

LOCALIZATION OF ELECTRONIC EXCITATION AND CHANGE IN THE DIRECTION OF ELECTROPHILIC SUBSTITUTION REACTIONS IN SOME PHENYLAZOLES, 2-FURYLAZOLES, AND 2-THIENYLAZOLE*

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NMR, IR, UV, and fluorescence spectral data and semiempirical quantum chemical PPP and INDO/S methods were used to refine the electronic structure of several azoles and analyze the change in course of electrophilic aromatic substitution reactions involving addition and dissociation in going from free bases to protonated forms. The electronically excited singlet and triplet states of the protonated forms of the mono- and bicyclic systems studied feature excitation localization different from the free molecules. The results of quantum chemical modelling of the change in the reactivities of these systems are given.

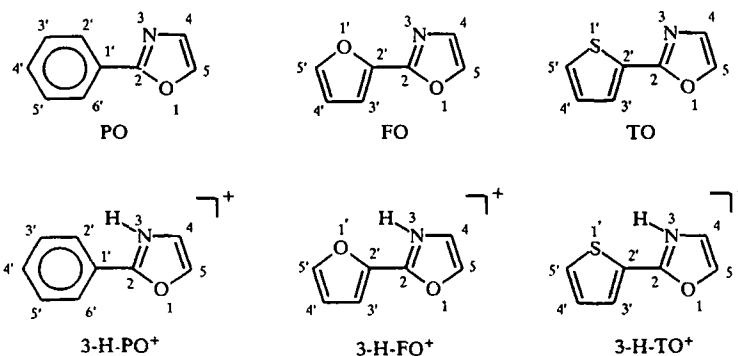
INTRODUCTION

The study of the properties of excited singlet and triplet states of organic molecules contributes to our understanding of both the intramolecular mechanisms leading to their various physical and photophysical characteristics and the chemical nature of their transformations. Nonfused tri- and pentacyclic systems containing one or two oxazole or 1,3,4-oxadiazole fragments are used as luminophors and active media for optical lasers in vapor and solutions [1-6]. 2-Phenyloxazole (PO), 2-(2-furyl)oxazole (FO), and 2-(2-thienyl)oxazole (TO) contain the same structural elements (atoms, groups, and rings) found in tri- and pentacyclic polyatomic systems with high luminescence capacity and may serve as their synthetic precursors [7]. Thus, we have already analyzed the reasons for the low luminescence activity of mono- and bicyclic systems [8] and the change in the photophysical characteristics [5] and course of their electrophilic substitution reactions [7, 9] due to protonation or formation of an $n\nu$ -complex with a Lewis acid at the pyridinic nitrogen atom of the heterocycle.

In the present work, we studied the interrelationship between the selective change in the reactivity of PO, FO, and TO and their analogs and the electronic structure of the excited electronic singlet and triplet states depending on the experimental conditions such as specific solvation, protonation, and complexation. The effect of protonation and complexation for the ground state has been studied both experimentally [7, 10-12] and theoretically [9, 12]. Synthetic methods permit us to alter the course of reactions and introduce electrophiles either into the aryl or hetaryl fragment if the azole ring is deactivated due to protonation or complexation with a Lewis acid or into the azole fragment if the molecule reacts as the free base [7]. There is presently no information on the reactions of bicyclic nonfused compounds of this type.

Photochemical electrophilic and nucleophilic aromatic substitution reactions proceed much more rapidly than the "dark" reactions. The orienting effects of the substituents also are significantly altered [13, 14]. We should note that acid-base properties are markedly enhanced in the excited states of aromatic molecules [15]. For example, the basicity of aromatic hydrocarbons is enhanced in the triplet state by 10-15 orders of magnitude [16, 17].

*Dedicated to Prof. A. Katritzky on his seventieth birthday.



In light of the structures of the compounds studied in this work, we shall initially consider several properties of monocyclic compounds such as benzene, furan, thiophene, and oxazole and, then, bicyclic systems containing the same cyclic fragments. 1,3,4-Oxadiazole will also be examined for comparison with oxazole.

1. CALCULATION METHODS AND EXPERIMENTAL

1.1. Experimental Methods

The preparation of 2-phenyloxazole (PO) has been described in our previous work [10] and the preparation of the other compounds were described in a subsequent study [18]. The ¹H NMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz, while the ¹³C NMR spectra were taken on a Bruker WM-250 spectrometer for solutions in CDCl₃ and presented in our previous work [10-12, 18]. The IR spectra were taken for KBr pellets on a Specord M-40 spectrometer. The precision for calculation of the vibrational bands in the UV spectra was a function of the systematic error of the instrument (≤ 10 -100 cm⁻¹), while the error in determining the optical density (D_{abs}^v) was not greater than 3-5%. The concentrations of the solutions were in the range from $\sim 10^{-3}$ to 10^{-7} moles/liter. The spectra are given as the molar extinction coefficient vs. the frequency ν , cm⁻¹.

The excitation and fluorescence spectra were taken on an SLM-4800S spectrofluorimeter and given in accordance with the literature [19]. The solution concentration was about 10^{-5} mole/liter.

