On the Electronic Effects of the Heteroatom in Five-Membered Heterocycles. Photoelectron Spectra of Selenolo and Pyrrolo Analogues of Thieno[2,3-*b*]thiophene and Thieno[3,2-*b*]thiophene[1]

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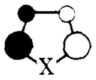
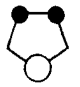
In order to study the effects of the heteroatoms, the photoelectron spectra of thieno[2,3-*b*]selenophene (**3**), selenolo[2,3-*b*]selenophene (**4**), thieno[3,2-*b*]selenophene (**5**), selenolo[3,2-*b*]selenophene (**6**), thieno[2,3-*b*]pyrrole (**7**), selenolo[2,3-*b*]pyrrole (**8**), pyrrolo[2,3-*b*]pyrrole (**9**), thieno[3,2-*b*]pyrrole (**10**), and selenolo[3,2-*b*]pyrrole (**11**) have been measured and analyzed. Replacement of sulfur by selenium can be considered as a minor perturbation, i.e., simple perturbation theory is valid. The effect on the π electronic system of a replacement of sulfur or selenium by an NH group is governed by a balance between the influence of the increase of the resonance integral for the bonds involving the heteroatom and a strongly destabilizing inductive effect due to the polarity of the N–H bond. The effective electronegativity of the NH group is found to be not too different from that of a sulfur atom.

A description of the electronic effects associated with the heteroatom in a heterocyclic compound is of fundamental importance in chemistry and biology. Heterocyclic chemistry is a rich field for the application of perturbation theoretical arguments, and qualitative descriptions of the influence of the heteroatom are in most cases based directly or indirectly on simple perturbation theory.[5] A prominent example of a series of heterocycles is the compounds C_4H_4X, where X may be O, S, Se, NH, etc. In Figure 1 we have indicated the positions of the first two ionization potentials[6,7] of the compounds furan, pyrrole, thiophene, and selenophene, arranged in the order of decreasing electronegativity of the heteroatom. Within the validity of Koopmans' theorem (see later), the first and the second ionization potential correspond to removal of an electron from the highest and the second highest molecular orbital, $a_2(\pi)$ and $b_1(\pi)$, respectively. The general shape of these orbitals is indicated below. According to simple perturbation theory, the energy of the $a_2(\pi)$ level should be much less affected by a change of heteroatom than the energy of the $b_1(\pi)$ level. Inspection of Figure 1 shows that this expectation holds excellently for the series furan, thiophene, and selenophene, but pyrrole is a striking exception. Consider for instance the passing from thiophene to pyrrole: the shift of the $a_2(\pi)$ level is much larger than the shift of the $b_1(\pi)$ level, and both shifts are toward lower binding energies, which is apparently inconsistent with an increase of electronegativity of the heteroatom.



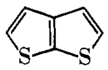
$a_2(\pi)$



$b_1(\pi)$

In order to obtain a better understanding of the effects operating in these systems, we have studied the PE spectra of thieno[2,3-*b*]selenophene (**3**),[8] selenolo[2,3-*b*]selenophene (**4**),[9] thieno[3,2-*b*]selenophene (**5**),[10] selenolo[3,2-*b*]selenophene (**6**),[11] thieno[2,3-*b*]pyrrole (**7**),[12] selenolo[2,3-*b*]pyrrole (**8**),[13] pyrrolo[2,3-*b*]pyrrole (**9**),[13] thieno[3,2-*b*]pyrrole (**10**),[13] and selenolo[3,2-*b*]pyrrole (**11**).[13] The PE spectra of thieno[2,3-*b*]thiophene (**1**) and thieno[3,2-*b*]thiophene (**2**) have been measured previously.[14]

In the first section of the paper we discuss the compounds **1–6**, where simple perturbation theoretical arguments appear to be valid. In the second and largest part of the paper we discuss the compounds **7–11** in order to describe the effects leading to the breakdown of simple perturbation theory when sulfur or selenium is replaced by NH. We use the results of current semiempirical methods and refer to recent ab initio results, but the emphasis has been put on a conceptual analysis in terms familiar to most organic chemists.



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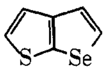

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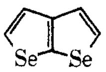

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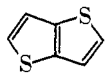

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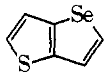

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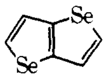

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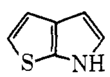

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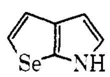

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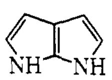

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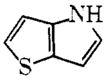

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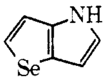

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I. PE Spectra of 1–6

The PE spectra of **3–6** are shown in Figure 2 and the vertical ionization potentials of the first four bands are listed in Table I. The PE spectra of **1** and **2** have been published previously,[14] and the vertical ionization potentials are included in Table I. The PE spectra of the series **1–3–4** all look very similar, as do the PE spectra of the series **2–5–6**. This is not surprising, since sulfur and selenium have very similar electronegativities,[15] and substitution of sulfur by selenium can be expected to be a minor perturbation of the valence electronic system. In the following section is given a more detailed discussion of this matter in connection with a description of the effects due to the NH group.

In our interpretation of these spectra we assume the validity of Koopmans' theorem.[16] In this approximation, the negative value of the orbital energy, ϵ_J, is set equal to the vertical ionization potential, $I_{V,J}$:

$$-\epsilon_J = I_{V,J} \tag{1}$$

As in the case of **1** and **2**[14] we take the steep onset of the first few PE bands as an indication that the bands correspond to ionizations from π orbitals. From the similarity of the PE spectra mentioned above, the correlation diagram given in Figure 3 can be drawn. To check this diagram we have carried out semiempirical calculations using a parametrized Hückel (HMO) procedure,[5] and the EWMO,[17,18] CNDO/2,[19] and MINDO/3[20] methods. The results of the HMO and MINDO/3 calculations are summarized in Table I, and a correlation diagram based on the HMO results is presented in Figure 4.

