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The Electronic Structure of Heterotropones. Photoelectron Spectra and Molecular Orbital Calculations

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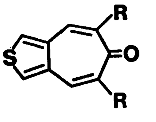
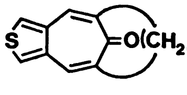
Using a helium discharge lamp with an energy of 21.21 eV (He(I)$_\alpha$ line) the photoelectron (PE) spectra of the heterotropones **1**—**7** have been investigated and compared with the PE spectra of benzologue tropones and with the PE data of thiophene, furan and pyrrole. The first five ionization events in the PE spectra of **1** to **7** could be assigned to electron ejections from $2a_2(\pi)$, $4b_1(\pi)$, $9b_2(n)$, $3b_1(\pi)$, and $1a_2(\pi)$ orbitals. This assignment has been deduced by means of experimental correlation techniques and using ZDO calculations of the LCBO and HMO type as well as semiempirical SCF versions (MINDO/3 and PPP).

The photoelectron (PE) spectra of tropone, benzotropone, naphthotropone and related alkylderivatives have been investigated by several groups[1–3] using an open helium discharge lamp with an energy of 21.21 eV (He(I)$_\alpha$ line). Although the variations due to alkyl substitution and due to hydrocarbon annelation have been studied in great detail,[1] informations concerning the effect of hetero atoms are sparse.

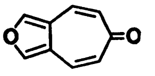
Therefore we felt it of interest to investigate the PE spectra of tropone derivatives with variable hetero fragments. The investigated systems are collected below:



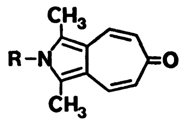
1 R=H
2 R=CH$_3$



3 n=5
4 n=6



5



6 R=H
7 R=CH$_3$

The measured vertical ionization potentials are compared with results of semiempirical MO calculations.

The PE Spectra of Thiophene-fused Propones 1 to 4

The He(I) PE spectra of 6*H*-cyclohepta[*c*]thiophen-6-one (**1**), 5,7-pentamethylene-6*H*-cyclohepta[*c*]thiophen-6-one (**3**), 5,7-hexamethylene-6*H*-cyclohepta[*c*]-thiophen-6-one (**4**), 6*H*-cyclohepta[*c*]furan-6-one (**5**), 1,3-dimethyl-2*H*,6*H*-cyclohepta[*c*]pyrrol-6-one (**6**), and 1,2,3-trimethyl-6*H*-cyclohepta[*c*]pyrrol-6-one (**7**) are shown in Fig. 1 and the measured vertical ionization potentials, $I_{v,j}$, of the first PE bands of **1** to **4** collected in Tables 1 and 2. For the assignment of these data we assume the validity of Koopmans' theorem.[4]

$$I_{v,j} = -\varepsilon_j \qquad (1)$$

This approximation relates the vertical ionization potentials to the one-electron energies of canonical molecular orbitals derived for the electronic ground state.

The PE spectrum of **1** shows below 12 eV two band systems with strongly overlapping ionization events. The first peak with approximate maxima at 8.62, 8.77, and 9.09 eV is assigned to three ionization events (bands 1 to 3) while the two maxima at 10.68 and 10.84 eV should correspond to two transitions. This assignment is supported by the comparison with the PE spectra of the alkyl derivatives **2**, **3**, and **4**. In the case of **2** and **3** the alkyl groups yield a definite separation of the first peak into three separated bands. The two latter molecules additionally provide evidence that the second peak between 10 and 11 eV is the result of two transitions (bands 4 and 5) as the small

Table 1. Comparison between measured ionization potentials $I_{v,j}$ and calculated orbital energies of **1**. All values in eV

Band	$I_{v,j}$	Assignment[a)]	LCBO A	LCBO B	MINDO/3[b)]	PPP
1	8.62	$2a_2(\pi)$	−8.36	−8.47	−8.68	−9.42
2	8.77	$4b_1(\pi)$	−8.16	−8.75	−8.98	−8.97
3	9.07	$9b_2(n)$			−9.65	
4	10.68	$3b_1(\pi)$	−9.99	−10.59	−10.88	−11.23
5	10.84	$1a_2(\pi)$	−11.29	−11.02	−11.33	−11.76

a) The orbital numbering corresponds to the valence electrons; the core orbitals are neglected. b) Some σ orbitals between the π levels have been omitted.

