ELECTRONIC STRUCTURES, PHYSICAL PROPERTIES, AND REACTIVITIES OF FIVE-MEMBERED AROMATIC HETEROCYCLES

(REVIEW)

I. A. Abronin and G. M. Zhidomirov

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The possibilities of modern quantum-chemical methods for the investigation of the electronic structures and reactivities of five-membered heteroaromatic compounds are examined.

The criteria that have long been at the disposal of chemistry are presently inadequate for the explanation and, especially, the prediction of the chemical behavior of heterocyclic compounds. For this reason the number of quantum-chemical studies whose final aim is the creaction of a broader theoretical basis for organic chemistry is presently growing at an increasing rate.

The task that we set for ourselves in the compilation of the present review was to make it possible for the organic chemist-reader to evaluate the arsenal of means and possibilities now at the disposal of quantum chemistry. As objects for this examination we selected relatively simple aromatic systems – furan, pyrrole, and thiophene – which form a single "triad" of similar and, in addition, different in several respects five-membered heterocycles. It seemed expedient to us to discuss precisely those aromatic systems that have a definite well-known sum of chemical properties.

The present review is devoted to quantum-chemical calculations performed primarily after 1968: i.e., after both semiempirical methods, which take into account all of the valence electrons, and nonempirical methods, which take into account all of the electrons of the system, began to be widely used. The application of these methods to calculations of typical π-electron systems such as heteroaromatic molecules was justified primarily by the fact that in calculations within the π-electron approximation there is considerable arbitrariness in the selection of the computational parameters, and this leads to ambiguity in the results.

The review consists of two parts. The first part is devoted to the calculation of the physical properties of heteroaromatic molecules and to the application of the methods of quantum chemistry for the interpretation of the spectra (photoelectronic, UV, NMR, and ESR) of these systems. A brief description of the quantum-chemical methods of calculation is given at the beginning of this part. The second part is devoted to the strictly chemical properties of five-membered heteroaromatic molecules; i.e., to their reactivities.

The problems of the aromatic character of five-membered heterocycles are not discussed in the review, since the recently published large review of Cook, Katritzky, and Linda [1] was devoted to this topic.

Calculation of the Electronic Structures and Physical Properties of Five-Membered Heteroaromatic Molecules

Quantum-Chemical Methods of Calculation. Self-consistent-field (SCF) methods within the MO LCAO approximation developed by Hartree, Fock, and Roothaan [5-7] have found wide application in the calculations of molecular systems. However, their application even in the LCAO form is fraught with a number of computational difficulties. The problems in the calculation of multicenter integrals that arise when Slater type orbitals (STO)

$$\chi_{nlm}{}^{\mathrm{STO}}=[(2n)!]^{-1/2}\cdot(2\xi)^{n+1/2}\cdot r^{n-1}\cdot\exp(-\xi r)\cdot Y_{lm}(\theta,\xi),$$

N. D. Zelinskii Institute of Organic Chemistry, Academy of Science of the USSR, Moscow 117913.
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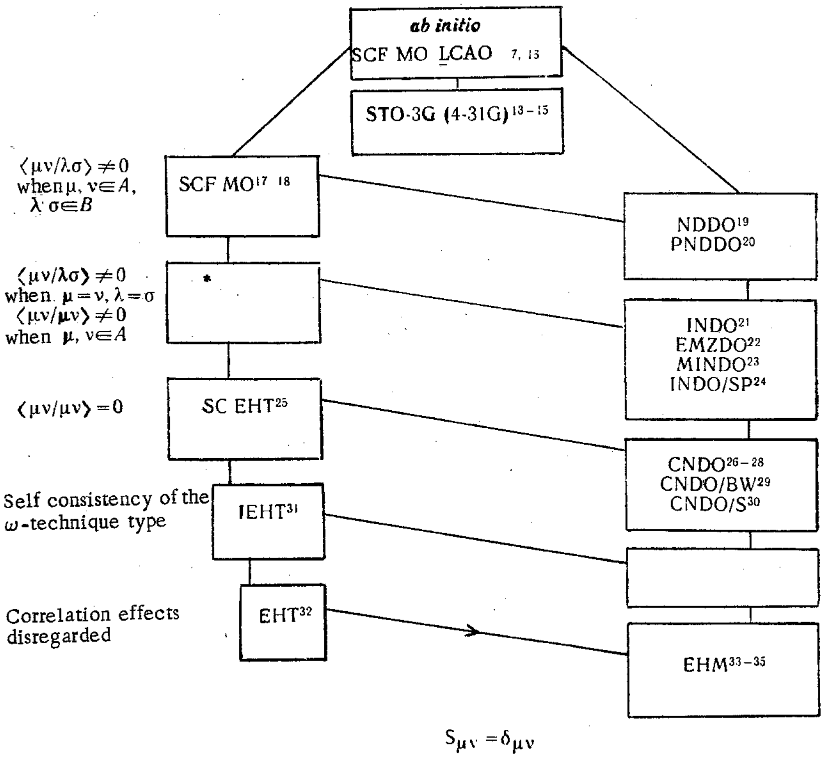
TABLE 1



*Not discussed.

are used in molecular calculations are overcome by means of approximation of the STO by a set of Gaussian type functions (GTO) [8-10]:

$$\chi_{nlm}^{GTO}=2^{n+1}[(2n-1)!!]^{-1/2}\cdot(2\pi)^{-1/4}\cdot\alpha^{(2n+1)/4}\cdot r^{n-1}\cdot\exp(-\alpha r^2)\cdot Y_{lm}(\theta,\xi).$$

However, since the STO rather than the GTO are the solutions of the central field problem, many more GTO are necessary for an adequate representation of the problem. The radial Hartree–Fock (HF) functions when $r\to\infty$ behave like $\exp(-\xi r)$, and a minimum of two GTO are therefore necessary to describe the solution in this region [11]. The expansion of the HF AO with respect to the GTO, which leads to energies close to the HF limit, contains 15-16 terms for atoms of the second period [12]. Calculation, within this basis, of rather large molecules is extremely time consuming and laborious, since it requires calculation of an enormous number of integrals. The development of simplified nonempirical and numerous semiempirical MO LCAO methods for the examination of the behavior of the electron in molecular systems is therefore completely natural. The simplified nonempirical methods are characterized by the fact that a limited expansion of the STO with respect to the GTO is used for the calculation. The STO-3G method* is the most well-known variant of this approach [13-15].

