Photoelectron Spectra, Electronic Structures, and Conformational Properties of (*E*)-Stilbene, Styrylthiophenes, and (Thienylethenyl)pyridines[‡]

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Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

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The UV photoelectron spectra of two isomeric styrylthiophenes (**5**, **6**) and six isomeric (thienylethenyl)pyridines (**7**–**12**) have been recorded and analyzed, making use of DFT Becke3LYP calculations. The spectra were compared with those of (*E*)-stilbene (**1e**) and the isomeric styrylpyridines (**2**–**4**), which are π-isoelectronic with **5**–**12**. Using quantum chemical analyses, planar molecular structures were obtained for all these compounds. However, from the separation Δ*IP* of the ionization bands associated with the π_7 and π_3 MOs, it is possible to make a distinction between planar and twisted molecular structures. Accordingly in these compounds, 2-substituted pyridine rings and 3-substituted thiophene rings are nearly untwisted, whereas phenyl rings, 3- and 4-substituted pyridine, and 2-substituted thiophene rings are twisted to an extent similar to that in **1e**. The apparent distortion of the molecules is probably caused by torsional vibrations, so that twisted average geometries correspond to planar equilibrium structures. The B3LYP data permit detailed conclusions to be drawn with regard to the conformational preferences of 2- and 3-substituted thiophene and pyridine rings in heterocyclic analogues of **1e**, as well as the to relative stabilities of isomers **7**–**12**. The results clearly indicate that PE spectroscopy is a powerful method for analysis of conformational properties of stilbene-like molecules.

Introduction

1,2-Diaryl- or 1,2-diheteroaryl-substituted ethylenes have been studied by various methods as model compounds possessing delocalized π electron systems with torsional mobility, and because of this, the relationship between conformation and electronic structure is of particular interest. The parent compound stilbene is stable in both *E* (**1e**) and *Z* configurations (**1z**). While there can be no doubt that, in the *Z* isomer, the phenyl groups are twisted about the central ethylene group,[2] the question of whether (*E*)-stilbene (**1e**) has a planar or twisted structure seems to be difficult to answer unequivocally (see below).[3] Since torsion limits the delocalization of the π electrons, these compounds are "classical" examples for the interplay of steric effects and resonance, and the question of the actual structure of **1** and related molecules can be considered as decisive for the concept of steric resonance inhibition,[4] as well as for the performance of experimental and theoretical methods to answer such subtle questions. Both the electronic and the conformational properties of these molecules are also of utmost importance for their thermal and photochemical behavior.[3,5–9]

We have investigated hetero analogues of **1e** possessing pyridine and thiophene groups instead of benzene rings. In the (thienylethenyl)pyridines **7**–**12**, an ethylene group has been substituted with a π-electron-overrich thiophene and a π-electron-deficient pyridine group, making these compounds push-pull systems,[10] which should be stabilized relative to ethylene derivatives with matching substituents. Since there are two geometrically different carbon atoms in thiophene, and three different carbon atoms in pyridine, six constitutional isomers are possible; all were synthesized and investigated. Styrylpyridines **2**–**4** and styrylthiophenes **5** and **6** were also included in this study for comparison. All compounds (**2**–**12**) are π-isoelectronic with **1e**, presenting seven occupied π MOs (π_1–π_7).

Results and Discussion

Structures and Energies

The conformational problems to be addressed in compounds **1**–**12** (Scheme 1) can be reduced to the simpler molecules: styrene (**13**), vinylpyridines (**14**–**16**), and vinylthiophenes (**17**, **18**) (Scheme 2). In particular, the parent hydrocarbon (**13**) has been investigated by numerous experimental and theoretical methods, but unfortunately the results are nonuniform. No detailed account of these studies can be given here; instead reference is made to a recent gas phase electron diffraction (GED) investigation by Traet-

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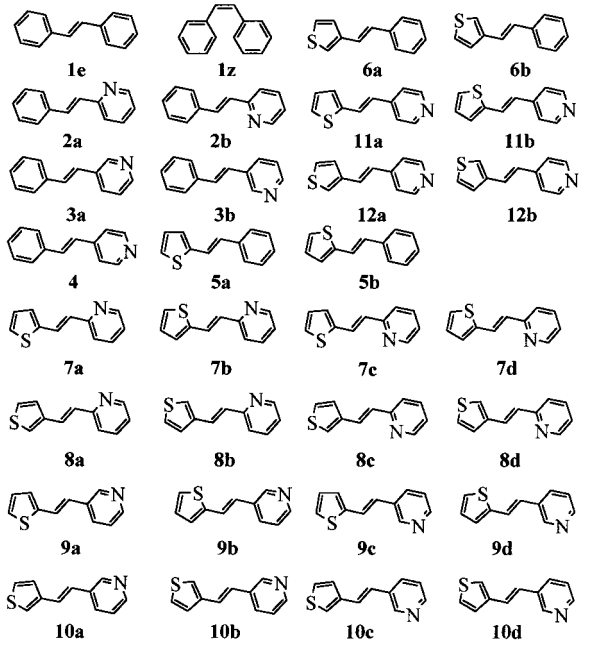
teberg et al.[11] and to a theoretical investigation by Choi and Kertesz.[12] According to these studies, the vinyl torsional motion can be described in terms of a double-minimum potential function, with a barrier of 1.0 kJ mol^{-1} corresponding to the planar form, and with the minimum at about 27°. The conformation of 4-vinylpyridine (**16**) has been investigated in the gas phase by microwave spectroscopy;[13] it was found to be planar. 2-Vinylpyridine (**14**)[14] and 2-vinylthiophene (**17**) have been investigated by ^{1}H NMR spectroscopy, and a conformational equilibrium is suggested for both compounds, with a preponderance of the *synperiplanar* (*sp*) conformers (**14b**, **17b**). We could not obtain any information relating to the conformational properties of 3-vinylpyridine (**15**) and 3-vinylthiophene (**18**). As far as planarity of the structures is concerned, it may be expected that because of their five-membered rings the molecules **17** and **18** have fewer problems than **13**−**16**.