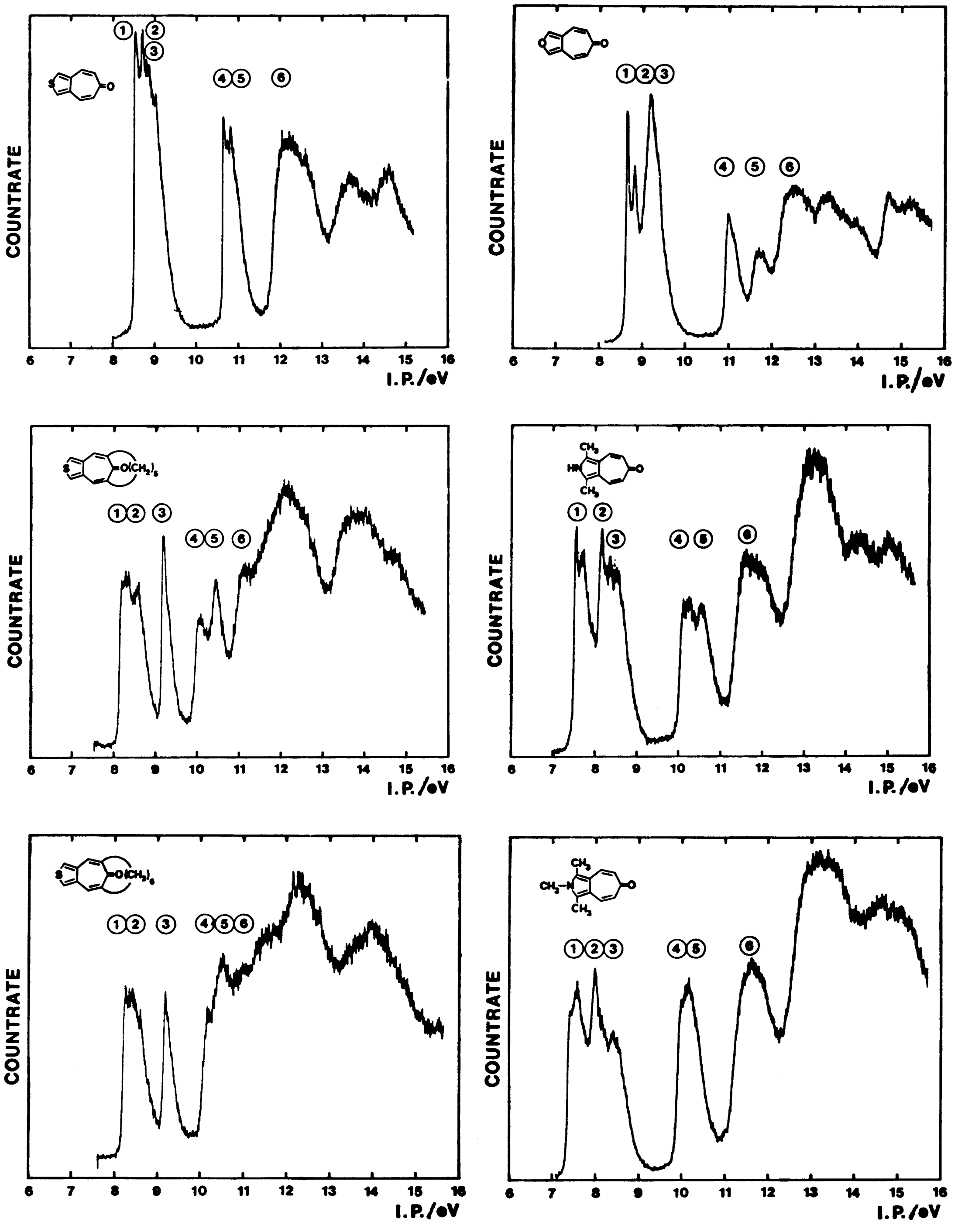


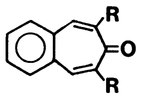
Fig. 1. He(I) PE spectra of **1**, and **3**—**7**.