Let us examine the principal approximations that reduce the SCF MO LCAO of the Roothaan equation [7]

$$\sum_{\nu} F_{\mu\nu}c_{\nu i}=\sum_{\nu} S_{\mu\nu}c_{\nu i}\varepsilon_i \tag{1}$$

to equations of one or another semiempirical method. In equation (1)

$$F_{\mu\nu}=H_{\mu\nu}+G_{\mu\nu} \tag{2}$$

is the Fockian matrix element

$$H_{\mu\nu}=\int\varphi_\mu\left[-\frac{1}{2}\nabla^2-\sum_{A}V_A(\vec{r})\right]\varphi_\nu d\tau \tag{3}$$

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*Here and subsequently, we will use the abbreviated names of the computational methods generally adopted in the literature. The expansions of these names can be found in the original communications, the citations to which are given in the review.

TABLE 2. Range of Application of Methods of the CNDO and INDO Type

CNDO/2[27,28], INDO[21]	CNDO/BW[29], MINDO/1(2,3)[20,41,42]	CNDO S[30], INDO SP[24]
Charge distributions, dipole moments, spin-density distributions, and magnetic properties	Heats of formation, geometries, and force constants	UV spectra and ionization potentials

TABLE 3. Literature Sources Containing Quantum-Chemical Calculations of Five-Membered Aromatic Heterocycles

Method	Compound		
	pyrrole	furan	thiophene
HMO	43–54	47, 54, 83, 84	47, 54, 90–98
PPP	55–60	50, 59, 61, 63, 85	58, 61, 85, 99–105
EHT	64–68	65, 67	106, 107
CNDO	68–76	69, 71, 72, 74, 75, 86–88	87, 108–110
ab initio	68, 77–82	80, 82, 89	82, 111–115

takes into account the interaction of the electrons with the nuclei,

$$G_{\mu\nu}=\sum_{\nu\sigma} P_{\lambda\sigma}\left[\langle\mu\nu/\lambda\sigma\rangle-\frac{1}{2}\langle\mu\sigma/\nu\lambda\rangle\right] \tag{4}$$

is the interelectron interaction,

$$\langle\mu\nu/\lambda\sigma\rangle=\int\int\varphi_\mu(1)\varphi_\nu(1)\frac{1}{r_{12}}\varphi_\lambda(2)\varphi_\sigma(2)d\tau_1 d\tau_2 \tag{5}$$

is the integral of interaction between the AO, and

$$P_{\lambda\sigma}=2\sum_i^{\text{occ}} c_{i\lambda}c_{i\sigma} \tag{6}$$

is the density matrix element.

The principal approximation, which is practically common to all of the semiempirical methods, is approximation of the $H_{\mu\nu}$ matrix elements by several empirical values. The remaining approximations pertain to approximation of the integrals, neglect of some or other integrals, etc. In this case, all of the semiempirical approaches can be divided into two large subgroups. The first subgroup includes methods with allowance for overlap in which a system of equations of the (1) type is solved. The second subgroup includes the so-called methods of zero differential overlap, in which it is assumed that $S_{\mu\nu}=\int\varphi_\mu(1)\varphi_\nu(1)d\tau=0$ when $\mu\neq\nu$, i.e., $S_{\mu\nu}=\delta_{\mu\nu}$. An exemplary scheme of various semiempirical methods discussed in the literature is presented in Table 1.

When the π-electron approximation is used (the σ electrons and the inner electrons are considered to be a nonpolarizable framework), the scheme presented in Table 1 simplifies to the series ab initio → PPP [36, 37] (CNDO analog) → ω-HMO [38] → HMO [39] (simple Hückel method). The advantages and disadvantages of the various approaches have been examined in quite some detail and quite graphically by Clark [40]. We note only two peculiarities of the semiempirical computational methods that are fundamental, in our opinion, for the subsequent exposition. The first is the impossibility of the correct description of all or a sufficiently extensive set of physical properties of a molecule within the framework of one semiempirical method. A consequence of this was the development of different variants, particularly of methods of the CNDO or INDO type. The range of their application is presented in Table 2.

The second peculiarity pertains more to semiempirical than to empirical approaches (EHT, HMO, and particularly PPP). This involves not only the need to use different sets of parameters for the calculation of different properties but also to the limitation due to the fundamental impossibility of the application of the same parameters for the calculation of different types of molecules. This circumstance led to the development of a

TABLE 4. Calculated and Experimental Values (eV) of the First and Second Ionization Potentials in Pyrrole, Furan, and Thiophene

Method	Pyrrole		Furan		Thiophene	
	I_1-type	I_2-type	I_1-type	I_2-type	I_1-type	I_2-type
ab initio	8,13 $(a_2\text{—}\pi)$	9,50 $(b_1\text{—}\pi)$[81]	9,06 $(a_2\text{—}\pi)$	11,03 $(b_1\text{—}\pi)$[89]	9,04 $(a_2\text{—}\pi)$	9,30 $(b_1\text{—}\pi)$[113]
CNDO/2	11,68 $(a_2\text{—}\pi)$	13,34 $(b_1\text{—}\pi)$[68]	12,16 $(a_2\text{—}\pi)$	14,96 $(b_1\text{—}\pi)$*	11,87 $(a_2\text{—}\pi)$	13,13 $(b_1\text{—}\pi)$*
EHT	10,29 $(a_2\text{—}\pi)$	11,20 $(b_1\text{—}\pi)$[68]	—	—	12,51 $(a_2\text{—}\pi)$	12,80 $(b_1\text{—}\pi)$[106]
Exptl. value	8,21 (π)	9,20 (π)[117]	8,88 (π)	10,3 (π)[117]	8,87 (π)	9,52 (π)[117]

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*This review.

TABLE 5. Results of Calculation of the UV Spectra of Pyrrole, Furan, and Thiophene by the CNDO/S Method

Compound	Symmetry	ΔE, eV		f		Type of transition
		exptl.	calc.	exptl.	calc.	
Pyrrole	$^1B_2$	5,7[118]	5,0[73]	—	0,080	$\pi\rightarrow\pi^*$
	$^1A_1$	6,5	5,4	—	0,006	$\pi\rightarrow\pi^*$
	$^1B_2$	7,1	7,0	—	0,129	$\pi\rightarrow\pi^*$
	$^1A_1$	—	7,0	—	0,479	$\pi\rightarrow\pi^*$
Furan	$^1B_2$	5,9[118]	5,2[73]	0,12	0,078	$\pi\rightarrow\pi^*$
	$^1A_1$	6,5	5,8	0,08	0,009	$\pi\rightarrow\pi^*$
	$^1A_1$	7,4	7,3	—	0,368	$\pi\rightarrow\pi^*$
	$^1B_2$	—	7,3	—	0,097	$\pi\rightarrow\pi^*$
Thiophene	$^1B_2$	5,2[119]	5,4 5,0[110]	0,1	0,2 0,1	$\pi\rightarrow\pi^*$
(The upper calculated value pertains to the sp basis, and the lower value pertains to the spd basis)	$^1A_1$	5,3	5,5 5,4	0,1	0,1 0,2	$\pi\rightarrow\pi^*$
	$^1A_1$	5,6	6,9 6,2	Weak	0,6 0,08	$\pi\rightarrow\pi^*$
	$^1B_2$	6,6	7,1 6,7	Strong	0,08 0,4	$\pi\rightarrow\pi^*$

