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A Simple Theoretical Molecular Orbital Model for Five-Membered Heterocycles

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Abstract: A one-electron MO approach is utilized to discuss the physical properties of heteroaromatic five-membered rings (C_4H_4X). The observed changes in geometry, resonance energy, and PE spectra as X is varied are adequately rationalized. The question of d-orbital participation when X is a second period element is discussed. In most cases, it is found that d-orbital participation is not necessary for the qualitative rationalization of trends, although its presence cannot be excluded. The electrophilic substitution patterns in these molecules as well as their benzo derivatives are discussed along the same lines.

The physical and chemical properties of C_4H_4X heteroaromatic five-membered rings change dramatically as the heteroatom X is changed from a first row element to a second row element.^{2a} It has been suggested that participation of empty, low-lying d orbitals in the case of the second row element can account for the observed differences. Longuet-Higgins has utilized a molecular orbital (MO) model including d orbitals in order to rationalize the difference between thiophene and furan.³ However, dramatic changes are also noted as the heteroatom is changed from an element in one column of the periodic table to an element of the adjacent column but same row.^{2b} Obviously, these changes cannot be explained by invoking d-orbital participation. In this paper, we wish to present a one-electron MO (OEMO) approach with neglect of overlap that is capable of explaining the differences observed in five-membered ring heteroaromatic compounds. In particular, we wish to compare the chemical and physical properties of furan and thiophene, a case where the heteroatom is changed from one row to another, and to make the analogous comparison between furan and pyrrole, a case where the heteroatom is changed from one column to another. The approach should only be used when comparing heteroaromatics that are similar, e.g., furan vs. thiophene and furan vs. pyrrole, but not pyrrole vs. thiophene.

The model consists of the π MO's of butadiene interacting with the heteroatom lone pair atomic orbital (AO). The typical interaction diagram (for furan) is shown in Figure 1. We have labeled the orbitals as symmetric (S) or antisymmetric (A) with respect to a mirror plane that bisects the five-membered

ring. The interaction between the lowest filled MO of the butadiene fragment and the p_z AO of X results in neither stabilization nor destabilization, since overlap has been neglected. Consequently, the primary interaction of interest is between the lowest unfilled MO (LUMO) of the butadiene fragment and the p_z AO of the heteroatom. This interaction results in net stabilization given by the expression⁴

$$SE = H_{ij}^2/\Delta\epsilon \quad (1)$$

where SE is the stabilization energy, H_{ij} is the off-diagonal matrix element of the interacting MO's, i.e., $\int \phi_i H \phi_j d\tau$, and $\Delta\epsilon$ is the difference between the unperturbed energies of the interacting MO's. The matrix element will be approximated in the usual manner, that is,⁵

$$H_{ij} = kS_{ij} \quad (2)$$

where S_{ij} is the overlap integral between ϕ_i and ϕ_j and k is a constant. The stabilization energy is then

$$SE = k^2 S_{ij}^2/\Delta\epsilon \quad (3)$$

Using this simple model we shall now investigate the chemical and physical differences between furan and thiophene and between furan and pyrrole.

Ground-State Geometries

The ground-state geometries of furan,⁶ thiophene,⁷ and pyrrole⁸ are shown below. The C(1)-C(2) bond length in furan is considerably shorter than in thiophene or pyrrole. Likewise,

