STRUCTURAL FEATURES OF THE π-ELECTRON SHELLS OF MESOIONIC HETEROCYCLES

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The computational method is described and the results of calculations of various characteristics of the ground and excited states of tropone, azulene, and 42 molecules belonging to 24 types of heterocyclic systems containing planar conjugated cyclic fragments with seven π electrons are presented. The results are compared with the experimental characteristics, including data on the photochemistry of the investigated molecules. Several features of mesoionic systems that distinguish them from ordinary heterocycles are revealed.

It has been decided to use the term "mesoionic heterocycles" for conjugated heterocycles that cannot be depicted by classical covalent formulas without the use of formal charges and unpaired electrons. The structure of the π-electron shells of such systems within the basis of 2p atomic orbitals (AO) cannot be conveyed by a combination of one-center and two-center molecular orbitals. In the present research we made an attempt, within the framework of the π-electron approximation of the self-consistent field (SCF) MO LCAO method, to reveal the features of mesoionic systems that distinguish them from isomeric nonmesoionic heterocycles.

In all, 24 possible simplest types of heterocyclic systems containing planar conjugated cyclic fragments with seven π electrons are examined, 12 of which, denoted by an asterisk, are mesoionic (Fig. 1). In contrast to the latter, heterocycles of the I, IV, VII, X, XII, XIV-XVI, and XVIII-XXI types can be depicted by single classical covalent formulas. It might be supposed that localized orthogonal MO corresponding to the depicted structures are a possible means of interpretation of the SCF wave functions for such molecules.

A large number of heterocycles that differ with respect to the number and types of heteroatoms and their mutual orientation is included among the indicated 24 types. In the present paper only nitrogen- and oxygen-containing systems, the probability of the participation in the bonds of which of the vacant orbitals of atoms that have a formally increased valence is lower* than for the corresponding atoms (P and S) of the third period [1], are investigated in the present paper.

The σ skeletons and molecular diagrams of the 42 calculated heterocycles and their carbocyclic analogs (tropone and azulene) are presented in Figs. 2 and 3. Heterocycles that are assigned to a certain type of system, regardless of their composition, have molecular orbitals with similar structures (Fig. 4). In the present study we used the Kagan [2] program for calculations of the π-electron shells of the conjugated molecules by the Pariser–Parr–Pople (PPP) method. In order to obtain results that are qualitatively independent of the parametrization used in the calculations we utilized four variants for evaluation of the elements of the electron Hamiltonian H_{pq} that lead to results that differ quantitatively to a great degree. The parameters of variants of A and A' were taken from [3], and the parameters of variants of C were taken from a communication [4] in which the parameters were selected for transmission of the energies of the triplet states of carbocycles and heterocycles. In variant B the ionization potentials of the atoms and the one-center integrals (γ_{pp}) were assumed to be linear functions of the effective nuclear charges (see [2]). The γ_{pq} integrals in variants A-C were calculated from the Pariser–Parr formula, whereas the integrals in variant A' were calculated from the Mataga–Nishimoto formula for $R_{pq} \geq 2.8$ Å or from the first formula for smaller distances. For lack of data on the geometry of most of the 24 calculated molecules, the geometries of all of the systems were assumed

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*And, consequently, those that have a greater tendency to form mesoionic structures.

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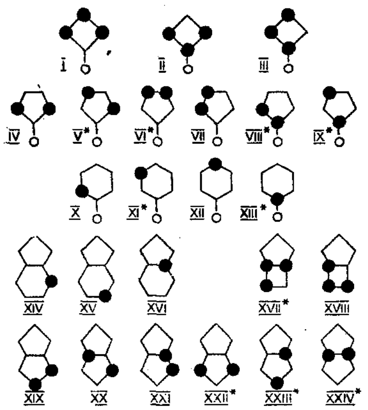

Fig. 1. Examined types of heterocycles containing planar conjugated cyclic fragments with seven π electrons. Atoms with a pair of π electrons are indicated by •, and mesoionic systems are denoted by an asterisk.