TABLE 2. VERTICAL IONIZATION POTENTIALS IN THE THIOPHENE SERIES **1**, **2**, **3**, AND **4** FOR THE FIRST FIVE IONIZATION EVENTS. THE IRREDUCIBLE REPRESENTATIONS CORRESPOND TO THE UNSUBSTITUTED MOLECULE **1**. ALL VALUES IN eV

Peak	Assignment	**1**	**2**	**3**	**4**
1	$2a_2(\pi)$	8.62	8.40	8.25	8.22
2	$4b_1(\pi)$	8.77	8.59	8.57	8.38
3	$9b_2(n)$	9.07	9.09	9.15	9.14
4	$3b_1(\pi)$	10.68	10.48	10.01	10.11
5	$1a_2(\pi)$	10.84	10.61	10.43	10.48

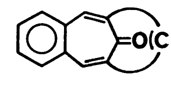
gap of 0.16 eV in **1** is increased to 0.38 and 0.37 eV in **3** and **4**.

The PE spectra of the four thiopheno-tropones are similar to the PE data obtained for benzotropones with the corresponding substituents (**8** to **11**) as counterparts of **1** to **4**.[1)]



8 R=H

9 R=CH_3



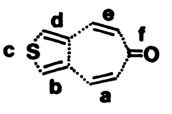
10 n=5

11 n=6

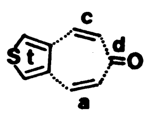
This close resemblence, at least for the first band system is not surprising since the first ionization events in **8** to **11** correspond to MO's predominantly localized in the seven-membered ring. The replacement of one double bond by a sulfur will not cause large variations in the IP's as the electronegativities of carbon and sulfur are of comparable size.[5] The difference between the two types of tropones is caused by the inclusion of a 3p-orbital on the sulfur center only. As a result of this restriction all coefficients in the a_2 orbitals are set to 0 in the hetero position as shown below.

The pairwise analogy between **1**/**8**, **2**/**9**, **3**/**10**, and **4**/**11** suggests that two bands of the first peak are the result of ionization events out of π orbitals (b_1 and a_2) while the third one is due to the lone pair of the carbonyl group.[1-3] The correspondence between the second band system with two strongly overlapping maxima leads to the assumption that the π-orbitals of b_1 and a_2 symmetry lead to these peaks. To assign the ionization events in the sulfur derivatives explicitly we discuss the sequence of the π-orbitals in the unsubstituted molecule **1** in some detail.

a) ZDO Models: To derive the orbital energies of the π MO's of **1** we make use of the linear combination of bonding orbitals (LCBO)[6] successfully applied in the benzologue tropone series by Heilbronner *et al.*[1] Two alternatives for the construction of the molecular orbitals of **1** are displayed below:



A



B

In the case of **A** the MO's are constructed from bonding orbitals of C=C and C=O double bond fragments and from the sulfur 3p AO. In the alternative model we couple the orbitals of the thiophene moiety to the remaining bonding fragments. To calculate the orbital energies in the zero differential overlap (ZDO) model we have to estimate the energies of the basis orbitals in **A** and **B**.

For the complete fragmentation scheme **A** one has to know the diagonal elements $A_a=A_e$, $A_b=A_d$, A_f and A_c as well as the interaction parameters $B_{ab}=B_{ed}$, $B_{ef}=B_{af}$, $B_{bc}=B_{dc}$, and B_{bd} respectively. For the fragments of the tropone unit we use the parameters derived by Heilbronner *et al.*:[1]

$$A_a = A_e = -10.64\,\text{eV},$$
$$A_f = -13.70\,\text{eV},$$
$$B_{af} = B_{ef} = -0.9\,\text{eV}.$$

For the double bonds b and d of the thiophene moiety we neglect the inductive effect of the carbonyl group, an approximation which should be allowed due to the remarkable separation between b and d and the carbonyl chromophore. As the electronegativity of C and S are of comparable magnitude we neglect this influence too. These simplifications lead to a basis orbital energy of $A_b=A_d=-10.22$ eV.[1] From our previous experience with thiophene derivatives we choose the following S dependent parameters:[7] $A_c=-9.4$ eV and $B_{bc}=B_{dc}=-1.8$ eV. The interaction integrals that couple the thiophene moiety to the triene fragment once again were taken from Ref. 1 $B_{ab}=B_{ed}=-1.215$ eV. The same value also has been used in the case of B_{bd}.

