 137.8 (s), 136.6 (s), 135.2 (s), 133.8 (s), 133.3 (s), 131.6 (d), 129.5 (d), 129.0 (d), 128.5 (d), 128.3 (d), 127.6 (d), 125.4 (d), 122.6 (d), 115.8 (d), 111.5 (d), 83.6 (s), 27.6 (q); IR (KBr) ν_{max}/cm^{-1} 1739 (CO); MS *m*/*z* (%) 381 (5, M$^+$), 379 (15, M$^+$), 323 (25), 278 (20), 168 (30), 57 (100).

Removal of the Boc Group. *N*-Boc-2-{2-[2-(4-substituted phenyl)ethenyl]phenyl}pyrrole (**6a**−**c**) (6.88 mmol) was dissolved in 50 mL of CH_3OH. A solution of freshly prepared sodium methoxide [prepared by reacting 950 mg of Na (41 mmol) in 20 mL of CH_3OH] was added and the reaction mixture was heated under reflux over 1 h. The solvent was evaporated and the residue treated with water (100 mL) and extracted with CH_2Cl_2 (4 × 50 mL). The organic extracts were dried over anhydrous $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on a column with silica gel using CH_2Cl_2/petroleum ether (1:4) as eluent. In the first fractions *cis*-2-{2-[2-(4-substituted phenyl)-ethenyl]phenyl}pyrroles (**1a**−**c**) were isolated, followed by the isolation of *trans*-isomers. Reaction furnished the following yields: 81.5% (*p*-Me),[7] 99% (*p*-OMe), and 86% (*p*-Cl).

cis-2-{2-[2-(4-Methoxyphenyl)ethenyl]phenyl}pyrrole (**1b**): yellowish crystals; mp 50−51 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 8.18 (br s, 1H), 7.35 (d, 2H, J = 8.7 Hz), 7.17 (d, 2H, J = 8.7 Hz), 7.05 (ddd, 1H, J = 7.5 Hz, J = 7.5 Hz, J = 1.2 Hz), 6.89 (ddd, 1H, J = 7.5 Hz, J = 7.5 Hz, J = 1.2 Hz), 6.75 (ddd, 1H, J = 3.6 Hz, J = 2.1 Hz, J = 1.5 Hz), 6.56 (d, 2H, J = 8.7 Hz), 6.55 (d, 1H, J = 12.0 Hz), 6.47 (dd, 1H, J = 2.7 Hz, J = 1.5 Hz), 6.41 (d, 1H, J = 12.0 Hz), 6.38 (dd, 1H, J = 3.6 Hz, J = 2.7 Hz), 3.20 (s, 3H); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 159.8 (s), 135.1 (s), 132.9 (s), 131.7 (s), 131.2 (d), 131.0 (d), 129.9 (s), 129.7 (d), 128.1 (d), 128.0 (d), 126.7 (d), 119.4 (d), 114.4 (d), 110.4 (d), 110.1 (d), 55.06 (q); IR (KBr) ν_{max}/cm^{-1} 3436 (NH); UV (EtOH) λ_{max}/nm (ϵ) 282.0 (17 185), 301.0 (18 190); MS *m*/*z* (%) 275 (100, M$^+$), 168 (40, M$^+$ − CH_3OPh).

trans-2-{2-[2-(4-methoxyphenyl)ethenyl]phenyl}pyrrole (**1b**): colorless crystals; mp 112−113 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.57 (d, 1H, J = 7.2 Hz), 7.42 (br s, 1H), 7.42 (d, 1H, J = 16.2 Hz), 7.23 (d, 2H, J = 8.4 Hz), 7.10−7.26 (m, 3H), 6.95 (d, 1H, J = 16.2 Hz), 6.72 (d, 2H, J = 8.4 Hz), 6.54 (ddd, 1H, J = 1.8 Hz, J = 2.7 Hz, J = 3.3 Hz), 6.40 (ddd, 1H, J = 1.2 Hz, J = 1.5 Hz, J = 2.7 Hz), 6.37 (ddd, 1H J = 0.9 Hz, J = 2.7 Hz, J = 3.3 Hz), 3.28 (s, 3H, OCH_3); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 160.2 (s), 136.4 (s), 133.2 (s), 131.4 (s), 131.2 (s), 130.4 (d), 129.4 (d), 128.6 (d), 127.8 (d), 127.5 (d), 127.4 (d), 126.7 (d), 119.2 (d), 114.9 (d), 110.6 (d), 110.2 (d), 55.1 (q); IR (KBr) ν_{max}/cm^{-1} 3363 (NH); UV (EtOH) λ_{max}/nm (ϵ) 283.0 (24940), 301.0 (20987). Anal. Calcd for $C_{19}H_{17}NO$: C 82.88, H 6.22, N 5.09. Found: C 82.54, H 6.51, N 5.12.