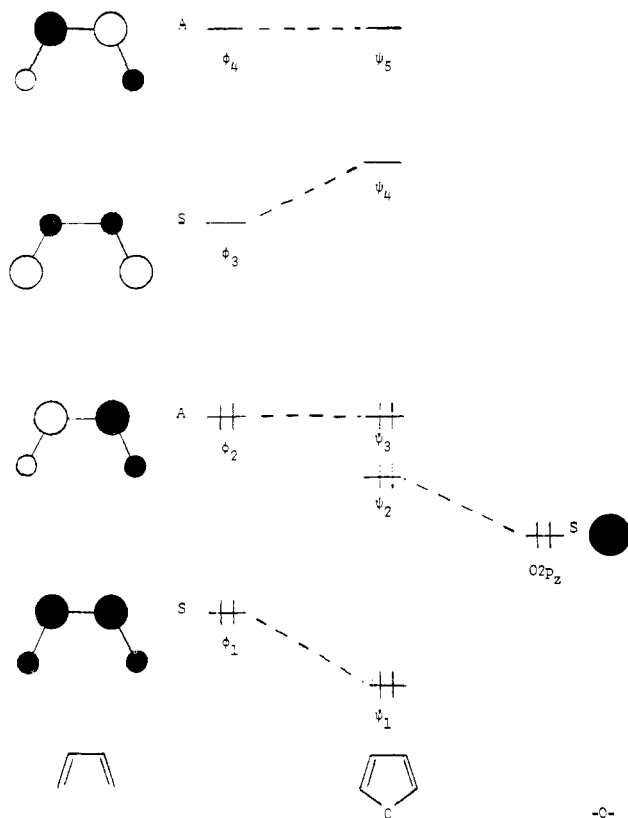


Figure 1. The interaction diagram for furan.

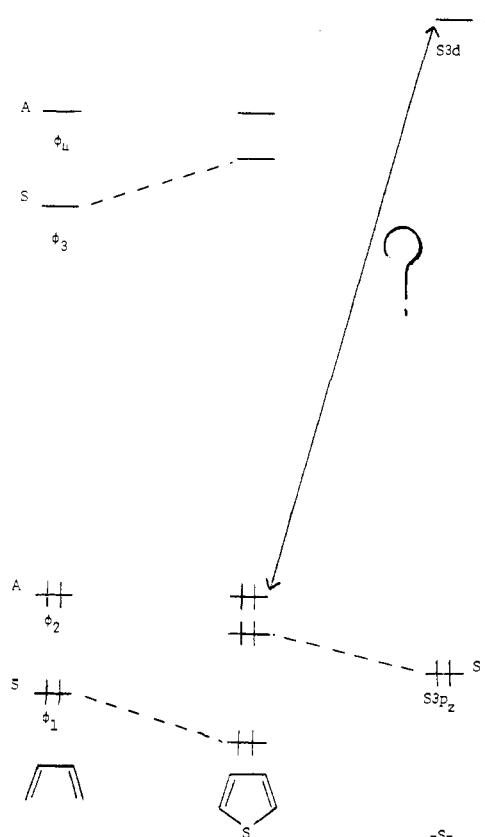
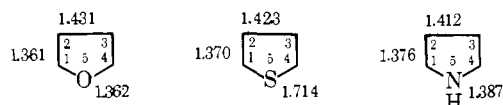


Figure 2. The interaction diagram for thiophene.



the C(2)-C(3) bond length in furan is considerably longer than in thiophene or pyrrole. We shall focus our attention on the two-electron stabilizing interaction between ϕ_3 of the butadiene fragment and the p_z lone pair AO of the heteroatom. As mentioned, this interaction is directly proportional to the square of the matrix element and inversely proportional to the energy separation of the interacting orbitals. Typical ionization potentials of several -OH, -SH and -NH₂ containing molecules are shown below.

H ₂ O	12.61 ⁹	CH ₃ OH	10.83 ⁹
H ₂ S	10.42 ⁹	CH ₃ SH	9.44 ¹⁰
H ₃ N	10.16 ⁹	CH ₃ NH ₂	9.18 ¹¹

From these results we may conclude that the denominator in eq 3 will be greater for furan than for thiophene or pyrrole. That is, just considering the energy factor, we expect the interaction between the LUMO of the butadiene fragment and the p_z AO of the heteroatom to be greater for thiophene or pyrrole than for furan.

The expression for the overlap integrals between ϕ_3 of the butadiene fragment and the Xp_z AO is given below.

$$\langle \phi_3 | Xp_z \rangle = \langle c_1 p_{1z} + c_2 p_{2z} + c_3 p_{3z} + c_4 p_{4z} | Xp_z \rangle$$

By symmetry, $c_1 = c_4$ and $c_2 = c_3$, so

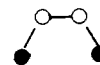
$$\langle \phi_3 | Xp_z \rangle = 2 \langle Xp_z | c_1 p_{1z} + c_2 p_{2z} \rangle = 2 [c_1 \langle Xp_z | p_{1z} \rangle + c_2 \langle Xp_z | p_{2z} \rangle]$$

The values for the π overlap integrals over AO's calculated by standard procedures are listed below.^{12,13}

	X:	O	S	N
Overlap integral: ($\langle \phi_3 Xp_z \rangle$)		0.1611	0.1756	0.2007

It can be seen that the overlap factor slightly favors a stronger interaction between the sulfur p_z AO and the butadiene fragment than between the oxygen p_z AO and the butadiene fragment. The same is true when comparing the N case to the O case, but here the magnitude of the difference is somewhat larger.