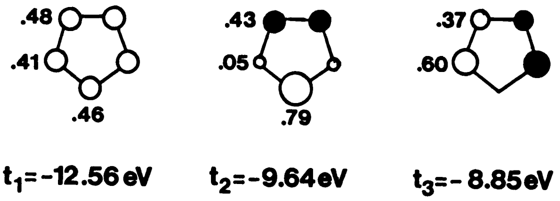


Fig. 2. HMO levels for thiophene.

In the case of **B** one has to determine the LCAO coefficients and the orbital energies of the thiophene fragment, t, which are then coupled to the basis orbital energies and resonance integrals of a, b, and c, the values of which already have been explained. The basis energies for thiophene are taken from experiment:[8] $A_s=-9.4$ eV, $A_c=-7.0$ eV, $B_{cc}=-3.0$ eV, and $B_{cs}=-1.8$ eV. The MO wave functions obtained by the Hückel (HMO) model[9] are displayed in Fig. 2. With these LCAO coefficients it is possible to calculate the B parameters of the second LCBO alternative. The new interaction integrals for the LCBO approach **B** are listed below:

$$B_{at_1} = B_{ct_1} = -0.8188\,\text{eV},$$
$$B_{at_2} = B_{ct_2} = -0.7374\,\text{eV},$$
$$B_{at_3} = -0.6388\,\text{eV}, \qquad B_{ct_3} = +0.6388\,\text{eV}.$$

Solving the secular determinants for the two LCBO models **A** and **B** described above yields the eigenvalues for the π orbital energies given in Table 1. It is seen that both sets are in line with the measured ionization energies. A closer look into the corresponding columns, however, demonstrated that model **B** leads to the better agreement in comparison with the experiment. Thus a more realistic description of the orbitals of **1** is obtained if the thiophene orbitals are coupled to the remaining bonding fragments.

*b) Semiempirical MO Calculations on **1***: To support the assignment based on the LCBO model we also performed semiempirical calculations using the MINDO/3 method[10] and the PPP-Hamiltonian.[12,13] The results of both approaches are included in Table 1. In the case of the PPP model the canonical orbital energies were corrected according to Eq. 2:[14]

$$\varepsilon_j = 0.168\,\text{eV} + 0.932 \times \varepsilon_j^{\text{PPP}} \qquad (2)$$

This linear dependence has been obtained earlier and is based on a regression analysis on several thiophene derivatives. The agreement between the measured IP's and the semiempirical calculations is as good as can reasonably be expected. Both types confirm the assignment derived within the LCBO framework and experimentally deduced from the benzologue tropone.

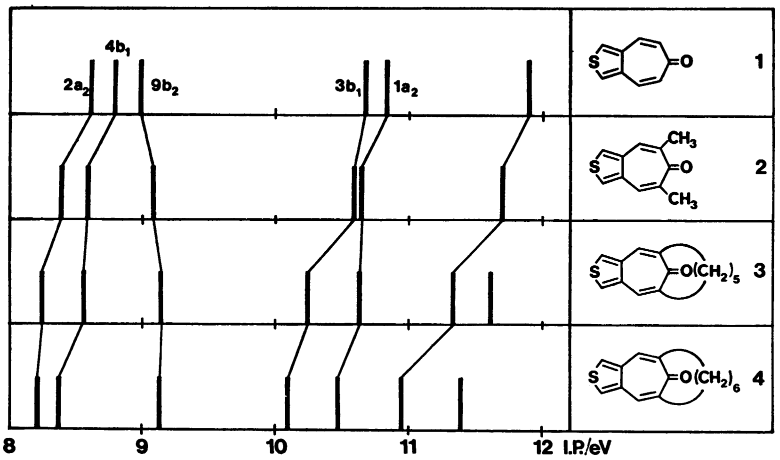


Fig. 3. Correlation between the first bands in the PE spectra of **1**, **2**, **3**, and **4**.