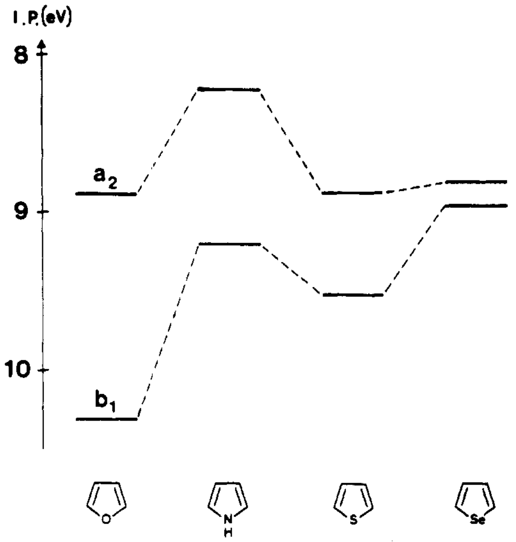


Figure 1. Correlation of the observed first and second ionization potentials of the compounds furan, pyrrole, thiophene, and selenophene.

HMO Model. The parameters for the HMO calculations were chosen in a straightforward way. α_X and β_{CX} values for X = S and Se were taken as those used previously: $\alpha_S = -9.4$, $\alpha_{Se} = 8.5$, $\beta_{CS} = -1.8$, and $\beta_{CSe} = -1.5$ eV.[21] The β_{CC} value was also kept in accordance with the previous work: $\beta_{CC} = -3.0$ eV.[21] The α_C value was then adjusted to reproduce the observed first ionization potential of thiophene (8.87 eV[6]) and selenophene (8.80 eV[7]). The HOMOs of these compounds have a node through the position of the heteroatom X, and are thus independent of the choice of α_X and β_{CX} parameters in the HMO model. A good agreement is found for $\alpha_C = -7.0$ eV, which yields a common value of −8.85 eV for the energies of these levels. The results for thiophene and selenophene are then (eV)

	Thiophene	Selenophene
$a_2(\pi)$	−8.85	−8.85
$b_1(\pi)$	−9.64	−8.93
$b_1(\pi)$	−12.56	−12.23

The agreement with the observed energies[6,7] is satisfactory; in particular, the consistency with the recent analysis of the PE spectrum of thiophene by Niessen et al.[22] is gratifying.

Results and Discussion. The results of the HMO calculations on the compounds **1–6** agree reasonably well with the experimental energies; see Table I. The results support the assignments suggested previously[14] for **1** and **2**; this assignment is furthermore supported by the MINDO/3 results for **1** and **2** given in Table I. Comparison of the correlation diagrams in Figures 3 and 4 shows that the HMO calculations reproduce the significant trends in the PE spectra for this series of compounds. Most of the observed shifts of the bands can be understood in terms of simple first-order perturbation theory applied to the HMOs of **1** and **2** (see Figure 4). The HOMO of **1** has a small amplitude on the sulfur atoms, while the next MO has a large amplitude in these positions. These orbitals are thus destabilized to different extents by replacement of sulfur by selenium, and a reversal of the ordering of these two closely spaced levels is predicted in the series **1–3–4**. Similar shifts are shown by the two highest occupied orbitals in **2**, which have the same symmetry (a_u in C_{2h}). At first glance it may appear strange that the energy of the second highest MO approaches the energy of the HOMO in the series