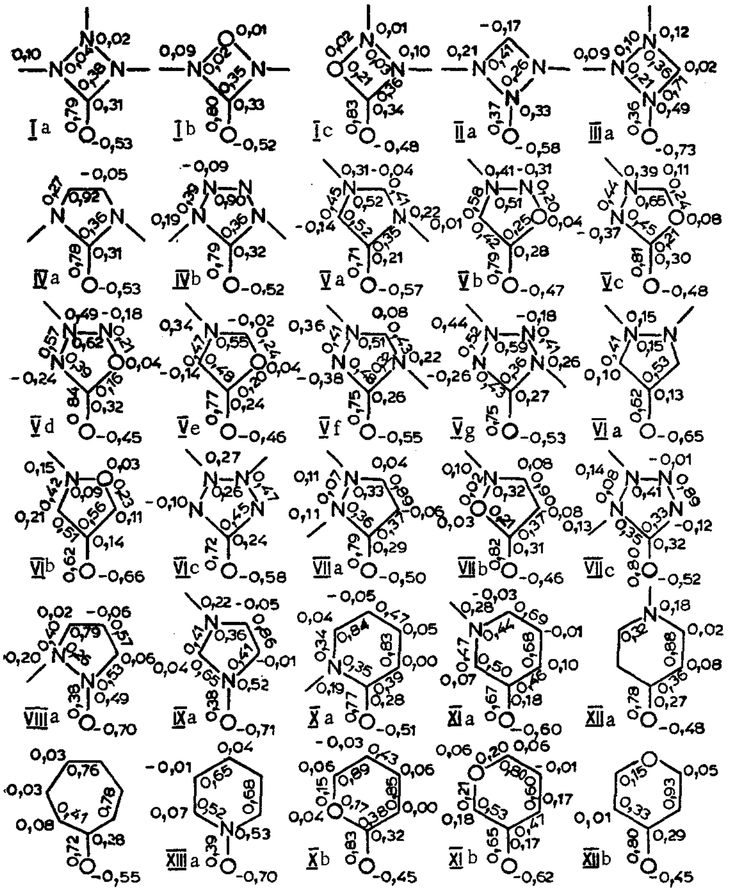

Fig. 2. Skeleton and molecular diagrams of molecules Ia-XIIIa.

to be idealized – regular polygons with 1.40 Å sides, and the C=O and N–O (in N-oxides) bond lengths were assumed to be 1.21 and 1.25 Å, respectively. The length of the bond common to the two rings in two-ring compounds XIV, XV, XIX, and azulene was assumed to be 1.45 Å. The β_{pq} integrals, which were identical for all of the computational variants, were estimated from data in [5]. No attempt to render the β_{pq} integrals self-consistent was made.

The heats of atomization (E_{at}) are necessary for evaluation of the relative stabilities of the mesoionic and isomeric nonmesoionic systems. The appropriate experimental data for heterocycles Ia-XXIVa (with all substituents R=H) are not available in the literature. For most of the investigated molecules