cis-2-{2-[2-(4-Chlorophenyl)ethenyl]phenyl}pyrrole (**1c**): yellowish crystals; mp 61−62 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.76 (br s, 1H), 7.23 (d, 1H, J = 7.8 Hz), 7.16 (d, 1H, J = 7.5 Hz), 7.03 (dd, 1H, J = 7.5 Hz, J = 7.8 Hz), 6.93 (d, 2H, J = 8.7 Hz), 6.89 (d, 2H, J = 8.7 Hz), 6.82 (dd, 1H, J = 7.5 Hz, J = 7.5 Hz), 6.69 (ddd, 1H, J = 3.6 Hz, J = 2.7 Hz, J = 1.5 Hz), 6.59 (d, 1H, J = 12.0 Hz), 6.46 (ddd, 1H, J = 1.2 Hz, J = 1.5 Hz, J = 2.7 Hz), 6.38 (dd, 1H, J = 2.7 Hz, J = 3.6 Hz), 6.20 (d, 1H, J = 12.0 Hz); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 135.9 (s), 134.3 (s), 133.5 (s), 133.0 (s), 132.3 (d), 131.2 (s), 131.0 (d), 129.8 (d), 129.1 (d), 127.9 (d), 126.7 (d), 119.6 (d), 110.6 (d), 110.4 (d); IR (KBr) ν_{max}/cm^{-1} 3428 (NH); UV (EtOH) λ_{max}/nm (ϵ) 281.0 (18 509), 298.0 (18 190); MS *m*/*z* (%) 281 (30, M$^+$), 279 (100, M$^+$), 168 (60, M$^+$ − ClPh).

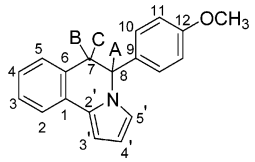
trans-2-{2-[2-(4-Chlorophenyl)ethenyl]phenyl}pyrrole (**1c**): colorless crystals, mp 92−93 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.47 (d, 1H, J = 7.3 Hz), 7.36 (d, 1H, J = 16.2 Hz), 7.30 (br s, 1H), 7.06−7.20 (m, 3H), 7.04 (d, 2H, J = 8.4 Hz), 6.93 (d, 2H, J = 8.4 Hz), 6.72 (d, 1H, J = 16.2 Hz), 6.45 (ddd, 1H, J = 1.5 Hz, J = 2.7 Hz, J = 3.3 Hz), 6.39 (ddd, 1H, J = 1.5 Hz, J = 1.5 Hz, J = 2.7 Hz), 6.35 (ddd, 1H, J = 2.7 Hz, J = 2.7 Hz, J = 3.3 Hz); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 136.8 (s), 135.7 (s), 133.7 (s), 133.5 (s), 131.0 (s), 129.6 (d), 129.5 (d), 129.30 (d), 129.26 (d), 128.42 (d), 128.37 (d), 127.51 (d), 127.46 (d), 119.4 (d), 110.9 (d), 110.4 (d); UV (EtOH) λ_{max}/nm (ϵ) 280.0 (27956), 302.0 (20298); IR (KBr) ν_{max}/cm^{-1} 3348 (NH). Anal. Calcd for $C_{18}H_{14}ClN$: C 77.28, H 5.04, N 5.01. Found: C 77.15, H 5.43, N 5.13.

Irradiation of 2-{2-[2-(4-Methylphenyl)ethenyl]phenyl}-pyrrole. In a quartz vessel, 200 mg of the SP (0.77 mmol; c = 1.5 × 10^{-3} M) was dissolved in 500 mL of benzene (or acetonitrile). The solution was purged with argon for 30 min, sealed, and irradiated in a Rayonet reactor at 300 nm over 30 min. The solvent was removed on the rotary evaporator and the residue chromatographed on a column filled with silica gel using CH_2Cl_2/petroleum ether (3:7) as eluent. In the first fractions, 9 mg (4.5%) of 4*H*-4-(4-methylbenzyl)-pyrrolo[2,1-*a*]isoindole was isolated, followed by 19 mg (9.5%) of 2-{2-[2-(4-methylphenyl)ethyl]phenyl}pyrrole and 65 mg (32.5%) of 4,5-dihydro-4-(4-methylphenyl)benzo[*g*]indole. High molecular weight material remained on the column.[7]

