Studies on the Conjugated Double Bond Systems. VIII. On the Electronic Structures of Furan, Pyrrole and Thiophen

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Introduction

Recently, remarkable advances have been made in the theoretical study on the electronic structures of unsaturated hydrocarbons containing conjugated double bonds. In particular, the electronic structures of benzene and other relatively simple molecules have been investigated in detail. Under these circumstances, therefore, the study on the electronic structure of hetero-cyclic compounds may be regarded not only as desirable from the stand-point of the theory of resonance, but also as necessary for the progress of the electronic theory of organic chemistry.

The first quantum mechanical treatment on hetero-cyclic compounds was made, probably, by Wheland and Pauling,[1] who used the molecular orbital method. It was, however, no more than merely making a guess at the π-electron distributions in the molecule which, apparently agreed with experimental facts on the condition that their assumed constant of electron affinity for the hetero-atom and of induced affinity for the adjacent atoms was suitable. Longuett-Higgins and Coulson[2] applied the same method to many hetero-cyclic compounds containing nitrogen, under some original assumptions about coulomb integrals. The method of Orgel *et al.*[3] which was applied to many hetero-cyclic molecules was essentially identical with that of Longuett-Higgins and Coulson. They calculated the values for dipole moment and compared them with the experimental results.

In the present paper, the molecular orbital method has been employed in the investigation of electronic structures of furan, pyrrole and thiophene under suitable assumptions about coulomb- and exchange-integrals. The results have been used for discussiug resonance energies, dipole moments and near ultraviolet absorption spectra of these substances.

Outline of Method

In our treatment of furan, pyrrole and thiophene, we assume that they are all planar, and consider five $p\pi$ orbitals and six electrons, including an unshared pair on the hetero-atom. With the approximation of LCAO, the wave functions of molecular orbitals are as follows:

$$\Psi_j = C_{1j}\varphi_1 + C_{2j}\varphi_2 + C_{3j}\varphi_3 + C_{4j}\varphi_4 + C_{5j}\varphi_5 \quad (j=1,2,\ldots 5) \qquad (1)$$

(1) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(2) H. C. Longuett-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

(3) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *ibid.* **47**, 113 (1951).

where φ_1 is the $2p\pi$ or $3p\pi$ wave function of the hetero-atom, O, N or S, respectively, and $\varphi_2 \sim \varphi_5$ are the $2p\pi$ wave functions of the carbon atoms numbered as in Fig. 1. Assuming that φ_ts are all

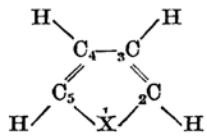

Fig. 1.

normalized and mutually orthogonal, we reach to the following equation by the usual variation method:

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & H_{14} & H_{15} \\ H_{21} & H_{22}-E & H_{23} & H_{24} & H_{25} \\ H_{31} & H_{32} & H_{33}-E & H_{34} & H_{35} \\ H_{41} & H_{42} & H_{43} & H_{44}-E & H_{45} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55}-E \end{vmatrix} = 0 \qquad (2)$$

where E is the energy of the molecular orbital Ψ_j, and $H_{rs}=\int \varphi_r H \varphi_s d\tau$.

Since these molecules belong to the symmetry group C_{2v}, the equation (2) is reduced to the following form

$$\begin{vmatrix} \alpha_1-E & \sqrt{2}\beta_1 & \sqrt{2}\beta_1' & 0 & 0 \\ \sqrt{2}\beta_1 & \alpha_2+\beta'_3-E & \beta_2+\beta_2' & 0 & 0 \\ \sqrt{2}\beta_1' & \beta_2+\beta_2' & \alpha_3+\beta'_3-E & 0 & 0 \\ 0 & 0 & 0 & \alpha_2-\beta_3'-E & \beta_2-\beta_2' \\ 0 & 0 & 0 & \beta_2-\beta_2' & \alpha_3-\beta_3-E \end{vmatrix} = 0 \qquad (3)$$

where following notations have been used, considering the symmetry of these molecules,

$$H_{11}=\alpha_1, \quad H_{22}=H_{55}=\alpha_2, \quad H_{33}=H_{44}=\alpha_3$$
$$H_{12}=H_{15}=\beta_1, \quad H_{23}=H_{45}=\beta_2, \quad H_{34}=\beta_3$$
$$H_{13}=H_{14}=\beta'_1, \quad H_{24}=H_{35}=\beta'_2, \quad H_{25}=\beta'_3.$$

That is, β_t $(t=1, 2, 3)$ is the exchange integral between adjacent atoms, and β_t' $(t=1, 2, 3)$ is the exchange integral between non-adjacent atoms. β_t' used to be neglected so far, but we will not neglect it, because in the penta-cyclic compounds, $|\beta_t'|$ is relatively large, owing to the smaller atomic distances compared with that of benzene. To make this point clear we have made calculations with and without neglecting β_t' in the case of furane and the results of two calculations have been compared with each other. (The method neglecting β_t' is named the first method, and the one including it, the second.)