In conclusion, the interaction between ϕ_3 of the butadiene fragment and the p_z AO of the heteroatom is predicted to be greater in thiophene and pyrrole than in furan. In other words, the numerator and denominator of eq 3 vary in the same direction. This interaction results in charge transfer into the ϕ_3 unoccupied MO which is depicted below. As charge is trans-



ferred into this MO, the bond order between C(1)-C(2) decreases, while at the same time the C(2)-C(3) bond order increases. Consequently, as this interaction increases on going from furan to thiophene or pyrrole, the C(1)-C(2) bond length is expected to increase and the C(2)-C(3) bond length is expected to decrease. Indeed, this is what is observed experimentally.

The geometric changes from furan to thiophene can also be explained on the basis of the interaction between ϕ_2 of the butadiene fragment and the empty 3d levels of the sulfur atom, as is shown in the interaction diagram for thiophene (Figure 2). If one assumes this interaction to be negligible in furan but not in thiophene, then the charge transfer from the HOMO of the butadiene fragment to the 3d AO's on sulfur leads to electron density removal from the bonding C(1)-C(2) region and this results in a lengthening of this bond. There is also a reduction of the antibonding density in the C(2)-C(3) bond, leading to a shortening of this bond.

The ϕ_2 -3d interaction represents in MO terms what is called "3d-orbital participation", and its effects on the bond lengths

Table I. Calculated Stabilization Energy and Resonance Energy of Furan, Pyrrole, and Thiophene

X	SE	Resonance energy, kcal/mol		
		I ^a	II ^b	III ^c
O	0.0721	23	22	16
N	0.1338	31	24.5	21
S	0.1112	31	28	29

^a L. Pauling "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960. ^b G. W. Wheland, "Resonance in Organic Chemistry", Wiley, New York, N.Y., 1955. ^c F. Klagan, *Chem. Ber.*, **82**, 358 (1949).

of the ring just parallel those caused by the interaction between the LUMO of the butadiene fragment and the p_z AO of X, as discussed before. Therefore, it would appear that from a *qualitative* point of view it is not necessary to invoke 3d-orbital participation to explain the geometric differences between furan and thiophene.

Resonance Energy

The difference in the resonance energies of furan and thiophene or furan and pyrrole can be explained along the same lines. Specifically, the stabilization energy upon union of the heteroatom X and the diene fragment reflects the corresponding resonance stabilization of the molecule. As we have seen, the major stabilizing interaction involves the lone pair of the heteroatom and the LUMO of the diene. This stabilizing interaction is greater when X is sulfur or nitrogen than when it is oxygen due mainly to the energy separation of the interacting levels. Using energy differences ($\Delta\epsilon$) and overlap integrals which were obtained from CNDO/2¹³ calculations, we can evaluate the stabilization energies by way of eq 3. These calculated stabilization energies are shown in Table I. Also shown in Table I are the resonance energies for the three heterocycles obtained from various methods. It can be seen from this tabulation that the trends observed in the experimental resonance energies agree well with the trends of the calculated stabilization energies.

The increased resonance energy of thiophene relative to furan can also be rationalized by invoking d-level participation. As shown in Figure 2, the HOMO of the diene fragment can mix with the empty d levels on the sulfur atom. This additional stabilization will consequently increase the resonance energy of thiophene relative to that of furan. However, as seen before, it would appear that it is not necessary to invoke 3d-orbital participation to explain qualitatively the difference in resonance energy between furan and thiophene.

Photoelectron Spectra

The photoelectron spectra of the three heterocycles afford the energies of the two highest filled π MO's.¹⁴ These are shown in Table II. The ionization potential of the lowest filled π MO cannot be obtained by this method at the present due to the intermingling of bands corresponding to ionization from the higher filled σ MO's.¹⁵ The HOMO in these molecules (i.e., ψ_3) is essentially the ϕ_2 MO of the butadiene fragment. Since this MO cannot mix with the lone pair AO on the heteroatom, its ionization potential is not expected to change much on going from one of these heteroatoms to another. However, if d-level participation is important, this MO will be depressed in thiophene relative to furan, since it can mix with the empty d orbitals.