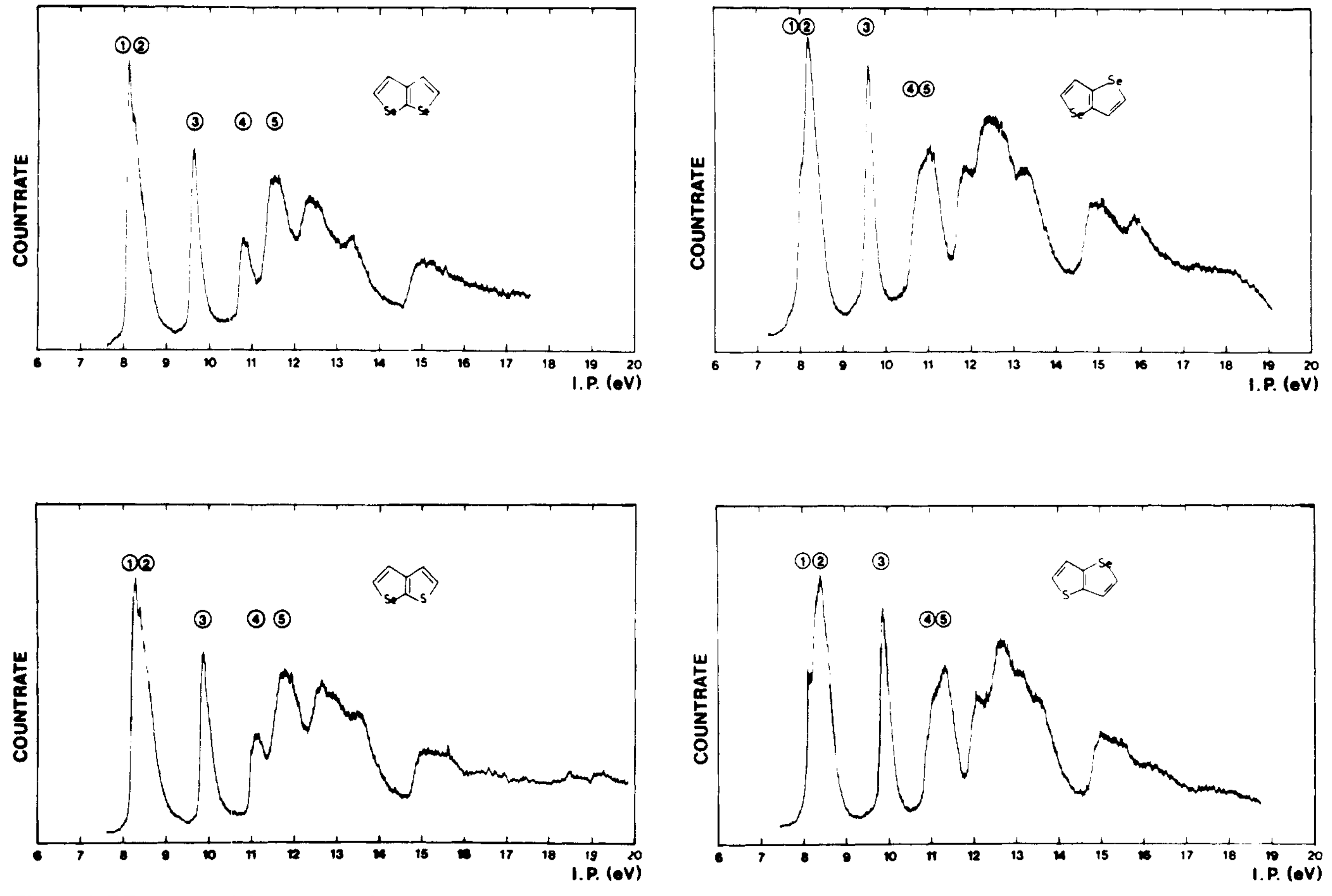


Figure 2. PE spectra of the compounds **3–6**.

Table I. Measured Vertical Ionization Potentials, $I_{V,J}$, and Orbital Energies, ϵ_J, for **1–6**. All Values in eV

Registry no.	Compd	Band	$I_{V,J}$[a]	Assignment[a]	ϵ_J (HMO)	ϵ_J (MINDO/3)[b]
250-84-0	**1** (C_{2v})	①	8.32	$4b_1$ (π)	−8.48	−8.27
		②	8.41	$3a_2$ (π)	−8.60	−8.47
		③	10.08	$3b_1$ (π)	−10.28	−9.76
		④	11.27	$2a_2$ (π)	−11.10	−11.50
23787-71-5	**3** (C_s)	①②	8.28	$8a''$ (π)	−8.32	
				$7a''$ (π)	−8.49	
		③	9.88	$6a''$ (π)	−9.87	
		④	11.12	$5a''$ (π)	−10.91	
250-85-1	**4** (C_{2v})	①②	8.16	$4a_2$ (π)	−8.16	
				$5b_1$ (π)	−8.45	
		③	9.66	$4b_1$ (π)	−9.51	
		④	10.82	$3a_2$ (π)	−10.59	
251-41-2	**2** (C_{2h})	①	8.10	$4a_u$ (π)	−8.25	−8.15
		②	8.61	$3a_u$ (π)	−8.94	−8.57
		③	10.04	$3b_g$ (π)	−10.25	−9.67
		④⑤	11.5	$2b_g$ (π)	−11.11	−11.53
				$15a_g$ (σ)		−9.33
20503-37-1	**5** (C_s)	①	8.08	$8a''$ (π)	−8.19	
		②	8.39	$7a''$ (π)	−8.61	
		③	9.86	$6a''$ (π)	−9.97	
		④⑤	11.3	$5a''$ (π)	−10.93	
				$32a'$ (σ)		
251-49-0	**6** (C_{2h})	①	8.05	$5a_u$(π)	−8.09	
		②	8.20	$4a_u$ (π)	−8.50	
		③	9.63	$4b_g$ (π)	−9.47	
		④⑤	11.1	$3b_g$ (π)	−10.84	
				$18a_g$ (σ)		

[a] The ionization potentials and assignments reported for **1** and **2** are taken from ref 14. [b] Some σ orbitals between the π orbitals have been omitted. The calculations were based on geometries derived from the experimental structure of thiophene; see ref 25.

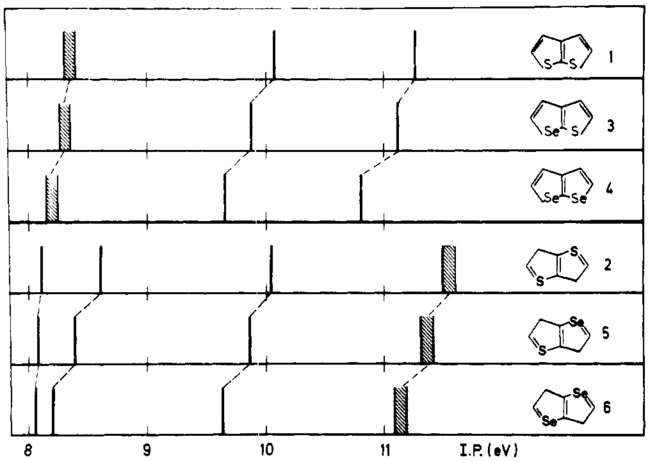


Figure 3. Correlation of the observed first four ionization potentials in the series **1–3–4** and **2–5–6**; see Table I.

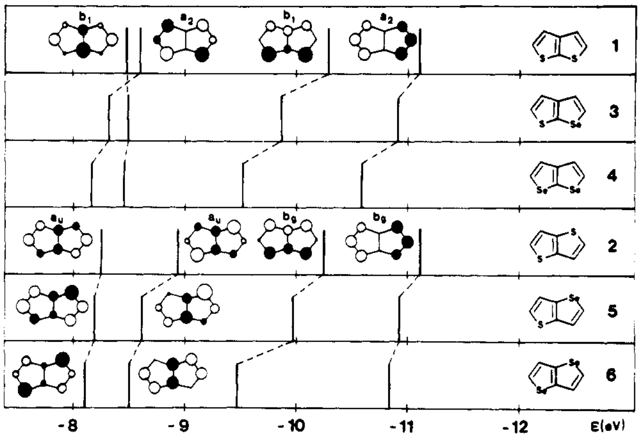
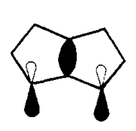


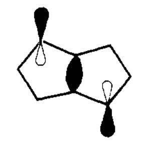
Figure 4. Correlation of the calculated energies of the four highest occupied HMO levels for the series **1–3–4** and **2–5–6**; see Table 1. The shape of the most important orbitals is indicated schematically.

2–5–6 without shifting the latter much. The shapes of the orbitals shown in Figure 4, however, indicate that the interaction is considerable, corresponding to the initial stages of an avoided crossing.

