Photoelectron Spectra, Electronic Structures, and Conformational Properties of Substituted 2-Styrylpyrroles[‡]

Paul Rademacher,*[a] Nikola Basaric,[b] Klaus Kowski,[a] and Marija Šindler-Kulyk[b]

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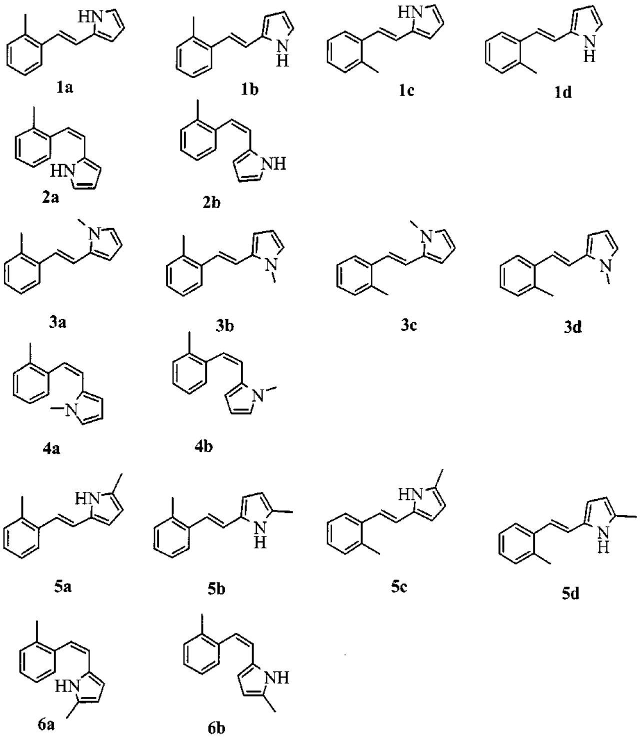
The UV photoelectron spectra of three pairs of *cis*/*trans*-isomers of 2-(2-methylstyryl)pyrroles (**1**–**6**) have been recorded and analysed, making use of density functional theory (DFT) calculations at the B3LYP level. Compounds **1** and **2** have no further substituents in the pyrrole ring. In the other compounds the pyrrole ring is substituted by a methyl group in the 1- (**3**, **4**) or 5-position (**5**, **6**). Twisted conformations were calculated for **1**–**6** in which the toluene ring is generally much more distorted from the plane of the central C=C double bond than the pyrrole ring. In the *cis*-isomers (**2**, **4**, **6**) the torsion angle of the toluene groups amounts to about 50°, while in the *trans*-isomers (**1**, **3**, **5**) the torsional angle is only about half as large. The energy difference ΔIP of the ionization bands associated with the molecular orbitals (MOs) π_7 and π_3 is related to this torsion. Calculated ΔIP values are generally 5–10% larger than the experimental values, indicating that torsional vibrations contribute to the apparent distortion of the molecules. The results clearly indicate that PE spectroscopy — in combination with high-level quantum chemical calculations — is a versatile method to distinguish *E*/*Z* isomers of heterocyclic stilbene-like molecules.

Introduction

We have recently investigated several (*E*)-stilbene-like styrylthiophenes and (thienylethenyl)pyridines by UV photoelectron spectroscopy (PES) and quantum chemical calculations.[1] The torsional angle of the molecules was estimated from the splitting of two ionization potentials. We have now investigated by similar techniques some related compounds that are π-isoelectronic with stilbene, namely the 2-styrylpyrroles **1−6** (Scheme 1). Three of these compounds (**1**, **3**, **5**) have an *E*-configuration at the central C=C double bond while the others (**2**, **4**, **6**) are in the *Z*-configuration. As for the parent stilbene,[1−3] differences in the stereochemical properties and the electronic structure are of prominent interest. They are of particular importance because changes in configuration or conformation may strongly affect the electronic structure and, as a consequence, may influence their photophysical and photochemical properties.[4−6] Furthermore, this study may be considered as a contribution to the better understanding of the conformational properties of stilbene-like molecules including the effects of hetero atoms and substituents.