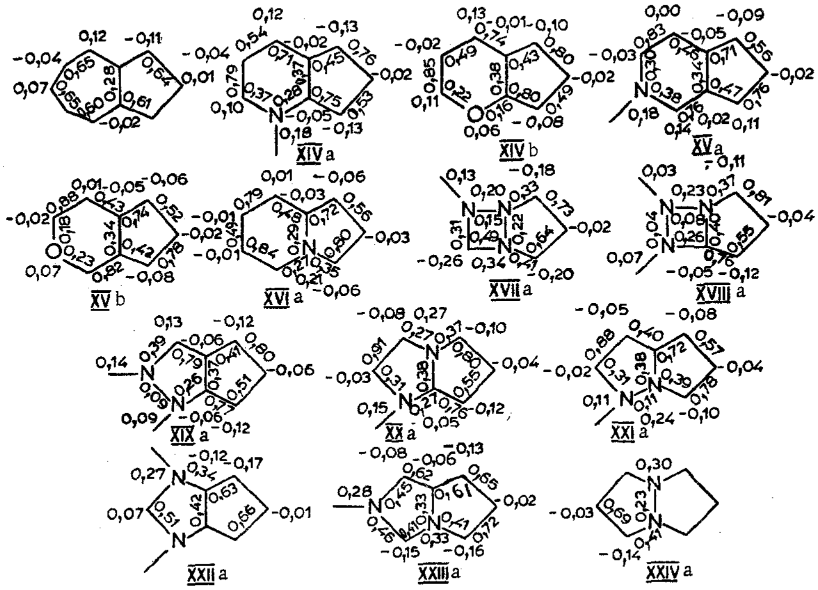

Fig. 3. Skeleton and molecular diagrams of molecules XIVa-XXIVa.

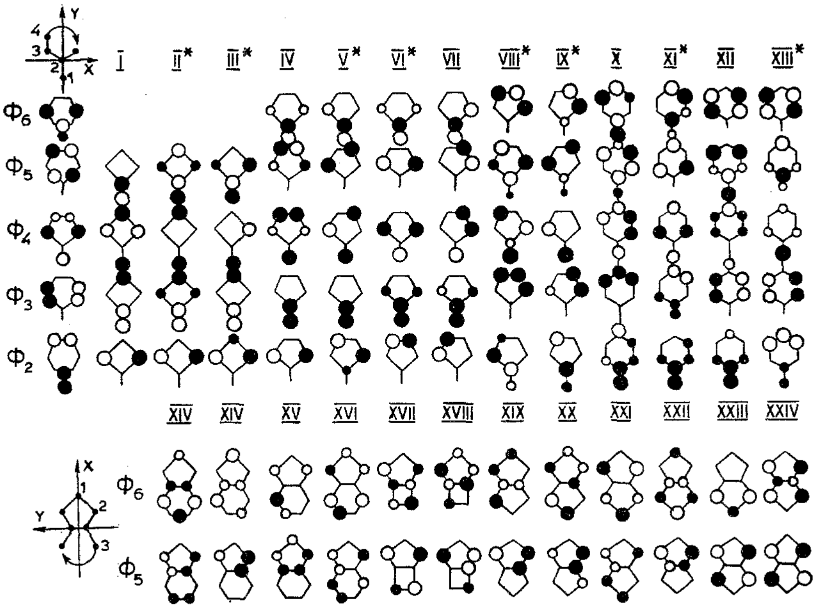

Fig. 4. Numbering of the atoms and structure of the Φ_2—Φ_6 molecular orbitals on the calculated analogs of tropone and N-oxides and of the Φ_5 and Φ_6 molecular orbitals of azulene analogs. The color and size of the circles correspond to the sign and magnitude of the coefficients of the atomic orbitals.

with R = H they probably cannot be determined at all experimentally. Dewar and co-workers [6] have pointed out the possibility of evaluation of E_{at} by means of the Pople method. The effectiveness of such calculations decreases as the number of heteroatoms and, consequently, the types of bonds increase. To a considerable degree this is due to the lack of the necessary parameters and the difficulty involved in realization of the entire program of such calculations. It is essential that "thermochemical" values of resonance integrals β_{pq} that are somewhat lower than those presented in [5] be used in the latter calculations for evaluation of E_{at}. An analysis of the corresponding expressions for E_{at} and π-bonding energies

$$E_{bond}{}^{\pi}=E_{Pople}{}^{\pi}+E_{skel}-\sum_{p}H_{pp}^{skel}$$

shows (see [6-9]) that the changes in the heats of atomization for molecules containing an identical number of bonds of a definite type depend only slightly on the β_{pq} values used in the calculations of the E_{bond}^{π} values

TABLE 1. Calculated Energies of Atomization (ΔE_{at}), π Bonding Energies (E^{π}_{bond}), Upper Occupied MO and Lower Vacant MO Energies (in eV), and Calculated and Experimental Dipole Moments (μ, D)