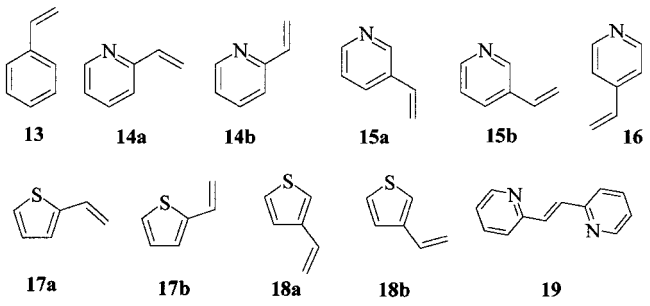
Scheme 1. Structures of compounds **1**−**12**

In *trans*- or (*E*)-stilbene (**1e**), phenyl group torsion may be mainly caused by steric interactions between the ethylene hydrogen atoms and the *ortho* hydrogens of the phenyl groups.[15] In a GED study,[15] which indicated phenyl group torsion of 28° and a large C=C−C valence angle of 128°, the smallest H---H distances were found to be 240 pm, which corresponds closely to the sum of the van der Waals radii. The corresponding H---H distances would be expected to be smaller than 200 pm in the planar conformation.[15] In the crystalline state, molecules of **1e** are essentially but not completely planar; average torsion angles of 5.2−6.6° were determined by X-ray analyses.[16] With spectroscopic methods, either the planar[19−23] or a twisted structure[8,18,24,25] has been found. The results of quantum chemical studies are also not uniform. Semi-empirical methods such as CNDO, MNDO, AM1, and PM3 have been used by several authors to investigate the structure of **1e**.[5−8,26−28] Baranovic et al.[8] calculated a phenyl torsion angle of 22.2° by AM1[29] and of 23.3° by means of the ab initio RHF method using the 6−31G(d) basis set. Galvao et al.[26] reported that PM3 geometries are superior to MNDO and AM1, and that PM3 predicts, in contrast with MNDO, AM1 and even ab initio 3−21G, a coplanar structure. Choi and Kertesz[12] found that when second-order Møller−Plesset perturbation (MP2) was used, the nonplanar conformation was preferred by 3.35 kJ mol^{-1}; however, B3LYP and similar methods favor a planar conformation, contradicting the MP2 results. The obvious discrepancies between experimental and theoretical methods may − at least in part − be caused by different vibrational states of the molecules. While quantum chemical methods refer to vibrationless equilibrium structures at 0 K, most experimental methods determine average structures at a certain − often elevated − temperature.

Both our PM3 and our B3LYP calculations on **1e** predicted a completely planar structure as the most stable conformation, even when a twisted input geometry was used. For a conformation fixed at a torsion angle of 30°, the energy was increased by 5.04 (PM3) or 5.22 kJ mol^{-1} (B3LYP).

We have investigated compounds **2**−**12** by the same quantum chemical methods, with often conflicting results. Of these, the PM3 data frequently seem to be unreasonable. Because of this, we will refrain from presenting PM3 data, but restrict the discussion to the more sophisticated B3LYP results.

For styrylpyridines in which one of the phenyl groups of **1e** is replaced by a pyridine ring, Sorriso and Lumbroso[30] deduced from electric dipole moment measurements in benzene solution that isomer **2** prefers the *antiperiplanar* (*ap*) conformer **2a**, while in isomer **3** both conformers (**3a** and **3b**) are of comparable importance. On the other hand, Bartocci et al.[31] measured absorption and fluorescence spectra in a rigid matrix of EPA at 77 K; spectral analysis clearly indicated the presence of two conformers for both **2** and **3**. With regard to 2-vinylpyridine (**14**), one would expect a preference for the *synperiplanar* (*sp*) conformer **2b**, because of weaker H---H interactions than in **2a**. For *trans*-1,2-bis(2-pyridyl)ethene (**19**) an essentially planar structure with both pyridine rings in *sp* orientations was determined by X-ray crystal structure analysis.[27]



Scheme 2. Structures of compounds **13**−**19**

For all conformational isomers of **2**−**4**, only planar structures were found by B3LYP. Conformer **2a** is calculated to be less stable than **2b** by 4.46 kJ mol^{-1}, and **3a** to be more stable than **3b** by 1.70 kJ mol^{-1}. Since **2**−**4** are constitutional isomers, it makes sense to compare their total energies *E*, and the sequence **2b** > **4** > **3a** is obtained.

For the styrylthiophenes **5** and **6**, in which one of the phenyl groups of **1e** is replaced by a thiophene ring, one might expect that the phenyl ring would be twisted while the thiophene ring should be able to adopt a coplanar orientation with the ethylene group without steric hindrance. For the thiophene group, two coplanar orientations − *ap* and *sp* − are possible, resulting in the conformers **a** and **b**. By the B3LYP method, **5b** is found to be 4.69 kJ mol^{-1} more stable than **5a**, and **6a** is favored over **6b** by 4.55 kJ mol^{-1}. All conformers are planar.

Finally, in the (thienylethenyl)pyridines **7**−**12**, torsion has to be expected for the pyridine ring; in particular for the 3- and 4-substituted isomers (**9**−**12**), because of steric interactions between the *ortho* hydrogens and ethylene hydrogen atoms. Even for completely planar structures, four conformational isomers (**a**−**d**) have to be considered for **7**−**10**, since each ring may be either *ap* or *sp* with respect to the ethylene group. For the 4-substituted pyridine derivatives **11** and **12**, only two different planar conformers (**a** and **b**) are possible.

We have performed MMX, PM3, and B3LYP calculations for all conformational isomers of **7**−**12**. In Table 1, some structure parameters are summarized; the corresponding data for the most stable conformers (according to B3LYP results) of **1**−**6** are included for comparison. In a surprising common result for all methods, only planar conformers were found for all compounds. The total energies *E* are given in Table 2−10 (see below). Most stable are the conformers **7d**, **8c**, **9b**, **10a**, **11b**, and **12a**. For the 2-substituted pyridine derivatives **7** and **8**, the conformers **c** and **d** with *sp* pyridine rings are favored over the *ap* conformers **a** and **b**, because of very short H---H distances of about 216 pm in the latter forms. In conformer **7d**, both heterocyclic rings are in their preferred *sp* orientations, as in 2-vinylpyridine (**14b**) and 2-vinylthiophene (**17b**).