TABLE 6. Charges on the Atoms and Dipole Moments of Pyrrole, Furan, and Thiophene

Position	Pyrrole		Furan		Thiophene	
	ab initio[79]	CNDO/2*	*ab initio*[89]	CNDO/2*	*ab initio*[113]	CNDO/2*
N, O or S σ	−0,748	−0,428	−0,637	−0,393	−0,225	−0,213
π	+0,341	+0,311	+0,230	+0,256	+0,240	+0,165
Σ	−0,407	−0,117	−0,407	−0,137	+0,015	−0,048
$C_{2(5)}$ σ	−0,031	+0,132	+0,151	+0,168	−0,160	−0,011
π	−0,075	−0,073	−0,032	−0,068	−0,085	−0,026
Σ	−0,106	+0,059	+0,119	+0,100	−0,245	−0,037
$C_{3(4)}$ σ	−0,159	+0,030	−0,066	+0,014	−0,208	+0,008
π	−0,096	−0,082	−0,143	−0,060	−0,035	+0,022
Σ	−0,255	−0,052	−0,143	−0,046	−0,243	+0,030
H_N (pyrrole)	+0,339	+0,112	—	—	—	—
2(5)-H	+0,202	−0,008	+0,114	+0,005	+0,249	+0,026
3(4)-H	+0,193	+0,003	+0,111	+0,009	+0,232	+0,004
μ_{calc}, D†	2,01	1,73	0,64	0,74	0,44	0,28
μ_{exp}, D	1,80		0,67		0,53	

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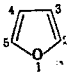
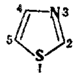
*This review.

† The results of ab initio calculations of the dipole moments are presented in [82].

large number of schemes and formulas for the selection of parameters, and, as a consequence of this, comparison of the results becomes impossible.

In conclusion, we present citations to studies in which sufficiently detailed data from calculations of the above-mentioned heterocycles by various methods (Table 3) are presented. A more detailed discussion of some of these studies will be presented below.

TABLE 7. Relative Bonding Energies of the 1s Electrons (ΔE_i) in Furan and Thiazole Calculated by the CNDO/2 Method [136]

		ΔE_i, eV	$\Delta E_{i\,exp}$, eV [135]
	$C_{2(5)}$	(0,0)	(0,0)
	$C_{3(4)}$	−1,2	−1,1
	C_2	(0,0)	−0,7
	C_4	+0,7	+0,4
	C_5	−1,2	(0,0)

Ionization Potential and UV Spectra. The first and second ionization potentials calculated by various methods that take into account all of the electrons or only the valence electrons and the corresponding experimental values are presented in Table 4. In conformity with Koopmans' theorem [116], the ionization potential was assumed to equal to the magnitude of the level of the upper (or second from the upper) occupied MO, taken with the opposite sign.

It is apparent from Table 4 that the nonempirical approach completely satisfactorily conveys the ionization potentials of the heteroaromatic molecules. The agreement is considerably worse both with respect to the magnitude of the first and second ionization potentials and with respect to the ratio between them in the case of semiempirical methods.

Precisely these circumstances led to the use of the so-called CNDO/S method with variable "spectroscopic" parametrization rather than the CNDO/2 method for the calculation of the electronic spectra within the all-valence approximation. The results of calculations of the UV spectra of pyrrole, furan, and thiophene (in the sp and spd bases) with allowance for the configurational interaction are presented in Table 5.

It is apparent from Table 5 that the calculated values and the experimental data are in quite satisfactory agreement. All of the lower transitions pertain to those of the $\pi \rightarrow \pi^*$ type; this was due to the extensive use of calculations within the π-electron approximation for the analysis of the UV spectra of compounds of the heteroaromatic series. Thus the PPP method was used for calculations of the UV spectra of condensed and dihetaryl compounds formed by pyrrole, furan, and thiophene [101, 102, 105, 120-131]. In addition, the CNDO/S method was also used for the calculation of some heteroaromatic derivatives [131-133].

Charge Distribution and Dipole Moments. The calculated charge densities and dipole moments are presented in practically all of the studies listed in Table 3. Isoelectronic density maps are also presented in some of them [67, 75, 107, 113] for thiophene, furan, and pyrrole. The distribution of charges in heteroaromatic derivatives obtained within the framework of the π-electron approximation is also presented in studies involving calculations of the UV spectra [120-131]. The π, σ, and total charges on the atoms and the dipole moments of pyrrole, furan, and thiophene (spd basis) calculated by the ab initio and CNDO/2 methods are presented in Table 6.

It is apparent that despite some quantitative differences, both the ab initio approach and the CNDO/2 method qualitatively identically convey the charge distribution in both the π and σ systems; the calculated dipole moments also sufficiently satisfactorily reproduce the experimental values.

The bonding energy E_i of the inner electrons determined from the x-ray electron spectra, may serve as yet another experimental criterion of the magnitude of the charge on the atoms. It is assumed [135] that

$$E_i = E_i^0 + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}},$$

where E_i^0 is the energy of a level in the atom, and the remaining terms determine the potential from the charge in the molecule. The k value depends on the choice of computational methods. The relative bonding energies of the 1s electrons in furan and thiazole calculated by the CNDO/2 method (k = 25 eV/unit of charge) are presented in Table 7.

