π-ELECTRON STRUCTURE OF THE NITROFURAN SYSTEM

I. Distribution of the Unpaired Electron in Anion Radicals of 5-Nitrofuran and Its 2-Substituted Derivatives

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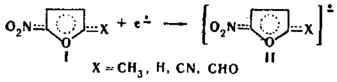
Distribution of the unpaired electron in the first free MO, the partial bond orders created by this electron, and the energy level corresponding to it in anion radicals of the nitrofuran series have been examined on the basis of quantum-chemical calculations by the MOH method of the π-electron system of 5-nitrofuran and its 2-substituted derivatives. Distribution of the spin density of the π electrons in the anion radicals has also been calculated by McLachlan's method. The parameters of the first free MO obtained by calculation agree satisfactorily with the physicochemical characteristics of the corresponding particulars measured experimentally (HFS constants in the EPR spectra and polarographic half-wave potentials).

By the electrochemical addition of one electron to the molecule of 5-nitrofuran and its 2-substituted derivatives of the general structure I we have obtained the corresponding anion radicals in sufficient concentration for the determination of some of their physicochemical characteristics [1–4]:



The EPR spectra of the anion radicals II have a well defined hyperfine structure (HFS), from which the HFS constants [4] characterizing the distribution of the unpaired electron in the anion radicals have been calculated. For a more complete description of the distribution of the unpaired electron in the first free molecular orbital of the π system of anion radicals II we have performed a quantum-chemical calculation of the molecular orbitals of the π-electron system of molecules I by means of the MO LCAO method in Hückel's approximation (MOH) [5, 6].

This type of calculation usually has an approximate nature, and the result obtained depends substantially on the selection of the initial parameters; the assumptions and approximations in the calculations are compensated by variable selection of the initial parameters. The values of the Coulomb integrals α_r and the bond integrals β_{rs} for the various atoms r and bonds rs are expressed in units of standard magnitude α and β, and the corresponding values for the benzene molecule were selected as

$$\alpha_r = \alpha + h_r\beta \text{ and } \beta_{rs} = k_{rs}\beta.$$

The initial values of k_{rs} for calculating the furan ring were given in such a way that k_{rs} was assumed to be proportional to the overlap integral S_{rs} [7, 8]:

$$k_{rs} = \frac{S_{rs}}{S_{\text{benz}}},$$

where S_{benz} is the overlap integral in the benzene ring. By using the values of the bond lengths for the furan ring found from microwave spectra [9], the values of the overlap integrals S_{rs} were determined from the tables of Mulliken et al. [10]. We selected the parameters h_r and k_{rs} for 5-nitrofuran (I, X = H). We judged the suitability of any particular set of parameters from the correspondence of the ratio of the calculated densities of the unpaired electron in positions 4 and 2 of the furan ring to the experimentally found ratio of the distribution constants due to the protons in the EPR spectra ($a_{H,4}/a_{H,2} = 1.3$), and also from the correspondence of the calculated densities of the unpaired electrons with McConnel's equation [11, 12]. For the substituents X = CH_3, CN, CHO, and NO_2 in the corresponding molecules I we used the parameters h_r and k_{rs} selected by Rieger and Fraenkel in calculations for compounds of the nitrobenzene series [13]. Our final choice of the parameters h_r and k_{rs} settled on the values given in Table 1.

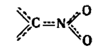
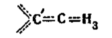
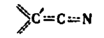
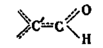
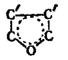
We also determined the spin density of the electrons of the π system in anion radicals II by McLachlan's method

[14] taking into account the mutual polarization of the π electrons:

$$\rho_{rL} = c_{ro}^2 - \lambda \sum_s \pi_{rs} c_{so}^2,$$

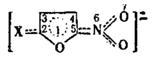
where c_{ro}^2 is the density of the unshared electron in the first free orbital, π_{rs} is the mutual polarizability of the atoms, and $\lambda = 1$ is an experimental constant [14].

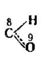
Table 1. Parameters for Calculations by the MOH Method

Groups		Atoms	h_r	Bonds	k_{rs}
Nitro		O	1.4	C=N	1.2
		N	2.2	N=O	1.67
Methyl		H_3	−0.5	C=H_3	2.5
		C	−0.1	C′=C	0.9
Nitrile		N	1.0	C=N	2.0
		C	0.0	C′=C	0.9
Carbonyl		O	1.5	C=O	1.6
		C	0.0	C′=C	0.9
Furan		C′	0.0	C′=C′	0.96
		C	0.0	C′=C	1.18
		O	2.7	C=O	0.664

The results of the calculations, which were performed on a BÉSM-2M high speed electronic computer are given in Table 2.

