

INVESTIGATION OF OXAZOLIUM COMPOUNDS BY THE
SELF-CONSISTENT-FIELD MO LCAO METHOD

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The electron densities, the lower singlet-singlet transitions, and the diamagnetic characteristics were calculated on the basis of the semiempirical self-consistent-field method for a number of oxazolium and variously substituted oxazolium cations. The results were found to be in agreement with the available experimental data. The parameters of the nitrogen atom in the oxazolium cations were adopted within the framework of a unified parametrization that unites the pyridine, pyrrole, and immonium nitrogen atoms. It was found that over a broad range of structural changes in the oxazolium cation the maximum positive charge is found in the 2 position; this determines the site of nucleophilic addition in reactions involving opening and recyclization of these heterocycles. It was shown that the phenyl substituent attached to the nitrogen atom is least conjugated with the heteroring as compared with the other positions in the oxazolium ring; as a consequence of this, the smallest bathochromic shift of the long-wave absorption band of the UV spectrum is observed in the series of phenyl-substituted oxazolium salts, and the N-methyl group markedly shifts the spectrum to the short-wave region. The scale of aromaticity of the investigated compounds, according to which the azolium cations are less aromatic than the corresponding bases, is given.

Little study has been devoted to the electronic structures of oxazolium cations and their manifestation in the spectral characteristics and reactivities, although this important class of aromatic cyclic cations assumes practical importance as fluorescent substances (for example, scintillators) and in organic synthesis.

The selection of the π -electron semiempirical parameters in quantum-chemical calculations of self-consistent-field (SCF) systems containing a nitrogen atom in various states presents certain difficulties [1, 2], since different semiempirical parameters that are not interrelated are ordinarily used for pyridine, pyrrole, and quaternized nitrogen atoms and even in calculations of different properties of systems with nitrogen atoms of a single type.

In the present research, following the procedure in [2], we will use the unified parametrization of the nitrogen atom that was previously tested in calculations of the electronic absorption spectra of pyridine, pyrrole, and their benzo derivatives [3]. This makes it possible to not only compare the various properties of nitrogen-containing compounds but also to make a more reliable estimate of the reactivities on passing from nonquaternized to quaternized heterocycles, which occurs in recyclization processes and in catalytic processes in which acidic agents participate.

The significance of the parametrization used in this research consists in the fact that the interelectron interaction integrals and the resonance integrals do not depend on the type of nitrogen atom, and the coulombic integral (W) is associated with the number of π electrons furnished by a given atom to the π -electron system. For example, the W values of pyrrole and pyridine nitrogen atoms are interrelated by the expression

$$W_N = W_N^* + \frac{V_{NN}}{2}$$

The numerical values of the π -electron parameters of the carbon atom are identical to those used in [4], whereas those of the pyridine nitrogen atom are identical to those used in [5], in which an extensive number of molecular properties were used for compounds containing these atoms within the framework of a unified para-

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TABLE 1. Residual π -Electron Charges

Compound	Molecule	Charges on the heteroring					Total charges	
		q_1	q_2	q_3	q_4	q_5	hetero-ring	phenyl rings
I	Furan	0.275	-0.038	-0.099	-0.099	-0.038	0	
II	Pyrrole*	-0.113	-0.072	0.370	-0.072	-0.113	0	
III	Oxazole	0.281	0.057	-0.251	-0.043	-0.045	0	
IV	Oxazinium ion	0.285	0.241	0.115	0.015	0.046	1.000	
		(0.361)	(0.090)	(0.471)	(0.029)	(0.049)		
V	Oxadiazole	0.284	0.055	-0.197	-0.197	0.055	0	
VI	Oxadiazonium ion	0.279	0.310	0.442	-0.254	0.222	1.000	
VII	2-Phenyloxazolium ion	0.267	0.203	0.386	0.004	0.030	0.890	0.110
VIII	3-Phenyloxazolium ion	0.312	0.231	0.457	0.039	-0.056	0.983	0.017
IX	4-Phenyloxazolium ion	0.286	0.228	0.400	0.014	0.020	0.948	0.052
X	5-Phenyloxazolium ion	0.273	0.222	0.417	-0.013	0.041	0.940	0.060
XI	2,3-Diphenyloxazolium ion	0.265	0.180	0.121	-0.012	0.031	0.888	0.103 0.009
XII	2,4-Diphenyloxazolium ion	0.269	0.195	0.373	0.006	0.012	0.855	0.102 0.043
XIII	2,5-Diphenyloxazolium ion	0.257	0.190	0.389	-0.016	0.029	0.849	0.101 0.050
XIV	4,5-Diphenyloxazolium ion	0.275	0.217	0.402	-0.007	0.021	0.907	0.042 0.051
XV	2,3,5-Triphenyloxazol. ion	0.255	0.168	0.427	-0.033	0.030	0.847	0.095 0.004 0.049
XVI	2,4,5-Triphenyloxazol. ion	0.258	0.186	0.375	-0.009	0.013	0.823	0.096 0.040 0.042