We finally briefly mention a few results regarding the highest occupied σ level in these compounds. According to the results of an extended Hückel calculation reported previously,[14] the highest occupied σ orbital in **1** and **2** transforms according to A_1 and A_g, respectively. The corresponding amplitudes are indicated schematically below.

These results are confirmed by the CNDO/2 and MINDO/3 methods, and by the results of EWMO calculations for **1–6**. The calculations predict a destabilization of the $a_g(\sigma)$ orbital relative to the $a_1(\sigma)$ orbital due to a very strong antibonding interaction between the n_+ "lone pair" combination and the central C–C σ bond in the series **2–5–6**. Our assignment of the overlapping bands ④ and ⑤ in the spectra of this series of compounds to ionization out of a π and a σ level is consistent with this result.


$a_1(\sigma)$


$a_g(\sigma)$

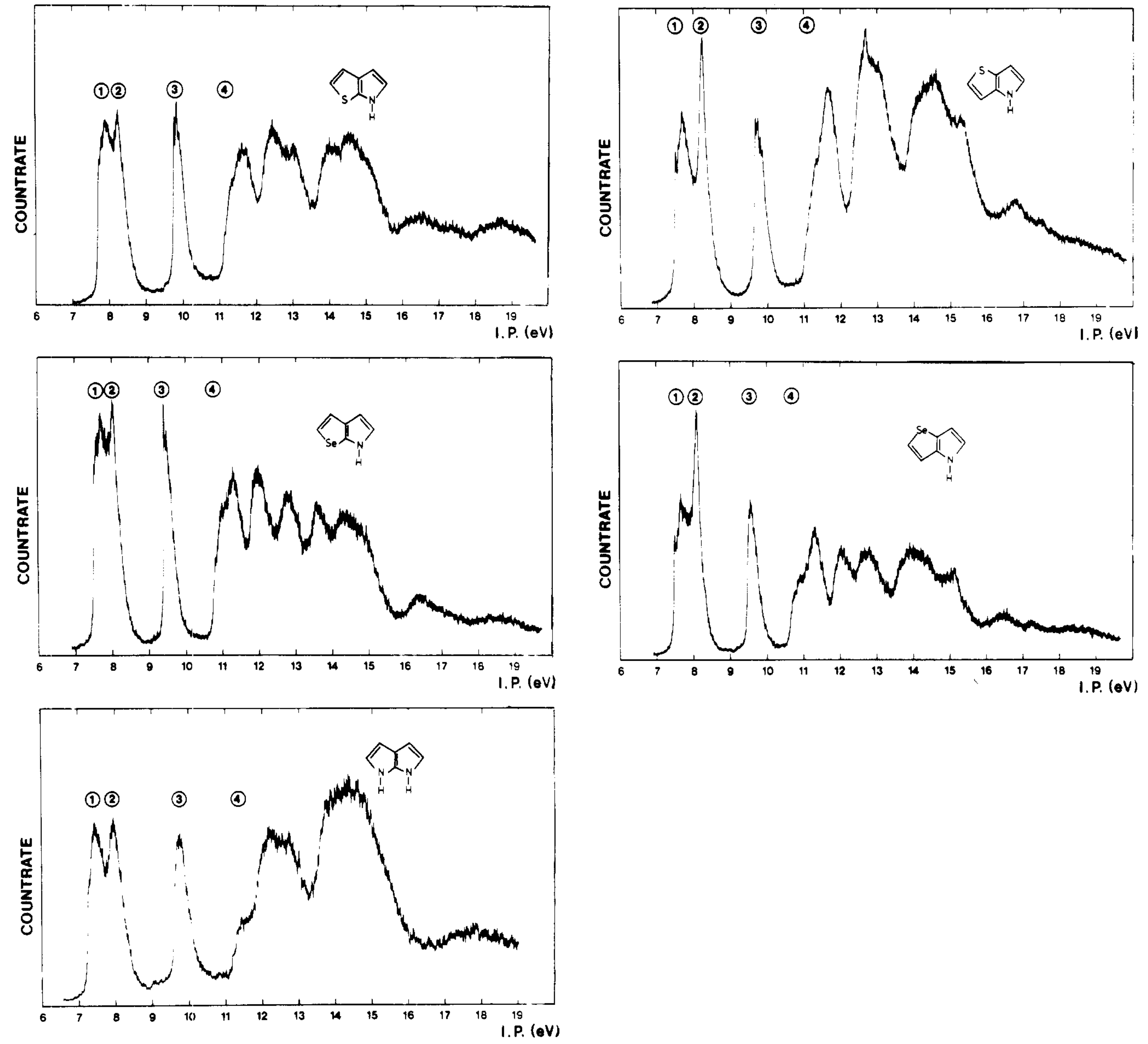


Figure 5. PE spectra of the compounds **7–11**.

II. PE Spectra of 7–11

Replacement of sulfur or selenium in the compounds **1–6** by an NH group yields the compounds **7–11**. The PE spectra of these compounds are shown in Figure 5, and the vertical ionization potentials are given in Table II. The assignment of the first broad peak in the spectra of the compounds **1–6** to two overlapping transitions (band ① and ②) is immediately supported by the comparison with the spectra of **7–11**: the peak is clearly split into two components.

Electronic Effects of the NH Group. The discussion of the PE spectra of **1–6**, was simplified by the circumstance that replacement of sulfur by selenium can be considered as a minor perturbation. Replacement of sulfur or selenium by an NH group, however, is not a small perturbation, and simple perturbation theory is no longer valid. As indicated in the introduction, this is easily seen by a comparison of the PE spectrum of pyrrole with the PE spectra of thiophene and selenophene (see Figure 1). Usual π electron theory will fail to describe this phenomenon properly, since the dominant interactions in pyrrole take place through the σ system; while the pyrrole nitrogen is a π electron donor, it is a much stronger σ electron acceptor.[23] An all-valence electron model with inclusion of electron interaction terms is appropriate for an understanding of these effects. In closed-shell SCF theory the orbital energy ϵ_J can be considered as a sum of two terms,[24]

$$\epsilon_J = H_{JJ} + \sum_{K}(2J_{JK} - K_{JK}) = H_{JJ} + G_{JJ} \qquad (2)$$

where the summation is over the occupied orbitals. The first term, H_{JJ}, represents the kinetic energy of an electron in the orbital J plus its potential energy due to the attraction by the nuclei. The second term, G_{JJ}, represents an average value of the repulsion between the electron in the orbital J and all other electrons in the molecule. The orbital energy ϵ_J is thus the sum of two large contributions with opposite sign.