NMR Spectra. Information regarding the electronic structures and the structures of compounds can be obtained from the NMR spectra both from the magnitudes of the chemical shifts (σ) and from the

TABLE 8. Calculated (by the CNDO/2 method) Chemical Shifts of the ^{13}C Nuclei in Furan and Pyrrole

Compound		$\sigma_p+\sigma_d$ (calc)	$\Delta\sigma_{2,3}$ (calc), ppm	$\Delta\delta_{2,3}$ (exp), ppm
Furan	C_2	−208,92	14,91	16,00
	C_3	−194,01		
Pyrrole	C_2	−205,66	9,16	10,20
	C_3	−196,50		

TABLE 9. Spin–Spin Coupling Constants $J_{H_M H_N}$ (Hz) in Furan, Thiophene, 2- and 3-Formylthiophenes, and Furfural

Molecule	M, N	CNDO/SP	INDO-FPT	Exptl.
Furan	2,3	1,9[154]	1,8[155]	1,8[156]
	2,4	1,7	2,1	0,8
	2,5	1,7	2,8	1,5
	3,4	3,8	3,8	3,3
Thiophene	2,3	6,8*	4,6[155]	4,9[156]
	2,4	1,9	2,0	1,0
	2,5	2,7	2,4	2,8
	3,4	4,2	4,7	3,5
2-Formylthiophene, cis-S,O/ trans-S,O	3,4	3,1/3,1[157]	3,4[158]	3,5[161]
	4,5	5,2/5,2	4,1	5,0
	3,5	1,4/1,4	1,9	—
	CHO, 3	0,2/0,1	—	—
	CHO, 4	0/0,5	—	—
	CHO, 5	0,7/0	—	0,9
3-Formylthiophene, cis-S,O/trans-S,O	2,5	1,8/1,7[159]	1,9[158]	1,4[161]
	2,4	2,6/2,6	2,1	2,7
	4,5	6,5/6,5	3,8	5,2
	CHO, 2	0,3/0,2	—	—
	CHO, 4	0,3/0	—	—
	CHO, 5	0/0,6	—	0,7
Furfural, cis-O,O/ trans-O,O	3,4	2,9/2,9[157]†	—/2,8[160]	3,5[162]
	4,5	1,5/1,5	—/1,3	1,7
	3,5	1,3/1,3	—	0,8
	CHO, 3	0/0,1	—	
	CHO, 4	0/0,5	—	0,45
	CHO, 5	0,5/0	—	0,45

*This review.

† Data for calculations with $\lambda_J=5.5$ are presented.

spin–spin coupling constants (J_{MN}). On the basis of the general theory of chemical shifts proposed by Ramsey [137], the chemical shift tensor can be divided into three contributions [138]

$$\sigma=\sigma_d+\sigma_p+\sigma', \tag{7}$$

where σ_d is the diamagnetic contribution to shielding, σ_p is the paramagnetic contribution to shielding, and σ' is the contribution from the adjacent atoms. The theory of chemical shifts was developed by Karplus and Pople [139] within the framework of the MO method. In conformity with this theory

$$\sigma_d^{AA}=\frac{e^2}{3mc^2}\sum_i\left\langle\frac{1}{r_i}\right\rangle \tag{8}$$

where summation is performed over all electrons, and r_i is the distance from a given electron to the nucleus. The diamagnetic contribution can be expressed in terms of the effective charge of the nucleus Z_A^* [140]. In the case of the carbon atom

$$\sigma_d^{AA}=4{,}45Z^*_A Q_A, \tag{9}$$

where

$$Z^*=3{,}25-0{,}35(Q_A-4), \tag{10}$$

and Q_A is the total electron density on a given atom

$$\sigma_p^{AA}=\frac{1}{3}(\sigma_{XX}^{AA}+\sigma_{YY}^{AA}+\sigma_{ZZ}^{AA}), \tag{11}$$

$$\sigma_{ZZ}^{AA}=-\frac{2e^2\hbar}{m^2c^2}\left\langle\frac{1}{r^3}\right\rangle\sum_i^{\text{occ}}\sum_j^{\text{vac}}\Delta E_{i\to j}^{-1}[c_{iX_A}c_{jY_A}-c_{iY_A}c_{jX_A}]\sum_B(c_{iX_B}c_{jY_B}-c_{iY_B}c_{jX_B}) \tag{12}$$

with analogous expressions for σ_{XX}^{AA} and σ_{YY}^{AA}.

Finally, σ' is a quantity that, in the general case, is most difficult to calculate. However, it is of importance only for the chemical shifts of protons. It can be disregarded for heavy nuclei (for example, ^{13}C).

In the case of cyclic molecules there is yet another contribution to the magnetic shielding of the nuclei – σ_{del} – the delocalization contribution or contribution of the ring current. The effect of the ring current of an aromatic ring on the chemical shifts of the nuclei of a side chain is widely used in the discussion of stereochemical problems. Insofar as the cyclic system of bonds itself is concerned, attempts are currently being made to link data on ring currents with the aromaticity of the ring. These problems have been discussed in [141-143] for heteroaromatic systems.

Further simplifications in theoretical calculations of the chemical shifts of ^{13}C nuclei involve the introduction in Eq. (12) of the average energy of excitation [144] etc., up to the construction of correlations between the ^{13}C chemical shift and the magnitude of the total charge on a given carbon atom. It should be noted that correlations between the chemical shift of the proton and the charge on the carbon atom bonded to it are also completely satisfactorily fulfilled for aromatic (including heteroaromatic) compounds. A more detailed description of methods for the calculations of chemical shifts and correlations between chemical shifts and charges on atoms is given in [145, 146].

The calculated (within the framework of the CNDO/2 method [70]) and experimental chemical shifts of the ^{13}C nuclei in furan and pyrrole are presented in Table 8. It is quite difficult to compare the absolute values of the chemical shifts in this case, but the $\Delta\sigma$ and $\Delta\delta$ values are in completely agreement with one another.

Calculations of the ^{13}C chemical shifts by various methods and correlations between the chemical shifts of ^{13}C nuclei or protons and the charges on carbon atoms are also presented in [64, 148-152].

In addition to the chemical shifts, other important parameters of the PMR spectra of molecules are the spin–spin coupling constants (J). There are three contributions to spin–spin coupling: interaction of the nuclear magnetic moments with the orbital moments of the electrons (orbital contribution), dipole interaction between the magnetic moments of the electrons and the nuclei (spin–dipole contribution), and Fermi interaction (contact contribution). The latter plays the most important role, at least in the spin–spin coupling of protons.