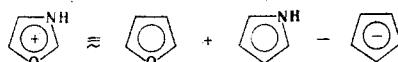
* The nitrogen atom is the 3 atom, as in oxazole.

metrization. The parameters of the furan (it will also be the pyrrole) oxygen atom ($W_O^{**} = -10.1$, $\beta_{C=O}^{**} = -3.5$, and $\gamma_{OO} = 15.57$ eV) and of the pyrrole nitrogen atom $W_N^{**} = -6.86$, $\beta_{C-N}^{**} = -3.1$, and $\gamma_{NN} = 10.4$ eV) were used for the calculation of the UV spectra of furan and pyrrole [3].

Since, first of all, the quaternized and pyrrole nitrogen atoms each furnish two electrons to the π -electron system (in heteroaromatic cyclic cations, including oxazolium ions, one of them is then transferred from the π -electron system to the gegenion) and, second, the closest chemical surroundings of the pyrrole nitrogen atom and the immonium nitrogen atom in oxazolium, pyridinium, etc. cations are identical, we assume that the π -electron parameters of these nitrogen atoms are equivalent.*

The chemical properties of these atoms are also similar, as indicated, for example, by a physicochemical value such as the pK_B , which is intimately associated with the charge on the nitrogen atom: pyrrole 16.5 [6], 4-phenyloxazolium ion 15.2 [7], 5-phenyloxazolium ion 13.7 [7], and oxazolium ion 13.2 [7]. As one might have expected, the trend of the change in the pK_B value is the opposite of the trend of the residual π -electron charge on the nitrogen atom (see Table 1); however, with respect to their pK_B values the oxazolium cations, as acids, are found in the same series as pyrrole.

It is curious that whereas we obtain pyrrole if the oxygen atom in the oxazolium cation is formally replaced by CH, we obtain furan if the quaternized nitrogen atom is replaced by CH. The oxazolium cation can then be represented by superimposition of the pyrrole and furan structures after subtraction of the cyclopentadienyl anion:



In fact, the electron distribution obtained by summation in conformity with the scheme presented above gives an accurate picture of the charge distribution in the oxazolium cation (see the numbers in parentheses in Table 1, where the results of quantum-chemical calculations of furan, pyrrole, and the oxazolium cation are also presented). The bond orders obtained by this scheme (the numbers in parentheses) are also in good agreement with the quantum-chemical calculation: $P_{1-2} = 0.514$ (0.572), $P_{2-3} = 0.621$ (0.617), $P_{3-4} = 0.482$ (0.450), $P_{4-5} = 0.797$ (0.856), and $P_{5-1} = 0.426$ (0.404).

The results of calculations of the charge distribution of the oxazolium cations are presented in Table 1. It follows from Table 1 that a sharp decrease in the residual π -electron charge in the 2 position is observed, whereas the charge density in the other positions changes extremely insignificantly. Allowance for the inter-electron interaction simplifies the picture of the electron distribution only somewhat (compare with [8]).

* In this case we follow the CNDO (complete neglect of differential overlap) method, in which the parameters for any type of nitrogen are identical and the manifestation of the nature of the atom in the quantum-chemical calculation depends only on its environment.