Following the Reaction Course of Cis−Trans Isomerization of 2-{2-[2-(4-Methylphenyl)ethenyl]phenyl}pyrrole (1a) by ^{1}H NMR. In a NMR tube was placed 10 mg of *cis*-2-{2-[2-(4-methylphenyl)ethenyl]phenyl}pyrrole (**1a**) and it was dissolved in 1 mL of C_6D_6. In the other NMR tube was placed 10 mg of the *trans*-isomer and it was dissolved in 1 mL of C_6D_6. To both NMR tubes was added 1 μL of cyclohexane. NMR tubes were irradiated in a Rayonet reactor (equipped with 2 lamps) at 300 nm for short period of time, after which the ^{1}H NMR spectra were recorded. From the ratio of integrals of signals in ^{1}H NMR spectra, the ratio of the compounds was calculated.

Irradiation of 2-{2-[2-(4-Methoxyphenyl)ethenyl]phenyl}-pyrrole (1b). In a quartz vessel, 184 mg (0.67 mmol; c = 1.3 × 10^{-3} M) of the SP was dissolved in 500 mL of benzene (or acetonitrile). The solution was purged with argon for 30 min, sealed, and irradiated in a Rayonet reactor at 300 nm over 2 h. The solvent was removed by rotary evaporation and the residue chromatographed on a column filled with silica gel using CH_2Cl_2/petroleum ether (3:7) as eluent. In the first fractions, 7 mg (3.8%) of 4,5-dihydro-4-(4-methoxyphenyl)pyrrolo[2,1-*b*]isoquinoline (**8b**) was isolated, followed by 18 mg (9.8%) of 4*H*-4-(4-methoxybenzyl)-pyrrolo[2,1-*a*]isoindole (**3b**), 20 mg (10,9%) of the mixture of cis- and trans-isomers of the starting material (**1b**), and 51 mg (27.8%) of 4,5-dihydro-4-(4-methoxyphenyl)benzo[*g*]indole (**2b**). High molecular weight material remained on the column.

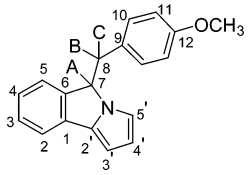
4,5-Dihydro-4-(4-methoxyphenyl)pyrrolo[2,1-*b*]isoquinoline (**8b**): colorless crystals; ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.65



(d, 1H, J = 7.2 Hz, H-2), 7.17 (dd, 1H, J = 7.2 Hz, J = 7.2 Hz, H-3), 6.99 (dd, 1H, J = 7.2 Hz, J = 7.2 Hz, H-4), 6.92 (d, 1H, J = 7.2 Hz, H-5), 6.86 (dd, 1H, J = 3.6 Hz, J = 1.2 Hz, H-3′), 6.80 (d, 2H, J = 9.0 Hz, H-10), 6.66 (d, 2H, J = 9.0 Hz, H-11), 6.43−6.47 (m, 2H, H-4′ and H-5′), 4.69 (t, 1H, J = 6.6 Hz, H-A), 3.25 (s, 3H, OCH_3), 2.90 (d, 2H, J = 6.6 Hz, H−B and H−C); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 160.1 (s), 130.6 (s), 130.3 (s), 128.8 (d, 2C-10), 128.7 (d), 127.8 (d), 126.0 (d), 122.9 (d, C-2), 121.3 (d, C-5′), 114.7 (d, 2C-11), 109.9 (d, C-4′), 105.2 (d, C-3′), 58.6 (d, C-8), 55.1 (q, OCH_3), 38.6 (t, C-7), two singlets were not seen;

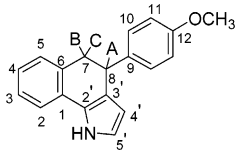
MS *m*/*z* (%) 275 (75, M^+), 168 (60, M^+ − *p*-methoxyphenyl); HRMS calcd for $C_{19}H_{18}NO$ 276.1388, found 276.1391.