With regard to conformational preferences, the total energies *E* (B3LYP results) of the isomeric (2-thienyl-ethenyl)-pyridines **7**−**12** permit the following conclusions:

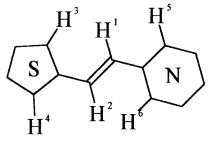
the *sp* orientation of the 2-substituted pyridine ring is favored by about 5 kJ mol^{-1},

the *sp* orientation of the 2-substituted thiophene ring is favored by about 5 kJ mol^{-1},

the *ap* orientation of the 3-substituted pyridine ring is favored by about 1.5 kJ mol^{-1},

the *ap* orientation of the 3-substituted thiophene ring is favored by about 4.5 kJ mol^{-1}.

The relatively strong preference of the 3-substituted thiophene ring for the *ap* orientation is certainly unexpected and difficult to explain. However, this result is confirmed by inspection of the two conformers of 3-vinylthiophene (**18a**, **18b**) for which an energy difference of 4.87 kJ mol^{-1} is calculated by B3LYP; both conformers are found to be planar. The nonbonded H---H distances H^1---H^3 and H^2---H^4 (Scheme 3) in **18a** are 236.3 and 258.8 pm, and in **18b** 254.2 and 245.0 pm, so the energy difference cannot simply be ascribed to steric effects. Since some reservation with respect to noncovalent interactions is appropriate to DFT methods,[32] we have repeated calculations for **18a** and **18b** at the MP2/6−31G* level. Here, again, planar conformers resulted, and the energy difference was found to be 3.89 kJ mol^{-1}, not much at variance with the B3LYP result.



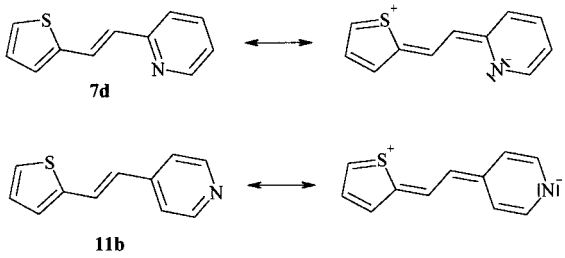
Scheme 3. Atom numbering for 1,2-bis(hetero)arylethylenes **1**−**12**

For **7**−**12**, comparison of the total energies *E* of their most stable conformers reveals the relative magnitude of interaction of the two heteroaromatic rings through the C=C double bond in the isomers. Most stable is **7d** and least stable is **10a**, with an energy difference of 15.27 kJ mol^{-1}. This can be explained by a dipolar resonance structure of **7d** (Scheme 4), in which the donor character of the thiophene ring and the acceptor character of the pyridine ring are evident (Scheme 4). No such equivalent resonance structure can be drawn for **10a**, and in the 4-substituted pyridine derivative **11b**, resonance is less effective than in 2-substituted **7d**. Relatively short C(S)−C and C(N)−N bond lengths and long C=C bond lengths (Table 1) in **7d** and the opposite tendency in **10a** are consistent with this interpreta-

Table 1. Selected structure parameters (pm, °) of compounds **1**−**12** (B3LYP results); atom numbering see Scheme 3

	C=C	C(S)−C	C(N)−C	C(S)−C=C	C(N)−C=C	H^1---H^3	H^1---H^5	H^2---H^4	H^2---H^6
1e	135.0	146.8	146.8	127.2	127.2	214.1	231.8	231.8	214.1
2b	135.0	144.6	146.7	127.4	124.2	217.9	239.2	223.2	---
3a	135.0	146.7	146.5	127.2	126.8	214.4	232.9	231.9	218.0
4	135.0	146.7	146.6	127.3	126.5	214.9	236.8	231.7	216.3
5b	135.3	144.8	146.5	126.8	127.2	---	232.5	256.8	215.9
6a	135.1	145.9	146.7	126.1	127.2	228.5	232.5	257.2	214.9
7d	135.2	144.5	146.5	127.2	124.2	---	240.3	258.8	---
8c	135.0	145.7	146.7	126.3	124.2	232.7	239.9	259.6	---
9b	135.3	144.7	146.2	126.9	126.9	---	233.7	256.6	219.5
10a	135.1	145.8	146.4	126.1	126.8	229.0	233.5	257.2	218.8
11b	135.3	144.6	146.3	126.9	126.5	---	237.5	256.5	218.1
12a	135.0	146.1	146.5	126.7	126.6	237.2	237.3	252.8	217.3

tion. Generally, it is found that 3-substituted thiophenes are less stable than 2-substituted ones by 3.5−4.4 kJ mol^{-1}. 2-Substituted pyridine derivatives are more stable than 3- and 4-substituted ones by about 11−12 and 9−10 kJ mol^{-1}, respectively.



Scheme 4. Resonance structures of compounds **7d** and **11b**

The structure parameters of **1**−**12** summarized in Table 1 reveal a rather uniform picture with only minor differences in individual data. The length of the central C=C double bond varies only between 135.0 and 135.3 pm. In the thiophene derivatives (**5**−**12**), the largest value is found for 2-substituted molecules and the smallest for 1-substituted ones. On the other hand, variation of the substituent position on the pyridine ring does not affect this bond length by more than 0.1 pm. The length (C(S)−C) of the bond between the thiophene ring and the central C=C double bond varies between 146.2 and 146.7 pm; for 2-substituted thiophenes it is slightly shorter than for 3-substituted ones. The length of the C(N)−C bond − the bond between the pyridine ring and the C=C double bond − shows a variation, between 146.2 and 146.7 pm, that seems to depend on both substituents. The shortest value is found in **9b** and the longest in **8c**. For **1e**, the calculated value of the C=C bond length is 2 pm longer than found by GED.[15]

The valence angles C(S)−C=C and C(N)−C=C adjacent to the central C=C double bond are very close to the large value of 128° found for *trans* stilbene (**1e**) by GED.[15] As far as the H---H distances between the ethylene hydrogens and the *ortho* hydrogen atoms of the rings are concerned, corresponding distances are calculated as longer than in **1e** for all molecules **2**−**12**, with the only exception being H^2---H^4 in **4**, which is 0.1 pm shorter than in **1e**. The H---H distances can be up to 28 pm longer than in **1e**; the largest variation is found for H^2---H^4 and the smallest (only 5.4 pm) is found for H^2---H^6. However, if only the (thienylethenyl)pyridines (**7**−**12**) are considered, H^2---H^4 varies only by 6.8 pm. Working on the assumption that the H---H interactions are the reason for the torsion in **1e**, molecules **2**−**12** should be expected to be less twisted than the parent compound.

