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Photochemical Formation of Indanylpyrrole Derivatives from 2,2′-(*o*-Phenylenedivinylene)dipyrrole

Nikola Basarić,[a] Slavica Tomšić,[a,†] Željko Marinić[b] and Marija Šindler-Kulyk[a,*]

[a]*Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10000 Zagreb, Croatia*

[b]*NMR Center, The Rugjer Boškovic Institute, Zagreb, Croatia*

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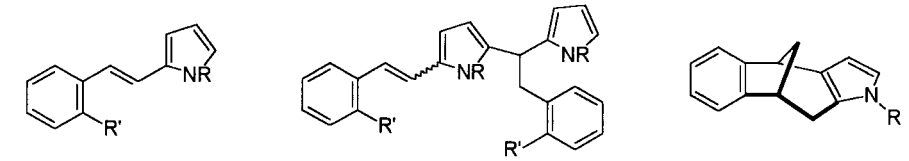
Abstract—Photochemically induced intra- and inter-molecular reaction of 2,2′-(1,2-phenylenedivinylene)dipyrrole (**4a**) led to a mixture of geometric isomers of 5-{2-pyrrolyl[2-(2-pyrrolyl)-1-indanyl]methyl}-2,2′-(1,2-phenylenedivinylene)dipyrroles (**8**) in 40% yield. The compounds were isolated and characterized spectroscopically and by catalytic hydrogenation to 5-{2-pyrrolyl[2-(2-pyrrolyl)-1-indanyl]-methyl}-2,2′-(1,2-phenylenediethylene)dipyrrole (**10**). Traces of 4,5-dihydro-4-(2-pyrrolyl)benzo [5,6]cycloocta[1,2-*b*]pyrrole (**7**) were isolated in addition to **8**. Under the same conditions *N*,*N*′-dimethyl-2,2′-(1,2-phenylenedivinylene) dipyrrole (**4b**) undergoes only *cis*–*trans*-isomerization.

Introduction

As a result of our interest in the synthesis and photochemistry of unsaturated heterocyclic derivatives,[1] we turned our attention to styrylpyrroles **1** (Scheme 1).[2]

Irradiation of **1a** or **1b** gives products **2a** and **2b**, respectively, by regiospecific intermolecular addition of the pyrrole to the double bond. With **1a**, no intramolecular formation of bicyclic product **3a** was observed, as we expected on analogy with furan derivatives.[1a] The bimolecular photoaddition does not occur upon irradiation of the *N*-methylpyrrole derivative **1c** and only traces of the bicyclic product **3b** were formed. In addition to *cis*–*trans* isomerization, the formation of some tarry material was also observed. We proposed[2] that the formation of dimeric products **2a**,**b** occurs via photoinduced electron transfer, followed by proton transfer and radical combination. In order to exploit the potential of our efficient intermolecular photodimerization of styrylpyrroles and to develop a short route to pyrrole derivatives, which are new nitrogen heterocycles, we synthesized the compounds **4** (Scheme 2).

Compound **4a** upon irradiation might give the intermolecular addition product **5**. This could subsequently close to the interesting larger aromatic pyrrole-containing systems, the so-called ‘expanded’ porphyrin-like compounds.[3] More likely, because of the presence of the two pyrrolyl-styrylgroups in the same molecule, an intramolecular ring closure is expected to give an annelated azepine compound such as **6**. Although Lewis[4] and co-workers reported the intramolecular photoaddition of



1a: R = H, R' = CH=CH$_2$
b: R = H, R' = CH$_3$
c: R = CH$_3$, R' = CH=CH$_2$
d: R = CH$_3$, R' = CH$_3$

2a, b

3a: R = H
b: R = CH$_3$

Scheme 1.

Keywords: indanes; hydrogenation; photochemistry; pyrroles.

* Corresponding author. Tel.: +385-1-4597246; fax: +985-1-4597250; e-mail: marija.sindler@pierre.fkit.hr

† Present address: Pliva-Research Institute, Zagreb, Croatia.

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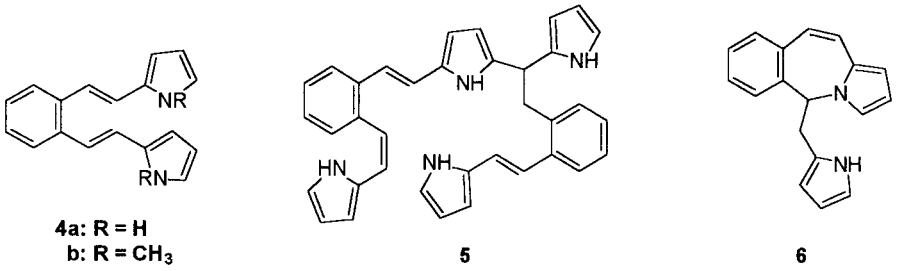


Scheme 2.