The fluorescence quantum yield (γ) for this series of compounds was measured relative to γ of ethanolic anthracene: $\gamma = 0.22$ [2-6].

1.2. Quantum Chemical Calculations

The semiempirical INDO/S (*sp* basis) and PPP (Pariser–Parr–Pople) methods were used to calculate the excited electronic singlet and triplet states and characteristics of the following electronic transitions: $S_0 \rightarrow S_n^*$, $S_1^* \rightarrow S_0^*$, $S_1^* \rightarrow S_n^*$, $T_1 \rightarrow T_n$, and $T_1 \rightarrow S_0$ [20-22]. The two-electron integrals $\gamma_{\mu\nu}$ were found using the formula of Mataga and Nishimoto [23, 24]. The atomic spectral parameters (ionization potentials I_μ and electron affinities A_μ) of the free atomic gases were used in the calculations [24, 25]. Some results of these calculations are given in Tables 1 and 2.

2. RESULTS AND DISCUSSION

2.1. Structures of Phenyl-, 2-Furyl-, and 2-Thienyloxazoles and -1,3,4-Oxadiazoles

The aryl and hetaryl oxazoles and 1,3,4-oxadiazoles examined are liquids under ordinary conditions, which hinders the study of their structure by x-ray diffraction analysis. X-ray, electron diffraction, and quantum chemical data for their com-

ponent benzene, furan, thiophene, oxazole, thiazole and 1,3,4-oxadiazole rings [26-28] as well as for 2,2'-dithiophene and 2,5-diphenyl-1,3,4-oxadiazole [29] are available. Thus, we encounter the problem of determining the physicochemical characteristics of aryl- and hetaryloxazoles for the geometry optimized by the LCAO MO SCF method taking account of the configurational interaction (using standard spectroscopic parametrization) and their comparison with the experimental data for ionization potentials, electron affinities, and various types of bond lengths and corresponding bond angles [30, 31].

The structural data for several tricyclic nonfused azoles obtained either experimentally or by quantum chemical calculations (for the optimized ground state geometry) indicate alternation of the single and double bonds in these heterocycles and that the intercylic carbon-carbon bond is always single, i.e., its order $p_{\mu\nu} < 0.3$ [3-6, 8, 32]. Thus, the structural features are rather reliably reproduced independently of the semiempirical method used to obtain the molecular geometry. The differences observed in the bond lengths calculated by the PPP, INDO/S, MNDO, AM1, and other methods are slight [31].

2.2 Infrared Absorption Spectra

The IR spectra for polyatomic heterocyclic molecules have complex structure featuring overlapping bands of different intensity in the range $1700-400\text{ cm}^{-1}$. All the IR bands correspond both to the fundamental and combination bond vibrations [32]. The band at 1592 cm^{-1} is assigned to a combination vibration $(992+606)\text{ cm}^{-1}$, which is active in the Raman and IR spectra [33, 34]. The line at 992 cm^{-1} corresponds to the fully symmetric vibration of the benzene ring carbon atoms A_{1g} , while the line at 606 cm^{-1} corresponds to the an incompletely symmetrical vibration B_{2u} . The strong bands at $1600-1630$ and $1540-1534\text{ cm}^{-1}$ should be ascribed to the asymmetrical vibrations of the oxazole ring with double and single C=N, C-N, and C=C bonds. The bands at $988-1008\text{ cm}^{-1}$ are assigned to deformation vibrations of the azocyclic bonds. The low-frequency strong IR bands at $625, 680, 750, \text{ and } 852\text{ cm}^{-1}$ indicate high activity of the out-of-plane and in-plane ring deformation vibrations in these molecules [33].

2.3. NMR Spectra and Electronic Structure of the Molecules in the Ground State

The PMR signals of 4-H and 5-H in the oxazole or oxadiazole rings are found downfield relative to the corresponding signals of benzene, furan, or thiophene rings (at $\delta = 7.4-8.4$ ppm for tricyclic systems containing an oxazole ring [7] and up to 9.3 ppm in the case of 1,4-phenylenebis-1,3,4-oxadiazole [35]). This is seen in the chemical shifts of the carbon atoms (for example, $\delta = 128.5-144.1$ ppm for $C_{(4)}$ [12]), indicating high aromaticity ($\sigma\pi$ -bonding of the atoms).

The structural subsystems of these molecules in the ground state display electronic vibrational quasiautonomy [2]. We could not establish which of the conformers of the polycyclic molecules are favored at room temperature since, in accord with the estimates of various workers [36-38], the energy barriers for isomerization do not exceed 2.0-2.5 kcal/mole.

The ^{13}C NMR spectral data show that the chemical shifts for $C_{(2)}$ in 2-methyloxazole and 2-methylthiazole differ from the shifts for benzene carbon atoms by 33-36 ppm, while this difference for $C_{(4)}$ and $C_{(5)}$ is only 1.55 and 13.95 and 9.95 and 10.15 ppm, respectively [11, 12]. The downfield shift for the ^{13}C nuclei for bicyclic 2-phenyloxazole and 2-thienyloxazole for the same free positions in the azocycles is 1.25 ppm greater than for the ^{13}C nuclei in benzene. We note that the difference in the chemical shifts of the ^{13}C nuclei for the benzene residue in PO and TO relative to benzene is not more than 2-6 ppm. Thus, the downfield chemical shift for the azocycles reflects a strong reduction in electron density on the nuclei. This reduction is much less for the benzene fragment.