Photoelectron Spectra

PE spectra of styrene (**13**), [19,33] and 2- and 4-vinylpyridine (**14**, **16**)[34] have been published. To interpret the spectrum of **13**, a planar conformation was anticipated. For **14** and **16** no conclusion was drawn regarding conformations. To the best of our knowledge, PE spectra of 3-vinylpyridine (**15**) and the vinylthiophenes (**17**, **18**) have not previously been measured.

PE spectra of compounds **1e** and **5**−**12** are depicted in Figure 1. The ionization potentials are summarized in Table 2−10, together with the relevant results of B3LYP calculations. We refrain from presenting the results obtained by other quantum chemical methods in order to limit the amount of data. We have also omitted σ orbitals, which are irrelevant for spectral assignments. In Figure 2, a correlation diagram is shown for π and *n* ionization potentials.

In most cases, semi-empirical and B3LYP methods lead to the same assignment for the *IP*s, using the Koopmans theorem[35] ($IP_i = -\varepsilon_i$) to relate vertical ionization energies and MO energies. For the first vertical *IP* (IP_{1v}), much better agreement between experimental and theoretical values can be expected 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 ($M^{\bullet+}$) using the molecule's (M) geometry. This has been done for **1e** and all conformers of **5**−**12**. The corresponding energy values are given in Table 2−10. We can now correct other ε^{B3LYP} values by the difference Δ = 1.53 eV (compound **1e**, Table 2) between $-\varepsilon$(HOMO) and the calculated IP_{1v}, in order to obtain higher IP_v values.[36] The corresponding Δ values for the other compounds are between 1.56 and 1.61 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 values are linearly correlated with the experimental IP_i values, with correlation coefficients very close to 1.00.

(*E*)-Stilbene (1e)

According to investigations by Maier and Turner[19] and by Kobayashi et al.,[18] the first and the fifth ionization bands of stilbenes are the so-called conjugation π bands. These ionizations correspond to the π_7 and π_3 MOs, which are delocalized over the entire molecular frameworks. The energy difference between these two MOs is quite sensitive to the change in the torsion angles of the two aromatic substituents, relative to the central C=C double bond. In **1e**, the separation (ΔIP) of these two ionizations is about 2.6 eV; in agreement with sizeable resonance inhibition caused by phenyl group torsion. As has been shown by GED structure analysis, the two phenyl groups in **1e** are twisted by about 30° from the olefinic group plane.[15] McAlduff and Chan[37] found ΔIP values of 2.53−2.70 eV for 4-monosubstituted (*E*)-stilbenes and concluded that these molecules exist in a planar or nearly planar conformation.

Styrylpyridines 2−4

The PE spectra of compounds **2**−**4** were investigated by Distefano et al.[38] *IP* values and their assignments are closely related to those of **7**−**12**. For **2**−**4**, ΔIP values between $IP(\pi_7)$ and $IP(\pi_3)$ were found to be 2.68, 2.87, and 2.86 eV, respectively. Other azastilbenes such as dipyridylethylenes[39,40] and 1-diazinyl-2-pyridylethylenes (triazastilb-