TABLE 2. Lower Singlet-Singlet Transitions (nm)

Compound	Molecule	Calc.	Compound	Molecule	Calc.
III	Oxazole	205.3	X	5-Phenylloxazolium ion	286.3
IV	Oxazolium ion	216.0	XI	2,3-Diphenyloxazol. ion	317.1
V	Oxadiazole	193.4	XII	2,4-Diphenyloxazol. ion	331.5
VI	Oxadiazolium ion	194.4	XIII	2,5-Diphenyloxazol. ion	336.0
VII	2-Phenyloxazol. ion	286.3	XIV	4,5-Diphenyloxazol. ion	322.0
VIII	3-Phenyloxazol. ion	267.2	XV	2,3,5-Triphenyloxaz. ion	348.0
IX	4-Phenyloxazol. ion	285.0	XVI	2,4,5-Triphenyloxaz. ion	363.6

The introduction of a phenyl substituent in any position of the heteroring leads to a small decrease in the positive charge in the 2 position and on the heteroring, which is larger, the larger the number of phenyl rings incorporated in the heterocyclic cation — the latter displays an appreciable electron-acceptor effect. The charges in the other positions of the heteroring remain almost the same in this case. In monosubstituted oxazolium cations the highest positive charge in the 2 position (and on the heteroring) is observed when there is a phenyl substituent attached to the nitrogen atom; this is associated with stabilization of the cationic state in the heteroring as a result of the least conjugation with the phenyl substituent. This is confirmed by the heteroring-phenyl ring bond orders, which, according to the calculation, have their lowest values when there is a phenyl ring attached to the nitrogen atom of the heteroring and are practically independent of the presence of other phenyl rings in the heterocycle: $P_{2-Ph} = 0.383-0.386$, $P_{3-Ph} = 0.245-0.299$, $P_{4-Ph} = 0.351-0.362$, and $P_{5-Ph} = 0.360-0.372$. The total charge on the phenyl rings therefore also depends on their position in the heteroring and changes symbiotically with the phenyl-heteroring bond orders, which characterize their degree of conjugation: q_{tot} for 2-phenyl = 0.10, as compared with 0.04-0.05 for 4- and 5-phenyl and 0.01 for 3-phenyl.

To make allowance for the effect of functional substituents in the phenyl rings and the heteroring on the charge distribution of the systems that we investigated we successfully tested the associated variant of perturbation theory in the SCF MO LCAO method during a study of the effects of chemical substitution on the proton and ^{13}C chemical shifts, the electrical polarizabilities, and the dipole moments [9]. The calculations show that quaternization of the oxazole and oxadiazole rings does not lead to a substantial change in the self-polarizability and mutual polarizability (π_{rs}). The introduction of functional substituents in the phenyl rings has practically no effect on the charge distribution in the oxazolium ring. The electron density changes least of all in the 2 position ($\pi_{2-Ph} = 0.00-0.04$, while $\pi_{4-Ph} \approx \pi_{5-Ph} = 0.02-0.05$; the results are presented in -3.8972 eV units; the maximum absolute values of the limits pertain to the atoms to which the phenyl group is connected). The self-polarizabilities of the carbon atoms of the oxazolium ring in unsubstituted and various mono-, di-, and triphenyl-substituted systems range from 0.4 to 0.5, whereas the mutual polarizabilities between these atoms are negative and lie in the following ranges: $\pi_{24} = 0.00-0.11$, $\pi_{25} = -0.09$ to -0.20 , and $\pi_{45} = -0.24$ to -0.32 .

It follows from the calculations that the highest positive residual charge in unsubstituted and various phenyl-substituted oxazolium cations corresponds to the 2 position, to which nucleophilic addition should also take place. In fact, it has been proved in a number of simplest examples [10] that nucleophilic opening of the ring in phenyl-substituted oxazolium cations proceeds precisely at the $O-C_2$ bond. In more complex processes — in recyclization reactions — we also proceeded from the same premises by way of analogy. The calculations performed in this research make it possible to consider these assumptions to be substantiated in various aryl derivatives of the oxazolium cation.