Table 2. Electron-Spin Density Calculated by Hückel's Method (ρ_{rH}) and McLachlan's Method (ρ_{rL}), and the Corresponding Experimental Values ($\rho_{rH}^{exp}, \rho_{rL}^{exp}$) for the Anion Radicals II



X	ρ \ r	1	2	3	4	5	6	7	8	9
$\overset{8}{C}=\overset{9}{H_3}$	ρ_{rH}	0.016	0.152	0.003	0.208	0.039	0.206	0.179	0	0.019
	ρ_{rH}^{exp}	—	0.176	0.029	0.232	—	—	—	—	—
	ρ_{rL}	0.011	0.202	-0.050	0.264	-0.018	0.216	0.178	-0.005	0.024
	ρ_{rL}^{exp}	—	—	0.034	0.274	—	—	—	—	—
H	ρ_{rH}	0.016	0.155	0.003	0.216	0.040	0.210	0.182	—	—
	ρ_{rH}^{exp}	—	0.168	0.032	0.218	—	—	—	—	—
	ρ_{rL}	0.012	0.212	-0.052	0.269	-0.018	0.219	0.180	—	—
	ρ_{rL}^{exp}	—	0.198	0.038	0.257	—	—	—	—	—
$\overset{8}{C}=\overset{9}{N}$	ρ_{rH}	0.018	0.152	0.019	0.182	0.055	0.183	0.168	0.017	0.039
	ρ_{rH}^{exp}	—	—	0.054	0.200	—	—	—	—	0.040
	ρ_{rL}	0.014	0.195	-0.026	0.225	0.012	0.189	0.167	0.012	0.045
	ρ_{rL}^{exp}	—	—	0.063	0.236	—	—	—	—	0.042
	ρ_{rH}	0.020	0.130	0.049	0.143	0.073	0.149	0.147	0.079	0.064
	ρ_{rH}^{exp}	—	—	0.054	0.157	—	—	—	—	—
	ρ_{rL}	0.016	0.156	0.022	0.166	0.049	0.152	0.148	0.081	0.062
	ρ_{rL}^{exp}	—	—	0.063	0.186	—	—	—	—	—

From the measured EPR spectra [4], the experimental values of the distribution of the unpaired electron in the anion radicals II were determined on the basis of the HFS constants $a_{H(N)}$ from McConnell's equation

$$a_{H(N)} \cong |Q|\, \rho_r^{exp}.$$

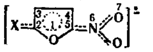
In the determination of the electron density in the first free MO, for the carbon atom of the C—H fragment, the σ–π parameters |Q| was taken as 28 G [15], and in the determination of the spin density of the electrons of the π system it was taken as 23.7 G [13]. A value of |Q| = 27.2 G was used for the carbon atom in the methyl group of I (X = CH_3) [16]. The experimental value of the density of the unpaired electron in the first free MO of the π system for the nitrogen atom of the CN group in I (X = CN) was determined with the value of |Q| = 19.8 G, and that for the spin-spin density of the electrons of the π system with the value of |Q| = 18.9 G [17].

The results of the MOH calculations (Table 2) show that in particles II the greatest density of the unpaired electron is concentrated on the nitro group; in anion radicals II it amounts to 0.57 to 0.44 of an electron, depending on the nature of substituent X. Within the nitro group, the unpaired electron is distributed almost uniformly between the nitrogen atom and the oxygen atoms. As the electron-accepting properties of substituents X increases, the density of the unpaired electron on the nitrogen atom decreases considerably more than on the oxygen atom.

On the oxygen atom of the furan ring, the density of the unpaired electron is negligible; it is also very small on the carbon atoms in positions 3 and 5 of the furan ring (symbols in Table 2). The highest density of the unpaired electron in the furan ring exists in position 4. As the electron-accepting properties of the substituent increases, the density of the unpaired electron increases in positions 3 and 5 of the ring, and decreases in positions 2 and 4.

The spin density of the electrons of the π system on the atoms of substituents as calculated by McLachlan's method differs little from the density of the unpaired electron in the first free orbital. In the furan ring, the spin density of the electrons of the π system differs considerably from the density of the unpaired electron in the first free orbital. In positions 3 and 5 of the anion radicals of the nitrofuran series, as the electron-donating properties of the substituent increases, a negative spin density of the electrons of the π system appears, and increases.

The addition of an unpaired electron to the molecule of I also changes the strength of the bonds between the ions. The addition of one electron to the first free molecular orbital (Table 3) strengthens the π bond between the substituent in the furan ring and between the carbon atoms in the β position of the furan ring; all the other π bonds in the anion radicals of II are weakened in comparison with the initial molecules.