	E^{π}_{bond}, eV		ΔE_{at}, eV	$-E_u$	$-E_l$	μ^{σ}	$\mu^{\pi+\sigma}_{calc}$	μ_{exp} [17-19]
	A	B	B	A	A			
Tropone	16,4	19.6		10,5	2.2	1,0	5.3	4,2
Ia	6.7	6,9		10,7	−1,6	1,4	5,6	
Ib	6.5	6.1		11,7	−1,4			
Ic	3.9	3,6		11,2	−1,1			
IIa	0.5	−0,8	5,5	9.0	1,0	1,5	5,2	
IIIa	5,6	4,5	0.0	10,4	0,4	0,7	6,8	
IVa	11,1	11,6	0,0	10,8	−0,1	1,1	4,3	
IVb	11,4	11.1	0,0	11,7	1,6	0,4	2,4	
Va	9.6	9,6	2,4	9,6	1,6	1,4	7.9	
Vb	10.9	4,0		10.9	2,6	2,4	6,6	6,0; 7,3
Vc	10.8	4,2		10.9	2,3	2,3	8,7	7,6
Vd	9,5	3,9		11,7	3,1	1,9	6,4	
Ve	8.2	3,9		9.9	2,0	2,7	8,0	
Vf	10.3	9,8		10,4	2,0	1,9	9,4	
Vg	9.9	9,9	1,2	11,0	2,6	1,0	6 8	
VIa	8,5	9.3	2,1	9,0	2,0	1,3	9,8	
VIb	7,4	5.2	3,0	9,2	2,6	1,1	7,9	
VIc	8.8	8,2	2,8	8,8	1,8	1,5	10,4	
VIIa	10.4	11,2	0.0	10,8	0,7	1,5	6,4	5—7
VIIb	9,7	7.9	0,0	9,2	−2,3	3,2	6 5	
VIIc	10,2	10.3	0,7	11,3	2,0	0,7	5,6	
VIIIa	9.8	9,5		10,4	1,5	0,9	5,7	
IXa	9.9	9,3		10,3	1,3	2,0	7,2	
Xa	14 3	15,9	0,0	10,7	1,6	1,1	5,1	4,0
Xb	13,3	10,2	0,0	10.9	1,8	2,2	5,5	
XIa	13.0	14,5	1,7	9,7	2.3	1,5	8.0	7,2
XIb	11,5	7,3	3,2	9,6	2.9	1,3	6,7	
XIIa	13,9	15,4	0,5	10,6	1,1	1.6	7,2	
XIIb	13,2	10,1	0,1	11,1	1,3	0,0	4,2	
XIIIa	13.8	14,7		10,4	1,6	1,3	5,3	4,24
Azulene	21.0	24,8		9,4	2,0	0,1	2,1	
XIVa	17.7	20,1		9,2	1,9	0.3	4,5	
XIVb	14.7	19,2		9,5	2.1	0,4	4.9	
XVa	17,5	20.0		9,0	1,6	1,3	4,0	
XVb	16.8	19,0		9,2	1,8	1,2	1,7	
XVIa	18,2	19.7		9,6	1,1	0,2	1,5	
XVIIa	8.7	13,6		8,5	0,5			
XVIIIa	10.2	15,8		9,3	−1,0			
XIXa	13 6	15,1	0,2	8,9	1,3	0,4	5,0	
XXa	14,7	15,4	0,0	9,7	2,1	0,4	2,2	
XXIa	14,3	15,4	0,0	9,5	0,3	0,1	2,6	
XXIIa	13.6	14,3	1,2	8,8	1,6	0,1	6,5	
XXIIIa	13.6	14,0	1,7	8,7	1,2	0,9	4,5	
XXIVa	13,4	13,8	3,2	9,2	1,1			

by the PPP method. The ΔE_{at} values (the 0.0-eV level corresponds to molecules with maximum energies of atomization) calculated from the E^{π}_{bond} values obtained in the variant B are presented in Table 1.† The calculated values of the energies of the upper occupied (E_u) and lower vacant (E_l) molecular orbitals and dipole moments μ^{σ} (calculated by the del Re method [10]) and $\mu^{\pi+\sigma}$ are also presented in Table 1. The corresponding experimental values are contrasted with the indicated values.