Analysis of the electron occupancies $\rho_{\pi z}^i$ (INDO/S method) of the atoms in the ground state shows that replacement of the benzene ring by a furan or thiophene ring (going from PO to FO or TO) leads to an increase in the electron density on the nitrogen atom, decrease in the electron density on $O_{(2)}$, and some change on $C_{(4)}$ and $C_{(5)}$ (Table 2). The density $\rho_{\pi z}^i$ on 4-H and 5-H correspondingly increases or decreases. In all cases, the excess density on $C_{(4)}$ and $C_{(5)}$ is positive, while it is negative on $C_{(3')}$ and positive on $C_{(4')}$ (the furan or thiophene ring is chemically bound at free positions). This is clearly seen in the chemical shifts for 4-H and 5-H and in the chemical shifts for 4'-H and 5'-H, which are at lower field than for 4'-H and 5'-H. The qualitative agreement of the ^{13}C NMR chemical shifts upon corresponding rearrangements of the similar rings in different samples or upon complexation and protonation at the nitrogen unshared electron pair of the same compound indicates that an

TABLE 1. Charges q_0 and q^* and Electronic Excitation Localization Numbers L_i^a on the Ring Atoms in the Ground S_0 and Excited Singlet and Triplet T_1 States for Several Monocyclic Azoles Calculated by the PPP/S (π approximation) and INDO/S (sp basis) Methods

Compound	State	Index	O(1)	C(2)	C(3) OR N(3)	C(4) OR N(4)	C(5)
Oxazole	S_0	q_0	0,334	0,036	-0,269	-0,003	-0,097
		q_i^*	-0,254	0,223	-0,468	0,314	0,185
		L_i	34,8	8,2	12	16,7	27,3
	T_1	q_i^*	0,193	0,018	-0,231	0,081	-0,061
		L_i	7,7	27,9	7,8	19,9	36,7
1,3,4-Oxa- diazole	S_0	q_0	0,332	0,044	-0,210	-0,210	0,044
		q_i^*	0,179	0,020	-0,109	-0,109	0,020
		L_i	8,7	33,4	12,2	12,2	33,4
	T_1	q_i^*	0,192	0,009	-0,105	-0,105	0,009
		L_i	7,2	30,6	15,8	15,8	30,6
2-Methyl- oxazole ^b	S_0	q_0	0,287	0,131	-0,373	-0,001	-0,153

^aThe electronic excitation in the singlet S_1^* , S_2^* , S_3^* , and S_4^* and triplet T_1 states in the benzene molecule is distributed evenly over the ring atoms ($L_i = 16.7\%$).

^b $q_0 = 0.110$ on the methyl group carbon atom.

induction effect (intramolecular mechanism), transmitted through the $\sigma\pi\pi$ -electron system and reflecting some variation of the parameters of its atoms and bonds, predominates in each case.

2.4. Ultraviolet Absorption Spectra

A strong dependence of the frequency and shape of the highly pronounced long-wavelength band (LWB) is observed on structural factors for aryl- and hetaryloxazoles. A bathochromic shift is found for the LWB in going from aryl- and hetaryloxazolines, which have saturated bonds, to the corresponding oxazoles with conjugated bonds $\Delta\lambda_{abs}^{max}$ 10-30 nm, while replacement of the benzene ring by a furan or thiophene ring gives a bathochromic shift $\Delta\lambda_{abs}^{max} \sim 6-12$ nm. For thiophene derivatives, $\Delta\lambda_{abs}^{max}$ is three times greater. The extinction ϵ_{abs}^v at the LWB maximum is $(35-40) \cdot 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for bicyclic structures PO, TO, FO, and PP (biphenyl). For bicyclic structures with saturated bonds, ϵ_{abs}^v decreases gradually, while it drops more sharply for monocyclic molecules to $\epsilon_{abs}^v \sim (2-7) \cdot 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$ [2, 32, 37] (Fig. 1). No $n\pi$ bands were observed in the UV spectra of these compounds in solution, which is in accord with the literature data [19, 38].

2.5. Fluorescence Characteristics of Azoles

The mono- and bicyclic molecules fluoresce with $\lambda_{osc}^{max} \sim 260-310$ nm and quantum yields $\gamma \sim 0.0001-0.1$ in chemically inert solvents such as cyclohexane, methylcyclohexane, chloroform, pentane, and hexane and in hydroxyl and viscous solvents such as ethanol, dimethylformamide, dimethylsulfoxide, and diethyleneglycol. The lowest value for γ was found for benzene (0.0001), while the greatest value (0.1) was found for 2-(2-furyl)oxazole in diethyleneglycol.