The calculated π_{rs} values provide evidence that the presence of functional substituents in the phenyl rings does not entail changes in the site of primary nucleophilic attack, but direct substitution of the heteroring by groups with high $\Delta\alpha$ values may lead to reorientation in nucleophilic addition (see [11] for experimental examples), as follows from Table 1 and the above-determined ranges of the changes in the π_{rs} values of the heteroring.

On the basis of the above-described charge distribution in oxazolium cations with allowance for the superimposition of all of the singly excited configurations by the method developed in [12] we determined the energies of the lower singlet-singlet transitions. The values found within the framework of the above-described parametrization are presented in Table 2, and the experimentally obtained UV spectra of the oxazolium salts are presented in Figs. 1 and 2.

Protonation of oxazole and 1,3,4-oxadiazole (Table 2) leads to a small shift in the spectra. Protonation of phenyl-substituted oxazoles leads to a more complex dependence (Fig. 1): the absorption maxima of the un-

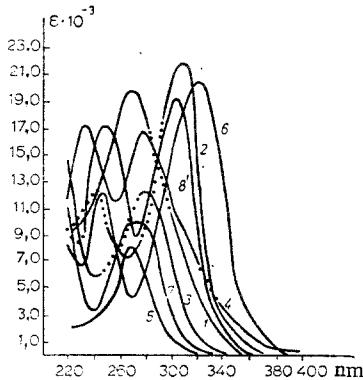


Fig. 1

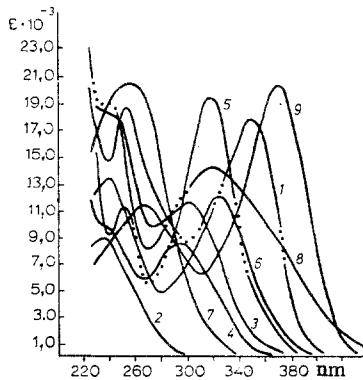
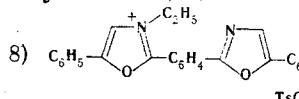


Fig. 2

Fig. 1. Experimental UV absorption spectra of oxazoles: 1) 5-phenyloxazole XVII; 2) 2,5-diphenyloxazole XVIII; 3) 4,5-diphenyloxazole XIX; 4) 2,4-diphenyloxazole XX in 96% ethanol (see [9]); 5) XVII; 6) XVIII; 7) XIX; 8) XX in 98% H_2SO_4 .

Fig. 2. Experimental UV absorption spectra of oxazolium salts in 96% ethanol: 1) 2,3,5-triphenyloxazolium perchlorate XV; 2) 2,3-dimethyl-5-phenyloxazolium perchlorate XXI; 3) 2,5-diphenyl-3-methyloxazolium tosylate XXII; 4) 2,5-diphenyl-3-ethyloxazolium tosylate XXIII; 5) 2-(*p*-methoxyphenyl)-3-methyl-5-phenyloxazolium tosylate XXIV; 6) 2-(*p*-diphenyl)-3-methyl-5-phenyloxazolium tosylate XXV; 7) 2-methyl-3,5-diphenyloxazolium perchlorate XXVI;

8)  (XXVII); 9) 2,3-diphenyl-5-furyloxazolium tosylate XXVIII.

protonated forms of X, XII, XIII, and XIV in ethanol are 261, 276, 314, and 280 nm, as compared with 268, 302, 319, and 275 nm, respectively, in concentrated sulfuric acid (Fig. 1). It follows from Table 2 and Figs. 1 and 2 that the introduction of a phenyl group in any position of the oxazolium cation leads to a bathochromic shift of ~ 60 –70 nm. A second phenyl residue has a lesser effect (a bathochromic shift of 30–40 nm), while a third phenyl group has an even smaller effect (20 nm). In this case a phenyl ring attached to the nitrogen atom has the smallest effect; this is in conformity with the lowest conjugation of the phenyl ring with the heteroring (see the corresponding bond orders presented above).

Quaternation of the nitrogen atom with alkyl groups leads to an appreciable shift in the spectra of these compounds as compared with the nonquaternized forms: oxazolium salt XXI absorbs at 235 nm, XXII absorbs at 298 nm, and XXIII absorbs at 295 nm.