Table 3. Comparison between measured ionization potentials, $I_{v,j}$, and calculated orbital energies of **5**, **6**, and **7**. All values in eV

Compd	Peak	$I_{v,j}$	Assignment[a]	LCBO **B**	HMO	MINDO/3[b]	PPP
	1	8.65	$2a_2(\pi)$	−8.68	−8.78	−8.50	−9.86
5	2	9.17	$4b_1(\pi)$	−8.82	−8.96	−9.26	−9.18
	3		$9b_2(n)$			−9.60	
	4	10.98	$1a_2(\pi)$	−11.03	−10.68	−11.23	−11.99
	5	11.70	$3b_1(\pi)$	−11.50	−11.74	−11.86	−12.20
[c]	1	7.55	$2a_2(\pi)$	−7.07	−7.75[d]	−8.14	−9.04[d]
	2	8.16	$4b_1(\pi)$	−7.87	−8.65	−8.57	−8.98
6	3	8.50	$9b_2(n)$			−9.33	
	4	10.21	$3b_1(\pi)$	−10.73	−10.75	−10.93	−11.68
	5	10.56	$1a_2(\pi)$	−10.85	−10.38	−10.90	−11.66
[c]	1	7.59	$2a_2(\pi)$		−7.75[d]	−8.11	−8.82
	2	8.01	$4b_1(\pi)$		−8.55	−8.43	−8.91
7	3	8.44	$9b_2(n)$			−9.30	
	4	10.14	$3b_1(\pi)$		−10.32	−10.66	−11.45
	5		$1a_2(\pi)$		−10.38	−10.87	−11.60

a) The orbital numbering corresponds to the valence electron configuration; the core orbitals are neglected. b) Some σ orbitals between the π levels have been omitted. c) The MO's of the methyl substituents have been neglected in the numbering of the irreducible representations. d) Results obtained by simple perturbation theory (formula 3).

In Table 2 and Fig. 3 we have correlated the different ionization potentials in the thiophene series **1** to **4**.

In analogy to the benzotropones **9** and **10** a remarkable separation between $4b_1$ and $9b_2$ is found for n= 5 and 6. This observation has been rationalized by the fact that for n=5/6 the carbonyl group is strongly bent out of the molecular plane and behaves as a predominantly unconjugated fragment.[1] This PE spectroscopic finding is in line with the results of various physicochemical investigations.[1]

The PE Spectra of 5, 6, and 7

The He(I) PE spectra of the furan derivative **5** and the two pyrrole descendents **6** and **7** are also shown in Fig. 1. The measured vertical ionization potentials are collected in Table 3 together with the results of the already discussed computational procedures. As the LCBO approach **B** gave better results only this model has been used in the case of **5**, **6**, and **7**. Additionally simple HMO results[9] are added in Table 3.

To rationalize the variation of the IP's in **5**, **6**, and **7** in comparison to **1** it is constructive to discuss the shift of the two highest occupied MO's in the series furan, pyrrole and thiophene.[8,15] A schematical representation is given in Fig. 4. A detailed explanation for the observed variations and the unexpected changes in pyrrole have been discussed elsewhere.[8] If we rely on the validity of Koopmans' theorem in the case of the tropone derivatives, we expect for the first two bands of **1** ($2a_2$, $4b_1$) a similar shift by replacing the sulfur atom by oxygen or NR as for the first two bands in the series thiophene, furane and pyrrole. According to Fig. 4 the $2a_2$ MO of the heterotropones should be constant if **1** and **5** are considered and shifted to higher energies if $2a_2$ of **1** is correlated with $2a_2$ of