These integrals are all represented with β[4], using the following approximations:

(a) the coulomb integral of the carbon atom in benzene is $4.1\,\beta$.[5]

(b) the coulomb integral of each atom is proportional to the electronegativity,[5] for which Pauling's values[6] have been adopted.

(c) the exchange integral is proportional to the overlap integral between two atoms.[7]

We have calculated the overlap integral with the aid of the table of Mulliken *et al.*[8] and the values of the atomic distances determined by Schomaker and Pauling.[9]

Under these assumptions, eigen values E_j $(j=1, 2, \ldots, 5$, numbered from the lowest level to the upper level) are evaluated and then C_{rj}s are determined for each value of E. With these values of C_{rj}s we can readily calculate the π-electron density q_r of r-atom by the following equation[1]

$$q_r = 2\sum_{j=1}^{3} C_{rj}^2$$

Now, it is possible to evaluate the formal charge of r-atom which is caused by π-electron migration from hetero- to carbon-atom. Owing to this formal charge, the correction term for the electronegativity and the overlap integral should be taken into consideration. We have obtained the correction for electronegativity according to Pauling,[10] and by the use of this corrected value the coulomb integral can be recalculated by the application of the above approximation (b). New values of overlap integrals are obtained from the tables of Mulliken *et al.*[8] and β_t's and β_t''s can be recalculated by the approximation (c). Using these values of the integrals, the equation (3) is resolved and q_rs are found.

These calculations are repeated several times until the final results are self-consistent.

Results and Discussion

In Table 1 are given our final values of energy integrals, energy levels and π-electron densities in the normal state.

Resonance Energy:—From the preceding results, we have calculated the resonance energy by the use of the following formula:

$$2(E_1+E_2+E_3)-2(\alpha_1+\alpha_2+\alpha_3+2\beta_2)$$

where α_1, α_2, α_3, and β_2 are the initial values of coulomb- and exchange integrals, *i. e.* the values

(4) β is the exchange integral between adjacent atoms of benzene.

(5) C. Sandorfy, *Bull. soc. chem. France*, (1949), 615.

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, (1940) p. 64.

(7) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(8) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(9) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

(10) L. Pauling, "The Nature of the Chemical Bond" Cornell University Press, (1940) p. 65.

Table 1[a]

Values of Various Energy Integrals, Energy Levels and π-electron Densities.

	Furan (The First Method)	Furan (The Second Method)	Pyrrole (The Second Method)	Thiophene (The Second Method)
α_1	5.811	5.796	5.062	4.327
α_2	4.092	4.080	4.069	4.046
α_3	4.074	4.092	4.061	4.040
β_1	0.575	0.576	0.718	0.674
β_2	1.077	1.076	1.085	1.096
β_3	0.900	0.892	0.936	0.945
β_1'	—	0.086	0.116	0.147
β_2'	—	0.197	0.201	0.177
β_3'	—	0.193	0.204	0.130
E_1	6.304 (A_1)	6.515 (A_1)	6.429 (A_1)	6.221 (A_1)
E_2	5.383 (A_1)	5.364 (A_1)	4.876 (A_1)	4.512 (B_1)
E_3	4.804 (B_1)	4.488 (B_1)	4.453 (B_1)	4.360 (A_1)
E_4	3.190 (A_1)	3.174 (A_1)	3.026 (A_1)	2.908 (A_1)
E_5	2.462 (B_1)	2.599 (B_1)	2.536 (B_1)	2.499 (B_1)
q_1	1.869	1.896	1.745	1.578
q_2, q_5	1.011	1.036	1.060	1.100
q_3, q_4	1.055	1.016	1.068	1.111

a) In this Table, the energy values are represented in units of β.

obtained without the consideration of the resonance of π-electrons. The results are given in Table 2 together with the observed values[9] [11] which are obtained from the heat of combustion or hydrogenation. By a glance at the table, it is seen that the observed values themselves are different from each other. However, the following values may be regarded as the most probable: the resonance energy of thiophene, *i. e. ca.* 30 kcal./mol, and the difference between the resonance energy of furan and of pyrrole, *i. e. ca.* 8 kcal./mol, which was deduced by Schomaker and Pauling[9] considering the resonance energies of many derivatives of furan and pyrrole. If these values are reliable, it is evident that the calculated values of these two quantities agree with the observed ones. In general, however, the calculated values are smaller than the observed, except in the case of the first method on furan. In addition, there is a serious difficulty in thiophene which requires a further discussion. It will be mentioned in the following section.