There are currently two alternative methods for the calculation of spin–spin coupling constants in molecules. A method for the calculation of J based on "finite perturbation theory" (FPT) was developed by Pople and co-workers [153] and was used within the INDO approximation for calculations of a large number of molecules. The MO theory and the FPT are found within the approximation of the unrestricted Hartree–Fock (UHF) method and, in conformity with the latter, differ somewhat for electrons with opposite (α and β) spins. The differences in the MO for α and β spins arise due to the perturbation terms added to the diagonal elements of the Hamiltonian matrix corresponding to the s-AO of atom B. The J_{AB} constants are calculated by means of differentiation techniques, since they are proportional to the derivatives of the induced (by magnetic nucleus B) spin populations of the s-AO of atoms A:

$$J_{AB} = J_0 \cdot \left(\frac{\partial}{\partial h_B} \rho_{s_A s_A}(h_B) \right)_{h_B=0}. \tag{13}$$

Here,

$$J_0 = \frac{1}{4} K_A K_B; \quad K_A = \frac{8\pi}{3} g_e \beta_e \hbar \gamma_A \cdot / s_A(0) /^2.$$

The second approach is based on the fact that the $\partial\rho/ph$ derivatives in the Hückel approximation are equivalent to the atom– atom polarizabilities

$$\pi_{s_A s_B} = -4 \sum_{i}^{occ} \sum_{j}^{vac} \frac{c_{is_A} \cdot c_{is_B} \cdot c_{js_A} \cdot c_{js_B}}{E_j - E_i}. \tag{14}$$

Then,

$$J_{AB} = \lambda_J \cdot J_0 \cdot \pi_{s_A s_B}. \tag{15}$$

The empirical coefficient λ_J takes into account the fact that simply the difference in the orbital energies is used in the denominator of Eq. (14) instead of the energies of the singlet–triplet excitations necessary in the case of self-consistent MO. This approach has been called the RHF/SP method [154].

TABLE 10. Experimental and Calculated (by the INDO method) ihfc Constants (Oe) in the Pyrrole Anion Radical [166]

a_H	Exptl.	INDO
2	45±2	45
3	11±2	8
4	—	0,5
5	11±2	5

TABLE 11. Experimental and Calculated (by the INDO method) ihfc Constants (Oe) in the Furan Anion Radical [167]

a_H	Exptl.	INDO
α	17	21
β	61	72
γ	(−)3	−2
δ	(−)3	−4

The results of calculations of J_{HH} in furan, thiophene, and formyl thiophenes by these two methods are presented in Table 9. A λ_J value of 7 was used in the calculations by the CNDO/SP method.

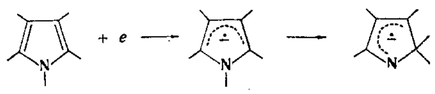
We note that calculations of the J constants may prove to be important in theoretical estimates of the preferred conformation. In fact, as we will demonstrate below, direct quantum-chemical calculations, because of some defects in the parametrization of the semiempirical methods, may give a practically zero difference in energies for the cis and trans conformations of 3-formylthiophene [163]. However, for the calculated $J_{CHO,\ 5}$ constants quite convincingly attest to the fact that 3-formylthiophene exists primarily in the trans-S,O conformation.* This is in agreement with the experimental data [164].

Calculations of Free Radicals of the Heteroaromatic Series. In ESR spectroscopy the most accessible information regarding the electronic structures of radicals in solution is associated with the hyperfine structure (hfs) of the spectrum determined by the isotropic hyperfine coupling (ihfc) of the unpaired electron with the nucleus. Within the MO LCAO approximation, the expression for the ihfc constant has the form

$$a_N = \frac{8\pi}{3} g\beta\hbar\gamma_N |\varphi_{s_N}(0)|^2 \rho_{s_N}, \qquad (16)$$

where ρ_{s_N} is the diagonal element of the spin density matrix corresponding to the s-AO of a given atom, which is also found by quantum-chemical calculation. The INDO method within the UHF approximation has found greatest application for calculations of the ihfc constants in free radicals. Initially formulated for elements from H to F [21], it was subsequently also extended to elements of the third period [165]. The elements of the spin density matrix within the UHF approximation are determined quite simply as the difference in the corresponding elements in the density matrix for electrons with α and β spins.

Radicals of two types have been calculated in the heteroaromatic series. The first type are anion radicals formed by the addition of an electron to a heteroaromatic molecule. In this case unsubstituted heteroaromatic molecules may undergo rather unexpected changes that are hardly characteristic of six-membered aromatic molecules. For example, in the pyrrole anion radical hydrogen is transferred from nitrogen to the α-carbon atom [166]:



The energetics of this process, calculated by the INDO method, are presented in the scheme below, and the experimental and calculated ihfc constants for the pyrrole anion radical are presented in Table 10.

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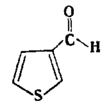
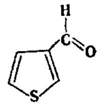
*We note that in [159], in analogy with 2-formylthiophenes, the following symbols were adopted:

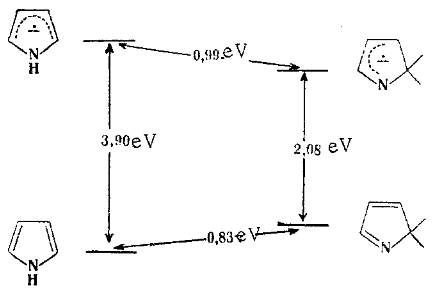


trans-S,O

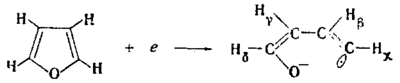


cis-S,O

these designations are the opposite of those used in [163], which should be considered to be incorrect.



In the furan anion radical the C−O bond is cleaved to give an acyclic σ-electron anion radical [167].



The ihfc constants of the resulting anion radical are presented in Table 11.

Calculations of anion radicals from nitrofuran and nitrothiophene derivatives, which retain their molecular structures when they capture an electron, were performed in [168, 169].

The second type of radicals consists of radicals formed by detachment of an H atom from the side chain of a substituted heteroaromatic molecule. Furfuryl and thienyl radicals [170, 171] are typical examples of such radicals (Table 12).

Calculations of radicals of the thiophene series within the π-electron approximation were made in [173].

Rotational Isomerism in Substituted Compounds of the Heteroaromatic Series. The problem of the conformations of substituted compounds of the heteroaromatic series is currently being discussed intensively, since it may be of fundamental value for the analysis and interpretation of experimental data (for example, NMR or IR spectroscopic data). The direct quantum-chemical solution of this problem by direct calculation and comparison of the energies of various conformations is complicated by the fact that the calculated (as well as the experimental) differences in the energies are relatively small, whereas the differences in the dipole moments of the conformations are quite large, so that the equilibrium may be shifted markedly to one or the other side depending on the polarity of the solvent. Calculations of the difference conformations of 2-formylfuran by the CNDO/2 method with allowance for the solvation energy on the basis of classical electrostatic

TABLE 12. Experimental and Calculated (by the INDO method) ihfc Constants (Oe) in 2-Furfuryl and 2- and 3-Thienyl Radicals