For example, Fig. 2 shows the UV absorption and fluorescence spectra of a solution of PO in ethanol and in an equimolar mixture of ethanol and H_2SO_4 as well as the spectra calculated by the INDO/S and PPP methods for the free PO molecule. A bathochromic shift for the LWB ($\Delta\lambda_{abs}^{max} = 8$ nm) and the fluorescence peak ($\Delta\lambda_{fl}^{max} = 16$ nm) is found upon change in the solution pH as an increase in the wavelength of the 0-0 transition ($\Delta\lambda_{00} = 16$ nm) [37]. The shape of the broad bands is retained in the optical spectra. The change in the spectral-fluorescent characteristics of these molecules is attributed

TABLE 2. Charges q_0 and q^* , Electronic Excitation Localization Numbers L_i and Change in Electron Density $\Delta\rho$ on Atoms in the Ground S_0 and Excited Singlet and Triplet T_1 States for Several Aryl- and Hetaryloxazoles Calculated by the PPP/S (π approximation) and INDO/S (sp basis) Methods

Compound	State	Index	$O_{(1)}$	$C_{(2)}$	$C_{(3)}$ or $N_{(3)}$	$C_{(4)}$ or $N_{(4)}$	$C_{(5)}$	$O_{(1)}$ or $S_{(1)}$	$C_{(1)}$ (FO, TO) $C_{(2)}$	$C_{(2)}$ $C_{(6)}$ or $C_{(3)}$	$C_{(3)}$ $C_{(5)}$ or $C_{(4)}$	$C_{(4)}$ (FO, TO) $C_{(5)}$
2-Phenyl-oxazole (FO)	S_0	$\Delta\rho$	-0,265	-0,268	-0,296	0,041	0,111		0,031	0,002 0,002	-0,014 -0,014	-0,023
		q_i^0	0,328	0,031	-0,270	0,002	-0,094		-0,012	0,017 -0,013	0,005 0,000	0,005
	S_1^*	q_i^*	0,317	0,033	-0,274	0,024	-0,054		-0,019	0,108 -0,123	-0,043 0,032	0,000
		L_i	1,1	2,5	3,3	1,2	4,0		12,7	16,0 16,7	14,6 14,0	13,8
	S_2^*	q_i^*	0,274	0,030	-0,325	0,126	0,099		-0,083	-0,114 0,052	0,032 -0,043	-0,048
		L_i	3,8	14,2	9,5	6,5	16,9		12,9	9,8 9,1	2,2 2,7	12,3
	T_1	q_i^*	0,287	0,017	-0,259	0,036	-0,062		-0,017	0,009 -0,015	0,003 0,001	0,000
		L_i	2,8	7,5	5,4	3,3	10,3		13,3	12,4 12,5	9,3 9,2	14,0

TABLE 2 (continued)

Cation 3-H-PO ⁺	S ₀	q _i ⁰	0,360	0,302	-0,778	0,169	-0,125	-0,036	0,063	0,008	0,029
	S ₁ [*]	q _i [*]	0,286	-0,015	-0,826	0,373	0,186	-0,005	0,057	-0,004	0,004
		L _i	7,0	22,7	4,2	15,5	18	7,4	7,6	0,8	8,3
									7,4	1,2	
	T ₁	q _i [*]	0,343	0,167	-0,799	0,252	-0,024	0,011	0,032	0,009	0,013
		L _i	4,2	8,7	1,8	6,1	6,7	13,4	12,7	9,4	14,9
									13,0	9,1	
trans-2- (2-Furyl)- oxazole (FO)	S ₀	Δρ	-0,191	0,240	-0,300	0,097	0,058	-0,203	-0,041	0,106	0,142
		q _i ⁰	0,332	0,030	-0,286	-0,001	0,097	0,327	-0,082	-0,073	-0,068
		q _i [*]	0,261	-0,072	-0,361	0,105	0,034	0,254	-0,059	-0,124	-0,006
		L _i	4,9	15,5	11,0	4,6	15,5	3,6	14,2	13,6	15,1
		q _i [*]	0,272	-0,010	-0,270	0,044	-0,063	0,241	-0,056	-0,064	-0,049
		L _i	4,0	10,2	7,4	4,6	13,9	4,8	17,4	13,9	18,3
trans-2- (2-Thienyl)- oxazole (TO)	S ₀	Δρ	-0,208	0,278	-0,322	0,062	0,074	-0,049	-0,027	0,035	-0,051
		q _i ⁰	0,328	0,029	-0,308	0,004	-0,092	0,061	-0,009	-0,027	0,000
		q _i [*]	0,286	0,028	-0,308	0,088	0,046	-0,048	-0,008	-0,090	-0,019
		L _i	3,1	9,1	9,0	4,1	13	1,2	18,0	17,6	19,6
		q _i [*]	0,313	0,022	-0,268	0,016	-0,076	0,036	-0,014	-0,026	-0,004
		L _i	1,7	2,3	4,6	1,0	4,8	1,3	25,7	18,8	27,5

Δρ is the change in electron density on the carbon and hydrogen atoms along the z-axis perpendicular to the plane of the bicyclic system (INDO/S method), q_i⁰ and q_i^{} are the charges on the carbon atoms (PPP/S method), and L_i are the electronic excitation localization numbers (PPP/S method).

to a change in the nature of the intramolecular (electronic–vibrational and spin–orbital) interactions of the structural subsystems, which is reflected in the energy of the quantum system [20, 21].