Consider now the HOMO of furan, $a_2(\pi)$. This orbital is localized in the butadiene fragment with zero amplitude on the heteroatom, as mentioned before (see Figure 6). Replacing the oxygen atom by a sulfur atom or an NH group leads to an increase of H_{JJ} and a decrease of G_{JJ} for this orbital, as illustrated in the top of Figure 6 where the results of a CNDO/2 calculation are shown. This can be explained by the change of geometry taking place;[25] part of the attracting core, as well as part of the repulsing electron density, is moved away from the region of the $a_2(\pi)$ orbital. The shifts are particularly large

Table II. Measured Vertical Ionization Potentials, $I_{V,J}$, and Orbital Energies, ϵ_J, for 7–11. All Values in eV

Registry no.	Compd	Band	$I_{V,J}$	Assignment	ϵ_J (HMO)	ϵ_J (MINDO/3)[a]
250-79-3	7 (C_s)	①	7.97	$6a''(\pi)$	-7.99	
		②	8.31	$5a''(\pi)$	-8.11	
		③	9.89	$4a''(\pi)$	-10.09	
		④	11.45	$3a''(\pi)$	-11.30	
42425-03-6	8 (C_s)	①	7.74	$7a''(\pi)$	-7.89	
		②	8.09	$6a''(\pi)$	-8.04	
		③	9.48	$5a''(\pi)$	-9.53	
		④	11.13	$4a''(\pi)$	-11.16	
58326-34-4	9 (C_{2v})	①	7.46	$2a_2(\pi)$	-7.60	-7.53
		②	7.91	$3b_1(\pi)$	-7.97	-7.51
		③	9.73	$2b_1(\pi)$	-9.96	-9.61
		④	11.47	$\left\{\begin{array}{l} 1a_2(\pi) \\ 16a_1(\sigma) \end{array}\right.$	-11.33	-11.89 -10.11
250-94-2	10 (C_s)	①	7.70	$6a''(\pi)$	-7.81	
		②	8.24	$5a''(\pi)$	-8.41	
		③	9.66	$4a''(\pi)$	-9.97	
		④	11.3	$3a''(\pi)$	-11.24	
58326-29-7	11 (C_s)	①	7.67	$7a''(\pi)$	-7.77	
		②	8.10	$6a''(\pi)$	-8.22	
		③	9.60	$5a''(\pi)$	-9.66	
		④	10.95	$4a''(\pi)$	-10.88	

[a] Some σ orbitals between the π orbitals have been omitted. The geometry of **9** was derived from the experimental geometry of pyrrole; see ref 25.

in going from furan to thiophene; the decrease of G_{JJ}, however, is found to practically compensate the increase of H_{JJ}, so that the orbital energy ϵ_J stays constant; see the bottom of Figure 6. This can be observed throughout the series furan, thiophene, selenophene, and tellurophene.[6,7,26] In the case of going from furan to pyrrole the increase of H_{JJ} is found to be larger than the decrease of G_{JJ}, leading to a net destabilization of the $a_2(\pi)$ level; see Figure 6. This is a direct consequence of the high polarity of the N–H bond, which tends to increase the G_{JJ} value by increasing the electron density in the ring: ab initio Hartree–Fock calculations[22,27] show that the total excess charge on the five ring atoms is ca. 25% larger in pyrrole than in furan or thiophene. Substitution of the NH hydrogen atom by an electron-donating methyl group leads to further destabilization of the $a_2(\pi)$ level.[28,29] We may thus summarize that although the individual shifts of H_{JJ} and G_{JJ} are much larger in the case of going from furan to thiophene than in the case of going from furan to pyrrole,[30] the destabilizing and stabilizing effects tend to cancel in the first case, but not in the second case.

We then turn briefly to the second highest occupied orbital in these compounds, $b_1(\pi)$. This orbital has a high amplitude on the heteroatom and it would appear reasonable to expect that the shifts of this level can be predicted by simple perturbation theory. One would thus predict a stabilization of this level when the heteroatom is replaced by a more electronegative atom. Calculated[22,27] and observed (Figure 1) energies support this prediction in the case of going from thiophene to furan, but not in the case of going from thiophene to pyrrole. The calculations by Niessen et al.[22,27] predict essentially the same energy of this orbital in thiophene and pyrrole, and the measured binding energies show a destabilization of 0.3 eV of the level in pyrrole relative to the level in thiophene (see Figure 1); the increase in electronegativity of the heteroatom is thus not able to outweigh the destabilizing inductive effect discussed in the preceding paragraph. This is largely due to the circumstance that although nitrogen is clearly more electronegative than sulfur,[15] the effective electronegativity of the NH *group* is probably not too different from that of a sulfur atom. The nitrogen atom in pyrrole gains approximately 0.4 electron, but ca. three-quarters of that is withdrawn from the hydrogen atom bonded to it;[27] the capacity to withdraw electrons from the neighboring carbon atoms is thus strongly deactivated, and the effective electronegativity of the NH group is much less than that of the nitrogen atom.

Contrary to the two highest occupied orbitals discussed above, $a_2(\pi)$ and $b_1(\pi)$, the third and most bonding π orbital in these compounds has large C–X bond contributions, and is thus quite sensitive to the strength of this π bond as measured by the value of the resonance integral β_{CX}. In the case of going from thiophene to furan, the large stabilizing effect due to the large magnitude of β_{CO} relative to β_{CS} cooperates with the increase of electronegativity of the heteroatom to yield a very large stabilization of the third π level, ca. 3 eV.[22] When passing from thiophene to pyrrole, it turns out that the stabilizing effect due to the bond contributions dominates over the destabilizing inductive effect of the NH group, and the level is stabilized by ca. 1 eV.[22,27] In this paper, however, we deal primarily with levels related to the two first π orbitals, $a_2(\pi)$ and $b_1(\pi)$.