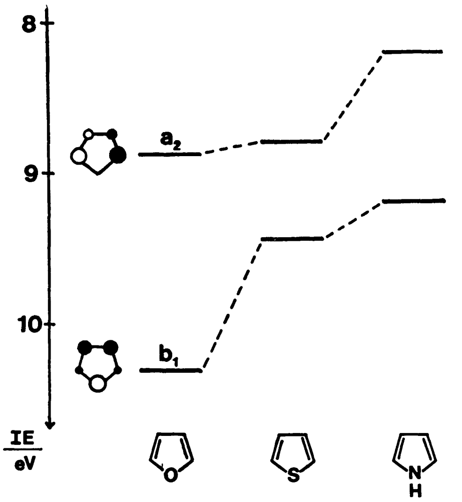
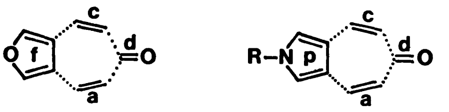


Fig. 4. Correlation of the two lowest ionization energies of furan, thiophene and pyrrole.

the pyrrole derivatives **6** and **7**. For the $4b_1$ MO one expects a stabilization going from **1** to the furane molecule **5** and a lowering if **1** is compared with **6** and **7**. These expectations are fulfilled as displayed in the correlation diagram of Fig. 5. For the comparison of the measured IP's of **5**, **6**, and **7** we follow the lines of the foregoing paragraph.

a) ZDO Models: For **5** and **6** we performed LCBO calculations of the type **B**. HMO data of the furane



B

moiety were chosen to fit the experimental IP's of furan.[16] With the following parameters ($A_0=-11.0$ eV, $A_c=-7.3$ eV, $A_{c'}=-7.0$ eV, all interaction integrals -3 eV) an almost perfect agreement between HMO energies and measured data is observed:

	$I_{v,j}$	ε_j^{HMO}/eV
$1a_2$	8.88	9.07
$2b_1$	10.31	10.31
$1b_1$	14.40	14.48

The MO coefficients obtained with this approximation are collected in Fig. 6a. The calculation of the unknown interaction integrals in **5** then is straightforward and not explicitly performed in this context. Inspection of the LCBO results in Table 3 demonstrates that the measured ionization energies are reproduced with high accuracy. Also the HMO results on the right hand of the LCBO calculations lead to a satisfactorical description of the ionization energies. The HMO parameters were taken from the literature.[17]

The pyrrole basis orbital energies were calculated with HMO parameters close to Eland's values:[17] $A_{NH}=-9.61$ eV, $A_c=-6.64$ eV, $A_{c'}=-6.37$ eV, all interaction integrals are set to -2.70 eV. The HMO energies are compared below with the measured ionization potentials of pyrrole:[18]

	$I_{v,j}$	ε_j^{HMO}/eV
$1a_2$	8.21	8.24
$2b_1$	9.20	9.24
$1b_1$	13.0	12.93

The HMO wave functions for the LCBO model are given in Fig. 6b. The calculated orbital energies for **6** confirm the qualitative assignment. Furthermore it is seen that also the HMO calculations with the parameters of Ref. 7 are in good agreement with the measured ionization energies. The inductive effect of the methyl groups in **6** and **7** has been taken into account by the simple first order perturbation theory:[9]

$$\delta\varepsilon_j = \sum_{\mu} c_{j\mu}^2 \delta\alpha_\mu + \sum_{\omega} c_{j\omega}^2 \delta\alpha_\mu / 3. \qquad (3)$$

For the perturbation parameter $\delta\alpha_\mu$ a value of 1.16 eV has been used. The indices ω refer to the position ortho to μ.

*b) Semiempirical MO Calculations on **5**, **6**, and **7***: The results of the semiempirical calculations of the MINDO/3 and PPP type in Table 3 suggest for all three heterotropones **5**, **6**, and **7** the same orbital sequence as in the thiophene derivative **1**. The variation of $2a_2$ and $4b_1$ upon changes of the hetero fragment have already been commended on. It is seen that MINDO/3 leads to the better agreement with the measured data while the PPP model fails to reproduce the sequence $2a_2$ on top of $4b_1$ in the case of **5** and **6**.