4*H*-4-(4-Methoxybenzyl)pyrrolo[2,1-*a*]isoindole (**3b**): yellowish crystals; mp 102−104 °C; ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.31



(d, 1H, J = 7.2 Hz, H-2), 7.08 (dd, 1H, J = 7.2 Hz, J = 7.2 Hz, H-3), 6.91 (dd, 1H, J = 7.2 Hz, J = 7.2 Hz, H-4), 6.82 (d, 1H, J = 7.2 Hz, H-5), 6.74 (d, 2H, J = 9.0 Hz, H-10), 6.68 (d, 2H, J = 9.0 Hz, H-11), 6.43−6.48 (m, 3H, H-3', H-4' and H-5'), 4.73 (dd, 1H, J = 6.0 Hz, J = 7.2 Hz, H-A), 3.25 (s, 3H, OCH_3), 2.84 (dd, 1H, J = 6.0 Hz, J = 14.1 Hz, H−B), 2.66 (dd, 1H, J = 7.2 Hz, J = 14.1 Hz, H−C); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 159.5 (s, OCH_3), 144.8 (s), 137.8 (s), 134.6 (s), 131.2 (d, 2C-10), 128.9 (s), 128.7 (d, C-3), 125.0 (d, C-4), 123.6 (d, C-5), 119.1 (d, C-2), 116.7 (d, C-5'), 114.5 (d, 2C-11), 113.4 (d, C-3'), 99.2 (d, C-4'), 62.8 (d, C-7), 55.0 (q, OCH_3), 41.5 (t, C-8); MS *m*/*z* (%) 275 (75, M^+), 154 (100, M^+ − methoxybenzyl); HRMS calcd for $C_{19}H_{18}NO$ 276.1388, found 276.1395.

4,5-Dihydro-4-(4-methoxyphenyl)benzo[*g*]indole (**2b**): colorless crystals; mp 122−123 °C; ^{1}H NMR (C_6D_6) δ/ppm (300 MHz) 7.26

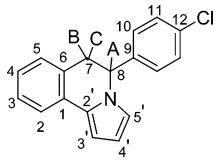


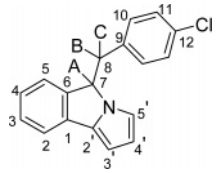
(br s, 1H, NH), 7.10−7.20 (m, 4H), 6.95−7.05 (m, 2H), 6.87 (d, 1H, J = 7.2 Hz, H-2 or H-5), 6.76 (d, 2H, J = 8.7 Hz, H-11), 6.31 (dd, 1H, J = 2.7 Hz, J = 2.7 Hz, H-5'), 6.24 (dd, 1H, J = 2.4 Hz, J = 2.7 Hz, H-4'), 4.09 (dd, 1H, J = 8.4 Hz, J = 8.7 Hz, H-A), 3.29 (s, 3H, OCH_3), 3.03 (d, 2H, J = 8.4 Hz, H−B and H−C); ^{13}C NMR (C_6D_6) δ/ppm (75 MHz) 158.6 (s, C-12), 137.4 (s), 134.4 (s), 129.5 (s), 129.0 (d, 2C-10), 128.6 (d), 126.5 (d), 125.1 (d), 124.1 (s), 118.5 (d, C-5'), 118.3 (d, C-2 or C-5), 113.9 (d, 2C-11), 108.2 (d, C-4'), 54.5 (q, OCH_3), 40.1 (t, C-7), 39.8 (d, C-8), one singlet was covered by solvent; MS *m*/*z* (%) 275 (75, M^+), 168 (70, M^+ − methoxyphenyl); HRMS calcd for $C_{19}H_{18}NO$ 276.1388, found 276.1389.

Irradiation of 2-{2-[2-(4-Chlorophenyl)ethenyl]phenyl}-pyrrole (1c). In a quartz vessel, 250 mg (0.90 mmol; c = 1.8 × 10^{-3} M) of the SP was dissolved in 500 mL of benzene (or acetonitrile). The solution was purged with argon for 30 min, sealed, and irradiated in a Rayonet reactor at 300 nm over 30 min. The solvent was removed by rotary evaporation and the residue chromatographed on a column filled with silica gel using CH_2Cl_2/petroleum ether (3:7) as eluent. In the first fractions, traces of 4,5-dihydro-4-(4-chlorophenyl)pyrrolo[2,1-*b*]isoquinoline (**8c**) were isolated, followed by 5 mg (2.0%) of 4*H*-4-(4-chlorobenzyl)pyrrolo-[2,1-*a*]isoindole (**3c**), 15 mg (6.7%) of 2-[2-(2-phenylethyl)phenyl]-pyrrole (**9c**), and 146 mg (58.4%) of 4,5-dihydro-4-(4-chlorophenyl)-benzo[*g*]indole (**2c**). High molecular weight material remained on the column.