The energies of the excited states (S^*_1 and T^*_1) calculated with allowance for interaction of all of the singly excited configurations and the oscillator forces of the $\pi-\pi^*$ transitions are presented in Table 2 along with the experimental data for known alkyl-substituted molecules. The molecular diagrams corresponding to the lower triplet excited states (T^*_1) of some of the calculated systems are presented in Fig. 5. Changes in the geometry of the molecules are usually disregarded in calculations of the characteristics of excited states [11]. The effect of intramolecular interaction makes a direct comparison of the calculated energies of the transitions with the experimental values corresponding to the maxima of the bands in the absorption spectra of pairs of real molecules extremely arbitrary and is valid only when a number of factors are observed [12]. It is most legitimate if the corresponding bands in the spectra of vapors of the conjugated systems under consideration that have extremely rigid skeletons are narrow and intense. However, in the general case it is expedient to evaluate the sensitivity of the calculated results to judiciously selected intervals of the parameters.

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† The σ-bond energies were estimated from the data in [6-8] by means of the Morse function starting from the bond orders calculated in variant B.

TABLE 2. Calculated and Experimental Characteristics of the Excited States (S^*_1 and T^*_1) of Ia-XXIVa, Tropone, and Azulene

	$E(S^*_1)$, eV	f	ΔE, eV	$E(S^*_1)$, eV	lg ε	Solvent	$E(T^*_1)$	
	A	A	B	experimental			A	C
Tropone	3,2	0,09	0,5	3,98	3,92	H_2O[21]	1,7	2,2
	4,1	0,17	0,0	4,08	3,70	iso-C_8H_{18}[21]		
IVa	5,5	0,30	0,4	4,86	3,60	H_2O	2,7	3,1
IVb	4,9	0,25					2,1	2,1
Va	3,5	0,40	2,4				0,6	1,5
Vb	3,9	0,57	0,6	4,34	3,78	H_2O	0,4	1,0
				4,16	3,73	$C_{10}H_{22}$		
Vc	3,8	0,43	2,0	4,86	3,81	C_2H_5OH[19]	0,7	1,4
Vd	3,9	0,41	1,4	4,77	3,95	C_2H_5OH[19]	0,7	0,9
Ve	3,5	0,55	1,4				0,2	1,2
Vf	3,7	0,30	4,1				1,0	1,7
Vg	3,6	0,26	3,0				0,9	1,1
VIa	2,4	0,19	4,2				−0,1	0,7
VIb	2,1	0,16	3,3				−0,5	0,4
VIc	2,2	0,12	5,6				−0,5	0,3
VIIa	5,2	0,58	0,6	4,76	4,00	C_2H_5OH[20]	2,3	2,3
				4,63	3,90	cis-C_6H_{14}		
VIIb	5,2	0,66	0,1	4,77	4,11	H_2O	2,3	2,2
				4,75	4,00	cis-C_6H_{14}		
VIIc	4,4	0,30	1,1				1,7	1,3
VIIIa	4,4	0,48	1,5	4,87	3,54	H_2O[22]	1,2	2,1
IXa	4,5	0,20	1,7				1,6	2,4
Xa	4,2	0,30	0,3	4,17	3,76	H_2O[23]	1,9	2,3
Xb	4,3	0,18	0,0	5,05	4,11	C_2H_5OH[23]	1,8	2,1
XIa	2,7	0,19	1,5	3,87	3,68	H_2O	0,6	1,4
				3,47	3,67	Dioxane[23]		
XIb	2,3	0,16					0,0	1,1
XIIa	4,4	0.02	0,5				2.2	2,3
	5,0	0,45	0,3	4,77	4,28	H_2O[23]		
XIIb	4,9	0,01		4,74	3,48	C_6H_{14}[24]	2,3	2,1
	5,2	0,44						
XIIIa	4,3	0,02	1,0	4,87	4,04	H_2O[14]	1,7	2,5
	4,3	0,20		4,40	4,10	iso-C_8H_{18}[14]		
Azulene	2,1	0,02	0.0	2,07	(f=0,01)[25]		1,8	1,9
XIVa	2,2	0,03	0.8	~2,7	~2,8	CH_3OH[26]	1,4	1,6
				~2,5	~2,9	cis-C_6H_{14}[26]		
XIVb	2,2	0,02	0,8				1,4	1,5
XVa	2,4	0,06	0,9	2,87	3,28	C_2H_5OH[27]	1,4	1,8
XVb	2,4	0,08	0,2				1,4	1,6
XVIa	3,6	0,12	0,1	3,59	3,29	cis-C_6H_{14}[23]	2,0	2,6
XVIIa	3,8	0,69					0,7	1,9
XVIIIa	5,0	0,36					2,8	3,1
XIXa	2,5	0,06	1,9				1,3	1,5
XXa	4,7	0,09	0,0				2,7	2,9
XXIa	4,5	0,43	0,2				2,1	2,6
XXIIa	2,1	0,02	3,3				1,3	1,5
XXIIIa	3,2	0,23	1,1				0,9	1,9
XXIVa	3,6	0,52					1,2	2,4