Dipole Moment:—The so called resonance moment which is caused by the migration of π-electron from the hetero-atom to the carbon atoms, *i. e.* μ_{mig}, can be calculated from the formal charges of the atoms and the atomic distances. The results are given in Table 3 together with the values which were determined by Schomaker and Pauling[9] using the observed values of dipole moments of these molecules and their tetrahydro-derivatives. As for pyrrole, however, they stated that it seemed to be impossible to make a reliable estimate for resonance moments on account of uncertainty regarding the orientation of the N-H bond in pyrrole and pyrrolidine, and further that various methods of making the calculation gave values lying between 1.0 and 2.5 D, 1.5 D being the most probable value.

Table 2

Resonance Energy (kcal./mol)

		Furan	Pyrrole	Thiophene
Calculated Values[a]	1st Method	17.6	—	—
	2nd Method	11.6	20.0	26.2
Observed Values	Schomaker and Pauling[9]	23	31	(31)
	Wheland (from heat of combustion)[11]	24	24	29
	Wheland (from heat of hydrogenation)[11]	17.2	—	—

(*a*) It is assumed that β is equal to -20 kcal./mol

Table 3

μ_{mig} (D)

	Furan	Pyrrole	Thiophene
Calculated Values: 1st Method	1.21	—	—
Calculated Values: 2nd Method	0.62	1.33	2.50
Estimated Values by Schomaker and Pauling[9]	0.95	*ca.* 1.5	1.25

If, μ_{mig} of pyrrole is calculated by the rule of vector addition using the bond moments 1.3 and 0.4 D for N-H and N-C bond,[9] respectively and assuming that pyrrole is planar, it will be found that μ_{mig} is about 1.0 D. Anyhow, in the case of pyrrole, the calculated value may be considered to be reasonable. Though the calculated value for furan by the first method is larger and by the second is smaller than the value estimated by Schomaker and Pauling, the discrepancies are not serious. On the contrary, in the case of thiophene, the calculated value is very large compared with that estimated by them. This disagreement seems to be due to the fact that the non-bonding electrons of sulphur have been represented only by the $p\pi$ wave function in our calculation. Longuett-Higgins[12] treated this molecule theoretically using the hybridisation functions of $3p\pi$ and $3d$ wave functions as those of the non-bonding electrons of sulphur atom.

Bond Order:—The bond order between neighbouring atoms r and s is defined[13] as

$$p_{rs} = 2 \sum_j C_{rj} C_{sj}$$

(11) G. W. Wheland, "The Theory of Resonance" John Wiley and Sons, New York (1947), Chapter III.

(12) H. C. Longuett-Higgins and C. A. Coulson, *Trans. Farad. Soc.*, **43**, 83 (1947).

(13) C. A. Coulson, *Proc. Roy. Soc.* (London), **A 169**, 413 (1939).

where the summation is extended over all occupied molecular orbitals. Calculated bond orders of present molecules are given in Table 4.

Table 4

Calculated Values of Bond Orders

	Furan	Furan	Pyrrole	Thiophene
	(The First Method)	(The Second Method)		
p_{12}	0.30	0.26	0.41	0.50
p_{23}	0.87	0.91	0.85	0.79
p_{34}	0.45	0.38	0.45	0.52

The difference between p_{12}, p_{23} and p_4 in the same molecule tends to decrease in the order of furan, pyrrole and thiophene. The result seems to be in agreement with the order of aromaticity of these molecules.(14)

Transition Energy and Near Ultraviolet Absorption Spectrum: — When the transition energies are calculated assuming that the electronic transition from E_3 to E_4 corresponds to the absorption spectra of the longest wave length and $\beta = 2.84$ e.V.,(15) it is found that they are 3.7, 4.0 and 4.1 e.V. in furan, pyrrole and thiophene, respectively. It is difficult to compare them with observed values, because we can not find reliable experimental data, but it seems that these values correspond to the absorption spectra,(16) 2650-2480 A. (4.6-4.9 e.V.), 2880-2540 A. (4.3-4.8 e.V.) and 2522-2246 A. (4.9-5.5 e.V.), respectively.

(14) The above mentioned view, however, is somewhat obscure owing to the following two reasons. Though it is reasonable to consider that p_{23} and p_{34} correspond to the strength of each bond, p_{12} does not do so, because as to the oxygen, nitrogen and sulphur atoms, which all have non-bonding electrons, the increase of the value of C means the decrease of bond formation character of these atoms. And as for thiophene, there is one more difficulty discussed in the preceding section.

Summary

Electronic structures of furan, pyrrole and thiophene were investigated by the use of the molecular orbital method. And values of energy levels, resonance energies, π-electron densities and bond orders were calculated. As the result of these calculations, it was found that non-bonding electrons of hetero-atoms migrate into carbon atoms and the degree of these electron migrations increases in the order of furan, pyrrole and thiophene.

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(15) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

(16) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).