Radical	a_H	Exptl.	INDO
2-Furfuryl	3	(−)8,79[170]	−9,40[170]
	4	1,28	3,29
	5	(−)7,87	−6,44
	CH_2 (1)	(−)13,32	−14,79
	CH_2 (2)	(−)13,01	−14,67
2-Thienyl	3	(−)8,26[172]	−9,45[171]
	4	1,62	3,62
	5	(−)7,89	−7,14
	CH_2 (1)	(−)14.22	−13,99
	CH_2 (2)	(−)13,97	−13,85
3-Thienyl	2	(−)8,94[172]	−10,61[171]
	4	(−)0,75	−2,61
	5	1,86	2,33
	CH_2 (1)	(−)16,89	−15,94
	CH_2 (2)	(−)16,39	−15,73

TABLE 13. Experimental and Calculated Stabilities (ΔE) of the cis-O,O and trans-O,O Isomers of Furfural in Various Solvents and Barriers to Rotation (ΔE*) of the CHO Group [174]

Solvent	ε	ΔE, kcal/mole		ΔE*, kcal/mole	
		exptl.	calc.	exptl.	calc.
Gas	1,0	1,5	(1,5)	8,1—8,7	8,5
CF_2Cl_2	2,9	0,34	0,29	10,5	10,4
Me_2O_2 (−120°)	12,0	−0,58	−0,60		
DMSO	45,0	−0,84	−0,85		

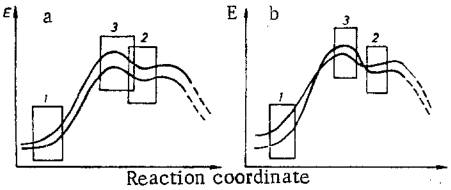


Fig. 1. Possible instances of a change in the energy of two systems during a reaction: 1) range of the effect of reactivity indexes in the isolated molecule approximation; 2) localization approximation; 3) activated complex approximation.

theory were made in [174]. The differences in the energies ($\Delta E = E_{cis} - E_{trans}$) and the barriers to rotation (ΔE^*) in various solvents are presented in Table 13. The experimental ΔE and ΔE^* values were determined on the basis of an analysis of the NMR spectra.

Similar calculations of pyrrole and thiophene carbonyl derivatives were made in [157, 159, 163, 175-177]. The fact that the conformation with the CHO group perpendicular to the plane of the ring is the most stable (from the calculation) in the case of 3-formylthiophene [163] is unexpected. This result can hardly be considered to be in agreement with fact, and it may most likely be associated with some errors in the parametrization of the CNDO/2 method for elements of the third period.

The EHT and CNDO/2 methods were used in [178] for calculation of the rotational barriers in isomeric dihetaryls.

Role of the d Orbitals of Sulfur in Thiophenes. The problem of the effect of the outer d-AO of sulfur on the physical and chemical properties of compounds of the thiophene series has frequently been discussed in the literature. In particular, a large review by Clark [179] has been devoted to it. Since then there have been a number of nonempirical calculations of thiophene [82, 111-115], on the basis of which it can be concluded that the inclusion of the d-AO of sulfur in the basis leads to the following results: 1) a decrease in the overall energy of the system; 2) a more uniform distribution of the π charge over the molecule; 3) improvement in the agreement between the calculated and experimental ionization potentials and dipole and quadrupole moments.

The qualitative picture of the spacing of the electronic levels and the charge distribution remains unchanged.

This effect of the 3d-AO coincides on the whole with the effect noted by Dyatkina and Klimenko for inorganic sulfur compounds [180], and the low populations of the 3d-AO in the thiophene (on the order of 0.18 electron [113]), together with the low valence of sulfur in thiophene, make it possible to consider them to be certain corrections that take into account the polarization of the valence s and p-AO during bond formation and give a more precise total wave function of the molecule. A detailed discussion of the modern state of the problem of the effect of the outer vacant AO has been given in the review mentioned above [180].

Reactivities of Five-Membered Heteroaromatic Compounds

Method of Reactivity Indexes. The presently used quantum-chemical estimates of reactivities are primarily based on a linear relationship between the free energies, i.e.,

$$\lg k_i = A + BW_i, \qquad (17)$$

where A and B are empirical constants, and W_i is the reactivity index calculated directly in the MO method.*

All of the reactivity indexes presently used can be divided into two groups. The first group includes indexes based on values obtained by calculation by the MO method of an individual molecule of the reactant, which is the so-called isolated molecule approximation. Values of this sort are free valences, charge densities, po-

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*In the general case, the indexes may be not only calculated values but also experimentally determinable values such as ionization potentials, dissociation constants of carboxylic acids, etc.

larities, boundary electron densities, etc. The indexes of the second group are determined by calculation of a possible system corresponding to the transition (or intermediate) state and pertain to the so-called localization approximation; it can also be regarded as the activated complex approximation.

The ranges of potential curves corresponding to different groups of reactivity indexes are presented in Fig. 1a.

An instance in which the use of reactivity indexes may lead to an incorrect representation of the relative reactivities of A and B molecules is presented in Fig. 1b. This is a case in which neither the indexes of the first or second group "work." A situation in which the indexes of only one group (more often the first group) give incorrect information regarding the reactivity is possible.

Finally, one should take into account another circumstance that has a direct bearing on heterocyclic systems. All of the reactivities of the first group enumerated above are substantiated theoretically only for alternating hydrocarbon systems, a peculiarity of which is uniform charge distribution and "symmetrical" disposition of the occupied and vacant orbital equations. Nonuniformity of the charge distribution and the MO levels, which, in particular, is also characteristic for heteroaromatic molecules, leads to the disappearance of the conformity between the different indexes, and a separate analysis of the applicability of the methods used is necessary in each case for the selection of the most suitable method for the theoretical description of the reactivity.

Electrophilic Substitution Reactions. The substitution (electrophilic, radical, or nucleophilic) reactions of pyrrole, furan, and thiophene are directed primarily to the ring α position. Data that make it possible to give a quantitative evaluation of the reactivities of five-membered heteroaromatic compounds (for example, see the review on electrophilic substitution [181]) have been recently obtained in a number of studies by means of direct kinetic measurements or by the method of competitive reactions.