Figure 3 shows schemes for the singlet and triplet transitions for PO, FO, and TO. Since the excited singlet or triplet $n\pi^*$ states for these molecules are low-lying (as for most bicyclic systems [8]), the electronic excitation energy is efficiently expended on transitions to triplet states with interconversion rate constant $k_{ST} \geq 10^8\text{-}10^{10} \text{ sec}^{-1}$. The optical $T_1 \rightarrow S_0$ transitions for most azoles are prohibited in the Franck–Condon approximation [2-6, 39]. Thus, some of the energy stored in the molecule is efficiently converted into heat. Hence, the importance of examining the relationship of the excitation localization characteristics and reactivity is obvious, specifically in the long-lived triplet state. The method of localization indices has been developed still only in the framework of the PPP/S approximation. However, since the same parametrization is used in the PPP/S and INDO/S methods [20, 23], such evaluations are fully justified and the data obtained by the two methods complement each other.

A common trait is found for the azoles studied: the interconversion rate is always greater than the rate of radiative decomposition of the fluorescent S_1^* state ($n\pi^*$ or $\pi\pi^*$ types), i.e., $k_{ST} \sim 10^8\text{-}10^9 \text{ sec}^{-1} \geq k_f \sim 10^6\text{-}10^8 \text{ sec}^{-1}$. The INDO/S calculations showed that the lowest triplet state (T_1) for oxazole, 1,3,4-oxadiazole, PO, FO, and TO is always a $\sigma\pi^*$ or $\pi\pi^*$ state (in the general case, π/π^* type). Internal or intercombinational conversion is a special case of nonradiative processes, which also encompass photoionization, preionization, and photochemical transformations [39]. Thus, we must examine the nature of the electronic excitation localization in molecules specifically in the fluorescent state.

3. EVALUATION OF THE REACTIVITY OF AZOCYCLIC MOLECULES BY ELECTRONIC EXCITATION LOCALIZATION NUMBERS

In strict Heisenberg matrix mechanics, there is no concept of the separation of energy into local contributions of atoms or molecular subsystems. However, the question of electronic excitation localization on atoms and fragments may be examined approximately by analyzing the localization numbers L_i [40].

The excitation localization numbers on atoms ($0 \leq L_\mu \leq 1$) and fragments ($\Sigma_\mu L_\mu$, %) in a molecule are evaluated using the following formula [40]:

$$L_\mu = \sum_{\nu=1}^m \left[D_{\mu\nu}^0 \right]^2. \quad (1)$$

In this case, the elements of the nonspin transition density matrix $[D_{\mu\nu}^0]$ are generated in an atomic (AO) basis of the molecular system where n is the number of occupied MO and m is the number of basis AO:

$$D_{\mu\nu}^0 = 1/\sqrt{2} \sum_{i=1}^n \sum_{p=n+1}^m d_{pi} (C_{\mu p} \cdot C_{\nu i} + C_{\mu i} \cdot C_{\nu p}),$$

where d_{pi} are the configurational coefficients of the configurational interaction (CI) matrix and $C_{i\mu}$ are the coefficients at the AO in the MO (obtained by the PPP, INDO/S, or CNDO/S methods).

Examination of the CI matrices obtained by the PPP or INDO/S methods shows that the $S_1^* \rightarrow S_0$ (similar to $T_1^* \rightarrow S_0$) for bicyclic molecules PO, FO, TO, and the corresponding forms 3-H-PO⁺, 3-H-FO⁺, and 3-H-TO⁺ protonated at N₍₃₎ is virtually single-configurational and is accomplished predominantly from the highest occupied to lowest unoccupied MO with coefficient $|\psi|^2 = 0.8\text{-}0.9$. Thus, it is important to determine the electronic characteristics of the molecules and their interacting states corresponding to the lowest energy of the quantum system [20].

Assuming complete localization of the n -orbital on the heteroatom (or its representation as a linear combination of n_j -orbitals of individual atoms), its energy ϵ_n is determined by the diagonal matrix element $\langle n|F|n \rangle$. The term $|n \rangle$ indicates the n -orbital, on which the n -electrons are located. For heterocyclic compounds, if the number of π -electrons of the heteroatom having n -electrons is equal to unity (in our case, this corresponds to an sp^2 -hybridized pyridinic nitrogen atom), the value of ϵ_n may be found from the following equation [39]:

$$\varepsilon_n = -I_n - \sum_{\nu} (P_{\nu\nu} - N_{\nu}) \cdot \gamma_{\nu n} - \frac{1}{2} \cdot p_n^{\pi} \cdot \chi, \quad (2)$$

where I_n is the ionization potential of the n -orbital of the unshared electron pair of the heteroatom in the valence state, $\gamma_{\nu n}$ are the integrals of the coulomb interaction of the n - and $p\pi$ -electrons of the ν -atom, p_n^{π} is the π -electron density on the heteroatom having n -electrons, and χ is the one-center integral of the exchange interaction of n - and $p\pi$ -electrons. In order of magnitude, we may assume: $\gamma_{\nu\nu} \sim 10$ eV, $\gamma_{\nu a} \leq 5$ -7 eV, $\beta_{\nu\nu} \leq 2$ eV, and $\chi \sim 1$ eV. Parameters found in Eq. (2) may be determined semiempirically.