Scheme 1. Structures of compounds **1−6**

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[a] Institut für Organische Chemie, Universität Essen,
Universitätsstraße 5−7, 45117 Essen, Germany
Fax: (internat.) + 49-(0)201/183-4252
E-mail: paul.rademacher@uni-essen.de
[b] Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb,
Marulicev Trg 19, 10000 Zagreb, Croatia
E-mail: marija.sindler@pierre.fkit.hr

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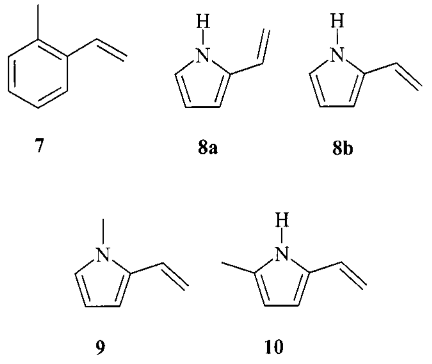
Results

We have investigated compounds **1−6** by UV PE spectroscopy and various quantum chemical methods. Semi-empirical (PM3[7]) as well as ab initio (B3LYP[8,9]) methods were used. Although interpretation of the PE spectra (see below) would have been possible with either method, structures and relative energies of the conformers were frequently at variance. Because the PM3 results are to be considered as less reliable, we refrain from presenting these data and restrict the discussion to the more sophisticated B3LYP results.

Structures and Energies

The most important question related to the structure of compounds **1−6** concerns the degree of torsion of the two rings with respect to the central C=C double bond. Model compounds with similar conformational properties are 2-methylstyrene (**7**), 2-vinylpyrrole (**8**), 1-methyl-2-vinylpyrrole (**9**) and 2-methyl-5-vinylpyrrole (**10**) (Scheme 2). For compound **7** a torsion of the vinyl group against the aromatic ring of 20−35° has been found by various experimental methods.[10,11] A literature search did not reveal any study concerning the structure or conformation of 2-vinylpyrroles (**8−10**).

For compounds **1−6** four conformers (**a−d**) can be drawn for each molecule starting from planar structures. These are depicted for the *E*-configured compounds (**1**, **3**, **5**) in Scheme 1. For the *Z*-configured isomers (**2**, **4**, **6**) only two planar conformers are considered; these differ in the orientation of the pyrrole or methylpyrrole ring. The two "missing" conformers with a *synperiplanar* (*sp*) orientation of the toluene ring are excluded because they would be much less stable than those with the *antiperiplanar* (*ap*) orientation (**a**, **b**). Total energies as calculated by the B3LYP method are included in Table 1−6. In almost all cases a single conformer (**1a**, **2a**, **3b**, **4b**, **5a**, **6a**) is clearly more stable by at least 3.4 kJ mol^{-1} than the others. With the exception of compounds **3** and **4**, all energetically preferred conformations have an *sp* pyrrole or methylpyrrole ring. In **3** and **4** the *N*-methyl group obviously hampers this orientation. The preference of the 2-vinylpyrrole unit for the *sp* conformation is confirmed by B3LYP calculations on compound **8**, which indicate that **8b** is less stable than **8a** by 4.61 kJ mol^{-1}. This result coincides with a smaller dipole moment of the latter form (**8a**: μ = 1.35 D; **8b**: μ = 1.80 D). Planar structures are calculated for both conformers.



Scheme 2. Structures of compounds **7−10**

The relative stability of the *E*/*Z*-isomers is indicated by energy differences of 7.23 (**1a**/**2a**), 15.94 (**3b**/**4b**) and 14.80 kJ mol^{-1} (**5a**/**6a**). These values are substantially

Table 2. Ionization potentials *IP* [eV], orbital energies ε [eV] and total energies *E* [au] of molecule M and radical cation M$^{+\bullet}$ for *cis*-2-(2-*o*-tolylvinyl)-1*H*-pyrrole (**2**)
(calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry)

IP	**2a** $-\varepsilon^{B3LYP}$	**2a** *IP*[a]	**2b** $-\varepsilon^{B3LYP}$	**2b** *IP*[b]	
7.43	5.38	7.06	5.31	6.96	π_7
8.77	6.76	8.44	6.60	8.25	π_6
9.0	6.88	8.56	6.78	8.43	π_5
9.2 sh	7.05	8.73	6.89	8.54	π_4
10.07	8.19	9.87	8.16	9.81	π_3
E(M)	−557.9675509		−557.9633291		
E(M$^{+\bullet}$)	−557.7079994		−557.7073639		

[a] Higher *IP*s: $IP_i = \varepsilon_i + 1.68$ eV (see text). [b] Higher *IP*s: $IP_i = \varepsilon_i + 1.65$ eV (see text).