the *o*-(aminoalkyl)stilbenes and formation of benzazepines, to the best of our knowledge no intramolecular secondary amine-like photoaddition of a pyrrole to a double bond has been previously observed. The intermolecular 1,4-photoaddition of aliphatic amines and pyrrole to benzene[5] and naphthalene[6] is well known. Besides the photodimerization of styrylpyrroles,[2] Gilbert's report of the photoaddition of pyrrole to styrenes[7] and photochemical coupling between pyrrole and pyridone derivatives,[8] and the photoaddition reactions of indole, carbazole and phenothiazine to *trans*-stilbene in the mixed crystal state as well as in solution have been described.[9]

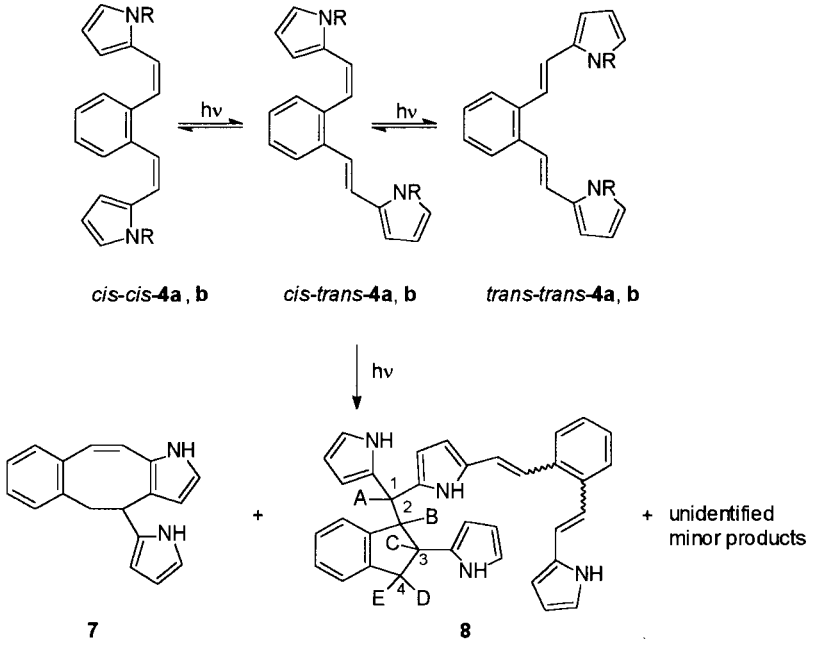
In the present paper we describe formation and structure determination of novel compounds **7** and **8** obtained by photochemical intra- and inter-molecular reaction of **4a** in benzene.

Results and Discussion

The starting compounds **4a** and **4b**, new pyrrole derivatives, were prepared as the mixtures of stereoisomers in 30 or 40% yield, respectively, by using the general procedure described for the heteroarylstilbene analogues.[1b–d] The yields are higher than those reported[10a] for Wittig reactions from *p*-substituted triphenylphosphonium salts and 1-methyl-2-pyrrole-carboxaldehyde but lower than those described for similar styrylpyrroles.[10b] In our case, because the diphosphonium salt is a starting material, a double Wittig reaction must occur to give **4a** or **4b**. Because of the lower reactivity of the pyrrolecarboxaldehydes, steric hindrance due to *o*-substitution and NH acidity of the pyrrole in a competing side reaction,[11] formation of a certain amount of styrylpyrroles **1b** and **1d** is unavoidable (see Experimental). In addition, the pyrrole derivatives are quite unstable in air and decompose during attempts at purification.

The geometric isomers of **4a** were separated by repeated column chromatography on silica gel and identified spectroscopically. The corresponding isomers **4b** have not been obtained pure because of poor chromatographic separation. All three isomers of **4a** and **4b** show a strong absorption in the region of 270–360 nm.

Irradiation of a degassed benzene solution of **4a** [10^{-3} M], followed by evaporation of the solvent, gave a dark residue from which a mixture of dimeric stereoisomers **8** was isolated in 40% yield after chromatography, besides traces of a minor product **7**. Starting material **4a** (40%, a mixture of isomers) was also recovered (Scheme 3).



Scheme 3.

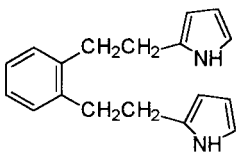
To improve the yield of the photoreaction, irradiation of **4a** (pure isomer or as a mixture of isomers) was performed at different wavelengths and irradiation times but without substantial influence on the reaction course. The yield of photoproducts did not increase due to their competitive absorbtion at the same wavelength as the starting material. On prolonged irradiation of isolated mixture of isomers **8**, some tetrameric structures are found in MS. No products were obtained from **4a** in a tube, which has been kept in darkness during the irradiation experiments. Irradiation of *N*-methyl derivative **4b**, a compound that cannot react as a secondary amine, failed to yield products other than the intractable tars deposited on the irradiation flask walls. The only detectable process was *cis–trans* isomerization.