In comparing the calculated results with the experimental results obtained from the spectra of the dissolved substances it is necessary to introduce a correction for the effect of the solvent. This effect may be significant. For example, the maximum of the longwave absorption band corresponding to $\pi-\pi^*$ transitions is shifted when a polar solvent (H_2O) is replaced by a nonpolar solvent (alkanes and benzene) for 3-phenylsyndone [13], pyridine N-oxide [14], and 2,3-diphenyltetrazole-5-thiolate [15] by 22, 28, and 135 (!) nm, respectively. The correction for the solvent effect can be estimated by means of equations linking the change in the energies of the transitions with the parameters (n, ε) of the solvent and the dissolved molecule: The Onsager radius (a_0) corresponding to the portion of the molecule to which the excitation is propagated [13, 16], the dipole moments of the molecule in the ground (μ_g) and excited (μ_e) states, and the angle (ψ) between them. We proposed a convenient method for the graphical solutions of these equations in [13]. It can be shown [13] that the difference in the energies of the excited states corresponding to the spectra of the substances dissolved in water and decane is determined by the approximate relationship $\Delta E\ (\text{eV}) = E_{H_2O} - E_{\text{decane}} = 1/a_0^3 \cdot 0.07 \cdot (\mu_e^2 - \mu_g^2) - 1.15\ (\mu_e\mu_g \cos\psi - \mu_g^2)$, which can be used as an additional criterion in the identification of the bands and comparison of the calculated and experimental energies of the excited states of the molecules. In the PPP method it is assumed that the dipole moment of the nonpolarizable rigid σ skeleton does not change during excitation of the π electrons. The μ^σ values of the ground state of the investigated systems are logically used also for calculations of the dipole moments of the excited states and, consequently, of the ΔE values. The Onsager radii can be estimated from the expression $a_0^3 = 2\alpha_{el}$, where α_{el} is the electron polarizability of the ground state of the molecule. The ΔE values calculated for the S^*_1 states of the molecules are presented in Table 2. An a_0 value of 3.2 Å was used in the calculation for tropone as compared with 3.6 Å for azulene, 2.5 Å for compounds of the IV-