Table 1. Ionization potentials *IP* [eV], orbital energies ε [eV] and total energies *E* [au] of molecule M and radical cation M$^{+\bullet}$ for *trans*-2-(2-*o*-tolylvinyl)-1*H*-pyrrole (**1**)
(calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry)

IP	**1a** $-\varepsilon^{B3LYP}$	**1a** *IP*[a]	**1b** $-\varepsilon^{B3LYP}$	**1b** *IP*[b]	**1c** $-\varepsilon^{B3LYP}$	**1c** *IP*[b]	**1d** $-\varepsilon^{B3LYP}$	**1d** *IP*[a]	
7.41	5.28	6.85	5.22	6.80	5.27	6.85	5.19	6.76	π_7
8.7 sh	6.72	8.29	6.69	8.27	6.74	8.32	6.74	8.31	π_6
8.82	6.90	8.47	6.88	8.46	6.91	8.49	6.88	8.45	π_5
9.0 sh	6.97	8.54	6.92	8.50	7.00	8.58	6.96	8.53	π_4
10.36	8.45	10.02	8.41	9.99	8.47	10.05	8.50	10.07	π_3
E(M)	−557.970307		−557.9690058		−557.9675619		−557.9662145		
E(M$^{+\bullet}$)	−557.718399		−557.7190988		−557.7159727		−557.7176000		

[a] Higher *IP*s: $IP_i = \varepsilon_i + 1.57$ eV (see text). [b] Higher *IP*s: $IP_i = \varepsilon_i + 1.58$ eV (see text).

Table 3. Ionization potentials IP [eV], orbital energies ε [eV] and total energies E [au] of molecule M and radical cation $M^{+\bullet}$ for 1-methyl-2-(2-*o*-tolylvinyl)-1*H*-pyrrole (**3**)
(calculation of first vertical IP: energy difference of molecule and radical cation with identical geometry)

	3a		**3b**		**3c**		**3d**		
IP	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[b]	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[a]	
7.27	5.22	6.77	5.15	6.71	5.22	6.77	5.10	6.65	π_7
8.60	6.66	8.21	6.61	8.17	6.65	8.20	6.60	8.15	π_6
8.8 sh	6.68	8.23	6.66	8.23	6.68	8.23	6.71	8.26	π_5
8.9 sh	6.86	8.41	6.83	8.39	6.89	8.44	6.91	8.46	π_4
10.23	8.36	9.91	8.33	9.89	8.34	9.89	8.44	9.99	π_3
E(M)	−597.2779988		−597.2794032		−597.2748234		−597.2764049		
$E(M^{+\bullet})$	−597.0293369		−597.0328271		−597.0259760		−597.0318303		

[a] Higher IPs: $IP_i = \varepsilon_i + 1.55$ eV (see text). [b] Higher IPs: $IP_i = \varepsilon_i + 1.56$ eV (see text).

Table 4. Ionization potentials IP [eV], orbital energies ε [eV] and total energies E [au] of molecule M and radical cation $M^{+\bullet}$ for *cis*-1-methyl-2-(2-*o*-tolylvinyl)-1*H*-pyrrole (**4**)
(calculation of first vertical IP: energy difference of molecule and radical cation with identical geometry)

	4a		**4b**		
IP	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[b]	
7.43	5.36	6.99	5.22	6.81	π_7
8.55	6.50	8.13	6.51	8.10	π_6
8.70	6.67	8.30	6.57	8.16	π_5
8.93	6.86	8.49	6.81	8.40	π_4
10.05	8.13	9.76	8.10	9.69	π_3
E(M)	−597.2719085		−597.2733290		
$E(M^{+\bullet})$	−597.0148618		−597.0223007		

[a] Higher IPs: $IP_i = \varepsilon_i + 1.63$ eV (see text). [b] Higher IPs: $IP_i = \varepsilon_i + 1.59$ eV (see text).