As can be seen from the PES data, the ionization potential of the HOMO's of thiophene and furan differ by only 0.03 eV, a result arguing against d-orbital participation. Also, it should

Table II. Ionization Potentials^a for the π MO's of Furan, Thiophene, and Pyrrole

	Furan		Thiophene		Pyrrole	
	$E(\psi_2)$	$E(\psi_3)$	$E(\psi_2)$	$E(\psi_3)$	$E(\psi_2)$	$E(\psi_3)$
Photoelectron spectroscopy ^b (PES)	10.32	8.90	9.49	8.87	9.16	8.20
Electron impact ^c (EI)	8.99		9.12			

^a In eV. ^b Reference 14. ^c Reference 18.

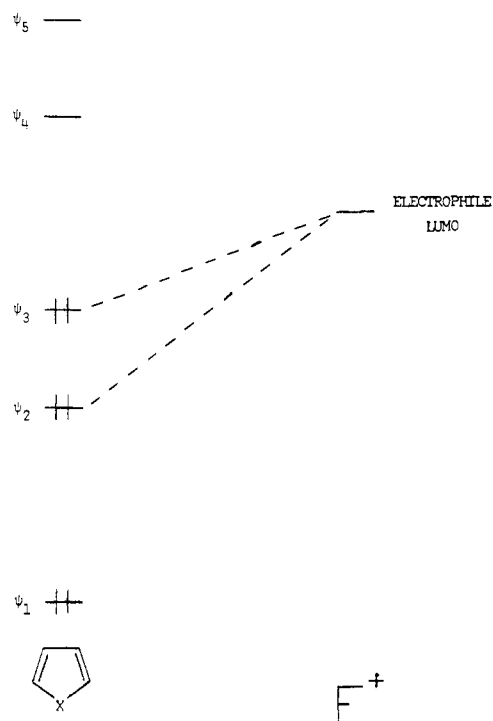


Figure 3. The frontier orbital interactions for electrophilic substitution on heteroaromatic compounds.

be mentioned that the band at 8.87 eV in the thiophene spectrum has recently been securely identified as being derived from the ϕ_2 MO of the butadiene fragment by an analysis of the vibrational fine structure.¹⁶ The raising of the HOMO of pyrrole relative to furan cannot be explained by our one-electron approach. The difference could be due to a two-electron effect, since furan and pyrrole are not completely analogous.¹⁷

The ionization potentials for the HOMO's of furan and thiophene have also been determined by electron impact studies.¹⁸ These results are also shown in Table II. From these data, it seems d-orbital participation is indeed important, since the HOMO of thiophene is depressed by 0.13 eV relative to furan. Thus, the experimentally determined ionization potentials of these molecules give conflicting results about the importance of d-level participation.

Chemical Reactivity

The positional selectivity observed in electrophilic attack on these heterocycles can be explained using the same simple approach. The pertinent orbital interactions are shown in Figure 3. According to frontier orbital theory,¹⁹ the position of attack in electrophilic substitution is determined by the magnitude of the HOMO electron density of each atomic center. This arises because the major contribution to the sta-

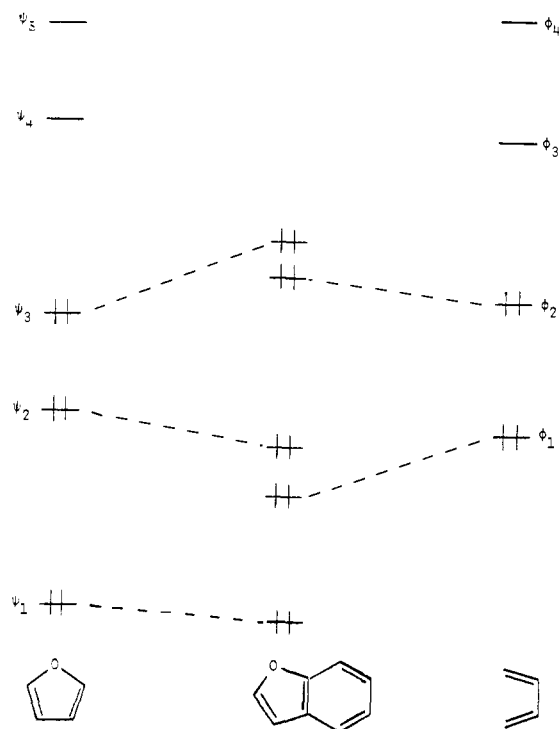


Figure 4. The interaction diagram for benzofuran; only the dominant orbital interactions are shown.