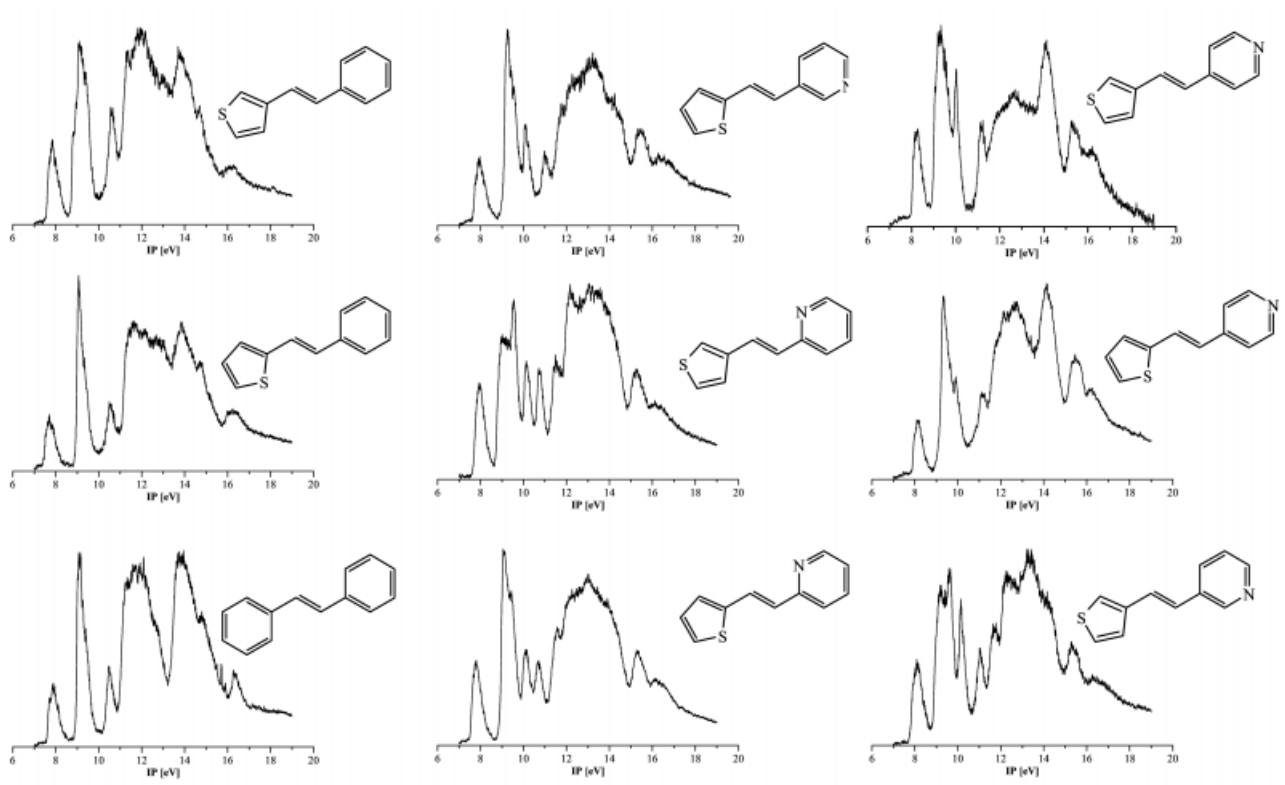


Figure 1. Photoelectron spectra of compounds **1e**, **5**−**12**

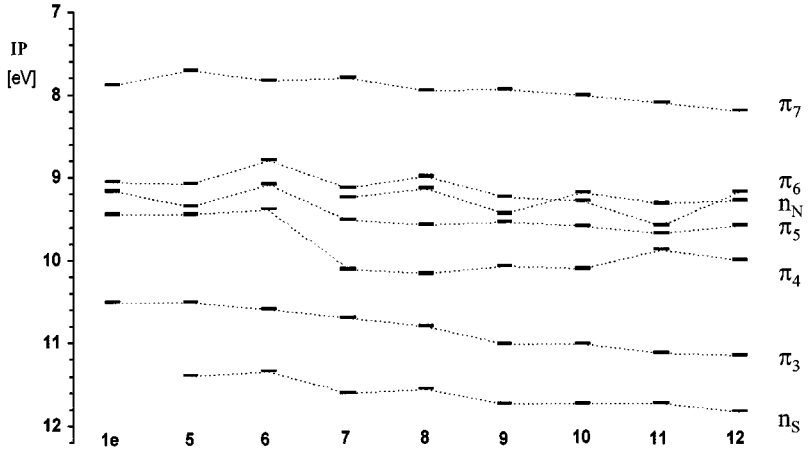


Figure 2. Correlation diagram of the ionization potentials *IP* of compounds **1e**, **5**−**12**

Table 2. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* stilbene (**1e**)

IP	$-\varepsilon^{B3LYP}$	*IP*[a]	
7.89	5.79	7.32	π_7 ($4a_u$)
9.06	7.07	8.60	π_6 ($3a_u$)
9.17	7.07	8.60	π_5 ($3b_g$)
9.45	7.39	8.92	π_4 ($2b_g$)
10.52	8.63	10.16	π_3 ($2a_u$)
11.35	9.30	10.83	σ
E(M)	−540.730039		
E(M^+)	−540.460868		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.53$ 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^+ for 2-styrylthiophene (**5**)

IP	**5a** $-\varepsilon^{B3LYP}$	*IP*[a]	**5b** $-\varepsilon^{B3LYP}$	*IP*[a]	
7.71	5.60	7.16	5.62	7.18	π_7 (7a")
9.08	7.08	8.64	7.07	8.63	π_6 (6a")
9.35 sh	7.09	8.65	7.08	8.64	π_5 (5a")
9.45 sh	7.26	8.82	7.27	8.83	π_4 (4a")
10.52	8.68	10.24	8.66	10.22	π_3 (3a")
11.4	9.40	10.96	9.28	10.84	n_S
E(M)	−861.483738		−861.485526		
E(M^+)	−861.220519		−861.221829		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.56$ 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^+ for 3-styrylthiophene (**6**)

IP	**6a** $-\varepsilon^{B3LYP}$	*IP*[a]	**6b** $-\varepsilon^{B3LYP}$	*IP*[b]	
7.84	5.72	7.28	5.70	7.27	π_7 (7a")
8.80/8.94	6.86	8.42	6.83	8.40	π_6 (6a")
9.09	7.06	8.62	7.07	8.64	π_5 (5a")
9.40/9.45	7.38	8.94	7.38	8.95	π_4 (4a")
10.60	8.68	10.24	8.68	10.25	π_3 (3a")
11.4	9.37	10.93	9.36	10.93	n_S
E(M)	−861.484041		−861.482306		
E(M^+)	−861.216394		−861.215133		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.56$ eV (see text). − [b] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.57$ eV (see text).

three ionization events contribute to the second band, centered at about 9.1 eV. In compound **5**, this band shows a steep increase on the low-energy side, while two shoulders are discernible on the high-energy flank. In the spectrum of **6**, this band is somewhat broader and exhibits a more complex shape. There are shoulders on both sides, originating from different vibrational transitions, and it is not possible to identify the vertical transitions of all three bands accurately. The shapes of the first and the third band indicate some vibrational transitions; however, it may be possible that the structure is also caused by superposition of the somewhat different *IP*s of various rotational isomers (cf. below). All *IP*s below 11 eV are assigned as π ionizations ($\pi_3-\pi_7$). The next ionization, at about 11.4 eV, is assigned as *IP*(n_S).

According to the sulfur-double bond (SD) model,[42−44] only minor perturbations in the π electron system are expected when a C=C double bond is replaced by a sulfur atom, and correspondingly the spectra of **5** and **6** are quite similar to that of (*E*)-stilbene (**1e**):[18] most *IP* values differ by less than 0.1 eV. The spectrum of compound **5** has been investigated previously;[45] however the published *IP* values differ from ours by up to 0.3 eV.

Table 5. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* 2-(2-thien-2-yl-ethenyl)pyridine (**7**)

IP	**7a** $-\varepsilon^{B3LYP}$	*IP*[a]	**7b** $-\varepsilon^{B3LYP}$	*IP*[a]	**7c** $-\varepsilon^{B3LYP}$	*IP*[b]	**7d** $-\varepsilon^{B3LYP}$	*IP*[a]	
7.81	5.79	7.37	5.80	7.38	5.72	7.29	5.73	7.31	π_7 (7a")
9.13	7.15	8.73	7.13	8.71	7.09	8.66	7.09	8.67	π_6 (6a")
9.25	7.20	8.78	7.18	8.76	7.17	8.74	7.17	8.75	n_N
9.52	7.43	9.01	7.43	9.01	7.39	8.96	7.40	8.98	π_5 (5a")
10.12	8.01	9.59	8.00	9.58	7.97	9.52	7.96	9.54	π_4 (4a")
10.70	8.82	10.40	8.81	10.39	8.75	10.32	8.74	10.32	π_3 (3a")
11.61	9.58	11.16	9.42	11.00	9.50	11.07	9.38	10.96	n_S
E(M)	−877.523135		−877.524710		−877.525138		−877.527075		
E(M^+)	−877.252333		−877.253350		−877.257152		−877.258374		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.58$ eV (see text). − [b] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.57$ 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^+ for *trans* 2-(2-thien-3-yl-ethenyl)pyridine (**8**)

