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Synthesis and photochemistry of 2-styrylpyrroles. Intermolecular photoaddition of pyrroles to a double bond

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Abstract. Irradiation of the 2-styrylpyrroles **3** and **5** resulted in intermolecular addition of the pyrrole derivative to the double bond of a second molecule in a regiospecific way to give the dimeric products **6** and **7** as the main products. The *N*-methyl-substituted derivative **4** did not show the same reaction, but reacts as the corresponding furan derivative.

Introduction

In continuation of our previous work on the synthesis[1] and intramolecular photocycloaddition reactions of 2-styrylfurans[2], the present investigation deals with the photochemical behaviour of pyrrole analogues.

Intramolecular photochemical cycloadditions of 1,2-divinylbenzene and its alkyl and/or aryl derivatives are well documented[3]. While the alkyl derivatives[4–5] (Scheme 1 R = alkyl) react to give cycloprop[*a*]indene, **C**, the aryl derivatives[6–9] undergo a [2 + 2] cycloaddition reaction to give 1,3-methanoindenes **A** (Scheme 1 R = aryl). Contrary to these results, the heteroaromatic furan analogue[2] gave on irradiation the tetracyclic compound **B** (Scheme 1 R = furyl) which is the first example of the photochemical one-step synthesis of such a compound. From a synthetic point of view, it was of interest to investigate whether the photoreaction is generally applicable to other heterocyclic compounds, thus providing a direct route to bicyclic compounds well suited to undergo different chemical transformations. We anticipated that the pyrrole derivative might react analogously to the furan derivative. However, in the present paper we describe a novel regiospecific *inter*-molecular photoaddition reaction of 2-(2-vinylstyryl)pyrrole (**3**) and of 2-(2-methylstyryl)pyrrole (**5**).

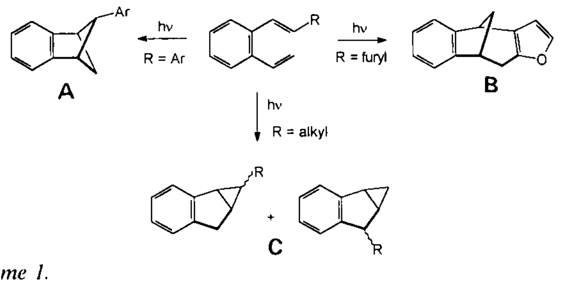
Results and discussion

The starting compounds for the photochemical experiments **3**, **4** and **5** (Scheme 2) were prepared applying the general procedure described for the heteroaryl stilbene analogues[1,10] and obtained in good yield as mixtures of *cis* and *trans* isomers. The isomers were separated by repeated column chromatography on silica gel and identified spectroscopically. They all show a strong absorption band near 300 nm with a bathochromic shift for the *trans* isomer.

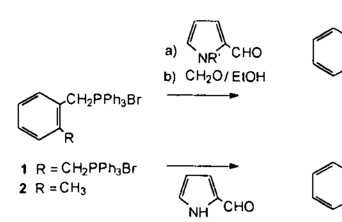
It should be noted that the compounds **3**–**5** and their photoproducts are unstable on exposure to air. They decompose during isolation and separation.

Irradiation of degassed 10^{-3}–10^{-2} molar solutions of **3** in petroleum ether at 300 nm for 6 hours, followed by evaporation of the solvent and chromatographic separation of the dark reaction mixture, gave 38% material from which, in addition to *cis*- and *trans*-**3** (29%), the dimer cis-**6** (Scheme 3) was isolated as the main photoproduct in 9% yield. By inspection of ^{1}H-NMR spectra of the crude reaction mixture prior to separation, the formation of *cis*- and *trans*-**6** was observed (in a 1.5 : 1 ratio). *trans*-**6** could not be isolated in pure form because of its decomposition during chromatographic separation.