The structures of the products were determined spectroscopically and by chemical means. The ^{1}H NMR spectrum of compound **7** was taken in three different solvents, $CDCl_3$, C_6D_6 and $(CD_3)_2CO$, to facilitate the structure determination and full assignment of the resonances. Combining the data from all three spectra it is evident that the molecule has one conjugated double bond in the *cis*-configuration, five pyrrolic CH, two NH and three aliphatic protons of a CH_2–CH moiety, according to the coupling constants and chemical shifts. Using COSY experiments, three pyrrole protons were ascribed to one ring and two to the other. Based on their chemical shifts and corresponding coupling constants, we concluded that the second pyrrole ring has to be substituted in positions 2 and 3. The three protons in the CH_2–CH moiety might give a similar pattern either as a part of a seven-membered ring, as in structure **6**, or as a part of an eight-membered ring. The mass spectrum showed the fragment M^+-66 (M^+-pyrrole) which confirmed the structure **7** and eliminated the cycloheptene-like structure, for which the preferred fragmentation would be M^+-80 (M^+-pyrrolylmethyl)[12] with formation of the tropylium-like cation.

The main product **8** consists mainly of three isomers according to ^{1}H NMR in a ratio 1:3:1 (**8a**:**8b**:**8c**). From the C,H-elemental analysis it is evident that the mixture consists only of dimeric isomers and not additional products. All three isomers **8a–c** show the molecular ion in the mass spectrum (M^+ 520) and the base peak of *m*/*z* 338 which corresponds to the mass of **4a** increased by a pyrrolylmethylenic group. ^{1}H NMR spectra of all three products **8a–c** show four signals from 2.0 to 4.5 ppm in a ratio of 1:1:1:2 in the aliphatic region. The aromatic region is complicated but the pattern resembles a structure with twice the number of pyrrole and benzene protons with respect to starting compound **4a**. However, in this multiplet, parts of AB-quartets could be detected. These are similar to *cis*- and *trans*-ethylenic protons of **4a**. From the COSY experiments it is shown that protons A–E are in mutual interaction. The ^{13}C NMR spectra of **8b** and **8c** show three doublets and one triplet in the aliphatic region. This corresponds to the carbons C(1)–C(4). In the aromatic region there are twenty-three doublets and nine singlets. When added to the aliphatic signals, this makes thirty-six total signals. Analysis of each ^{13}C NMR signal, assisted with HETCOR, results in the following assignments. The eleven doublets (not twelve) between δ 105–120 correspond to pyrrole carbons. Three pyrrole doublets (not four) are at δ 117–120 indicating that the product has one pyrrole ring substituted at the 2- and 5-positions. The four signals near δ 120 can be assigned to ethylenic carbons. Eight doublets at δ 125–130 correspond to benzene carbons and nine singlets at δ 130–145 belong to quaternary benzene and pyrrole carbons. Four isomers are possible for the two double bonds in **8**, but more are possible because of different configurations on the indane ring. Since the chemical shifts of the aliphatic protons of separable isomers of **8** differ hardly at all, and the coupling constants are nearly identical, we conclude that isomers **8a–c** all have the same configuration in the indane, and differ only in the configuration of the double bonds. *Cis*- and *trans*-coupling constants are very similar in indanes and the stereochemical relationship of the 1,2-substituents cannot readily be evaluated from coupling constant data.[13] However, it is clear from the NOESY spectra of **8** that protons A and C interact more strongly than protons B and C. The cross peak in the spectrum from A and C shows that they are on the same side of the indane ring. Consequently, products **8** should have the *trans*-configuration of the pyrrolic substituents on the indane ring.

To confirm that the only difference among **8a–c** is the configuration on the double bonds, hydrogenation was carried out (Scheme 4). The procedure was tried first for model compound **4a**, which gave a new compound **9**. Then, catalytic hydrogenation of the isomers **8** gave only one product **10** that was evident from the ^{1}H NMR spectrum of the crude reaction mixture prior to separation. The mass spectrum of the hydrogenated product **10** shows a molecular ion that is four units higher than compound **8** and a base peak at *m*/*z* 342 from the same fragmentation as in **8**. The aliphatic region in the ^{1}H NMR spectrum of **10** shows five indane protons (Fig. 1) in addition to resonances for eight CH_2 protons that are similar to those found in compound **9**. An attempt to make simpler derivatives of the compounds **8** by ozonolysis gave, as found with the model compound **4a**, polymeric material.

A plausible mechanism for the formation of photoproducts **7**



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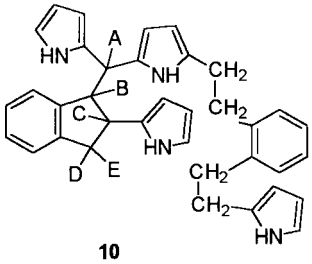

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Scheme 4.