IP	**8a** $-\varepsilon^{B3LYP}$	*IP*[a]	**8b** $-\varepsilon^{B3LYP}$	*IP*[b]	**8c** $-\varepsilon^{B3LYP}$	*IP*[a]	**8d** $-\varepsilon^{B3LYP}$	*IP*[a]	
7.96	5.92	7.51	5.90	7.48	5.84	7.43	5.83	7.42	π_7 (7a")
9.00	6.92	8.51	6.90	8.48	6.87	8.46	6.85	8.44	π_6 (6a")
9.15	7.18	8.77	7.18	8.76	7.15	8.74	7.15	8.74	n_N
9.58	7.51	9.10	7.51	9.09	7.48	9.07	7.49	9.08	π_5 (5a")
10.17	8.01	9.60	8.00	9.58	7.96	9.55	7.96	9.55	π_4 (4a")
10.81	8.83	10.42	8.82	10.40	8.75	10.34	8.75	10.34	π_3 (3a")
11.57	9.56	11.15	9.53	11.11	9.50	11.09	9.46	11.05	n_S
E(M)	−877.523581		−877.521811		−877.525400		−877.523595		
E(M^+)	−877.247710		−877.246764		−877.252468		−877.251079		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.59$ eV (see text). − [b] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.58$ eV (see text).

enes)[41] were also studied by PE spectroscopy (PES), and for these molecules it was concluded[39] that their angles of twist are rather small.

2-Styrylthiophene (5) and 3-Styrylthiophene (6)

The PE spectra of these two compounds are rather similar (Figure 1). As in the case of (*E*)-stilbene (**1e**), the region below 11 eV is characterized by a three-band system, the relative intensity ratios of which are roughly 1:3:1, indicating that

(Thienylethenyl)pyridines 7−12

As well as π ionizations, one additional band can be expected in the low-energy region of the PE spectra of com-

Table 7. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* 3-(2-thien-2-yl-ethenyl)pyridine (**9**)

IP	**9a** $-\varepsilon^{B3LYP}$	*IP*[a]	**9b** $-\varepsilon^{B3LYP}$	*IP*[b]	**9c** $-\varepsilon^{B3LYP}$	*IP*[a]	**9d** $-\varepsilon^{B3LYP}$	*IP*[a]	
7.95	5.83	7.41	5.84	7.43	5.82	7.40	5.84	7.42	π_7 (7a")
9.25	7.21	8.79	7.19	8.78	7.18	8.76	7.17	8.75	π_6 (6a")
9.4 sh	7.23	8.81	7.22	8.81	7.22	8.80	7.21	8.79	n_N
9.55	7.51	9.09	7.52	9.11	7.48	9.06	7.48	9.06	π_5 (5a")
10.09	7.99	9.57	7.98	9.57	8.00	9.58	7.99	9.57	π_4 (4a")
11.03	9.13	10.71	9.11	10.70	9.11	10.69	9.09	10.67	π_3 (3a")
11.75	9.66	11.24	9.52	11.11	9.63	11.21	9.54	11.12	n_S
E(M)	−877.520817		−877.522614		−877.520123		−877.522093		
$E(M^+)$	−877.248349		−877.249595		−877.248000		−877.249369		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.58$ eV (see text). − [b] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.59$ eV (see text).

Table 8. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* 3-(2-thien-3-yl-ethenyl)pyridine (**10**)

IP	**10a** $-\varepsilon^{B3LYP}$	*IP*[a]	**10b** $-\varepsilon^{B3LYP}$	*IP*[a]	**10c** $-\varepsilon^{B3LYP}$	*IP*[a]	**10d** $-\varepsilon^{B3LYP}$	*IP*[a]	
8.03	5.96	7.55	5.94	7.53	5.95	7.54	5.93	7.52	π_7 (7a")
9.20	7.00	8.59	6.98	8.57	7.00	8.59	6.97	8.56	n_N
9.3	7.19	8.78	7.19	8.78	7.16	8.75	7.17	8.76	π_6 (6a")
9.60	7.59	9.18	7.59	9.18	7.56	9.15	7.56	9.15	π_5 (5a")
10.12	8.00	9.59	8.00	9.59	8.01	9.60	8.01	9.60	π_4 (4a")
11.03	9.12	10.71	9.12	10.71	9.10	10.69	9.10	10.69	π_3 (3a")
11.75	9.65	11.24	9.61	11.20	9.67	11.26	9.64	11.23	n_S
E(M)	877.521258		877.519494		877.520638		877.518862		
$E(M^+)$	877.243860		877.242682		877.243650		877.242361		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.59$ eV (see text).

Table 9. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* 4-(2-thien-2-yl-ethenyl)pyridine (**11**)

IP	**11a** $-\varepsilon^{B3LYP}$	*IP*[a]	**11b** $-\varepsilon^{B3LYP}$	*IP*[a]	
8.12	6.02	7.62	6.03	7.63	π_7 (7a")
9.33	7.17	8.77	7.16	8.76	n_N
9.6 sh	7.33	8.93	7.32	8.92	π_6 (6a")
9.7 sh	7.36	8.96	7.34	8.94	π_5 (5a")
9.90	7.86	9.46	7.87	9.47	π_4 (4a")
11.14	9.27	10.87	9.25	10.85	π_3 (3a")
11.75	9.74	11.34	9.59	11.19	n_S
E(M)	−877.521449		−877.523326		
$E(M^+)$	−877.241584		−877.242792		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.60$ eV (see text).

Table 10. Ionization potentials *IP* [eV], orbital energies ε [eV], and total energies *E* [au] of molecule M and radical cation M^+ for *trans* 4-(2-thien-3-yl-ethenyl)pyridine (**12**)

IP	**12a** $-\varepsilon^{B3LYP}$	*IP*[a]	**12b** $-\varepsilon^{B3LYP}$	*IP*[b]	
8.22	6.16	7.76	6.13	7.74	π_7 (7a")
9.2	7.11	8.71	7.09	8.70	π_6 (6a")
9.3	7.16	8.76	7.16	8.77	n_N
9.6	7.34	8.94	7.34	8.95	π_5 (5a")
10.02	7.96	9.56	7.95	9.56	π_4 (4a")
11.17	9.26	10.86	9.26	10.87	π_3 (3a")
11.85	9.75	11.35	9.70	11.31	n_S
E(M)	−877.521930		−877.520144		
$E(M^+)$	−877.236695		−877.235553		

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.60$ eV (see text). − [b]Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry. Higher *IP*s: $IP_i = -\varepsilon_i + 1.61$ eV (see text).

pounds **7**−**12**; namely, that of the electron lone pair (n_N) on the pyridine ring nitrogen atom. In pyridine itself, the corresponding ionization band is found at 10.51 eV[46] and a somewhat lower value can be expected for **7**−**12**. For styrylpyridines (**2**−**4**), $IP(n_N)$ values between 9.2 and 9.4 eV were associated with this orbital,[38] but strong overlap with $IP(\pi_6)$ and $IP(\pi_5)$ denied more precise data. Because of the higher electronegativity of N relative to CH, values a little higher than for the phenyl derivatives **5** and **6** are anticipated for the π ionizations of **7**−**12**.