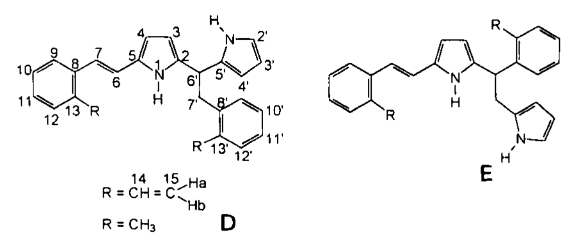
The structures of the photoproducts were determined spectroscopically using different techniques. The mass spectrum of **6** revealed a molecular ion which was indicative of a dimeric structure and the presence of two nitrogen atoms. The strong IR absorption at 3410 and 3370 cm^{-1} pointed in favour of an NH-containing compound. In the ^{1}H-NMR spectrum the characteristic signals of two vinyl groups were seen and only one two-proton AB pattern of an ethylenic group (*cis*-**6**; *J* 12 Hz) at 6.38 and 6.24 ppm. The two-proton AB part of the deceptively simple ABX pattern (3.12 and 3.00 ppm) with apparent coupling constants of 13.5 and 7.5 Hz, was ascribed to the benzylic diastereotopic hydrogens, while the X part was found as a triplet at 3.95 ppm. The signals in the ^{13}C-NMR at 38.57 and 39.02 ppm corresponded unequivocally with the *sp*^{3}-hybridised carbon atoms of the $-CH_2-CH=$ moiety. In the ^{1}H-NMR spectrum at lower field seven multiplets were found. Using COSY experiments, the multiplets at 5.76, 6.04, 6.53 and 7.56 ppm were ascribed to one pyrrole ring and those at 5.73, 6.0 and 7.41 to the other. The signals at 7.56 and 7.41 confirm the presence of pyrrolic NH protons. The remaining five multiplets imply the structure of a mono- and a disubstituted pyrrole ring. Based on their chemical-shift values and corresponding coupling constants one pyrrolic ring has to be substituted at the 2 and 5 position as shown in Scheme 4. From these



Scheme 1.



Scheme 2.



Scheme 4.

data, two structures (**D** and **E**) might be viewed as candidates (Scheme 4). However, the basic peak in the mass spectrum (M^{+}− 117; M^{+}− 2-vinylbenzyl for **6** and M^{+}− 105; M^{+}− 2-methylbenzyl for **7**), which indicates the most preferred fragmentation, undoubtedly eliminates structure **E**.

To confirm that the vinyl group in **3** is not involved in the photoreaction it was replaced by a methyl group. Thus, 2-(2-methylstyryl)pyrrole (**5**) was irradiated (Scheme 3) under the same conditions as **3**. The main reaction, as in the former case along with *cis–trans* isomerization, was intermolecular photoaddition giving a mixture of *cis*- and *trans*-**7** (Scheme 3). In this case both *cis*- and *trans*-**7** were obtained in pure form. The second photoproduct, compound **8**, was formed by an electrocyclodehydrogenation reaction.

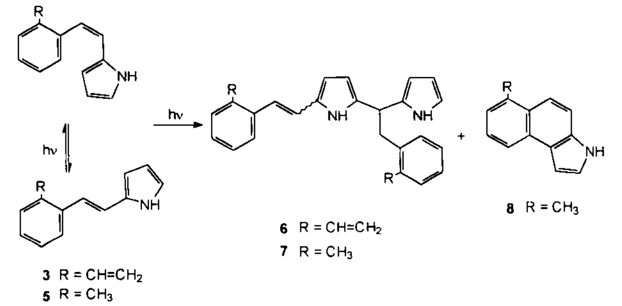
To improve the yield of the photoreaction, irradiation of **3** was performed at different concentrations and in various solvents (petroleum ether, benzene, acetonitrile, methanol) at different wavelengths and irradiation times. These changes had no substantial influence on the course of the reaction. The only detectable products by ^{1}H-NMR were *cis*- and *trans*-**6** and the starting compound **3** in varying isomer ratios. Upon prolonged irradiation of both diluted ($\approx 10^{-3}$ M) and more concentrated ($\approx 10^{-1}$ M) solutions, more of the unidentified high-molecular-weight materials were formed. The yield of photoproduct **6** did not increase and the starting material was still present. This could be explained by competition of excitation of starting material **3** and already formed photoproduct **6**, which absorbs at the same wavelength. Thus, the formed **6** could be consumed by reacting further, either with itself or with starting compound **3**, giving high-molecular-weight products. The same effect was observed upon irradiation of **5**.

The formation of dimeric product **6** instead of some kind of bicyclic product (Scheme 1) was rather unexpected. Some structural pyrrole rearrangements have been described[11] but to the best of our knowledge no secondary-amine-like addition of pyrrole to a double bond has been observed previously[12]. To ensure that the pyrrole derivative **3** was not active as a secondary amine, we substituted the hydrogen on the pyrrolic nitrogen for a methyl group and prepared the *N*-methyl-pyrrole derivative **4**. Irradiation of this compound under the same conditions as **3** resulted mainly in *cis–trans* isomerization and formation of unidentified high-molecular-weight products. Besides these products, only traces of the tetracyclic compound **9** and small amounts of the electrocyclization product **10** are formed. No dimeric products such as **6** were detected. The structure of the tetracyclic product **9** was determined by comparison of its ^{1}H-NMR spectrum with that of an analogous compound from the furan series[2].