Let us examine the data in Table 1 as an example. The lowest excited $\pi\pi^*$ states have charge separation q_i^* , $\sum_i q_i^*$, and numbers L_i (or $\sum_i L_i$) different from the ground state. An enhancement of the electronic-vibrational interaction of the structural subsystems and collectivization of the electronic-vibrational groups, which are quasiatomic in the ground state, are observed for bicyclic molecules in the lowest excited singlet and triplet states. The electronic structure of these bicyclic molecules is characterized by two basic properties, namely, localization and delocalization, which is reflected in the L_i values [3-6, 20, 37].

The excitation in monocyclic compounds is localized in individual bonds and atoms. With increasing number of subsystems in the structure, the charges q_i and indices L_i (or $\sum_i L_i$) depend on the number and sequence of chemical bonds between them. For example, in free PO, FO, TO, PT, and PP molecules, the excitation in the S_1^* and T_1 states is localized uniformly ($\sum_i L_i \sim 50\%$) on the rings independently of their electronic nature, while in their monosubstituted derivatives, 12-16, 53% and 35, 60, and 23% of the excitation is localized on the chromophore groups, respectively [20].

The greatest negative charge in the ground state is concentrated on the nitrogen atom of the oxazole, oxadiazole, or other heterocycle: $q_i = -(0.269-0.300)$. Positions 4 and 5 in oxazole have charges $q = -0.003$ and -0.097 , respectively. Position 5 should be the most active, which is in accord with the results of electrophilic substitution through an addition-dissociation mechanism [9]. However, the localization numbers indicate that position 2 is the most reactive in the excited state since $L_i = 35\%$ for this site, while $L_i = 18$ and 27% for positions 4 and 5, respectively (see Table 1). The data for 1,3,4-oxadiazole are also in accord: $L_i = 34\%$, $q = 0.044$. The heteroatoms take the least part in the electronic excitation of these azocycles; $L_i = \sim 12$ and 8% for nitrogen and oxygen, respectively. The introduction of a heteroatom into the ring not only gives rise to different atomic reaction sites but also may lead to greater reactivity than in the case of benzene [4].

The greatest electron density in the bicyclic PO, FO, and TO systems in the S_0 state is also localized on the nitrogen atom: $q = -0.270$, -0.286 , and -0.308 , respectively. The value of q in theazole fragment increases upon replacing the benzene ring with a furan and thiophene ring (the basicity increases). Positions 2 and 5 of the oxazole ring in the excited triplet T_1 state in free PO, FO, and TO molecules should be the most reactive ($L_i = 14.2$, 8.7 , and 10.2% and $L_i = 16.9$, 6.7 , and 13.9% , respectively), while the *para* positions should be most reactive in the benzene ring ($L_i = 12.9$ and 12.3%), positions 2' and 5' should be most reactive in the furan ring ($L_i = 17.4$ and 18.3%), and positions 2', 3', and 5' should be the most reactive in the thiophene ring ($L_i = 25.7$, 18.8 , and 27.5% , respectively).

Thus, we may expect that the thiophene ring in the bicyclic system acquires greater reactivity in comparison with the benzene and furan rings, which significantly enhances the reactivity of the azocycle atoms. The values of L_i in the S_1^* singlet state of FO molecules in positions 2 and 5 are equalized in the furan and azocycle, while they are significantly higher in the azocycle in the TO molecule than in the T_1 state.

The PPP calculation data indicating a diminution of the contribution of the group of azocyclic bonds to the formation of vibrational progressions in the UV absorption and fluorescence bands upon the introduction of a furan or thiophene ring instead of the benzene ring have been supported experimentally. In previous work [2, 37], we have shown that the bathochromic shift for λ_{abs}^{max} , λ_{osc}^{max} , and λ_{00} for the PO, FO, and TO molecules drops steadily upon protonation.

The results of the calculations for the free PO molecule and its protonated form 3-H-PO⁺ show that the change in the electronic state of the oxazole nitrogen atom, i.e., only one of the subsystems, leads to change in the distribution of charges q , localization numbers L_i , and bond orders $p_{\mu\nu}$ both in the azocycle and in the molecule as a whole [37]. The greatest electron density in the PO molecule is localized on the nitrogen atom and, thus, facile protonation is observed for this site (characteristic for all azoles). The $\sigma\pi$ -charge on the nitrogen atom in the ground state of PO and 3-H-PO⁺ is -0.270 and -0.778 . Furthermore, the total charge on the azocycle increases upon protonation from $\sum_i q_i^0 = -0.003$ to $\sum_i q_i^0 = -0.072$ (Table 2).