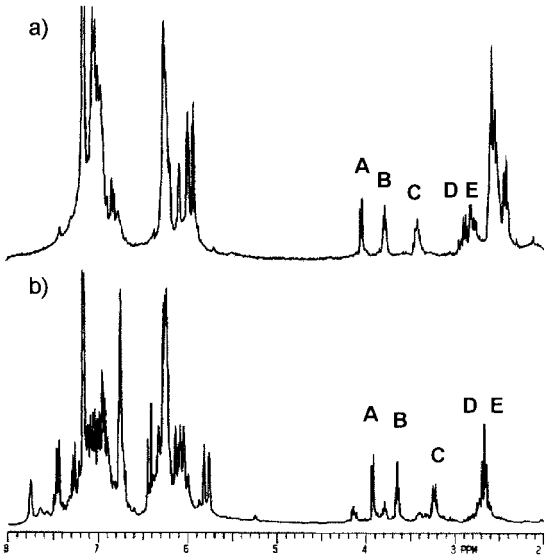


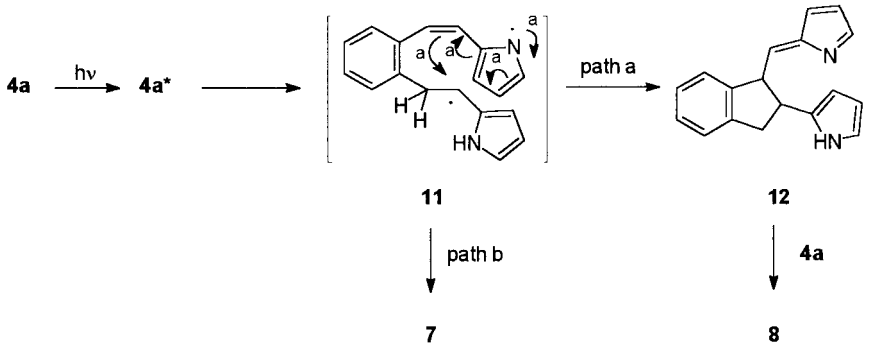
Fig. 1. ^{1}H NMR spectra of: (a) **10**; and (b) **8b**.

Me_4Si as an internal standard. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on Perkin–Elmer LAMBDA 20 Spectrophotometer. HRMS spectra were measured on an Auto Spec Q (VG Analytical). Elemental analyses were carried out in the Microanalytical Laboratory at the Rugjer Boskovic Institute. Melting points were obtained on a Original Kofler Mikroheitztisch apparatus (Reicherdt, Wien) and are uncorrected.

Pyrrole-2-carboxaldehyde and *N*-methylpyrrole-2-carboxaldehyde were obtained from commercial source and used without further purification.

Notation of H atoms in NMR assignments: e.g. H_{5p}=H in pyrrole at the position 5, H_{et}=H in ethylene, H_{et}-ct_c=H in *cis*-ethylene part of *cis–trans* isomer, H_{et}-ct_t=H in *trans*-ethylene part of *cis–trans* isomer etc.

Preparation of 2,2′-(1,2-phenylenedivinylene)dipyrrole (4a) and *N*,*N*′-dimethyl-2,2′-(1,2-phenylenedivinylene)-



Scheme 5.

and **8** is shown in Scheme 5. After photoexcitation of **4a**, an electron transfer followed by hydrogen transfer can occur[2,7] to give the intermediate **11**. This could close (path a) to the indane derivative **12** that easily reacts with the starting compound **4a** and give dimeric products **8**. Compound **7** can be formed from the same intermediate **11** but by the different intramolecular ring closure (path b) (Scheme 5).

Based on the results thus far obtained, we can conclude that the preferred process in the photochemical reaction of 1,2-di(pyrrolylvinyl)benzene is ring closure to the substituted indanes followed by nucleophilic attack of the starting compound. Although the absolute configurations on the chiral centers of the isolated isomers **8** are not known, all of them have *trans*-configuration of the pyrrolic substituents on the indane ring.

Experimental

General

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian GEMINI 300 spectrometer at 300 and 75 MHz, respectively, in $CDCl_3$ and when necessary in C_6D_6 with

dipyrrole (4b) by the Wittig reaction from diphosphonium salt *o*-$C_6H_4(CH_2PPh_3Br)_2$ and corresponding aldehydes, pyrrole-2-carboxaldehyde and *N*-methylpyrrole-2-carboxaldehyde, respectively. To a stirred solution of *o*-xylylenebis(triphenylphosphonium bromide)[1] (7.88 g, 10 mmol) and the corresponding aldehyde (20 mmol) in 250 ml of absolute ethanol a solution of sodium ethoxide (700 mg, 30 mmol in 20 ml ethanol) was added dropwise. Stirring was continued under a stream of dry nitrogen for two days at 30°C (**4a**) and 24 h under reflux (**4b**), respectively. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was chromatographed on silica gel with dichloromethane to separate the products **4a** and **4b**, respectively, from triphenylphosphine oxide and unreacted aldehydes, which remained on the column. The *cis*- and *trans*-isomers were separated and fully characterized by repeated column chromatography using petroleum ether/dichloromethane mixture as eluent.