Table 6. Ionization potentials IP [eV], orbital energies ε [eV] and total energies E [au] of molecule M and radical cation $M^{+\bullet}$ for *cis*-2-methyl-5-(2-*o*-tolylvinyl)-1*H*-pyrrole (**5**)
(calculation of first vertical IP: energy difference of molecule and radical cation with identical geometry)

	6a		**6b**		
IP	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[b]	
7.22	5.19	6.83	5.13	6.74	π_7
8.72	6.69	8.23	6.54	8.15	π_6
8.95	6.80	8.34	6.69	8.30	π_5
9.2 sh	6.98	8.52	6.80	8.41	π_4
9.85	8.05	9.59	8.03	9.64	π_3
E(M)	−597.2885874		−597.2841894		
$E(M^{+\bullet})$	−597.0376854		−597.0365925		

[a] Higher IPs: $IP_i = \varepsilon_i + 1.53$ eV (see text). [b] Higher IPs: $IP_i = \varepsilon_i + 1.54$ eV (see text).

Table 5. Ionization potentials IP [eV], orbital energies ε [eV] and total energies E [au] of molecule M and radical cation $M^{+\bullet}$ for 2-methyl-5-(2-*o*-tolylvinyl)-1*H*-pyrrole (**5**)
(calculation of first vertical IP: energy difference of molecule and radical cation with identical geometry)

	5a		**5b**		**5c**		**5d**		
IP	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[b]	$-\varepsilon^{B3LYP}$	IP[a]	$-\varepsilon^{B3LYP}$	IP[b]	
7.13	5.12	6.65	5.02	6.56	5.11	6.64	5.02	6.56	π_7
8.6 sh	6.65	8.18	6.61	8.15	6.68	8.21	6.68	8.22	π_6
8.69	6.79	8.32	6.75	8.29	6.81	8.34	6.79	8.33	π_5
8.9 sh	6.88	8.41	6.84	8.38	6.88	8.41	6.84	8.38	π_4
10.25	8.31	9.84	8.28	9.82	8.34	9.87	8.38	9.92	π_3
E(M)	−597.2915116		−597.2888046		−597.2887130		−597.2870352		
$E(M^{+\bullet})$	−597.0470322		−597.0475317		−597.0445951		−597.0461219		

[a] Higher IPs: $IP_i = \varepsilon_i + 1.53$ eV (see text). [b] Higher IPs: $IP_i = \varepsilon_i + 1.54$ eV (see text).

smaller than the corresponding value for the *E*/*Z*-isomers of stilbene (20.67 kJ mol^{-1}).[1] This finding is in agreement with less twisted pyrrole rings in the *Z*-configuration (see below) compared to the benzene rings in *Z*-stilbene. Delocalization of the π electrons is thus less limited in the *cis* isomers of **1−6** than in *Z*-stilbene.

The most important structure parameters of the most stable conformers of **1−6** are summarized in Table 7. The length of the central C=C double bond remains the same in all compounds, even in those with the *Z*-configuration (**2a**, **4b**, **6a**). On the other hand, the lengths of the two formal single bonds between the central double bond and

Table 7. Selected structure parameters (pm, °) of compounds **1−6** (B3LYP results)

	C=C	C(To)−C	C(Py)−C	C(To)−C=C	C(Py)−C=C	τ[a]	φ[b]
1a	135.5	146.9	144.4	126.0	127.2	22.3	4.5
2a	135.5	148.0	144.9	128.9	131.6	51.8	3.3
3b	135.5	146.8	144.8	125.7	125.5	24.6	12.7
4b	135.6	147.7	145.3	130.0	130.6	43.6	16.1
5a	135.6	146.8	144.2	125.9	127.3	22.9	5.3
6a	135.6	148.0	144.7	128.9	131.8	51.0	3.7

[a] Torsion of toluene group with respect to central C=C bond. [b] Torsion of pyrrole group with respect to central C=C bond.

the two rings, i.e., C(To)−C and C(Py)−C are lengthened by about 1 and 0.5 pm, respectively, when the configuration is changed from *E* to Z. The C(Py)−C length shows a somewhat larger variation because of the different substitution of the pyrrole ring. The torsion angle of the toluene ring is 22−23° in the *E*-configuration and 51−52° in the *Z*-configuration. The former value is close to that observed for 2-methylstyrene (**7**) (see above), while the latter value is similar to that found for *Z*-stilbene (43°).[3]

The pyrrole ring of the *trans* isomers seems to be essentially coplanar with the central double bond. This is also the case in **2a** and **6a** even though these compounds have the *Z*-configuration. Only in **3b** and **4b** does the pyrrole ring show a substantial torsion (13−16°) that can be ascribed to the *N*-methyl group.