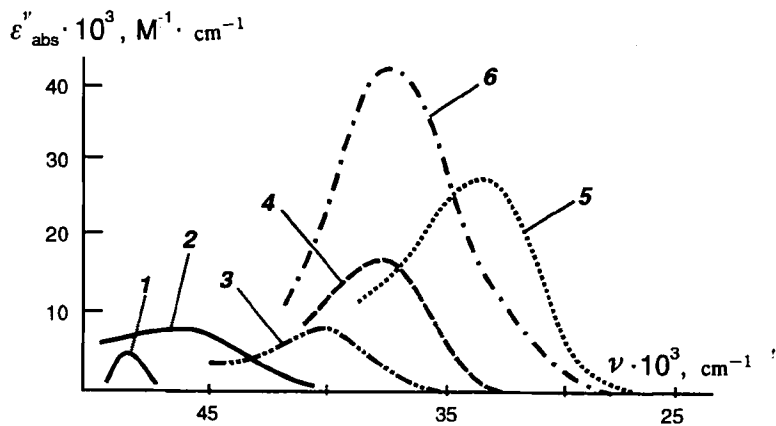


Fig. 1. Evolution of the UV spectra of azoles in solution: 1) 2-methyloxazole, 2) 4,5,4',5'-tetrahydro-2,2'-bisoxazole, 3) 4,5-dihydro-2-(2-furyl)oxazole, 4) 4,5-dihydro-2-(2-thienyl)oxazole, 5) 2-phenyloxazole, 6) 2-(2-furyl)oxazole.

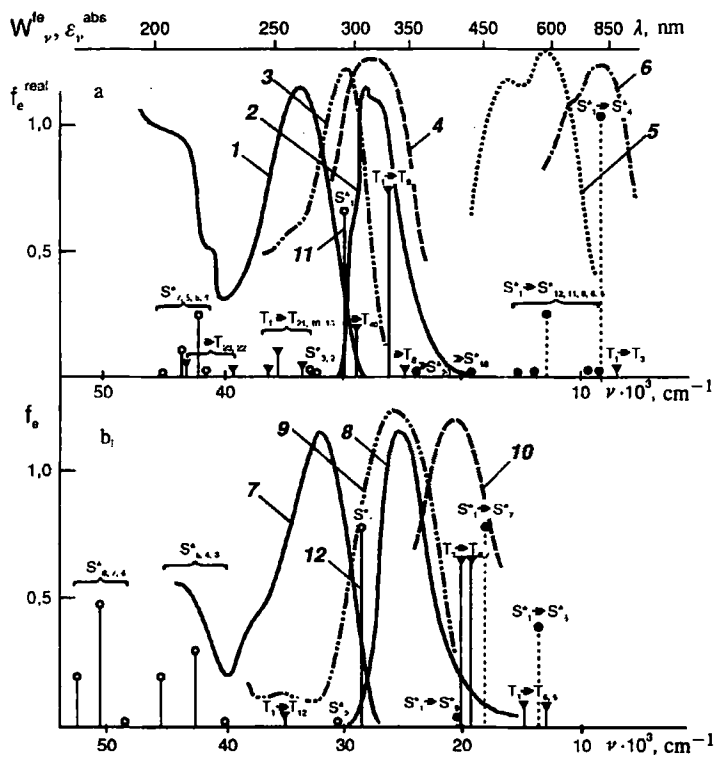


Fig. 2. UV absorption ε_{abs}^{ν} (1, 7) and fluorescence spectra $w\nu^{fl}$ (2, 8) of induced triplet-triplet $T_1 \rightarrow T_n$ (3, 4, 9) and singlet-singlet $S_1^* \rightarrow S_n^*$ reabsorption (5, 6, 10). For 2-phenyloxazole: a) in ethanol (1, 2, 3, 5), in the vapor phase (4, 6) and b) in equimolar ethanol- H_2SO_4 (pH \sim 2) (7, 8, 9, 10); 11, 12 according to data from the INDO/S and PPP/S methods, respectively. The vertical solid lines indicate the oscillator strengths f_e of the following electronic transitions: $S_0 \rightarrow S_n^*$, $S_1^* \rightarrow S_0$, $S_1^* \rightarrow S_n^*$, $T_1 \rightarrow T_n$, and $T_1 \rightarrow S_0$.

The change in properties of the PO molecule upon protonation is related to the selective change in the structure of one of its subsystems (analogous behavior was demonstrated for 1,4-phenylene-2,2-bisoxazole [3]). In this case, a decrease is found in the length $l_{\mu\nu}$ of the intercyclic C-C bond from 1.464 to 1.454 Å along with a corresponding increase in the order $p_{\mu\nu}$ from 0.295 to 0.336, shortening of the C=C bonds in the oxazole ring from 1.377 to 1.365 Å (with an increase in the bond order