2,2′-(1,2-Phenylenedivinylene)dipyrrole (4a). 0.845 g, yield 32.5%: a mixture of 14% *cis*, *cis*-**4a**, 32% *cis*, *trans*-**4a** and 54% *trans*, *trans*-**4a**. In the first fractions *cis*- and *trans*-2-(2-methylstyryl)pyrrole (**1b**) were isolated as by products and were identical to a sample obtained previously.[2]

cis, *cis*-**4a**: colorless crystals, mp 75–76°C; UV (EtOH) λ_{max} (ϵ) 285 (11529), 325 (13872); IR (KBr) 3400 (N–H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92 (bs, 2H, NH), 7.50–7.58 (m, 2H, H_{ar}), 7.30–7.38 (m, 2H, H_{ar}), 6.54 (dt, 2H, H_{5p}, J=2.6, 1.3 Hz), 6.41 (d, 2H, H_{et}, J=12.2 Hz), 6.23 (d, 2H, H_{et}, J=12.2 Hz), 6.15 (ddd, 2H, H_{4p}, J=3.5, 2.6, 1.3 Hz), 6.10 (dt, 2H, H_{3p}, J=3.5, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 137.71 (s), 129.54 (s), 129.28 (d), 127.83 (d), 121.99 (d), 120.86 (d), 118.91 (d), 111.71 (d), 108.83 (d); MS *m*/*z* 260 (M^+, 90%), 193 (70), 180 (100), 145 (98), 80 (90); HRMS for $C_{18}H_{16}N_2$ 260.1313, found 260.1311; Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.85; H, 6.19; N, 11.00.

cis, *trans*-**4a**: colorless crystals, mp 95–97°C; UV (EtOH) λ_{max} (ϵ) 242 (10228), 325 (21571), 340 (24546); IR (KBr) 3380 (N–H), 3440 (N–H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.29 (bs, 1H, NH), 7.89 (bs, 1H, NH), 7.67 (d, 1H, H_{ar}, J=7.6 Hz), 7.20–7.38 (m, 3H, H_{ar}), 6.95 (d, 1H, H_{et}, J=16.5 Hz), 6.82 (d, 1H, H_{et}, J=16.5 Hz), 6.79 (dt, 1H, $H_{5'p}$, J=2.6, 1.3 Hz), 6.54 (d, 1H, H_{et}, J=12.1 Hz), 6.53 (dt, 1H, H_{5p}, J=2.6, 1.3 Hz), 6.36 (d, 1H, H_{et}, J=12.1 Hz), 6.31 (ddd, 1H, $H_{4'p}$, J=3.5, 2.6, 1.3 Hz), 6.22 (dt, 1H, $H_{3'p}$, J=3.5, 2.6 Hz), 6.19 (ddd, 1H, H_{4p}, J=3.5, 2.6, 1.3 Hz), 6.10 (dt, 1H, H_{3p}, J=3.5, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 136.43 (s), 136.07 (s), 130.81 (s), 129.70 (s), 129.50 (d), 127.95 (d), 127.20 (d), 125.04 (d), 121.89 (d), 121.44 (d), 120.67 (d), 120.37 (d), 119.35 (d), 119.31 (d), 111.85 (d), 109.92 (d), 109.75 (d), 108.65 (d).

trans, *trans*-**4a**: colorless crystals, mp 151–152°C; UV (EtOH) λ_{max} (ϵ) 312 (30446), 325 (24710); IR (KBr) 3430 (N–H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.37 (bs, 2H, NH), 7.45–7.50 (m, 2H, H_{ar}), 7.20–7.25 (m, 2H, H_{ar}), 6.95 (d, 2H, H_{et}, J=16.1 Hz), 6.83 (d, 2H, H_{et}, J=16.1 Hz), 6.81 (dt, 2H, H_{5p}, J=2.6, 1.3 Hz), 6.37 (ddd, 2H, H_{4p}, J=3.5, 2.6, 1.3 Hz), 6.26 (dt, 2H, H_{3p}, J=3.5, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 135.68 (s), 131.07 (s), 127.21 (d), 126.25 (d), 121.44 (d), 121.35 (d), 119.21 (d), 110.09 (d), 109.24 (d).

***N*,*N*′-Dimethyl-2,2′-(1,2-phenylenedivinylene)dipyrrole (4b).** In the first fractions *cis*- and *trans*-*N*-methyl-2-(2-methylstyryl)pyrrole (**1d**) were isolated as by products (745 mg, *cis*:*trans*=2:3, 26.9%, based on the quantity of diphosphonium bromide) follwed by a mixture of *cis*, *cis*-**4b**, *cis*, *trans*-**4b** and *trans*, *trans*-**4b** (44%). Unreacted pyrrolecaroxaldehyde remained on the column by elution with dichloromethane.

cis-**1d**: light yellow oil; UV(EtOH) λ_{max} (ϵ) 233 (13586), 294 (14554); ^1H NMR ($CDCl_3$) δ 7.08–7.32 (m, 4H, H_{ar}), 6.53 (dd, 1H, $J_{3,5}$=1.6, $J_{4,5}$=2.7 Hz, H_{5p}), 6.47 and 6.44 (AB_q, 2H, J=12.2 Hz, H_{et}), 5.92 (dd, 1H, $J_{3,4}$=3.7, $J_{4,5}$=2.7 Hz, H_{4p}), 5.68 (dd, 1H, $J_{3,4}$=3.7, $J_{3,5}$=1.6 Hz, H_{3p}), 3.58 (s, 3H, N–CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 137.66 (s), 135.85 (s), 129.86 (d), 129.58 (s), 128.46(d), 126.96 (d), 125.84 (d), 125.64 (d), 122.33(d), 118.57 (d), 108.24 (d), 107.55 (d), 33.87 (q), 19.61 (q).