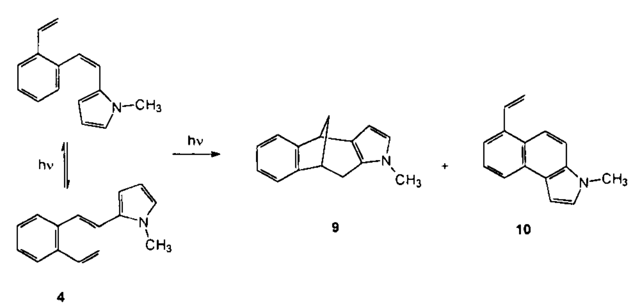
From the results it is clear that the exchange of a furan ring for a pyrrole ring in a heteroaryl-arylethylene system gives rise to a different photochemistry. Though the photophysical and photochemical behaviour of diarylethenes and their aza analogues has been systematically investigated[13], less is known[14] about the photochemistry of monopyrrole analogues.

Based on our experiments, one has to conclude that the formation of dimeric products **6** and **7** results from the presence of an *N*-unsubstituted pyrrole and that one of the steps of this reaction is an intermolecular hydrogen transfer. In the absence of N-H, as in **4**, the bimolecular photoaddition does not occur.

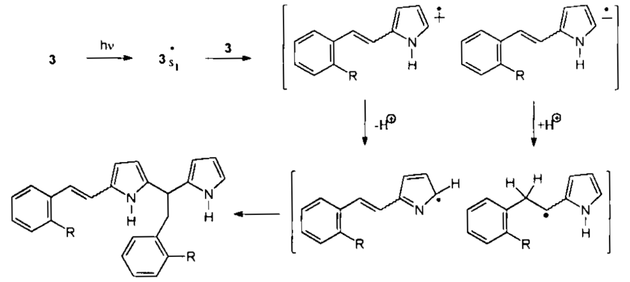
A plausible mechanism for the formation of dimeric products **6** and **7** might be as follows (Scheme 6). The first step after photoexcitation of **3** (or **5**) is an intermolecular electron transfer and formation of radical ions as is well known from the photochemistry of stilbene in the presence of amines[15-17]. By NH proton transfer in the contact radical-ion pair, followed by radical pair coupling at the pyrrole α position to form a carbon–carbon bond, and 1,5 H shift from C_{α} to nitrogen to regain the pyrrole configuration, the end product can be formed (Scheme 6). Intramolecular charge delocalization due to the pyrrole nitrogen could be the reason for regiospecific addition and formation of only one isomer, isomer **D**.



Scheme 3.



Scheme 5.



Scheme 6.

Experimental

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian GEMINI 300 spectrometer at 300 and 75 MHz, respectively. All NMR spectra were measured in $CDCl_3$ solution with tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. IR spectra were recorded on a Perkin-Elmer M-297 spectrophotometer. UV spectra were measured using a Perkin-Elmer Double Beam Spectrometer 124. High-resolution mass spectra (HRMS) were measured on an Extrel FTMS 2001 DD. Column chromatography was performed on silica gel (60–220 nm) using petroleum-ether/ether as eluent. A Rayonet reactor equipped with 253.7-, 300-, or 360-nm lamps was used for irradiation. Irradiations were performed in a Quartz or Pyrex vessel in petroleum ether, benzene, acetonitrile, or methanol solutions. All irradiation experiments were carried out in degassed solutions by bubbling a stream of oxygen-free nitrogen prior to irradiation. Solvents were purified by distillation. Melting points were uncorrected. Pyrrole-2-carboxaldehyde and 1-methyl-pyrrole-2-carboxaldehyde were commercially available.