4,5-Dihydro-4-(4-chlorophenyl)pyrrolo[2,1-*b*]isoquinoline (**8c**): aliphatic part of the ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 4.61 (dd, 1H, J = 5.4 Hz, J = 6.6 Hz, H-A), 2.81 (dd, 1H, J = 5.4 Hz, J = 15.0 Hz, H−B), 2.68 (dd, 1H, J = 6.6 Hz, J = 15.0 Hz, H−C); MS *m*/*z* (%) 281 (30, M^+), 279 (100, M^+), 168 (12, M^+ − chlorophenyl).

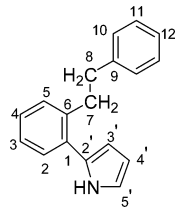
4*H*-4-(4-Chlorobenzyl)pyrrolo[2,1-*a*]isoindole (**3c**): colorless crystals; mp 101−103 °C; ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.27





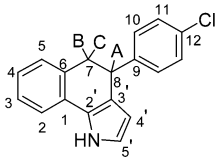
(d, 1H, J = 7.2 Hz, H-2), 7.07 (dd, 1H, J = 7.2 Hz, J = 7.8 Hz, H-3 or H-4), 6.97 (d, 2H, J = 8.1 Hz, H-10), 6.88 (dd, 1H, J = 7.2 Hz, J = 7.8 Hz, H-3 or H-4), 6.71 (d, 1H, J = 7.2 Hz, H-5), 6.45 (d, 2H, J = 8.1 Hz, H-11), 6.42 (dd, 1H, J = 3.3 Hz, J = 2.7 Hz, H-4'), 6.40 (d, 1H, J = 3.3 Hz, H-3'), 6.34 (d, 1H, J = 2.7 Hz, H-5'), 4.56 (dd, 1H, J = 6.0 Hz, J = 7.2 Hz, H-A), 2.64 (dd, 1H, J = 6.0 Hz, J = 13.8 Hz, H−B), 2.47 (dd, 1H, J = 7.2 Hz, J = 13.8 Hz, H−C); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 131.5 (d, 2C-11), 129.0 (d, 2C-10), 128.9 (d, C-3 or C-4), 125.0 (d, C-3 or C-4), 123.4 (d, C-5), 119.1 (d, C-2), 116.5 (d, C-5'), 113.6 (d, C-4'), 99.4 (d, C-3'), 62.2 (d, C-7), 41.4 (t, C-8), singlets were not seen due to the small quantitie of the sample; MS *m*/*z* (%) 281 (30, M^+), 279 (100, M^+), 154 (75, M^+ − chlorobenzyl); HRMS calcd for $C_{18}H_{15}NCl$ 280.0893, found 280.0895.

2-[2-(2-Phenylethyl)phenyl]pyrrole (**9c**): colorless oil; ^{1}H NMR



(C_6D_6) δ/ppm (600 MHz) 7.13−7.17 (m, 2H), 7.05−7.12 (m, 5H), 7.00−7.05 (m, 1H), 6.96 (dd, 2H, J = 7.8 Hz, J = 1.2 Hz), 6.41 (m, 1H), 6.37 (m, 1H), 6.35 (m, 1H), 2.95 (t, 2H, J = 7.8 Hz), 2.72 (t, 2H, J = 7.8 Hz); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 141.4 (s), 139.3 (s), 133.2 (s), 130.3 (s), 129.4 (d), 129.2 (d), 128.1 (d), 127.9 (d), 126.7 (d), 125.6 (d), 125.5 (d), 117.2 (d), 108.8 (d), 108.1 (d), 37.2 (t), 35.1 (t); MS *m*/*z* (%, fragment) 247 (100, M^+), 156 (25, M^+ − benzyl); HRMS calcd for $C_{18}H_{18}N$ 248.1439, found 248.1437.