It should be noted that when an electron-donor grouping that shifts the spectrum to the longer-wave region is introduced in the 2 position (compare XXII, XXIV, and XXV), the effect of the methyl group is leveled: oxazolium salt XXIV absorbs at 318 nm, XXV absorbs at 326 nm, while the nonquaternized forms of these compounds absorb at 308 and 320 nm [13], respectively. However, the introduction of an electron-acceptor grouping does not change the bathochromic effect characteristic for the N-alkyl group: oxazolium salt XXVII absorbs at 321 nm, and the nonquaternized form absorbs at 358 nm, which, in conformity with [9] ($\Delta\lambda = K_\lambda r \cdot \Delta\alpha$), can be ascribed to the effect of electron-donor and electron-acceptor groups with different signs. The introduction of electron-donor substituents in the 5 position also leads to a bathochromic shift of the bands (compare XV and XXVIII). We note that the nature of the gegenion (ClO_4^- , TsO^-) has practically no effect on the position of the absorption of the oxazolium salts.

On the basis of the data obtained let us also examine the problem of the aromaticity of azolium cations; this problem has not been studied previously. As the principal index of aromaticity we will adopt the relative π -electron diamagnetic susceptibility ($\chi^\pi / \chi^\pi_{C_6H_6}$) of these compounds; this value was calculated by the method developed in [4] within the framework of the associated variant of perturbation theory in the MO LCAO method of the above-described charge distribution of the ground state and tested in calculations of both uncharged and

TABLE 3. Diamagnetic Susceptibilities (in $10^{-6} \text{ cm}^3/\text{mole}$ units) and Induced π -Electron Currents (in units based on the current in the benzene ring)

Compound	Molecule	π -Electron calculation			χ^m		$\chi^{\pi}/\chi_{C_6H_6}^{\pi}$	Induced currents	
		χ^d	χ^p	χ^{π}	calc.	exptl.		I_i	phenyls
I	Furan	16,67	-1,09	15,58	43,1	43,1	0,499	0,754	
II	Pyrrole	16,54	-0,68	15,86	41,3	47,6	0,508	0,767	
III	Oxazole	17,00	-1,34	15,66	37,8	38,0	0,502	0,758	
IV	Oxazolium ion	17,42	-2,47	14,95	37,9		0,464	0,723	
V	Oxadiazole	17,23	-1,61	15,62	32,5		0,501	0,756	
VI	Oxadiazolium ion	17,30	-3,76	13,54	31,7		0,434	0,655	
VII	2-Phenylloxaz. ion	210,98	-168,97	42,01	91,61		1,346	0,648	0,917
VIII	3-Phenylloxaz. ion	214,13	-169,80	44,34	92,39		1,421	0,701	0,956
IX	4-Phenylloxaz. ion	212,83	-169,38	43,44	92,09		1,392	0,682	0,941
X	5-Phenylloxaz. ion	212,54	-169,36	43,18	92,00		1,384	0,676	0,936
XI	2,4-Diphenyloxa- zolum ion	406,69	-335,97	70,72	140,89		2,267	0,614	0,919 0,942
XII	2,5-Diphenyloxa- zolum ion	406,45	-335,95	70,50	140,82		2,260	0,610	0,919 0,937

charged systems. The results of the calculation of the diamagnetic susceptibility and the π -electron currents induced in the rings are presented in Table 3, in which the results of π -electron calculations of the diamagnetic (χ^d), paramagnetic (χ^p), and total π -electron (χ^{π}) contributions to the diamagnetic susceptibility are given in the first three columns. The molar diamagnetic susceptibility (χ^m), which is presented in the fourth column of Table 3, in which it is compared with the available experimental data [7, 14], was found with allowance for these contributions by means of an additive scheme in which all of the bonds in the cation were assumed, as in [5], to be magnetically equivalent with an additivity constant of $-3.61 \cdot 10^{-6} \text{ cm}^3/\text{mole}$ and the unshared pair of electrons of the oxygen atom was considered to be an additive parameter equal to $-5.41 \cdot 10^{-6} \text{ cm}^3/\text{mole}$, selected with respect to furan [7].