General procedure[1] for the synthesis of **3** *and* **4**

To a stirred solution of [1,2-phenylenebis(methylene)]bis(triphenylphosphonium bromide) (**1**) (7.88 g, 0.01 mole) and the aldehyde (0.01 mole, pyrrole-2-carboxaldehyde or 1-methyl-pyrrole-2-carboxaldehyde) in absolute ethanol (300 ml, dried over molecular sieves 3A) was added dropwise a solution of sodium ethoxide (prepared by dissolving 0.01 mole of sodium in 10 ml absolute ethanol). While warming to 35°C, the stirring was continued for 1/2 h. Under a stream of dry nitrogen, gaseous formaldehyde was introduced and sodium ethoxide (0.011 mole in 10 ml absolute ethanol) was added dropwise. The reaction mixture was left to stand overnight. After removal of the solvent under reduced pressure, the residue was worked up by adding water and then extracting with benzene. The benzene extracts were dried (anhydrous $MgSO_4$), the benzene evaporated and the reaction mixture was purified and separated by repeated column chromatography on silica gel using petroleum ether-ether as eluent. The first fractions yielded the *cis* and the later fractions the *trans* isomer.

2-(2-Vinylstyryl)pyrrole (**3**). Yield 1.27 g (65%; based on ^{1}H-NMR, a mixture of 43% *cis*- and 57% *trans*-**3**). *cis*-**3**: white crystals, m.p. 41°C. ^{1}H-NMR ($CDCl_3$): δ 7.79 (br. s, 1H, NH), 7.62–7.66 (m, 1H, Ar-H), 7.23–7.39 (m, 3H, Ar-H), 6.93 (dd, 1H, $CH=CH_2$, J 11.02 and J 17.55 Hz), 6.51 (m, 1H, 2-Pyr-H), 6.50 (d, 1H, Et-H, J 12.05 Hz), 6.34 (d, 1H, Et-H, J 12.05 Hz), 6.16 (m, 1H, 4-Pyr-H), 6.09 (m, 1H, 3-Pyr-H), 5.70 (dd, 1H, $=CHH_a$, J 1.13 and J 17.55 Hz), 5.25 (dd, 1H, $=CHH_b$, J 1.13 and J 11.02 Hz). ^{13}C-NMR ($CDCl_3$): δ [136.75 (s), 136.20 (s), C-8,13], 134.50 (d, C-14), 129.55 (s, C-5), [129.15 (d), 127.99 (d), 127.72 (d), 125.57 (d), C-9-12], [121.52 (d), 121.38 (d), C-6,7], 119.04 (d, C-2), 115.35 (t, C-1), [111.72 (d), 108.52 (d), C-3,4]. IR (KBr): ν 3440 (N-H), 1625 cm^{-1}. UV (EtOH) λ_{max} (ε): 250 (16039), 285 (9484), 305 (7811, sh).

trans-**3**: white crystals, m.p. 63-64°C. ^{1}H-NMR ($CDCl_3$): δ 8.35 (br. s, 1H, NH), 7.34–7.51 (m, 2H, Ar-H), 7.18–7.29 (m, 2H, Ar-H), 6.82 (m, 1H, 2-Pyr-H), 6.36 (m, 1H, 4-Pyr-H), 6.26 (m, 1H, 3-Pyr-H), 7.06 (dd, 1H, $CH=CH_2$, J 10.86 and J 17.37 Hz), 6.92 (d, 1H, Et-H, J 16.36 Hz), 6.83 (d, 1H, Et-H, J 16.36 Hz), 5.63 (dd, 1H, CHH_a, J 1.30 and J 17.37 Hz), 5.34 (dd, 1H, CHH_b, J 1.30 and J 10.86 Hz). ^{13}C-NMR ($CDCl_3$): δ [135.89 (s), 135.55 (s), C-8,13], 135.02 (d, C-14), 130.88 (s, C-5), [127.82 (d), 127.00 (d), 126.56 (d), 125.61 (d), C-9-12], [121.09 (d), 120.85 (d), C-6,7], 119.18 (d, C-2), 116.32 (t, C-15), [109.83 (d), 109.04 (d), C-3,4]. IR (KBr): ν 3380 (N-H), 1615 cm^{-1}. UV (EtOH) λ_{max}/nm (ε): 255 (7904), 335 (17318). MS m/z (%; fragment): 195 (100, M^+), 179 (17), 129 (21), 128 (21), 80 (79), 41 (94). HRMS found: M^+, 195.10475; calcd. for $C_{14}H_{13}N$: 195.10480.