The bond angles listed in Table 7 are considerably larger than the values expected for sp^2-hybridized carbon atoms. This is particularly obvious for the *cis*-isomers (**2a**, **4b**, **5a**).

Photoelectron Spectra

The PE spectra of compounds **1−6** are depicted in Figure 1. They are characterized by three ionization bands be-

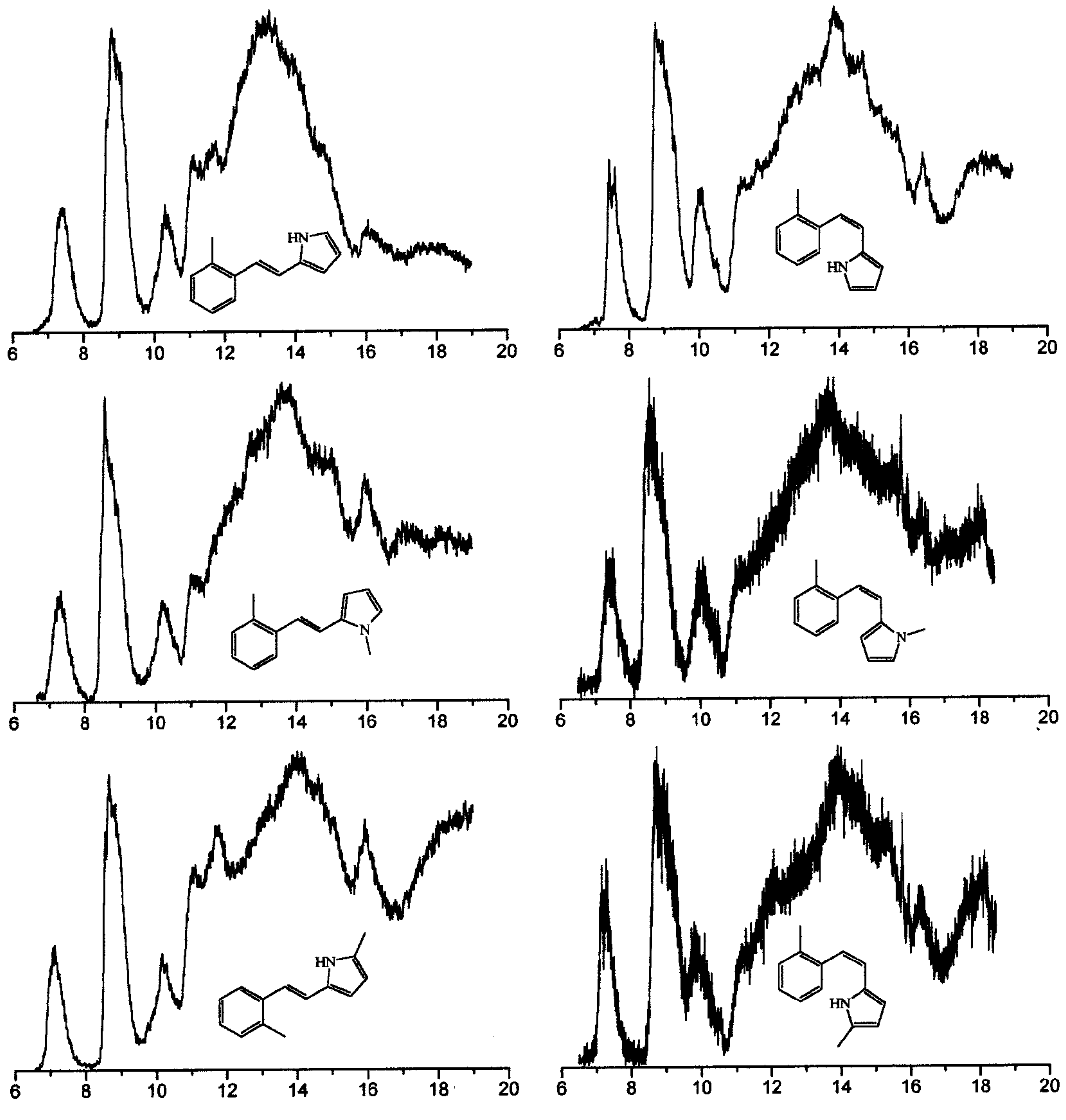


Figure 1. Photoelectron spectra of compounds **1−6**

low 11 eV of which the second band is of considerably higher intensity than the others and can be interpreted as a composite band to which three different ionizations contribute.