trans-**1d**: light yellow crystals, mp 44°C; UV (EtOH) λ_{max} (ϵ) 237 (10660), 335 (16793); ^1H NMR ($CDCl_3$) δ 7.53 (d, 1H, J=7.3 Hz, H_{ar}), 7.10–7.30 (m, 3H, H_{ar}), 6.85 and 7.07 (2d, 2H, J=15.9 Hz, H_{et}), 6.64 (m, 1H, H_{5p}), 6.49 (m, 1H, H_{3p}), 6.16 (m, 1H, H_{4p}), 3.65 (s, 3H, N–CH_3), 2.38 (s, 3H, ar-CH_3); ^{13}C NMR ($CDCl_3$) δ 136.81 (s), 135.37 (s), 132.31(s), 130.31 (d), 126.93 (d), 126.07 (d), 124.68 (d), 123.89 (d), 123.44 (d), 118.29 (d), 108.10 (d), 106.48 (d), 33.87 (q), 19.68 (q); MS *m*/*z* 197 (M^+, 100%), 182 (64), 167 (93), 165 (95), 152 (47), 141 (26), 139 (27), 115 (43). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 85.14; H, 7.44.

4b (overall yield 1.27 g, according to ^1H NMR spectrum a mixture of 13% *cis*, *cis*-**4b**, 67% *cis*, *trans*-**4b** and 20% *trans*, *trans*-**4b**): viscous oil which crystallizes by standing in refrigerator; UV(EtOH) λ_{max} (ϵ) of the mixture 324.0 (18598); ^1H NMR ($CDCl_3$) δ 7.10–7.65 (m, H_{ar}, $2H_{et}$-*tt*), 7.05 and 6.89 (2d, 2H, J=16.1 Hz, H_{et}-ct_t), 6.85 (d, 2H, J=15.9 Hz, H_{et}-*tt*), 6.65 (m, 2H, H_{5p}-*tt*), 6.62 (m, 1H, H_{5p}-ct_t), 6.48–6.55 (m, 5H, $2H_{5p}$-*cc*, H_{5p}-ct_c, $2H_{3p}$-*tt*), 6.52 (s, 2H, H_{et}-ct_c), 6.41 (bs, 5H, $4H_{et}$-*cc*, H_{3p}-ct_t), 6.17 (m, 2H, H_{4p}-*tt*), 6.13 (m, 1H, H_{4p}-ct_t), 5.96 (m, 2H, H_{4p}-*cc*), 5.92 (m, 1H, H_{4p}-ct_c), 5.88 (m, 2H, H_{3p}-*cc*), 5.77 (m, 1H H_{3p}-ct_c), 3.69 (s, 6H, CH_3-*tt*), 3.66 and 3.60 (2s, 6H, CH_3-*ct*), 3.55 (s, 6H, CH_3-*cc*); MS *m*/*z* 288 (M^+, 64%), 207 (31), 206 (46), 194 (80), 173 (100), 165 (43), 152 (29), 115 (30), 94 (59), 81 (40); Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99. Found: C, 83.33; H, 7.19.

Irradiation experiments

A solution of **4a** and **4b**, respectively, in 500 ml of benzene (2×10^{-3} M) was purged with argon for 30 min and irradiated in a quartz tube in the Rayonet reactor for 18 h at 300 nm (**4a**) and at 350 nm (**4b**) at rt. Solvent was removed in vacuum and the dark oily residue chromatographed on the silica gel column using petroleum ether–dichloromethane as eluents.

Irradiation of 2,2′-(1,2-phenylenedivinylene)dipyrrole (4a). Unreacted **4a** was isolated in first fractions (110 mg, 41%) followed by traces of **7** and then 108 mg (40%) of the dimeric products **8**. After repeated and tedious column chromatography of the dimeric mixture of **8** the enreached fractions of **8a**, **8b** and **8c**, respectively were isolated with dichloromethane/petroleum ether (7:4) as eluents.

4,5-Dihydro-4-(2-pyrrolyl)-benzo[5,6]cycloocta[1,2-*b*]-pyrrole (7): colorless crystals, mp 112°C; ^1H NMR ($CDCl_3$) δ 7.76 (bs, 1H, NH), 7.65 (bs, 1H, NH), 6.98–7.20 (m, 4H, H_{ar}), 6.63 (m, 1H, H_p), 6.61 (dd, 1H, H_{et}, J=12.1 Hz), 6.55 (dd, 1H, H_{et}, J=12.1 Hz), 6.55 (m, 1H, H_p), 6.16 (m, 1H, H_p), 6.13 (m, 1H, H_p), 5.96 (m, 1H, H_p), 4.62 (t, 1H, J=6.4 Hz), 3.23 (d, 2H, J=6.3 Hz); ^1H NMR (C_6D_6) δ 6.80–7.22 (m, 6H, H_{4ar}, 2 NH), 6.48 (d, 1H, H_{et}, J=12.4 Hz), 6.32 (m, 1H, H_p), 6.25 (m, 1H, H_p), 6.19 (m, 1H, H_p), 6.14 (d, 1H, H_{et}, J=12.4 Hz), 6.08 (m, 1H, H_p), 5.98 (m, 1H, H_p), 4.64 (dd, 1H, J=3.1 Hz), 3.30 (dd, 1H, J=3.0, 12.6 Hz), 3.16 (dd, 1H, J=8.4, 12.6 Hz); ^1H NMR ($(CD_3)_2CO$) δ 9.80 (bs, 1H, NH), 9.60 (bs, 1H, NH), 7.20–7.36 (m, 4H, H_{ar}), 6.79 (d, 1H, H_{et}, J=12.3 Hz), 6.68–6.73 (m, 2H, H_p), 6.66 (d, 1H, H_{et}, J=12.3 Hz), 6.05 (m, 1H, H_p), 5.96 (m, 1H, H_p), 5.92 (m, 1H, H_p), 4.58 (dd, 1H, J=3.2, 10.8 Hz), 3.43 (dd, 1H, J=12.5, 10.8 Hz), 3.21 (dd, 1H, J=12.5, 3.2 Hz); ^{13}C NMR (C_6D_6) δ 140.18 (s), 138.14