1-Methyl-2-(2-vinylstyryl)pyrrole (**4**). Yield 1.25 g (60%; based on ^{1}H-NMR, a mixture of 67% *cis*- and 33% *trans*-**4**). *cis*-**4**: colourless oil. ^{1}H-NMR ($CDCl_3$): δ 7.54–7.59 (m, 1H, Ar-H), 7.15-7.31 (m, 3H, Ar-H), 6.92 (dd, 1H, $CH=CH_2$, J 11.00 and J 17.58 Hz), 6.51 (dd, 1H, 2-Pyr-H, J 1.60 and J 2.60 Hz), 6.50 (d, 1H, Et-H, J 12.07 Hz), 6.47 (d, 1H, Et-H, J 12.07 Hz), 5.91 (dd, 1H, 3-Pyr-H, J 2.60 and J 3.70 Hz), 5.69 (dd, 1H, 4-Pyr-H, J 3.70 and J 1.60 Hz), 5.68 (dd, 1H, $=CHH_a$, J 1.31 and J 17.58 Hz), 5.22 (dd, 1H, $=CHH_b$, J 1.31 and J 11.00 Hz), 3.58 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [136.90 (s), 135.72 (s), C-8,13], 134.80 (d, C-14), 129.33 (s, C-5), [129.02 (d), 127.59 (d), 127.15 (d), 125.14 (d)*, C-9-12], [125.03 (d)*, 122.46 (d), C-6,7], 119.13 (d, C-2), 114.83 (t, C-15), [109.73 (d), 107.59 (d), C-3,4], 33.85 (q). UV (EtOH) λ_{max}/nm (ε): 295 (8592).

trans-**4**: colourless oil. ^{1}H-NMR ($CDCl_3$): δ 7.45–7.52 (m, 2H, Ar-H), 7.19–7.31 (m, 2H, Ar-H), 7.14 (d, 1H, Et-H, J 15.84 Hz), 6.83 (d, 1H, Et-H, J 15.84), 7.07 (dd, 1H, $CH=CH_2$, J 10.96 and J 17.42 Hz), 6.64 (dd, 1H, 2-Pyr-H, J 2.80 and J 1.40 Hz), 6.49 (dd, 1H, 4-Pyr-H, J 3.50 and J 1.40 Hz), 6.16 (dd, 1H, 3-Pyr-H, J 3.50 and J 2.80 Hz), 5.63 (dd, 1H, $=CHH_a$, J 1.31 and J 17.42 Hz), 5.34 (dd, 1H, $=CHH_b$, J 1.31 and J 10.96 Hz), 3.68 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [135.95 (s), 135.92 (s), C-8,13], 134.95 (d, C-14), 132.08 (s, C-5), [127.68 (d), 126.99 (d), 126.46 (d), 125.67 (d), C-9-12], [123.57 (d), 123.49 (d), C-6,7], 119.35 (d, C-2), 116.18 (t, C-15), [108.11 (d), 106.60 (d), C-3,4], 34,02 (q). UV (EtOH) λ_{max}/nm (ε): 253 (9941), 338 (17658). MS m/z (%; fragment): 209 (100, M^+), 194 (15), 182 (17), 165 (18), HRMS found: M^+, 209.122472; calcd. for $C_{15}H_{15}N$: 209.119900.

2-(2-methylstyryl)pyrrole (**5**). Prepared analogously to the furan derivatives[10]; yield 1.59 g (87%; based on ^{1}H-NMR, a mixture of 40% *cis*- and 60% *trans*-**5**). *cis*-**5**: yellowish oil. ^{1}H-NMR ($CDCl_3$): δ 7.78 (br. s, NH), 7.19–7.35 (m, 4H, Ar-H), 6.48 (m, 1H, 2-Pyr-H), 6.46 (d, 1H, Et-H, J 12.00 Hz), 6.29 (d, 1H, Et-H, J 12.00 Hz), 6.14 (m, 1H, 4-Pyr-H), 6.08 (m, 1H, 3-Pyr-H), 2.26 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [137.68 (s), 136.61 (s), C-8,13], 129.16 (s, C-5), [130.37 (d), 128.49 (d), 127.54 (d), 126.08 (d), C-9-12], [122.28 (d), 120.72 (d), C-6,7], 118.81 (d, C-2), [111.45 (d), 108.47 (d), C-3,4], 19.70 (q). UV (EtOH) λ_{max}/nm (ε): 235 (7890), 287 (10850).