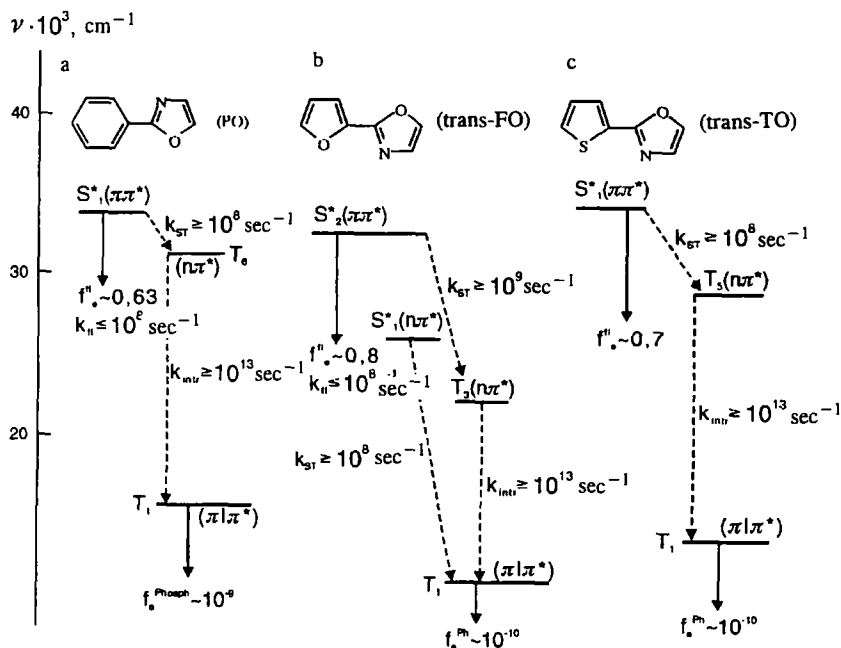


Fig. 3. Energy levels of excited singlet S_1^* and triplet T_j states of $\pi\pi^*$ and $n\pi^*$ types calculated by the INDO/S method for free molecules: a) 2-phenyloxazole (PO), b) 2-(2-furyl)oxazole (FO), and c) 2-(2-thienyl)oxazole (TO). The solid vertical lines indicate radiative transitions f_e with rate constants k_{fl} and k_{ph} , while the dashed lines indicate nonradiative transitions between states of different orbital nature and multiplicity with rate constants k_{ST} (intercombinational conversion) and k_{intr} (internal conversion).

$\rho_{\mu\nu}$ from 0.777 to 0.844), and extension of the two C–N bonds from 1.346 and 1.323 Å to 1.382 and 1.368 Å (the drop in the bond order is from 0.570 and 0.705 to 0.369 and 0.452, respectively). Thus, while the C–N bonds in the azocycle of the PO molecule had double and single bond orders, predominantly single and partial single bond order corresponds to these bonds in the protonated 3-H-PO⁺ form. The benzene and protonated azocycles in the 3-H-PO⁺ cation are more strongly interrelated than in the PO molecule.

The nature of the localization of the charges on the atoms and fragments in PO and 3-H-PO⁺ differs both in the ground and excited states. The increase in the basicity of the azocyclic systems in the electronically excited state observed by Kuz'min et al. [16] results from the expected strong increase in the electron density on the nitrogen atom upon protonation: $q^S = -0.799$ and $q^T = -0.826$ in the 3-H-PO⁺ cation and $q^S = -0.325$ and $q^T = -0.259$ in the PO molecule (in the singlet S_1^* and T_1 states, respectively).

The electronic excitation in the PO molecule in the fluorescent S_2^* state (as in the triplet T_1 state) is localized uniformly over the rings ($\sum_i L_i = 50\%$), while the excitation in the 3-H-PO⁺ cation in the fluorescent S_1^* state is localized 32 and 68% on the benzene and azocycle, respectively.

The oxazole ring in the PO molecule is an electron donor, while the benzene ring is an electron acceptor (the excess negative charge $q^* = -0.203$), while the oxazole and benzene rings in the 3-H-PO⁺ cation are virtually electroneutral ($\Sigma_i q_i^* = -0.004$). The excitation in the T_1 state is localized on the benzene ring: $\sum_i L_i = 70\%$ for PO and $\sum_i L_i = 60\%$ for 3-H-PO⁺. Negative charge is localized on the benzene ring: $\Sigma_i q_i^* = -0.018$ for PO and $\Sigma_i q_i^* = -0.061$ for 3-H-PO⁺. Thus, the values for $\sum_i L_i$ the triplet T_1 state reflect the nature of the electronic–vibrational deactivation of the atoms in the azocycle upon protonation of the PO molecule.

The L_i numbers for the PO molecule in the S_2^* state indicate greatest activity for C₍₂₎, C₍₅₎, C_(1'), and C_(4')

$$\sum_i L_i = 14.2 + 16.9 + 12.9 + 12.3 = 56.3\%;$$

and analogously for the 3-H-PO⁺ cation

$$\sum_i L_i = 22.7 + 18 + 7.4 + 8.8 = 56.9\%$$

i.e., approximately equal values. The atomic distribution of electronic excitation in the triplet T_1 state of the PO molecule approximately corresponds to the fluorescent S_2^* state. In the 3-H-PO⁺ cation, 14.9% of the excitation is localized in the *para* position of the benzene ring ($C_{(4')}$), while this value is 13.8% in the case of the PO molecule (Table 2).

Thus, variation of the characteristics of the $\pi\pi^*$ electronic–vibrational excitation is observed under conditions of complexation and selective protonation of the azocycle of heteroaromatic molecules for bond groups in the benzene, furan, or thiophene and azole fragments due to the appearance of efficient intermolecular hydrogen bonding in solution along with change in the geometry of the ground state. Correspondingly, we may expect a change in the chemical activity of the atoms (reaction sites), in particular, in electrophilic substitution reactions through an addition–dissociation mechanism.

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