It follows from Table 3 that the aromaticity of the investigated simple heterocycles decreases with respect to the relative π -electron diamagnetic susceptibility ($\chi^{\pi}/\chi_{C_6H_6}^{\pi}$) in the order

$$I > III \geq V > II > IV > VI.$$

On the scale that we established, the aromaticity of furan and pyrrole is in agreement with the data of Corradi and co-workers [15]. It should be emphasized that conversion of the azoles to the cationic state leads to a decrease in their aromaticity due to a decrease in the induced π -electron currents (I_i) in the heteroring. As one might have expected, the introduction of phenyl substituents leads to an increase in the aromaticity of the cation, and the increase is greater, the larger the number of phenyl residues introduced. The induced π -electron currents in the heteroring decrease symbatically in this case, and the decrease is greater, the higher the conjugation of the oxazolium ring with the phenyl substituent; the corresponding bond orders discussed above are indicative of this. The currents in the phenyl rings also decrease as their conjugation with the heteroring increases, and this leads to a decrease in the overall aromaticity of the cation as a whole, which, for example, in oxazole VIII, in which the phenyl residue is attached to the nitrogen atom and is least conjugated with the heteroring, is maximal among the monosubstituted oxazolium salts.

Thus an increase in the number of phenyl rings attached to the oxazolium ring leads, on the one hand, to an increase in the aromaticity of the system as a whole and a shift of the spectrum to the long-wave region and, on the other, to a decrease in the residual charge in the 2 position, i.e., to a decrease in the electrophilic activity of the cation. Although it also leads to a decrease in the overall aromaticity of the system, an increase in the conjugation of the phenyl rings with the heteroring in individual series of mono-, di-, and tri-phenyl-substituted oxazolium salts results in a bathochromic shift of the absorption spectra and a decrease in the charge in the 2 position of the heteroring.

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QUANTUM-CHEMICAL STUDY OF THE CH ACIDITIES OF
METHYL DERIVATIVES OF FIVE-MEMBERED AROMATIC
HETEROCYCLES

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The CNDO/2 (complete neglect of differential overlap) method was used for the study of the possibility of the quantum-chemical description of the electronic effects of substituents and heteroatoms on the CH acid properties of an extensive series of methyl derivatives of five-membered aromatic heterocycles. It is shown that the trend of the change in the relative rate constants of deuterium exchange of the methyl derivatives of furan, thiophene, thiazole, isothiazole, oxazole, isoxazole, pyrazole, imidazole, oxa- and thiadiazoles, and tetrazole corresponds in most cases to the changes in the deprotonation energies ($\Delta E = E_{\text{Het}-\text{CH}_2^-} - E_{\text{Het}-\text{CH}_3}$) and the charges on the hydrogen atoms of the methyl groups undergoing attack by the base. The factors responsible for violation of the indicated simple conformity are discussed.

Studies made in recent years have shown that within the limits of a series of similarly constructed compounds, the CNDO/2 (complete neglect of differential overlap) method can be successfully applied for the description of the kinetic and equilibrium acidities of carboxylic acids (for example, see the data on the CH acidities of substituted benzenes [1], some five- and six-membered nitrogen-containing heterocycles [2-4], methanes [5], ethylenes [6], phenylacetylenes [1], methyl derivatives of aromatic compounds [1], saturated rings [7, 8], etc.). In a continuation of our research on the relationship between the electronic structure and the lability of hydrogen atoms in organic compounds of different classes, we made a quantum-chemical examination of the CH acid properties of an extensive series of methyl derivatives of five-membered aromatic heterocycles. As in [5, 7, 9], we used the deprotonation energies ($\Delta E = E_{\text{Het}-\text{CH}_2^-} - E_{\text{Het}-\text{CH}_3}$) and the charges on the hydrogen atoms (q_H) undergoing attack by the base as the theoretical reactivity indices. The ΔE values were calculated for "planar" and pyramidal configurations corresponding to the model of complete detachment of a proton in the carbanion transition state. The experimental geometry of the corresponding unsubstituted heterocycles [9] was used as the basis of the calculation of the investigated series of methyl derivatives in most cases; the parameters of the idealized geometry recommended by Pople and Gordon [10] were used for

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