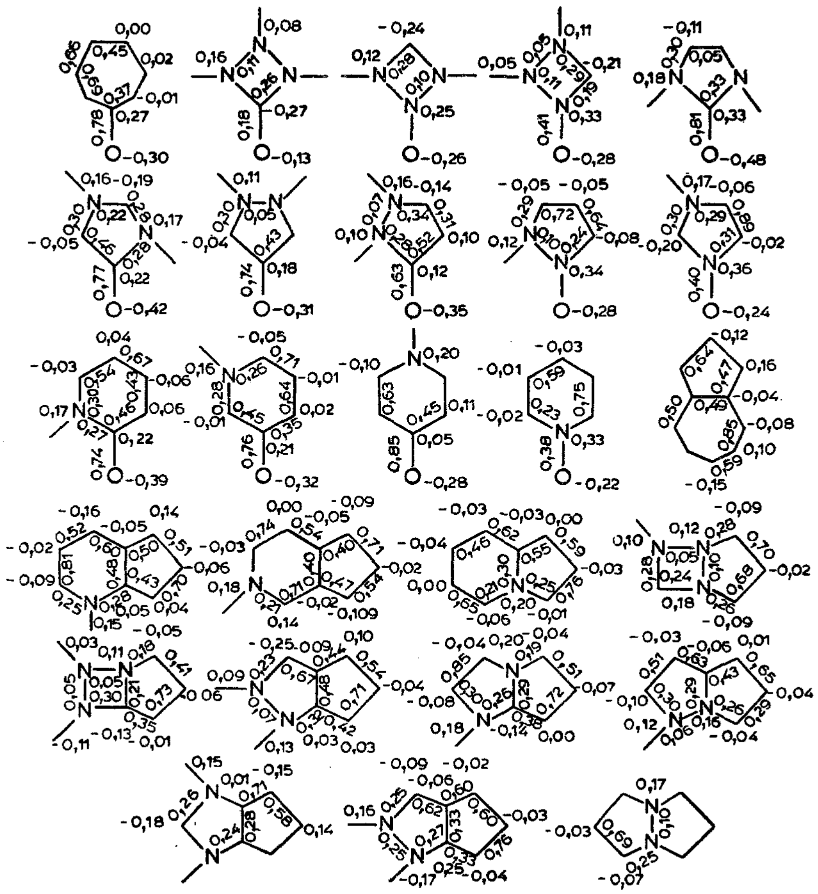

Fig. 5. Molecular diagrams corresponding to the lower triplet state of some of the calculated molecules.

VII type, 3.1 Å for X-XIII, 3.6 Å for XIV-XVI, and 2.8 Å for XIX-XXIV. The indicated values were calculated from the refractions of the investigated molecules or similarly constructed molecules.

Let us analyze the structure of the molecular orbitals that strictly determine the difference in the mesoionic and nonmesoionic systems.

The composition of the lower F_1, π-MO (they are not shown in Fig. 4) is determined mainly by the contribution from the AO atoms with a pair of electrons. Among the other MO of heterocycles that are tropone analogs one can isolate orbitals that are primarily localized on atoms having one π electron.

In the case of nonmesoionic heterocycles (IV, VII, XIV, XIX, and XX) and N-oxides (VIII, IX, and XIII) one can isolate MO that are primarily localized on the corresponding bonds that are close, judging from the molecular diagrams (Figs. 2-4), to double bonds.*

Judging from the structure of the MO and the molecular diagrams mesoionic heterocycles are characterized by high delocalization of the π electrons. Nevertheless, the π-bonding energies of mesoionic heterocycles are lower than the corresponding values for isomeric nonmesoionic systems (Table 1). The absence of a correlation of the π-bonding energies with the electron densities of the seven π-electron fragments seems extremely curious. This actually means that the increase in the π-bonding energy is not determined by the tendency for formation of "aromatic" π-electron sextets in the indicated fragments.

Replacement of the pyrrole nitrogen atom in the systems under consideration by a furan oxygen atom leads to a certain decrease in the π-bonding energies. This conclusion also does not depend on the parametrization used in the calculations.

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*The presence in tropone analogs of a π orbital localized on an exocyclic carbonyl group naturally explains the identical character of the C=O bond lengths in mesoionic sydnones Vb and, for example, isoazolones VIIb (see [28]).

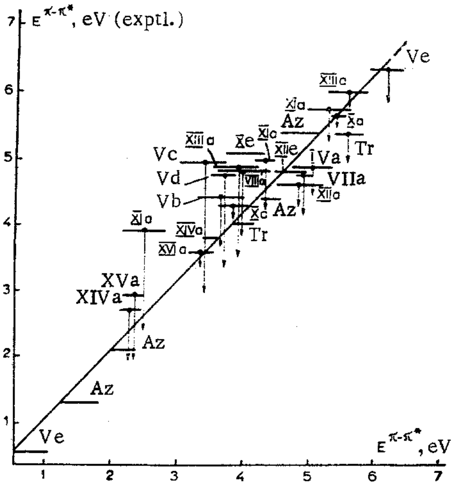

Fig. 6. Comparison of the experimental and calculated energies of the excited states. The experimental data were taken from the papers indicated in Table 2 and in the text.