trans-**5**: white crystals; m.p. 92°C. ^{1}H-NMR ($CDCl_3$): δ 8.36 (br. s, 1H, NH), 7.51 (d, 1H, Ar-H, J 7.25 Hz), 7.13–7.24 (m, 3H, Ar-H), 6.84 (s, 2H, Et-H), 6.82 (m, 1H, 2-Pyr-H), 6.36 (m, 1H, 4-Pyr-H), 6.26 (m, 1H, 3-Pyr-H), 2.39 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [136.43 (s), 135,15 (s), C-8,13], 131.11 (s, C-5), [130.37 (d), 126.94 (d), 126.20 (d), 124.74 (d), C-9-12], [121.16 (d), 120.19 (d), C-6,7], 119.03 (d, C-2), [109.96 (d), 108.95 (d), C-3,4], 19.95 (q). IR (KBr): ν 3400 (N-H), 1620, 1590 cm^{-1}. UV (EtOH) λ_{max}/nm (ε): 240 (5780), 330 (20707). MS m/z (%; fragment): 183 (17, M^+), 41 (100). HRMS found: M^+, 183.10476; calcd. for $C_{13}H_{13}N$: 183.10480.

Irradiation of **3**

A degassed mixture of *cis*- and *trans*-**3** (585 mg, 3 mmol) in 640 ml of petroleum ether in a quartz tube was irradiated in a Rayonet reactor equipped with 300-nm lamps for 6 h. The solvent was evaporated and the remaining dark oil was subjected to column chromatography on silica gel. Elution with petroleum-ether/ether (0–15%) gave 38% of material (222 mg). In the first fractions was isolated a mixture of *cis*- and *trans*-**3** (169 mg, 29%) followed by photoproduct **6** (53 mg, 9%). The remaining 62% of material was decomposed during the irradiation or by the chromatographic isolation. Similar results were obtained by separation on alumina.

cis-2-(2-vinylstyryl)-5-[1-(pyrrol-2-yl)-2-(2-vinylphenyl)ethyl]pyrrole (*cis*-**6**). Oil. ^{1}H-NMR ($CDCl_3$): δ 7.56 (d, 1H, Ar-H, J 7.69 Hz), 7.56 (br. s, 1H, NH), 7.41 (d, 1H, Ar-H, J 7.69 Hz), 7.41 (br. s, 1H, NH), 7.10–7.30 (m, 4H, Ar-H), 7.04 (dt, 1H, Ar-H, J 7.50 and J 1.50 Hz), 6.88 (dd, 1H, $CH=CH_2$, J 17.56 and J 11.02 Hz), 6.71 (dd, 1H, $CH=CH_2$, J 17.30 and J 10.95 Hz), 6.70 (dd, 1H, Ar-H, J 7.69 and J 1.50 Hz), 6.53 (ddd, 1H, 2′-Pyr-H[a], J 1.52, J 2.66 and J 2.73 Hz), 6.38 (d, 1H, Et-H, J 12.01), 6.24 (d, 1H, Et-H, J 12.01), 6.04 (ddd, 1H, 3′-Pyr-H, J 3.40, J 2.73 and J 2.66), 6.00 (dd, 1H, 4-Pyr-H, J 3.42 and J 2.68 Hz), 5.76 (ddd, 1H, 4′-Pyr-H, J 1.52, J 3.40 and J 2.46 Hz), 5.73 (dd, 1H, 3-Pyr-H, J 3.42 and J 2.68 Hz), 5.64 (dd, 1H, $=CHH_a$, J 17.56 and J 1.24 Hz), 5.55 (dd, 1H, $=CHH_a$, J 17.30 and J 1.47 Hz), 5.21 (dd, 1H, $=CHH_b$, J 11.02 and J 1.24 Hz), 5.20 (dd, 1H, $=CHH_b$, J 10.95 and J 1.47 Hz), 3.95 (t, 1H, 6′-H, J 7.55), 3.12 (dd, 1H 7′-H, J 13.50 and J 7.55 Hz), 3.00 (dd, 1H 7′-H, J 13.50 and J 7.55 Hz). ^{13}C-NMR ($CDCl_3$): δ [136.77 (s), 136.65 (s), 136.55 (s), 135.95 (s), C-8,8′,13,13′], [134.60 (d), 134.16 (d), C-14,14′], [134.16 (s), 131.87 (s), 128.95 (s), C-2,5,5′], [130.16 (d), 128.86 (d), 128.03 (d), 127.62 (d), 127.29 (d), 126.56 (d), 125.57 (d), 125.57 (d), C-9-12, 9′-12′], [121.46 (d), 120.83 (d), C-6,7], 116.62 (d, C-2′), [115.68 (t), 115.13 (t), C-15,15′], [111.77 (d), 108.13 (d), 106.28 (d), 105.43 (d), C-3,4,3′,4′], 39.03 (d, C-6′), 38.58 (t, C-7′). IR (NaCl): ν 3410 (N-H), 3370 (N-H), 3080, 3050, 3005, 2920, 2860, 1575, 1435 cm^{-1}. UV (EtOH) λ_{max}/nm (ε): 240 (14633), 297 (5211), 335 (5596). MS *m/z* (%; fragment): 390 (2, M$^+$), 273 (100), 258 (12), 115 (8). HRMS found: M$^+$, 390.201145; calcd. for $C_{28}H_{26}N$: 390.209049.