4,5-Dihydro-4-(4-chlorophenyl)benzo[*g*]indole (**2c**): colorless crystals; mp 170−171 °C; ^{1}H NMR (C_6D_6) δ/ppm (600 MHz) 7.24



(br s, 1H, NH), 7.14−7.24 (m covered by solvent, 1H H-2 or H-5), 7.06 (d, 2H, J = 8.4 Hz, H-10), 6.95−7.02 (m, 2H, H-2 and H-5), 6.92 (d, 2H, J = 8.4 Hz, H-11), 6.84 (d, 1H, J = 7.8 Hz, H-2 or H-5), 6.27 (dd, 1H, J = 2.4 Hz, J = 3.0 Hz, H-5'), 5.90 (dd, 1H, J = 2.4 Hz, J = 3.0 Hz, H-4'), 3.92 (dd, 1H, J = 6.6 Hz, J = 10.5 Hz, H-A), 2.89 (dd, 1H, J = 6.6 Hz, J = 15.0 Hz, H−B), 2.83 (dd, 1H, J = 10.5 Hz, J = 15.0 Hz); ^{13}C NMR (C_6D_6) δ/ppm (150 MHz) 144.5 (s), 134.4 (s), 132.6 (s), 130.1 (d, 2C-11), 129.9 (s), 129.2 (d), 129.1 (d, 2C-10), 127.3 (d), 125.9 (d), 123.6 (s), 119.2 (d, C-5'), 118.9 (d, C-2 or C-5), 108.5 (d, C-4'), 40.4 (d, C-8), 40.2 (t, C-7); MS *m*/*z* (%) 281 (30, M^+), 279 (100, M^+), 168 (70,

$M^+ - p$-chlorophenyl); HRMS calcd for $C_{18}H_{15}NCl$ 280.0893, found 280.0884.

Comparing Relative Photochemical Reactivity of 2-{2-[2-(4-Substituted phenyl)ethenyl]phenyl}pyrrole (1a−c). In three quartz cuvettes was placed 20 mg of a mixture of cis- and trans-isomer of SP **1a**, **1b**, or **1c**, respectively. The compounds were dissolved in 17 mL of benzene, purged with a stream of Ar, sealed, and irradiated in a Rayonet reactor over 15 min. After irradiation, solvent was removed and ^{1}H NMR spectra of the crude photomixtures were recorded. From the integrations of the signals, the relative amounts of the starting material and the photoproducts were obtained.

Laser Flash Photolysis (LFP). All LFP studies were conducted at the University of Victoria LFP facility using a XeCl excimer laser with 308-nm excitation. Flow cells (0.7 cm) were used and solutions were purged with nitrogen or oxygen for 30 min prior to measurements. Optical densities at 308 nm were ∼0.4. The measurements were performed in CH_3CN (HPLC grade).

Steady State and Time-Resolved Fluorescence Measurements. For the fluorescence measurements, solvents were of spectroscopic grade purity. All the compounds were additionally purified by three recrystallization using cyclohexane/chloroform. The steady state measurements were performed in three solvents: acetonitrile, methanol, and cyclohexane. Concentrations were adjusted to have absorbance at the excitation wavelength (280 nm) < 0.1. Solutions were purged with argon for 15 min prior to analysis. Corrected excitation and emission spectra were obtained on a fluorometer. Quantum yields were determined by comparison of the integral of emission bands with the one of quinine bisulfate ($\Phi = 0.55$ in 1.0 N H_2SO_4).[17] Typically, three absorption traces were recorded (and averaged) and three fluorescence emission traces, exciting at three different wavelengths (340, 300, and 280 nm). Three quantum yields were calculated, and the mean value was reported.

Fluorescence lifetimes were measured on an instrument equipped with a hydrogen flash lamp, using a time-correlated single photon counting technique in 1023 channels. Histograms of the instrument response functions (using LUDOX scatterer) and sample decays were recorded until they typically reached 3×10^3 counts in the peak channel. The half-width of the instrument response function was typically ∼1.5 ns. The time increment per channel was 0.020 or 0.049 ns. Three obtained fluorescence decays were fitted by global analysis as sums of exponentials using Gaussian-weighted nonlinear least-squares fitting based on Marquardt−Levenberg minimization implemented in the software package of the instrument. The fitting parameters (decay times and pre-exponential factors) were determined by minimizing the global reduced χ_g^2. An additional graphical method was used to judge the quality of the fit that included plots of surfaces ("carpets") of the weighted residuals vs channel number.

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Supporting Information Available: Detailed experimental procedures, UV and fluorescence spectra of SPs **1a**−**1c**, transient absorption spectra of **1a**−**1c** recorded on the nanosecond LFP, and ^{1}H and ^{13}C NMR spectra of all the prepared compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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