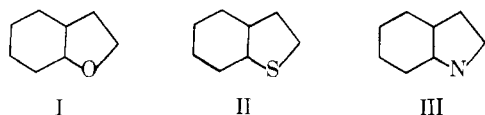
bilization energy of the transition state is due to the interaction of the HOMO of the substrate and the LUMO of the electrophile. It is thus predicted that C(1) in the heterocycles under consideration will be more reactive than C(2) because $C_{31}^2 > C_{32}^2$. Now, as the energy of ψ_2 approaches that of the ψ_3 , the stabilization energy of the transition state will reflect an increasing contribution of the $\psi_2-\chi_1$ interaction (where χ_1 is the LUMO of the electrophile). When the energy of ψ_2 becomes equal to that of ψ_3 , the stabilization energy of the transition state arises to an equal extent from the $\psi_2-\chi_1$ and $\psi_3-\chi_1$ interactions. At this limit ($X = C^\ominus$) the sum of the square of the coefficients of C(1) in ψ_2 and ψ_3 will equal the sum of the square of the coefficients of C(2) in ψ_2 and ψ_3 , and it is predicted that positions 1 and 2 will be equally reactive.

The experimentally determined energy gaps between these two higher filled π MO's and the ratios for electrophilic substitution at position 1 (the α position) relative to position 2 (the β position) are shown below.

X	$\Delta E (E(\psi_3) - E(\psi_2))^{14}$	$(\alpha:\beta)^2$
O	1.42	>1000
N	0.96	6
S	0.62	71.4

It can be seen that the trend in the ratio of $\alpha:\beta$ follows the trend in ΔE .

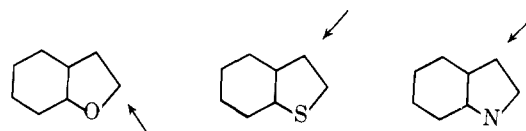
An interesting extension of this reasoning is provided by comparing the electrophilic substitution patterns of benzofuran (I), benzothiophene (II), and indole (III). The π MO's of these



molecules can be formed by the interaction of the appropriate heterocycle with *cis*-butadiene, as is shown in Figure 4. The important interactions to consider are between ϕ_2 and ϕ_1 of the butadiene fragment with ψ_2 and ψ_3 of the heterocycle, respectively. Now the HOMO of the benzoheterocycles will be determined by the extent of mixing of ψ_3 with ϕ_1 and ψ_2 with

ϕ_2 . If the strongest interaction is between ψ_3 and ϕ_1 , the HOMO will be $\psi_3-\lambda\phi_1$, and electrophilic substitution will occur mainly at position 2. However, as the energy of ψ_2 approaches that of ϕ_2 (which is approximately degenerate with ψ_3), this interaction becomes important and the HOMO will be of the type $\psi_2-\lambda\phi_2$, and electrophilic substitution should occur mainly at position 1. Thus, if the two MO's (ψ_2, ψ_3) are energetically close in the unperturbed heterocycle, the interaction with the diene fragment would tend to reverse the relative ordering in the benzo derivative.

The preferred position of electrophilic attack in these molecules is shown below.^{2b} Clearly, the position of electrophilic



attack changes as the energies of ψ_2 and ψ_3 become closer, as predicted by our model.

It should be emphasized that the comparative analysis of thiophene and furan is only suggestive. Specifically, OEMO theory can rationalize the differences in the properties of furan and thiophene without invoking d-orbital participation if interaction matrix elements are approximated by eq 2. However, other approximations lead to different conclusions. Accordingly, we can suggest, but not prove, that one-electron effects (s, p basis set) are at work in producing the aforementioned differences. Similarly, different d orbital parametrizations are possible which may emphasize or deemphasize their contribution. The final result is that no direct proof can be offered as to whether one-electron (s, p basis set) or d-orbital effects are primarily responsible for the observed differences between thiophene and furan. Rather, we can suggest an interpretation which does not involve d-orbital participation may well be reasonable.

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$$IP = -\epsilon_i = -(h_i + J_{ij} - 2K_{ij})$$

Here h_i is the one-electron contribution to the energy. Most likely, our approach, which involves an effective one-electron Hamiltonian, reproduces trends predominantly in h_i . The other two terms on the right side of the above equation are the two-electron contribution to the total energy. While these terms are expected to vary only by a small amount when comparing analogous systems, they may vary more drastically as the differences of the systems increases.

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