Irradiation of **4**

The irradiation was performed in the same way as the irradiation of **3**. 1-Methyl-7-vinylbenz[*e*]indole (**10**) was found in the first fractions by column chromatography separation and purification: δ 8.2 (d, 1H, Ar-H, *J* 8.5 Hz), 7.9 (d, 1H, Ar-H, *J* 9.2 Hz), 7.5–7.6 (m, 4H), 7.1 (d, 1H, Pyr-H, *J* 3.0 Hz), 7.0 (d, 1H, Pyr-H, *J* 3.0 Hz), 5.8 (dd, 1H, *J* 17.3 and *J* 1.6 Hz), 5.5 (dd, 1H, *J* 10.9 and 1.6 Hz), 3.9 (s, 3H, CH_3). From the ^{1}H-NMR spectrum of the enriched fraction the characteristic signals of 1,4,9,10-tetrahydro-1-methyl-4,9-methanobenzo-[4,5]cyclohepta[1,2-*b*]pyrrole (**9**) are: δ 6.31 (d, 1H, Pyr-H, *J* 2.5 Hz), 3.32 (s, 3H, NCH_3), 2.04 (d, 1H, *J* 10.2 Hz), 2.44 (dt, 1H, *J* 5.0 and *J* 10.2 Hz), 2.52 (dd, 1H, *J* 15.3 and *J* 1.5 Hz), 3.03 (dd, 1H, *J* 15.3 and *J* 5.0 Hz), 3.83 (d, *J* 4.4 Hz), one signal covered under the methyl of the **4**. The compound decomposed completely by TLC purification.

Irradiation of **5**

A degassed petroleum-ether solution of **5** (1 g, 5.4 mmol in 230 ml) was irradiated in a Rayonet reactor at 300 nm for 6 h. The solvent was evaporated and the dark, tarry residue was chromatographed on a silica-gel column with mixtures of petroleum-ether/diethyl-ether (0–15%) as eluents. The first fractions consisted of unreacted starting material **5** followed by *cis*-**7**, **8** and *trans*-**7**. After repeated column chromatography on silica gel in total 30% of material (300 mg) was isolated: 86 mg (8.6%) of *cis*- and *trans*-**5**, 105 mg (10.5%) of *cis*-**7**, 87 mg (8.7%) of *trans*-**7** and 22 mg (2.2%) of **8**.

*cis-2-(methylstyryl)-5-[1-(pyrrol-2-yl)-2-(2-methylphenyl)ethyl]pyrrole (cis-*7*)*. Oil. ^{1}H-NMR ($CDCl_3$): δ 7.60 (br. s, 1H, NH), 7.45 (br. s, 1H, NH), 6.97–7.22 (m, 7H, Ar-H), 6.77 (d, 1H, Ar-H, *J* 7.26 Hz), 6.55 (m, 1H, 2′-Pyr-H)[a], 6.35 (d, 1H, Et-H, *J* 11.96 Hz), 6.21 (d, 1H, Et-H, *J* 11.96 Hz), 6.05 (m, 1H, 3′-Pyr-H), 6.00 (t, 1H, 4-Pyr-H, *J* 2.99 Hz), 5.77 (m, 2H, 3/4′-Pyr-H), 3.94 (t, 1H, 6′-H, *J* 7.40), 3.05 (dd, 1H, 7′-H, *J* 7.40 and *J* 13.50 Hz), 2.95 (dd, 1H, 7′-H, *J* 7.40 and *J* 13.50 Hz), 2.17 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [137.73 (s), 137.66 (s), 136.43 (s), 136.37 (s), C-8,8′,13,13′], [134.30 (s), 132.26 (s), 129.21 (s), C-2,5,5′], [130.52 (d), 129.97 (d), 129.59 (d), 128.34 (d), 127.50 (d), 126.29 (d), 126.18 (d), 125.67 (d), C-9-12, 9′-12′], [121.85 (d), 120.78 (d), C-6,7], 116.67 (d, C-2′), [111.56 (d), 108.25 (d), 106.24 (d), 105.53 (d), C-3,4,3′,4′,], 38.94 (d, C-6′), 38.55 (t, C-7′), [19.74 (q), 18.06 (q), C-14,14′]. IR (KBr): ν 3400 (N-H), 3090, 3000, 2910, 2840 cm^{-1}. UV (EtOH) λ_{max}/nm (ε): 297 (8680). MS *m/z* (%; fragment): 366 (5, M$^+$), 261 (100), 194 (8), 91 (12). HRMS found: M$^+$, 366.204326; calcd. for $C_{26}H_{26}N$: 366.209049.