The results of calculations of the relative activities of the various positions of the heteroaromatic ring in electrophilic substitution reactions carried out within the framework of the π-electron approximation contradict not only the experimental results but also contradict one another. For example, the following theoretical estimates of the reactivities of various positions have been proposed for thiophene: $\alpha = S = \beta$ [92, 93], $S < \alpha < \beta$ [58, 94], $S < \beta < \alpha$ [47, 101, 182, 183], $\beta < S < \alpha$ [184], and $\alpha < S < \beta$ [185]. A similar situation has existed in calculations of other five-membered aromatic heterocycles. The situation improved somewhat with the development of semiempirical approaches that make it possible to take all of the valence electrons into account in the calculation. Thus in 1968 Hermann calculated pyrrole, furan, and their protonated (in the ring α and β positions) forms (σ complexes) by means of the CNDO/2 and EHT approaches [72]. In conformity with [186], the localization energy in calculations within the all-valence approximation can be defined as

$$\Lambda^{+} = E_b{}^{MH^{+}} - E_b{}^{M}, \tag{18}$$

where E_b^{M} and $E_b^{MH^+}$, respectively, are the energies of bonding of the aromatic molecule and its σ complex with a proton. The σ complex was postulated by Wheland [187] as the intermediate state of aromatic electrophilic substitution, and there is currently no doubt that it exists (see earlier reviews [181, 188]). The relative rate constant for electrophilic substitution in a series of similarly constructed aromatic molecules can then be defined as

$$\lg k/k_0 = -\text{const}\,\frac{\lg e}{RT}\,\Delta\Lambda^{+} \tag{19}$$

or, at constant temperature,

$$\lg k/k_0 = c\Delta\Lambda^{+}, \tag{20}$$

where k and k_0 are the rate constants for electrophilic substitution in the investigated (M) and standard (O) molecules (usually in benzene), $\Delta\Lambda^{+} = \Lambda_{M^+} - \Lambda_{O^+}$, and c is the coefficient of proportionality, which depends on the method of calculation and the chemical nature of the electrophile. The relative rate constants for deuteration in acid of thiophene, furan, and pyrrole [189], calculated by this method, and the corresponding experimental values [190] are presented in Fig. 2a. The Λ^+ values for furan and pyrrole were borrowed from [72], and the values for thiophene were calculated in [189]. Coefficient $c = -0.5203$ was determined by the method of least squares. Similar calculations for isomeric thienothiophenes and a comparison of the calculated Λ^+ values with the experimental data on the rate constants for acetylation, chlorination, formylation, and dedeuteration in acid for the isomeric thienothiophenes were made in [191]. On the basis of the data obtained in [189, 191] it could be concluded that the Λ^+ value calculated with allowance for all of the valence electrons qualitatively suf-

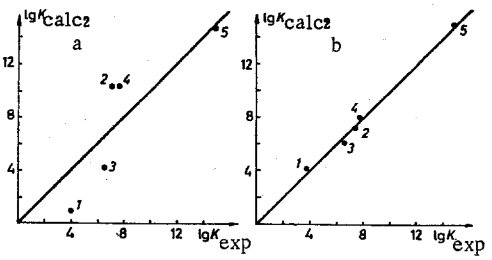


Fig. 2. Relationship between the calculated [from Eqs. (20) (a) and (23) (b)] and the experimental rate constants for deuteration in acid relative to benzene for five-membered heteroaromatic compounds: 1) thiophene (3); 2) thiophene (2); 3) furan (3); 4) furan (2); 5) pyrrole (2).

TABLE 14. Reactivity Indexes in the Diels–Alder Reaction [201]

Molecule	Overlap populations		R
	$C_{(2)}$—$C_{(3)}$	$C_{(3)}$—$C_{(4)}$	
Benzene	0,5206	0,5206	1,000
Pyrrole	0,5777	0,4916	1,175
Thiophene	0,5950	0,4774	1,246
Furan	0,6837	0,5326	1,283
Cyclopentadiene	0,6215	0,4288	1,449
cis-Butadiene	0,6076	0,4034	1,506

ficiently satisfactorily conveys the relative reactivities of the various positions of the rings of heteroaromatic molecules. At the same time, the quantitative agreement leaves much to be desired (see Fig. 2a).

As an alternative to the method of localization energies we examined an approach that takes into account the formation of a complex with partial or complete charge transfer [a charge transfer complex (CTC)] as an intermediate step in the reaction [189]. Variants of this sort of approach have been periodically examined in the literature [192–194]. It is assumed that the kinetic scheme of electrophilic substitution has the form

$$\mathrm{ArH}+\mathrm{X}^{+} \underset{k_{-m}}{\overset{k_m}{\rightleftarrows}} (\mathrm{ArH}\ldots\mathrm{X})^{+}, \qquad (1)$$

$$(\mathrm{ArH}\ldots X)^{+} \xrightarrow{k_i} \mathrm{ArHX}^{+} \qquad (\sigma\text{-complex}). \qquad (2)$$

The rate of this process in the case of a steady-state $(\mathrm{ArH}\ldots\mathrm{X})^+$ concentration and a shift to the left of the equilibrium of reaction (1) obeys the equation of a bimolecular reaction

$$\frac{d[\mathrm{ArHX}^+]}{dt}=k[\mathrm{ArH}][\mathrm{X}^+],$$

where $k=k_iK$ and $K=k_m/k_{-m}$. At constant volume or pressure

$$K=\exp\,(\Delta S_0/R)\,\exp\,\{f(I_\mathrm{M},Q_\mathrm{E})/RT\}, \qquad (21)$$

where I_M is the ionization potential of the molecule, and Q_E is the electron affinity of the electrophile. Then, for a series of similarly constructed molecules,

$$\lg\frac{k}{k_0}=\frac{\lg e}{RT}\,[-\Delta E^{*}+f(\Delta I_\mathrm{M},Q_\mathrm{E})]. \qquad (22)$$

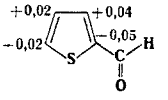
Assuming that the relative energy of formation of the CTC in the investigated series is proportional to the change in the ionization potential and, for the determination of ΔE*, that the resulting CTC has the properties of a radical pair and obeys the Semenov–Polanyi rule, we obtain an expression for the generalized reactivity index:

$$\lg\frac{k}{k_0}=A\Delta\Lambda^{+}+B\Delta I. \qquad (23)$$

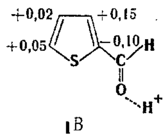
The relative constants for deuteration in acid [A = − 0.1543, B = − 0.4533 (kcal/mole)$^{-1}$], calculated from Eq. (23), and the corresponding experimental data for pyrrole, furan, and thiophene are presented in Fig. 2b. We note that this is the first known quantitative theoretical interpretation of experimental data on the relative reactivities of pyrrole, furan, and thiophene.

At the same time, simpler reactivity indexes also prove to be useful in the analysis of experimental data. In particular, the charges on the atoms have been used for the discussion of the reactivities of carbonyl compounds of the thiophene and furan series and their carbonyl- oxygen-protonated forms [157, 159].