The measured vertical ionization energies are summarized in Table 1−6 together with the relevant data of quantum chemical calculations. Assignment of the *IP*s can be achieved by using the Koopmans theorem,[12] $IP_i = -\varepsilon_i$, by which vertical ionization energies and MO energies are related. Although Kohn−Sham orbitals obtained by DFT methods are no molecular orbitals and their physical meaning is still debated it has been shown that they can be used with high confidence for the interpretation of PE spectra.[13,14] Much better agreement between experimental and theoretical values can be expected for the first vertical *IP* (IP_{1v}) when the energies of the molecule and the radical cation are calculated by the B3LYP method. For IP_{1v} a single point calculation is performed for the radical cation ($M^{\cdot+}$) using the molecule's (M) geometry. This has been done for all conformers of **1−6**. The corresponding energy values are included in Table 1−6. We can now correct the other ε^{B3LYP} values by the difference (Δ = 1.57 eV, compound **1a**, Table 1) between −ε(HOMO) and the calculated IP_{1v} in order to obtain higher IP_v values.[14] The corresponding Δ values for the other compounds are between 1.55 and 1.68 eV. Whereas typical energy differences between IP_i and $-\varepsilon_i^{B3LYP}$ values are about 2 eV, experimental and calculated IP_i values differ only by about 0.5 eV. Furthermore, both $-\varepsilon_i^{B3LYP}$ and calculated $IP_i(calcd.)$ values are linearly correlated with the experimental $IP_i(exp.)$ values with correlation coefficients very close to 1.00. The correlation equation obtained for IP_i values is $IP_i(calcd.) = 1.0508\ IP_i(exp.) - 0.8945$ [eV] with $R = 0.995$. Although the slope of the straight line is close to 1.00, higher IP_i values are slightly overestimated.

IP values calculated for different conformers of **1−6** generally differ by less than 0.1 eV. This indicates that it would be very difficult, if not impossible, to distinguish individual conformers by their PE spectra.

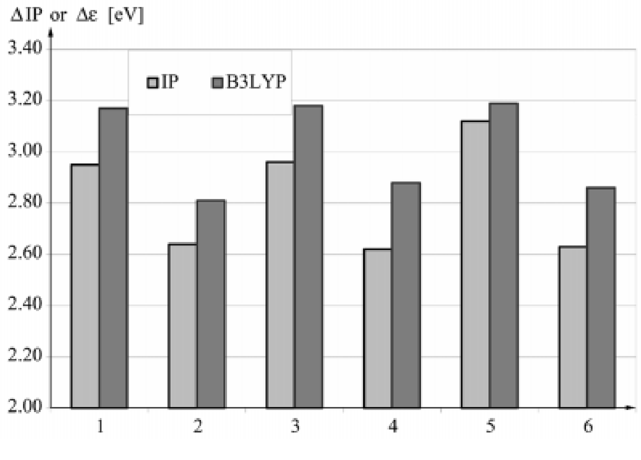


Figure 2. Splittings (ΔIP and $\Delta\varepsilon$ [eV]) of the MOs π_3 and π_7 of compounds **1−6**: calculated values refer to most stable conformers

It has been shown earlier for stilbenes[10] and related heterocyclic compounds[1] that the difference of the ionization energies related to π_3 and π_7 is a measure of the amount of torsion in the molecules. If we compare the values $\Delta IP = IP(\pi_7) - IP(\pi_3)$ measured by PE spectroscopy (Table 1−6) with those calculated by the B3LYP method we find that the experimental values are always smaller than the theoretical, usually by about 2−9% (Figure 2). Earlier,[1] this has been interpreted by a larger degree of torsion in the molecules under the conditions of the measurement of PE spectra (120−210 °C) than in the equilibrium state at 0 K in the calculations. However, it should be noted that the discrepancy between experimental and theoretical *IP* values has, at least in part, to be attributed to systematic errors in the calculation (see above).

Inspection of Figure 2 clearly reveals that ΔIP values are about 0.3 eV larger in the *E*- than in the *Z*-isomers, and there seems to be a close relationship with the torsion angle τ (Table 7), which is 20−30° larger in the *Z*- than in the *E*-configuration.