Table 3. Fractional Bond Orders (p_{rs}^{j+1}) Created by the Free Electron in Anion Radical II 

X	rs p_{rs}^{j+1}	12	23	34	45	56	67	15	28	89
$\overset{8}{C}{=}\overset{9}{H}_3$	p_{rs}^7	−0.05	−0.02	0.03	−0.09	0.09	−0.19	−0.03	0.00	0.00
H	p_{rs}^6	−0.05	−0.02	0.03	−0.09	0.09	−0.20	−0.03	—	—
$\overset{8}{C}{\equiv}\overset{9}{N}$	p_{rs}^7	−0.05	−0.05	0.06	−0.10	0.10	−0.18	−0.03	0.05	−0.03
$\overset{8}{C}HO$	p_{rs}^7	−0.05	−0.08	0.08	−0.10	0.10	−0.14	−0.04	0.10	−0.07

The experimental values of both the density of the unpaired electron in the first free MO and the spin density of the electrons of the π system are in satisfactory harmony with the corresponding calculated figures (Table 2). Thus, for example, in a correlation of the values that we have found for the HFS, $a_{H,4}$ constants from the EPR spectra for the proton in position 4 of the nitrofurans and from the calculated electron densities ρ_{4H} in the first free molecular orbital, treatment of the quantities by the method of least squares leads to the relation

$$a_{H,4} = 28.1\,\rho_H + 0.4 \text{ (correlation coefficient = 0.97).}$$

The value of the $\sigma-\pi$ parameter obtained, $|Q| = 28.1$ G, is close to that generally accepted (28 G). The other term (0.4) is apparently due to the contribution of the spin density caused by the mutual polarization of the π electrons, the inaccuracy of the determination of the HGS constants, and the fact that the parameters h_r and k_{rs} of the substituents in anion radicals II were not selected with allowance for the solvating influence of water molecules on the anion radicals, although the measurement of the EPR spectra were carried out in an aqueous medium.

In position 3, where, because of the mutual polarization of the π electrons, a comparatively small negative spin density prevails, the HFS constants do not correspond to the density of the unpaired electron in the first free orbital but qualitatively reflect the spin density of the electrons of the π system in this position.

Starting from the idea that in one-electron polarographic reduction the additional electron is arranged in the first free MO of the π system [6, 18], we may assume that in series I the reduction potentials ($E_{1/2}$) [2, 3] measured under conditions where previous protonation is absent will correlate linearly with the parameters m_{j+1} of the first free orbital: orbital:

$$E_{1/2} = \beta m_{j+1} + c.$$

In actual fact, the correlation of the values of $E_{1/2}$ (experiment) [3] and m_{j+1} (Table 4) by the method of least squares gave the equations: $E_{1/2} = 2.80\, m_{j+1} - 0.48$(V) (correlation coefficient = 0.986; water, pH 10), and $E_{1/2} = 2.81\, m_{j+1} - 0.45$(V) (correlation coefficient = 0.999; 10% ethanol, pH 10). These equations enable us to find the effective value of the bond integral $\beta = -2.8$ eV (-64.5 kcal · mole^{-1}). This result is in fairly good agreement with the values of β found by other authors (for aromatic hydrocarbons [6] $\beta = -64.6$ kcal · mole^{-1}, and for the nitrobenzene [13] $\beta = -52.5$ kcal · mole^{-1}).

Table 4. Comparison of the Parameters of the First Vacant Orbital m_{j+1} of Substituted Nitrofurans with the Half-Wave Potentials $E_{1/2}$ of the Polarographic Reduction of the Nitrofurans in Aqueous Buffer Media (pH 10) and in 10% Ethanolic Aqueous Buffered Media (pH 10)

Compound	$-m_{j+1}$	$-E_{1/2}$ (V; 1-st wave)			
		0% C_2H_5OH; pH 10		0% C_2H_5OH; pH 10	
		exp	calc	exp	calc
2-Methyl-5-nitrofuran	0,390	0,65	0,62	0,66	0,66
2-Nitrofuran	0,391	0,60	0,61	0,64	0,65
2-Cyano-5-nitrofuran	0,342	0,45	0,48	0,50	0,51
5-Nitro-2-furfural	0,281	0,32	0,31	0,34	0,34

Thus, a consideration of the properties of the first free molecular orbital, which is a particular result of a general quantum-chemical calculation of the π-electron system of molecules I, shows a satisfactory agreement between the theoretical figures and the measured physicochemical parameters of the corresponding molecules. The π-electron systems of the nitrofurans calculated by the MO LKAO method will be published in a subsequent paper.

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