So far we have not considered the effects due to a possible deviation from Koopmans' approximation (1). Niessen et al.[22,27] have recently calculated "Koopmans' defects" for furan, pyrrole, thiophene, and others, by means of highly sophisticated many-body perturbation theory. They obtained very small corrections for the $a_2(\pi)$ levels, in agreement with the close correspondence between calculated ab initio orbital energies and measured ionization potentials shown in Figure 6. This means that the analysis based on (2) is valid. The corrections obtained for the inner π levels were not negligible, but the shifts of the calculated ionization potentials were in all cases well predicted by the shifts of the corresponding orbital energies. This indicates that a description of the trends in the PE spectra of these compounds in terms of MO theory is reasonable.

HMO Model. The discussion given in the preceding paragraph of this section attempts to explain why the effects of replacement of sulfur or selenium atoms in compounds like **1–6** by NH groups cannot be described by simple perturbation theory. Any reasonable model must include the large inductive

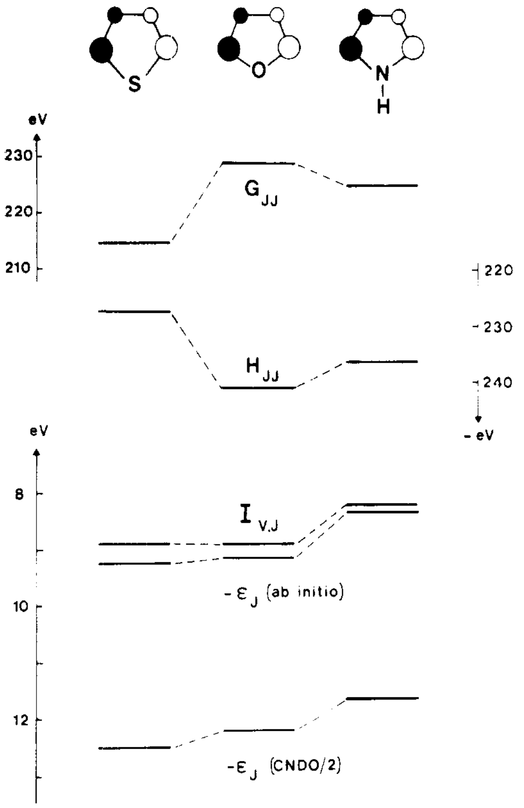


Figure 6. Top: Correlation of the calculated values of H_{JJ} and G_{JJ} (see the text) for the $a_2(\pi)$ orbitals in thiophene, furan, and pyrrole. The results were obtained by the CNDO/2 method and are based on the experimental geometries given in ref 25. Note that the values for H_{JJ} are negative. Bottom: Correlation of the measured ionization potentials $I_{V,J}$ and of the calculated orbital energies $\epsilon_J = H_{JJ} + G_{JJ}$ for the $a_2(\pi)$ levels in thiophene, furan, and pyrrole. The ab initio results are taken from ref 22 and 27; the CNDO/2 results correspond to the results mentioned above.

effect of the NH group on the carbon frame. Eland[6] has proposed a parametrization of the HMO model which leads to good agreement with the first few PE bands of pyrrole, indole, and aniline. This parametrization employs α_C values of smaller magnitude than the value −7.0 eV derived for thiophene and selenophene in the preceding section: $\alpha_C = -6.37$ eV and $\alpha_C^{adj} = \alpha_C - 0.27$ eV.[31] This is consistent with the destabilizing tendency described above (Elands's choice was not based on this argument, however; he was unable to obtain a good agreement for thiophene). The remaining parameters proposed by Eland are $\beta_{CC} = \beta_{CN} = -2.70$ eV and $\alpha_N = \alpha_C + \beta_{CC} = -9.07$ eV. It is interesting to note that this α_N value is not very different from the value −9.4 eV obtained for α_S,[21] indicating that the effective electronegativities are in fact quite similar (see also ref 5c, p 127).

We have performed a calculation using Eland's parameters on pyrrolo[2,3-*b*]pyrrole (**9**), and the results are in good agreement with experiment; see Table II.[32] We take this as an indication that the parametrization may be adequate for the series **7–11**. We apply Eland's parameters in the following way: for all atoms and bonds in a pyrrole fragment in **7–11** we use Eland's values, and in the remaining portions we keep the parameters derived in the previous section. It should be noted that the parameters lead to an underestimation of the binding energy of the third π level in the PE spectrum of pyrrole (~13.7 eV[27]); accordingly, we limit our attention primarily to the first three levels in **7–11** which are related to the first two levels in pyrrole.

Results and Discussion. The results of the calculations are listed in Table II, where also the results of a MINDO/3 calculation on **9** are included. The comparison of the observed and calculated energies shows that the HMO model, being pushed that far, is able to yield a very reasonable agreement with experiment. A correlation diagram of the first three PE bands in the series of [2,3-*b*]-fused compounds **1, 7, 9, 8,** and **4** is presented in Figure 7, and the corresponding diagram based on the HMO results is given in Figure 8. It is apparent that a number of significant trends are reproduced by the calculation, as discussed in the following. Successive replacement of sulfur atoms in **1** by NH groups to yield **7** and **9** is predicted to lead to a destabilization of the three highest occupied π levels, consistent with the destabilization of the two highest occupied π levels of pyrrole relative to the corresponding levels in thiophene. This is due primarily to the general shift toward lower binding energies introduced by the use of smaller α_C magnitudes for the pyrrole fragments. The two highest occupied near-degenerate π levels of **1** are predicted to experience very different shifts, leading to a considerable split of the levels as observed in the PE spectra (Figures 5 and 7). The a_2 level is destabilized more than the b_1 level, which means that the order is being reversed in the series **1–7–9.** A similar crossing was predicted in the series **1–3–4** (see Figure 4), although mainly for a different reason. The different shifts of the two levels are in the present case largely due to the difference in C–X bonding characteristics; the C–X bond contributions of the b_1 orbital are small and tend to cancel, while the a_2 orbital is significantly C–X antibonding. The large increase (0.90 eV) of the magnitude of β_{CN} relative to β_{CS} does thus produce a destabilization in the case of the a_2 level. Another factor contributing to the predicted splitting is the circumstance that the magnitude of the α_N value employed is actually somewhat less (0.34 eV) than the magnitude of α_S; this destabilizes the a_2 level relative to the b_1 level due to the large difference in amplitude on the heteroatoms; see Figures 4 and 8. The results of the MINDO/3 calculations listed in the tables also correspond to a larger destabilization of the a_2 level than of the b_1 level, although the difference is small. We thus tend to assign the ordering of these levels as indicated in Figures 7 and 8 and in Table II.