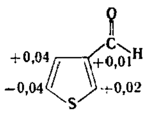
The total charges on the ring atoms in molecules of unprotonated and protonated 2- and 3-formylthiophene, calculated by the CNDO/2 method, are presented in the scheme below:



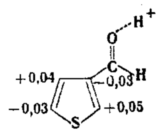
I A



IB



II A



IIB

As seen from the molecular diagrams presented above, of the free (unbonded with a substituent) ring positions in the case of Ia, the 5 position, to which the electrophilic attack should also be directed, has the most negative charge; this is in complete agreement with the available experimental data. In the case of protonated form IB the lowest positive charge is found in the 4 position. Thus the 4 position becomes preferred for reaction with an electrophilic agent, and this makes it possible to explain the charge in the direction of electrophilic attack in complexes of carbonyl compounds of the thiophene series with Lewis acids.

Protonation of II does not lead to a change in the character of the electron density distribution, and the 5 position retains the greatest negative charge.

Finally, the data obtained make it possible to understand why α-acylthiophenes are inclined to undergo transacylation and similar processes involving replacement of the acyl group by the attacking electrophile, whereas β isomers do not display this ability under similar conditions. In fact, the most negative charge in IA and IB is localized in the 2 position, and, although replacement of an acyl group by the electrophile is considerably more difficult than displacement of a proton, a large surplus negative charge should favor the former process to an appreciable extent.

In the case of II the charge in the 3 position is either positive (IIA) or negative (IIB) but is equal in magnitude to the charge in the 5 position. Considering the fact that the acyl group in the 3 position should be replaced, whereas the proton in the 5 position should be substituted, it can be concluded that substitution in the 5 position should be more likely.

The reactivities of five-membered heteroaromatic molecules in substitution reactions have also been discussed in [54, 74, 76, 84, 85, 98, 126, 131, and 195-199].

Cycloaddition Reactions. There are several studies in the literature devoted to an examination of the reactivities of five-membered heteroaromatic molecules in Diels–Alder reactions. In the first study [87] the reactivities of thiophene, thiophene 1,1-dioxide, and furan were analyzed within the framework of the reflection method [200]. The idea of this approach consists in an analysis of the stabilization energy of the level of the π orbitals of the diene during reaction with $-S-$, $-SO_2-$, or $-O-$ to give thiophene, thiophene 1,1-dioxide, or furan. The theoretical order of reactivities of the investigated compounds in cycloaddition was established on the basis of the data obtained: furan > thiophene 1,1-dioxide > thiophene. Dietmar [88] used the INDO method with transformation of the MO obtained to localized MO for analysis of the reactivities of pyrrole, furan, and cyclopentadiene. The diene character of the molecule was determined on the basis of the fraction of the π density localized on the double bonds. It follows from the results of the calculations that the reactivity of cyclopentadiene is higher than that of furan and higher than that of pyrrole. Finally, a similar study was made in [201] under the assumption that the tendency to undergo the Diels–Alder reaction can be correlated with the ratio (R) of the overlap populations in the formal double and single bonds. This "Hückel" series of reactivities obtained on the basis of ab initio calculations is presented in Table 14.

It should be noted that in contrast to substitution reactions in aromatic compounds, a unified approach to the theoretical evaluation of reactivities has not yet been formulated for cycloaddition reactions. This is also reflected in the contradictory results of the studies examined above. Thus, according to the data in [201], thiophene, which practically does not undergo reactions of this type, should be more reactive than pyrrole, and this clearly does not correlate with the experimental data.

CONCLUSIONS

In undertaking the present review, the authors attempted to make a comparative evaluation of the quantum-chemical methods currently used for the calculation of the physical properties and reactivities of heteroaromatic compounds. In summarizing all of the material set forth above, it may be concluded that a number of physical properties of heteroaromatic molecules such as the charge distribution, dipole moments, NMR spin–spin coupling constants, and ESR isotropic hyperfine coupling constants are quite satisfactorily described by the existing quantum-chemical methods. The situation is somewhat worse in the case of ionization potentials, UV spectra, ^{13}C nuclear chemical shifts, and conformational calculations. Finally, there have been practically no calculations of the vibrational spectra and the chemical shifts of protons (except for the simple correlation relationships between δ_H and the charge on the adjacent carbon atoms). The situation is similar in the case of calculations of the reactivities of heteroaromatic compounds. As seen from the data presented in this review, whereas the reactivities of the compounds under consideration in electrophilic substitution reactions can be theoretically evaluated quite reliably and unambiguously, the results of various approaches may differ substantially in the evaluation of the reactivities in reactions of the Diels–Alder type.

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MECHANISM OF HALOGEN SUBSTITUTION IN THE ELECTROCHEMICAL REDUCTION OF HALONITROFURANS IN DIMETHYLFORMAMIDE

I. M. Sosonkin, G. N. Strogov,
V. N. Novikov, and T. K. Ponomareva

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The polarographic reduction of 2-halo-5-nitrofurans in dimethylformamide, which leads ultimately to replacement of the halogen by hydrogen to give a nitrofuran, was studied. The ESR spectra of halonitrofuran anion radicals (Hal = Cl, Br) were recorded. Only the spectrum of the nitrofuran anion radical can be observed in the reduction of 2-I-5-nitrofuran. It is shown that the stabilities of the anion radicals of the halonitrofurans and the mechanism of their subsequent transformations depend to a considerable degree on the nature of the halogen.

The halogen in 2-halo-5-nitrofurans (HNF) is relatively easily exchanged by various nucleophilic groupings [1, 2], but the mechanism of these transformations has not yet been adequately ascertained. It is known that activated nucleophilic substitution reactions include acts involving electron transfer and the formation of anion radicals (AR) or dianions (DA) as intermediates [3, 4]. It therefore seemed of interest to follow the transformations of the HNF after electron transfer and to study the reactivities of their AR.

We investigated the polarographic behavior of HNF on a dropping mercury electrode (DME) in dimethylformamide (DMF) (Table 1). It is shown that 2-Cl-5-nitrofuran (CNF) adds the first electron reversibility to

TABLE 1. Reduction Potentials of HNF on a DME in DMF in a 0.1 N Bu_4NClO_4 Base Electrolyte (relative to a saturated calomel electrode)

Substituent	$-E'_{1/2}$*, V	$\Delta E'$ †, mV	i'_{lim}, μA	$-E''_{1/2}$, V	$\Delta E''$, mV	i''_{lim}, μA	$-E'''_{1/2}$, V	$\Delta E'''$, mV	i'''_{lim}, μA
Cl^-	0,995	58	1,6	2,290	140	7,8	—	—	—
Br^-	0,965	59	1,6	2,220	195	7,9	—	—	—
I^-	0,840	60	3,1	1,080	59	1,5	2,320	120	4,5
H^-	1,060	59	1,6	2,330	120	4,6	—	—	—

*The potentials are given with allowance for the resistance of the cell.
†$\Delta E = E_{3/4} - E_{1/4}$.

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