In the regions below 11.3 eV in the PE spectra of **7**−**12**, four to five different peak maxima are found, whereas six *IP* values would be expected. This indicates that in most cases band overlap is reduced relative to the situation observed for **1e**−**6**. However, the spectra of **7**−**12** are also all dominated by a strong composite band between 9 and 10 eV. The best spacing of the bands is found for compound **8**, and peak maxima are discernible for all six bands. The

assignment of *IP* values is uniformly $IP(\pi_7)$, $IP(\pi_6)$, $IP(n_N) \approx IP(\pi_5)$, $IP(\pi_4)$, $IP(\pi_3)$, and $IP(n_S)$ for all compounds, based on the results of B3LYP calculations.

Although there are some indications that several conformers with slightly different *IP* values might contribute to their PE spectra, in no case it is possible to identify such data and make any assignment to individual conformers of **5**−**12**. This is supported by the calculated MO energies. The data in Table 3−10 indicate that, with only a few exceptions, the energies of $\pi_3-\pi_7$ differ by less than 0.03 eV for the different planar conformers. The energy of the n_N orbitals of **7**−**12** also seems to be nearly invariant with respect to conformational change, which is obvious from the maximum energy shifts of 0.03 eV. Only the n_S orbital seems to show a systematic variation. For the 2-substituted thiophene derivatives (**5**, **7**, **9**, and **11**), the energy of this orbital varies between 0.1 and 0.2 eV for the individual conformers, while for the 3-substituted thiophene derivatives (**6**, **10**, **12**), this variation amounts only to 0.05 eV or less. The 3-substituted isomer **8** seems to be an exception, with a variation of 0.1 eV. Taking into account that the accuracy in the measurement of *IP* values of broad and overlapping bands is ±0.1 eV, we can only expect to find separate peaks for individual conformers in very few cases. However, the $IP(n_S)$ bands are difficult to identify because they are located above 11 eV, where they are obscured by strong σ ionizations.

Electronic Structures of Compounds 1−12

As is obvious from Figure 2, there are no drastic changes of *IP*s in the series of compounds summarized in this diagram. Compounds **5**−**12** are thus quite similar to **1e**, with which they are π-isoelectronic. However, with regard to their albeit small differences, some general trends may be recognized. Compared with the styrylthiophenes **5** and **6**, most *IP*s of the (thienylethenyl)pyridines **7**−**12** are increased by up to about 0.7 eV, which has to be attributed to the electronegative nitrogen atom in the pyridine ring. However, the first *IP*s of the pyridine derivatives **7** and **8** are nearly the same as in the analogous benzene derivatives **5** and **6**. In the series of compounds **7**−**12**, most *IP*s seem to increase in energy. This is particularly evident for $IP(\pi_7)$, $IP(\pi_5)$, and $IP(\pi_3)$. On the other hand, $IP(\pi_4)$ remains constant at 10.1 eV in **7**−**10** and then drops to 9.9 eV in **11**. This reflects the MO structure of π_4; there are only minor coefficients on atoms 2, 3, 5, and 6 of the benzene or pyridine ring, while on atoms 1 and 4 there are large coefficients. Surprisingly, this is not well reproduced by PM3 calculations, according to which $IP(\pi_4)$ should have more or less the same value in all these compounds, including **11**. This semi-empirical method is thus not suited for analysis of the subtle differences in the electronic structures of **7**−**12**. On the other hand, the B3LYP method indicates an $IP(\pi_4)$ value of 9.46 eV (Table 9), which is 0.15−0.20 eV smaller than in the other isomers.

Conformations of Compounds 1−12

As has been shown in numerous examples,[47,48] photoelectron spectroscopy is a powerful experimental method for conformational analysis, and by this method it has been found[18,19] that in *trans*-stilbene (**1e**) the phenyl groups are twisted by 30−40°. Above, it has been pointed out that neither the semi-empirical nor the DFT B3LYP method predicts a twisted structure. However, the splitting of the energy of the π_3 and π_7 MOs, which depends in a highly sensitive manner on the torsion of the phenyl groups, was predicted to be about 10% larger by the theoretical methods than was found by PES. Since the corresponding *IP* values can be determined with high accuracy and the spacing of the π MO energies for such systems calculated with high confidence, it has to be concluded from the PE spectrum that in **1e** the phenyl groups are not coplanar with the central C=C double bond, but are twisted. By trial and error, it can be shown that the PM3 method gives a Δε value of 2.61 eV, i.e. almost exactly the same value as $\Delta IP = 2.63$ eV (Table 2), for a torsion angle of 25°. This value is very close to that found by GED[15] as well as by PES.[18] By the B3LYP method, $\Delta\varepsilon = 2.52$ eV is obtained for a torsion angle of 30°, indicating that an angle of 15−20° would correspond to the observed Δ*IP* value.

In Figure 3, corresponding Δ*IP* and Δε values of compounds **5**−**12** are compared with those of **1e** and **2**−**4**. It is most remarkable that for all compounds, Δε (that always refers to a planar conformation) is greater than Δ*IP*. Taking into account that for **1e** a difference of Δ*IP* and Δε of about 0.2 eV or 10% was taken as evidence for a twisted structure, we have to conclude that the heterocyclic analogues of **1e**, with the exceptions of the 2-substituted pyridine derivatives **2**, **7**, and **8**, are actually clearly twisted, while the latter molecules are planar, or at least less twisted than **1e**. This result seems reasonable, since the most stable conformers **2b**, **7d**, and **8c** possess no H---H interaction between an *ortho* hydrogen atom in the pyridine ring and the β hydrogen atom of the ethylene group that would cause torsion.