Conclusion

Although the PE spectra of compounds **1−6** (Figure 1) appear to be rather similar they reveal clear differences that allow for a safe distinction of *cis*- and *trans*-isomers. In particular, this is apparent in the splitting of the ionization energies associated with the MOs π_7 and π_3, which is smaller in the *cis*- than in the *trans*-configuration because of a higher degree of torsion of the toluene ring with respect to the central C=C double bond in the former isomer.

Experimental Section

General: ^1H 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 $CDCl_3$ or C_6D_6 solution with tetramethylsilane as reference. 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. PE spectra were recorded on a UPG200 spectrometer from Leybold−Heraeus equipped with a He^I radiation source (21.21 eV). Samples were evaporated directly into the target chamber. Temperatures of 120−210° C were necessary in order to reach sufficient vapour pressure. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 eV and those of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionization energies, although for broad and overlapping signals it was only ±0.1 eV.

Semi-empirical PM3[7] calculations were performed with the MOPAC93[15] program package, and ab initio Becke3LYP[8,9] calculations with the program Gaussian 98.[16] For the latter method, the basis set 6-31+G* was used, unless stated otherwise. Geometries were fully optimized at the respective levels of theory. Prior to quantum chemical calculations, molecular geometries were pre-optimized by molecular mechanics calculations using the MMX[17] force field; these calculations were performed with the program PCMODEL, version 7.0.[18]

Materials: Styrylpyrroles, *trans*-2-(2-methylstyryl)pyrrole (**1**),[4] *cis*-2-(2-methylstyryl)pyrrole (**2**),[4] *trans-N*-methyl-2-(2-methylstyryl)pyrrole (**3**)[5] and *cis-N*-methyl-2-(2-methylstyryl)pyrrole (**4**)[5] were prepared as described in the literature.

***trans*-5-Methyl-2-(2-methylstyryl)pyrrole (5):** This compound was obtained by a Wittig reaction as a by-product in the synthesis of 5,5′-dimethyl-2,2′-(*o*-phenylenedivinylene)dipyrrole. Thus, *o*-xylenebis(triphenylphosphonium bromide) (5.42 g, 6.88 mmol) and 5-methyl-2-pyrrolecarbaldehyde (1.50 g, 13.8 mmol), made by formylation[19] of 2-methylpyrrole,[20] were dissolved in 200 mL of dry ethanol under nitrogen. A solution of sodium ethoxide (0.5 g of sodium in 20 mL of absolute ethanol) was then added dropwise to the stirred reaction mixture. After standing for six days in the dark at room temperature the solvent was evaporated and the residue treated with water (150 mL) and extracted with benzene. The benzene extracts were dried over anhydrous $MgSO_4$ and concentrated. The reaction mixture was chromatographed on a silica gel column using petroleum ether/dichloromethane as eluent. In the first fractions the *trans*-isomer (**5**) (679 mg, 50% yield) was isolated. M.p. 95−96 °C. UV(EtOH) λ_{max} (ε) = 339 nm (28000), 242 (9000). IR(KBr): $\tilde{\nu}$ = 3408 cm^{-1} (N−H). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.31 (s, 3 H, $CH_3^{ar/pyr}$), 2.39 (s, 3 H, $CH_3^{ar/pyr}$), 5.91 (m, 1 H, $H^{3pyr/4pyr}$), 6.21 (m, 1 H, $H^{3pyr/4pyr}$), 6.73 (d, J = 16.5 Hz, 1 H, H^{et}), 6.82 (d, J = 16.5 Hz, 1 H, H^{et}), 7.08−7.22 (m, 3 H, H^{ar}), 7.49 (d, J = 7.5 Hz, 1 H, H^{ar}), 8.05 (br. s, 1 H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.97 (q), 19.76 (q), 107.86 (d), 109.87 (d),119.28 (d), 120.25 (d), 124.51 (d), 126.12 (d), 126.57 (d), 129.55 (s), 129.95 (s), 130.29 (d), 134.92 (s), 136.66 (s). MS (70 eV, EI): *m*/*z* (%) = 197 [M^+] (100), 182 (40), 181 (25), 167 (20), 115 (17), 81 (25).