trans-**7**. Oil. ^{1}H-NMR ($CDCl_3$): δ 7.80 (br. s, 2H, NH), 7.45 (d, 1H, Ar-H, *J* 7.10 Hz), 7.02–7.20 (m, 6H, Ar-H), 6.94–7.00 (m, 1H, Ar-H), 6.73 (d, 1H, Et-H *J* 16.29 Hz), 6.60 (d, 1H, Et-H, *J* 16.29 Hz), 6.64 (m, 1H, 2′-Pyr-H), 6.22 (t, 1H, 4-Pyr-H, *J* 2.99 Hz), 6.15 (m, 1H, 3′-Pyr-H), 6.02 (m, 1H, 4′-Pyr-H), 5.95 (t, 1H, 3-Pyr-H, *J* 2.99 Hz), 4.24 (t, 1H, 6′-H, *J* 7.46 Hz), 3.27 (dd, 1H, 7′-H, *J* 7.46 and *J* 13.29 Hz), 3.24 (dd, 1H, 7′-H, *J* 7.46 and *J* 13.29 Hz), 2.34 (s, 3H, CH_3), 2.11 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ [137.77 (s), 136.63 (s), 136.30 (s), 134.96 (s), C-8,8′,13,13′], [134.39 (s), 132.37 (s), 130.44 (s), C-2,5,5′], [130.23 (d), 130.02 (d), 129.67 (d), 126.65 (d), 126.39 (d), 126.01 (d), 125.73 (d), 124.42 (d), C-9-12, 9′-12′], [120.20 (d), 119.86 (d), C-6,7], 116.97 (d, C-2′), [109.02 (d), 108.12 (d), 107.64 (d), 105.75 (d), C-3,4,3′,4′], 39.06 (d, C-6′), 38.36 (t, C-7′), [19.90 (q), 19.04 (q), C-14, 14′]. IR (NaCl): ν 3400 (N-H), 3080, 2995, 2900, 2840 cm^{-1}. UV (EtOH) λ_{max}/nm (ε): 340 (14857). MS *m/z* (%; fragment): 366 (8, M$^+$), 261 (100), 184 (40). HRMS found: M$^+$, 366.194141; calcd. for $C_{26}H_{26}N$: 366.209049.

7-Methylbenzo[e]indole (**8**). Oil. ^{1}H-NMR ($CDCl_3$): δ 8.43 (br. s, 1H, NH), 8.13 (d, 1H, Ar-H, *J* 8.20 Hz), 7.77 (d, 1H, Ar-H, *J* 8.95 Hz), 7.55 (dd, 1H, *J* 8.95 and *J* 0.80 Hz), 7.45 (dd, 1H, Ar-H, *J* 8.20 and *J* 6.98 Hz), 7.22–7.32 (m, 2H, Ar-H, Pyr-H), 7.08–7.12 (m, 1H, Pyr-H). ^{13}C-NMR ($CDCl_3$): δ 134.85 (s, C-9), 132.02 (s, C-1), [128.18 (s), 127.96 (s), C-5, 12], [125.45 (d), 124.46 (d), 122.25 (d), 121.32 (d), C-2,3,4,11], 122.95 (s, C-6), 119.00 (d, C-8), 112.29 (d, C-10), 102.10 (d, C-7), 20.24 (q). UV (EtOH) λ_{max}/nm (ε): 230 (19142), 251 (19482), 259 (14328), 305 (5436), 319 (4984), 335 (2945). MS *m/z* (%; fragment): 181 (100, M$^+$), 167 (22), 152 (33). HRMS found: M$^+$, 181.088471; calcd. for $C_{13}H_{11}N$: 181.088600.

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[a] For atomic position see **D**.