(s), 137.34 (s), 131.46 (d), 127.77 (d), 127.68 (d), 125.86 (d), 122.94 (d), 117.79 (d), 116.40 (d), 113.17 (d), 108.48 (d), 105.85 (d), 41.35 (d), 40.42 (t), 3 signals are covered; MS *m*/*z* 260 (M^+, 100%), 244 (33), 194 (28).

5-{2-Pyrrolyl[2-(2-pyrrolyl)-1-indanyl]methyl}-2,2′-(1,2-phenylenedivinylene)dipyrroles (8), according to ^{1}H NMR: **8a** (20%), **8b** (60%), **8c** (20%): UV(EtOH) λ_{max} (ϵ) of the mixture: 323 (5739), 344 (6659), 207 sh (11383); IR (KBr) of the mixture: 3385 (N–H), 3096, 3017, 2922, 2851, 1628 cm^{-1}; Anal. Calcd for $C_{36}H_{32}N_4$: C, 83.04; H, 6.20. Found: C, 83.23; H, 6.23.

8a: light yellow crystals, too small a quantity to be analyzed completely; ^{1}H NMR (C_6D_6) δ 5.7–7.8 (m, H_{ar}, H_{et}, H_p), 4.11 (d, 1H, *J*=5.7 Hz), 3.79 (t, 1H, *J*=5.7 Hz), 3.41 (m, 1H), 2.86–2.66 (m, 2H); MS *m*/*z* 521 (MH^+, 31%), 338 (100).

8b: light yellow crystals, 80–85°C (decomp.); ^{1}H NMR (C_6D_6) δ 5.7–7.8 (m, H_{ar}, H_{et}, H_p), 3.92 (d, 1H, *J*=5.4 Hz), 3.65 (t, 1H, *J*=5.4 Hz), 3.23 (ddd, 1H, *J*=5.4, 6.0, 7.8 Hz), 2.70 (dd, 1H, *J*=16.2, 7.8 Hz), 2.63 (dd, 1H, *J*=16.2, 6.0 Hz); ^{13}C NMR (C_6D_6) δ 144.49 (s), 144.10(s), 137.23 (s), 136.89 (s), 136.24 (s), 135.14 (s), 131.32 (s), 130.26 (s), 130.06 (d), 129.63 (s), 128.92 (d), 127.92 (d), 127.91 (d), 127.19 (d), 125.83 (d), 125.54 (d), 125.06 (d), 122.40 (d), 121.77 (d), 121.43 (d), 120.87 (d), 120.02 (d), 117.67 (d), 117.07 (d), 113.25 (d), 110.92 (d), 110.36 (d), 108.76 (d), 108.75 (d), 108.35 (d), 107.75 (d), 105.09 (d), 51.17 (d), 42.56 (d), 41.93 (d), 39.58 (t); MS *m*/*z* 520 (M^+, 18%), 338 (100), 271 (10), 180 (25), 145 (26), 80 (20); HRMS for $C_{36}H_{32}N_4$ 520.2627, found 520.2627.

8c: light yellow crystals, 100–103°C (decomp.); ^{1}H NMR (C_6D_6) δ 5.9–7.7 (m, H_{ar}, H_{et}, H_p), 4.14 (d, 1H, *J*=5.9 Hz), 3.77 (dd, 1H, *J*=5.4, 5.6 Hz), 3.39 (ddd, 1H, *J*=5.9, 7.9, 5.4 Hz), 2.84 (dd, 1H, *J*=16.0, 7.9 Hz), 2.72 (dd, 1H, *J*=15.9, 5.9 Hz); ^{13}C NMR (C_6D_6) δ 144.50 (s), 144.13 (s), 136.63 (s), 136.60 (s), 136.27 (s), 134.86 (s), 131.55 (s), 131.21 (s), 130.86 (s), 127.77 (d), 127.77 (d), 127.69 (d), 127.22 (d), 126.94 (d), 126.91 (d), 125.76 (d), 125.28 (d), 122.19 (d), 121.94 (d), 121.63 (d), 121.40 (d), 119.87 (d), 117.97 (d), 117.28 (d), 110.65 (d), 110.47 (d), 109.90 (d), 109.26 (d), 108.82 (d), 108.81 (d), 108.80 (d), 105.24(d), 57.09 (d), 42.70 (d), 42.07 (d), 39.56 (t); MS *m*/*z* 520 (M^+, 5%), 338 (100), 271 (20), 260 (38), 180 (43), 145 (28), 67 (48); HRMS for $C_{36}H_{32}N_4$ 520.2627, found 520.2579.