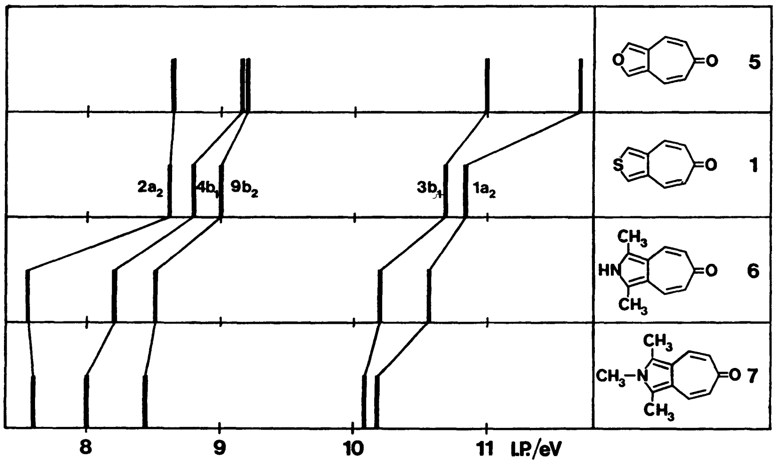


Fig. 5. Correlation between the first bands in the PE spectra of **1**, **5**, **6**, and **7**.

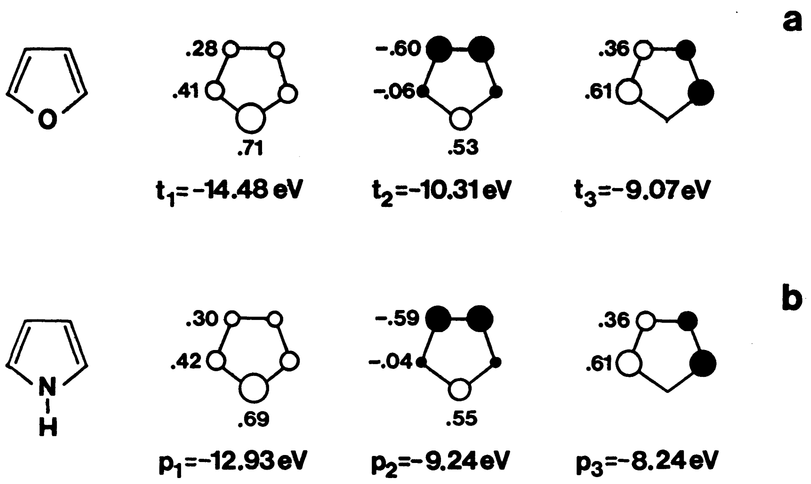


Fig. 6. HMO levels for furan (**a**) and pyrrole (**b**).

Conclusions

In the present publication we have investigated the He(I) PE spectra of seven heterotropones containing sulfur, oxygen and nitrogen as hetero fragment. The sequence of the ionization potentials has been derived by experimental correlation techniques and by simple LCBO considerations based on the validity of Koopmans' theorem. Although it has been demonstrated that ionization events in heterocycles are accompanied by significant reorganization effects of the electrons[19,20] that can be taken into account by sophisticated many-body procedures, our approach is as successful as the LCBO calculation of Heilbronner *et al.*[1] in the benzologue tropones. The comparison between the PE spectra of **1**/**2** with thiophene, of **5** with furane and **6**/**7** with pyrrole lead to an unambigous assignment of the ionization potentials of the tropone derivatives. It has been demonstrated that the variation of the hetero group leads to significant changes in the magnitude of the IP's but the sequence is constant in all investigated compounds.

The investigation of the PE spectra of the tropones **1** to **7** allowed a rationalization of the changes in the electronic structure of these molecules upon variation of the hetero fragment. However, it should be noted that no direct conclusions regarding the "aromaticity" or "reactivity" of these compounds should be drawn from these results.

Experimental

The heterotropones **1** to **5** were prepared according to methods described in the literature.[21] The PE spectra were recorded on a PS 18 spectrometer of Perkin-Elmer Ltd. (Beaconsfield, England) and calibrated with Ar. A resolution of about 20 meV of the Ar line was obtained.

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