For the styrylpyridines **2**−**4**, Δ*IP* values of 2.68, 2.87, and 2.86 eV have been measured by Distefano et al.[38] The corresponding $\Delta\varepsilon^{B3LYP}$ values are 2.78, 3.03, and 2.97 eV, respectively. The latter values refer to essentially planar structures; for isomers **2** and **3** they do not vary by more than 0.02 eV for the *ap* and *sp* conformers **a** and **b**. The experimental Δ*IP* values deviate by 0.1 eV or more from the calculated $\Delta\varepsilon^{B3LYP}$ values and, accordingly, slightly twisted structures are also most likely for these compounds.

The first ionization band in the PE spectra of the compounds studied here displays a broad and somewhat diffuse structure. Obviously, separate peaks originating from transitions to individual vibrational states of the respective radical cation are usually unresolved. The observed band is the envelope of slightly different spectra of a mixture of conformational isomers or − more accurately − different torsional states of a rotamer. If the latter is the case, the spectra should be temperature-dependant. In order to clarify this question, we measured PE spectra of compound **8**

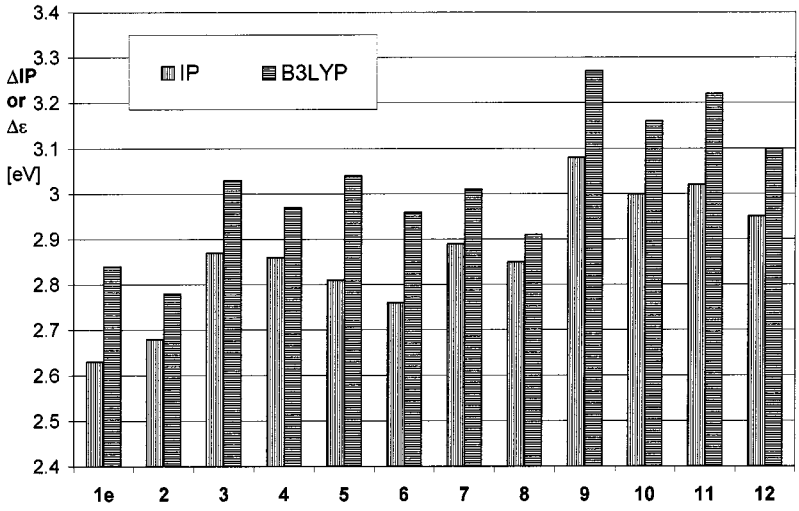


Figure 3. Splittings (ΔIP and Δε [eV]) of π_3 and π_7 MOs of compounds **1e**, **2**−**12**; calculated values refer to most stable conformers

at 120, 210, and 380 °C. The most remarkable observation is that the gap (Δ*IP*) between $IP(\pi_7)$ and $IP(\pi_3)$ decreases with increasing temperature. For the temperatures given, Δ*IP* values of 2.86, 2.81, and 2.77 eV, respectively, are obtained. This is strong support for the proposition that the torsion observed by PES may be mainly or entirely due to torsional vibration. Accordingly, there would hence be no conflict between the quantum chemical results that indicate planar *equilibrium* structures and spectroscopic results that indicate slightly twisted *average* structures. There are two vibrations for the simultaneous torsions of the two substituents. For **1e**, the fundamental frequencies are 9 and 118 cm^{-1},[9,49] respectively, so that the molecules are in highly exited states and consequently considerably twisted at the temperature at which the PE spectra of **1e** and **5**−**12** were measured (120−210 °C).

From Figure 3, it is apparent that the difference between Δ*IP* and $\Delta\varepsilon^{B3LYP}$ is always larger for 2-substituted thiophene derivatives than for the analogous 3-substituted isomers. This can be taken as an indication that in the former compounds the average twist angle of the thiophene ring is larger than in the latter.

Finally, we have investigated the torsion of the phenyl groups of (*Z*)-stilbene (**1z**). By PM3, a minimum-energy conformation with a twist angle of 50° was obtained. In this conformer, the calculated splitting $\Delta\varepsilon^{PM3}$ of the π_3 and π_6 MOs is 1.86 eV; about 10% smaller than that determined by PES (Δ*IP* = 2.10 eV).[18] When the torsion angle is fixed at 40° or 45°, Δε values of 2.19 and 2.05 eV, respectively, are obtained; quite close to the Δ*IP* value. It is noteworthy that the torsion angle (40−45°) estimated in this way from the PE spectrum is in excellent accord with the value determined by GED (43°).[2] By the B3LYP method, the twist angle is calculated as 35.1°, and in this conformer $\Delta\varepsilon^{B3LYP}$ has a value of 2.36 eV; i.e., the molecule should actually be a little more twisted than the calculation, which again gives an angle of about 40°, predicts. It may be appropriate to point out that the calculated energy difference between **1e** and **1z** (20.67 kJ mol^{-1}) is very close to the experimentally determined value (22.8±2.8 kJ mol^{-1})[50] and considerably better than that found by RHF/6−31G(d) (13.8 kJ mol^{-1}).[8]

Experimental Section

2-Styrylthiophene (**5**)[51] and 3-styrylthiophene (**6**)[52] were synthesized as described in the literature. Syntheses of (*E*)-pyridylthienylethenes **7**−**12** have been published.[53] The *trans* configuration of the compounds was verified by ethylenic vicinal H,H coupling constants ^3J of about 16 Hz.

PE spectra were recorded on a Leybold−Heraeus UPG200 spectrometer equipped with a He^I radiation source (21.21 eV). Samples were evaporated directly into the target chamber. In order to reach sufficient vapor pressure, temperatures of 120−210 °C were necessary. The energy scale was calibrated with the xenon lines at 12.130 and 13.436 and the argon lines at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ± 0.03 eV for ionization energies; for broad and overlapping signals it was only ± 0.1 eV.

Semi-empirical PM3[54] calculations were performed with the MOPAC93[55] program package, Becke3LYP[56,57] and MP2 calculations with the GAUSSIAN 98 program.[58] For the latter methods, the 6−31+G* basis set was used, if not stated otherwise. In the MOPAC calculations, the keyword "precise" was used in order to enhance the criteria for terminating the optimization. Geometries were fully optimized at the respective levels of theory. Molecular mechanics calculations using the MMX[59] force field were performed with the program PCMODEL, version 7.0.[60]

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