The fourth and fifth π levels are significantly C–X bonding, and a stabilization of these levels due to the increase of the magnitude of β_{CN} relative to β_{CS} is predicted to dominate over the destabilizing effects. As mentioned above, the predicted stabilization of these levels is expected to be underestimated as in the case of the third π level of pyrrole. The shifts of band ④ in the PE spectra are nevertheless quite accurately predicted by the shifts of the calculated fourth π level; see the tables. We consider it likely that this π level is involved in the ionization process corresponding to band ④, probably overlapping the onset of the σ levels.

The results for the series **4–8–9** can be understood in similar terms as the results for the series **1–7–9.** The increase of the magnitude of β_{CN} relative to β_{CSe} is very large (1.30 eV) and the increase of the magnitude of α_N relative to α_{Se} is also considerable (0.57 eV). This means that a domination of the stabilizing contributions is predicted already for the third π level; see Figure 8. The observed shifts of this level are not monotonic, however; see Figure 7. Successive replacement of the selenium atoms in **4** by NH groups to yield **8** and **9** shifts band ③ in the PE spectrum first toward lower, then toward higher binding energies, yielding a small overall shift toward higher binding energies. Such a behavior is hinted by the calculated results, and can be explained by a large distortion of the third π orbital in **8** which introduces a C–N antibonding contribution; see Figure 8.

Concluding Remarks

The results of the simple model not only describe a number of qualitative trends, but are also in satisfactory numerical

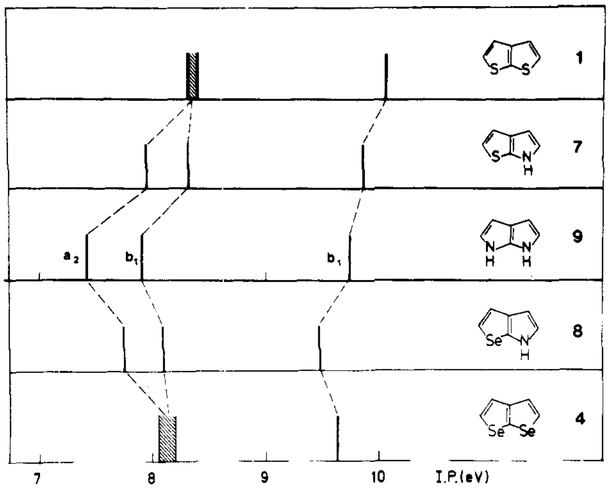


Figure 7. Correlation of the observed first three ionization potentials in the series 1–7–9–8–4; see the tables.

agreement with the PE data. This is illustrated by the linear regression of the measured ionization potentials on the calculated orbital energies for all the compounds 1–11; see Figure 9 (the linear regression coefficient is 0.993 and the standard deviation is 0.158 eV). The overall satisfactory performance of the model invites further confidence in the basic concepts behind it.

We may thus conclude that a description of the effects of the heterogroup NH relative to heteroatoms from group VI requires specific attention to the interactions taking place in the σ electron system. In particular, the large polarity of the N–H bond tends to increase the electron density on the ring atoms, implying a large destabilizing inductive effect on the carbon atom frame and a large reduction of the effective electronegativity of the NH group compared with the nitrogen atom. These effects can be described in terms of simple MO theory, which yields a good agreement with the PE data for the series 1–11. It appears that little evidence for these effects can be found from a study of electronic absorption spectra, since the influence on the excited states is similar to the influence on the ground state; this is indicated by the result that calculations with no representation of the effects described above give reasonable excitation energies.[33] We wish furthermore to point out that no direct conclusions regarding the "aromaticity" or "reactivity" of these compounds should be drawn from the present results, since these questions are probably much too complex to be meaningfully discussed in terms of one-electron properties.[34]

III. Experimental Section

The compounds 3–11 were prepared according to the prescriptions in the literature.[8–13]

The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) equipped with a heated probe. In the case of 9 the sample was heated to 105 °C; in the remaining cases the temperature was close to 30 °C. The spectra were calibrated with argon, and a resolution of about 20 meV on the argon line was obtained. Each spectrum was recorded several times to ensure the reproducibility of the results.

Calculations. The HMO[5] calculations were carried out on a Hewlett-Packard 9800-30 computer. The parameters applied are discussed in detail in the paper. The EWMO,[17,18] CNDO/2,[19] and MINDO/3[20] calculations were performed on the IBM 370/168 computer at the computing center of the TH Darmstadt, using double precision versions of computer programs published by QCPE, Indiana University. The standard parameters inherent in the programs were employed.[18–20]

For the calculations on furan, pyrrole, and thiophene the geometries determined by microwave spectroscopy[25] were employed. In case of the compounds 1–11 the geometries were estimated from the experimental geometries of thiophene,[25] selenophene,[35] and pyrrole[25] by simple fusion of the constituent rings. For the "mixed" compounds 3, 5, 7, 8, 10, and 11 the length of the central C–C bond was taken as 1.37 Å.