***cis*-5-Methyl-2-(2-methylstyryl)pyrrole (6):** *trans*-Isomer (**5**) (679 mg, 3.45 mmol) was dissolved in 500 mL of benzene. The solution was purged with argon and irradiated at 350 nm for 1 h in a Rayonet reactor. The solvent was removed under vacuum and the residue chromatographed on a silica gel column using petroleum ether/dichloromethane as eluent. In the first fractions the *cis*-isomer (**6**) (530 mg, 78% yield) was isolated. M.p. 34−35 °C. UV (EtOH): λ_{max} (ε) = 297 nm (8244). IR (neat): $\tilde{\nu}$ = 3445 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 2.08 (s, 3 H, $CH_3^{ar/pyr}$), 2.33 (s, 3 H, $CH_3^{ar/pyr}$), 5.81 (m, 1 H, $H^{3pyr/4pyr}$), 6.08 (dd, J = 2.7 and J = 3.0 Hz, 1 H, $H^{3pyr/4pyr}$), 6.22 (d, J = 12.0 Hz, 1 H, H^{et}), 6.44 (d, J = 12.0 Hz, 1 H, H^{et}), 7.18−7.32 (m, 3 H, H^{ar}), 7.43 (d, J = 6.3 Hz, 1 H, H^{ar}), 7.55 (br. s, 1 H, NH). ^1H NMR (C_6D_6): δ = 1.67 (s, 3 H, CH_3^{pyr}), 2.14 (s, 3 H, CH_3^{ar}), 5.85 (m, 1 H, $H^{3pyr/4pyr}$), 6.11 (d, J = 12.0 Hz, 1 H, H^{et}), 6.21 (m, 1 H, $H^{3pyr/4pyr}$), 6.36 (d, J = 12.3 Hz, 1 H, H^{et}), 6.96−7.05 (m, 4 H, 3H^{ar}, NH), 7.38 (d, J = 7.2 Hz, 1 H, H^{ar}). ^{13}C NMR ($CDCl_3$): δ = 12.79 (q), 19.63 (q), 106.53 (d), 112.10 (d), 120.79 (d), 120.86 (d), 126.00 (d), 127.49 (d), 128.54 (d), 128.74 (s), 129.08 (s), 130.40 (d), 136.69 (s), 138.03 (s). $C_{14}H_{15}N$ (197.28): calcd. C 85.24, H 7.66, N 7.10; found C 85.09, H 7.75, N 6.99.

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[1] P. Rademacher, A. Marzinzik, K. Kowski, M. E. Weiß, *Eur. J. Org. Chem.* **2001**, 121−130.

[2] M. Traetteberg, E. B. Frantsen, F. C. Mijlhoff, A. Hoekstra, *J. Mol. Struct.* **1975**, *26*, 57−68.

[3] M. Traetteberg, E. B. Frantsen, *J. Mol. Struct.* **1975**, *26*, 69−76.

[4] M. Šindler-Kulyk, S. Tomšic, Z. Marinic, B. Metelko, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 476−479.

[5] N. Basaric, S. Tomšic, Z. Marinic, M. Šindler-Kulyk, *Tetrahedron* **2000**, *56*, 1587−1593.

[6] N. Basaric, Z. Marinic, M. Šindler-Kulyk, *Tetrahedron Lett.* **2001**, *42*, 3641−3643.

[7] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209−220; J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 221−264.

[8] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372−1377.

[9] A. D. Becke, *J. Comput. Chem.* **1999**, *20*, 63−69.

[10] J. P. Maier, D. W. Turner, *J. Chem. Soc., Faraday Trans. 2* **1973**, *54*, 196−206.

[11] J. M. Hollas, P. F. Taday, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3335−3342.

[12] T. Koopmans, *Physica* **1934**, *1*, 104−113.

[13] R. Stowasser, R. Hoffmann, *J. Am. Chem. Soc.* **1999**, *121*, 3414−3420.

[14] See for example: A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641−6649.

[15] J. J. P. Stewart, MOPAC93.00 Manual, Fujitsu Limited, Tokyo, Japan **1993**.

[16] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1998**.

[17] J. J. Gajewski, K. E. Gilbert, J. McKelvey, *Adv. Mol. Model.* **1990**, *2*, 65−92.

[18] PCMODEL, Version 7.0, Serena Software, Bloomington, Indiana/USA, **1999**.

[19] R. M. Silverstein, E. E. Ryskiewcz, C. Willard, *Org. Synth.* **1956**, *36*, 74−77.

[20] J. W. Cornforth, M. E. Firth, *J. Chem. Soc.* **1958**, 1091−1099.

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