Irradiation of *N*,*N*′-dimethyl-2,2′-(1,2-phenylenedivinylene)dipyrrole (4b). Irradiation was performed under the same conditions as **4a**. This afforded only *cis*–*trans* isomerization, besides some tarry material.

Irradiation of 5-{2-pyrrolyl[2-(2-pyrrolyl)-1-indanyl]-methyl}-2,2′-(1,2-phenylenedivinylene)dipyrroles (8). A benzene solution of dimeric products **8** (45 mg in 17 ml, 0.09 M) was purged with nitrogen and irradiated in the Rayonet reactor at 300 nm for 1 h at rt. After removal of the solvent the dark brown residue was chromatographed on silica gel with dichloromethane–petroleum ether (7:3) as eluent. In the first fractions 21 mg (47%) of unreacted **8** was isolated followed by 10 mg (22%) of high molecular weight products. MS *m*/*z* 1041.3 (MH^+, 2%), 858.3 (18), 577.5 (60), 338.2 (65), 259.1 (100).

Hydrogenation experiments

To a benzene solution of **4a** or **8** (25 mg in 25 ml) a catalytic amount of Pd/C was added and the solution was purged with hydrogen for 3–5 days at rt. The solvent was removed in vacuum and the residue chromatographed on silica gel column using dichloromethane–petroleum ether (8:2 for **9** and 7:3 for **10**, respectively) as eluent. Unreacted **4a** or **8** was isolated from the first fractions followed by **9** or **10**, respectively.

Hydrogenation of 4a (*cis*–*trans*): 2,2′-(1,2-phenylenediethylene)dipyrrole (9). 19 mg (75%), oil; UV(EtOH) λ_{max} (ϵ) 211.6 (22190); IR (neat) 3383 (N–H), 3099, 3051, 2918, 2850 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.05–7.10 (m, 2H, H_{ar}), 6.99–7.04 (m, 2H, H_{ar}), 6.79 (bs, 2H, N–H), 6.30 (m, 2H, H_p), 6.26 (m, 2H, H_p), 6.02 (m, 2H, H_p), 2.65 (m, 4H, H_{et}), 2.55 (m, 4H, H_{et}); ^{13}C NMR (C_6D_6) δ 140.35 (s), 131.83 (s), 129.80 (d), 126.95 (d), 116.68 (d), 108.93 (d), 106.15 (d), 33.37 (t), 29.64 (t); MS *m*/*z* 264 (M^+, 100%), 184 (61), 80 (42); Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63. Found: C, 81.68; H, 7.46.

Hydrogenation of 8: 5-{2-pyrrolyl[2-(2-pyrrolyl)-1-indanyl]methyl}-2,2′-(1,2-phenylenediethylene) dipyrrole (10). 4 mg (16.5%); light yellow crystals, 47–48°C; UV(EtOH) λ_{max} (ϵ) 212 (39300); IR (as oil) 3386 (N–H), 2921, 2851 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.8–7.6 (m, H_{ar}, H_p), 4.05 (d, 1H, *J*=6.6 Hz), 3.79 (t, 1H, *J*=6.6, 5.1 Hz), 3.43 (ddd, 1H, *J*=5.1, 6.3, 8.1 Hz), 2.91 (dd, 1H, *J*=16.2, 8.1 Hz), 2.80 (dd, 1H, *J*=16.2, 6.3 Hz); ^{13}C NMR (C_6D_6) δ 144.98 (s), 144.10 (s), 140.35 (s), 140.26 (s), 136.60 (s), 131.86 (s), 131.60 (s), 131.57 (s), 131.46 (s), 129.85 (d), 128.92 (d), 128.92 (d), 127.06 (d), 126.92 (d), 126.85 (d), 125.99 (d), 125.09 (d), 117.64 (d), 117.04 (d), 116.74 (d), 109.06 (d), 108.75 (d), 108.75 (d), 108.29 (d), 107.07 (d), 106.26 (d), 106.13 (d), 105.03 (d), 57.29 (d), 42.96 (d), 42.22 (d), 39.55 (t), 33.38 (t), 33.26 (t), 29.64 (t), 29.34 (t); MS *m*/*z* 524 (M^+, 2%), 522 (12), 342 (100), 158 (40), 80 (75); Anal. Calcd for $C_{36}H_{40}N_4$: C, 81.77; H, 7.63. Found: C, 81.74; H, 7.80.

Ozonolysis of 4a. Into a dichloromethane solution of **4a** (35 mg in 30 ml) a stream of O_3 was introduced at −70°C for 15 min. The color of the solution changed from yellow to green. After warming up the reaction mixture to rt the solvent was evaporated. The residue of powdery material is not soluble in chloroform, benzene and only slightly soluble in acetone.

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