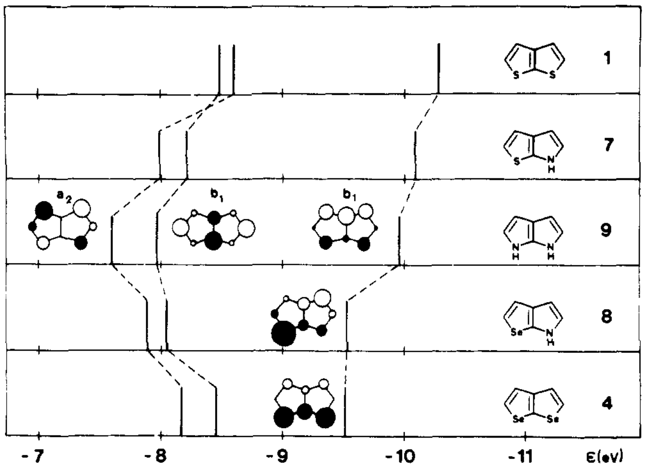


Figure 8. Correlation of the calculated energies of the three highest occupied HMO levels for the series 1–7–9–8–4; see the tables. The shape of the important orbitals is indicated schematically.

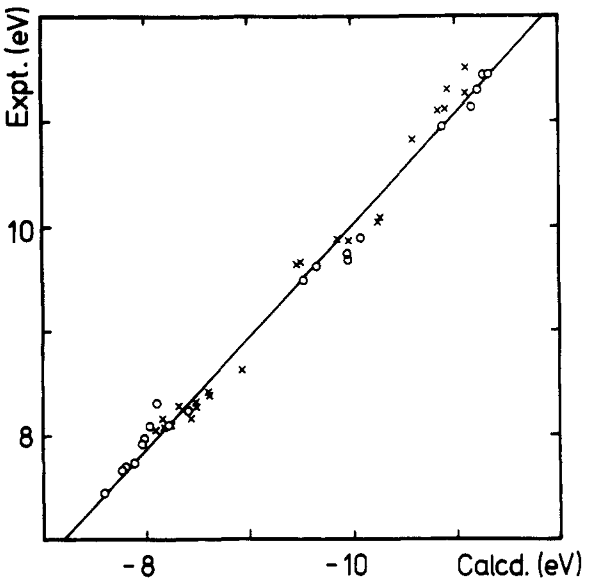


Figure 9. Linear regression of the experimental ionization potentials on the calculated HMO orbital energies for the compounds 1–11; see the tables. The crosses correspond to the compounds 1–6, and circles correspond to the NH containing species 7–11.

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Registry No.—Furan, 110-00-9; pyrrole, 109-97-7; thiophene, 110-02-1; selenophene, 288-05-1.

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Novel Aromatic Systems. 9.[1a] Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of the Heteroaromatic 6π 1,3-Dioxolium (Dithiolium) and 10π Benzo-1,3-dioxolium (Dithiolium) Ions

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The 6π heteroaromatic character of protonated (HSO_3F–SbF_5–SO_2) and methylated (CH_3F–SbF_5–SO_2) vinylene carbonate (**1a**) and its trithio analogue (**1b**) is investigated by ^{1}H and ^{13}C NMR spectroscopy. The 10π heteroaromatic character of the benzo derivative of **1a** in addition to the parent 1,3-benzodioxolium ion (**4**) and 1,3-benzodithiolium ion (**5**) has also been studied.

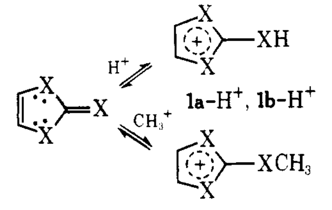
Aromatic character has been frequently attributed to molecules in which lone pair electrons on heteroatoms enter into conjugation with unsaturated bonds forming stable Hückel-type aromatic systems.[2] Heterocyclic compounds containing oxygen and sulfur represented by the 1,3-dioxolium and 1,3-dithiolium ions (as well as parent compounds) should, as 6π-electron systems, be quite stable. Few examples of substituted 1,3-dioxolium cations[3] have been reported in contrast to extensive reports concerning the 1,3-dithiolium salts.[4] The reactivity and electronic spectra of "pseudoaromatic" sulfur compounds have been studied using simple MO–LCAO methods.[5] We therefore thought it of interest to examine the ionic systems resulting from protonation and methylation of vinylene carbonate (**1a**) and 1,3-dithia-2-thione (**1b**). In addition, we have extended our studies to include 10π electron systems, 2-hydroxy-1,3-benzodioxolium ion (**2**-H$^+$), the parent 1,3-benzodioxolium ion (**4**), and 1,3-benzodithiolium ion (**5**).

Results and Discussion

Protonated and methylated ions, respectively, were prepared from their corresponding precursors with the general methods developed previously.[6a,b] ^{1}H and ^{13}C NMR data, for the precursors and the ions studied, are summarized in Tables I and II, respectively.

6π Heteroaromatic Ions. Stable ions result from protonation (**1a**-H$^+$, **1b**-H$^+$) using FSO_3H–SbF_5–SO_2 solution and, methylation (**1a**-CH_3^+) using CH_3F–SbF_5 "complex" in SO_2 solution at −60 °C. Methylated ion (**1b**-CH_3^+) was studied as the stable iodide salt[7] in SO_2 solution. Methylation of **1b** with CH_3F–SbF_5 "complex" in SO_2 solution resulted in, as yet, unidentifiable species in the ^{1}H NMR spectrum.

1a, X = O
1b, X = S



1a-H$^+$, **1b**-H$^+$

1a-CH_3^+, **1b**-CH_3^+

We consider the carbon-13 chemical shifts of ring carbons to be quite informative concerning trends of charge delocalization since extensive evidence has resulted indicating the sensitivity of charge and ^{13}C NMR shifts.[8] The assignment of resonances was made by the now familiar procedure of Grant and co-workers.[9,10] When needed, "off-resonance" proton decoupled spectra were obtained to assure correct peak assignments.

Vinylene carbonate (**1a**) in 1:1 M/M FSO_3H–SbF_5 in SO_2 solution was found to be protonated on the carbonyl oxygen. The ^{1}H NMR spectrum at −60 °C consisted of two peaks, one at δ 8.2 ppm of relative area 2, and one at δ 13.2 ppm of area 1. In addition, the olefinic protons are deshielded by 1.3 ppm