Our calculated increases in the heats of atomization of α- and γ-pyridones with respect to mesoionic β-pyridone of 1.7 and 1.2 eV correlate with the values calculated by Dewar and coworkers (2.1 and 1.5 eV) [8].

β-Pyrone (XIb) should be considerably less stable than α- and γ-pyrones (Xb and XIIb). A comparison of the ΔE_{at} values of isomeric tetrazolones (IVb, Vg, VIc, and VIIc) of molecules of the VI and IV, XIX and XXIV, and XX, XXII, and XXIII types shows that the lower energies of atomization correspond to the mesoionic molecules. The ΔE_{at} values of N-oxides IIa and IIIa differ appreciably.

The energies of the upper occupied and lower vacant MO and the size of the energy gap in the examined systems depend markedly on the parametrization used in the calculations. An analysis of the upper occupied molecular orbital (UOMO) and lower vacant molecular orbital (LVMO) energies shows that, regardless of the selection of the system of parameters, replacement of the carbon atoms by pyridine nitrogen atoms and of the pyrrole nitrogen atoms by furan oxygen atoms apparently will increase the ionization potential of the π electrons and the electron affinity of the molecules. As compared with isomeric nonmesoionic systems, the mesoionic systems are characterized (with certain exceptions) by higher UOMO energies, lower LVMO energies, and lower energies of excitation of an electron from the UOMO to the LVMO corresponding to the $\pi-\pi^*$ transitions to the S^*_1 and T^*_1 states (Tables 1 and 2). The literature data regarding the ionization potentials of N-methylated $\alpha-\gamma$-pyridones [29] and the 4-methyl derivative of pyridine N-oxide (8.58, 7.90, 8.48, and 8.12 eV)† and data from electronic spectra measured for solutions of the heterocycles in nonpolar solvents (Table 2) confirm the above conclusions.

With certain exceptions, the calculated dipole moments $\mu^{\pi+\sigma}$ for mesoionic systems are higher than the values for the isomeric nonmesoionic systems. The accuracy of ~1 D in the prediction of the $\mu^{\pi+\sigma}$ value, with allowance for the assumptions made, seems completely acceptable. This makes it possible to use the proposed method for the calculation of $\mu^{\pi+\sigma}$ for the evaluation of the ΔE values. The latter correlates in sign and, qualitatively, in magnitude‡ to the experimental values (Table 2); and the mesoionic heterocycles, with certain exceptions, are characterized by higher ΔE values than the isomeric nonmesoionic heterocycles.

The calculated excitation energies are compared in Fig. 6 with the experimental values that characterize the maxima of the absorption bands in the electronic spectra of the investigated molecules. The

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† The first ionization potentials of the Xa, XIa, XIIa, and XIIIa molecules correspond to detachment of a π electron.

‡ The deviation between the experimental and calculated ΔE values follows the trend of the ΔE values (Table 2). It might be supposed that more accurate calculations of the dipole moments of the S^*_i states would make it possible to evaluate the changes in the polarizabilities of the molecules during excitation (see [13, 16]).

horizontal segments correspond to the calculated (within the A, A', B, and C variants) intervals of the changes in the energies of the excited states, and the vertical segments correspond to the calculated ΔE values. The direction of the vertical arrows corresponds to the sign of the corrections for the solvent effect. The energy of the triplet state of azulene was taken from [25], and the energy of the triplet state of 3-methylsydnone was taken from [31].

It is shown in Fig. 6 that the calculated excitation energies of the molecules under consideration over a broad range of energies correlate with the experimental values, and explicit allowance for the effect of the medium in most cases improves the correlation.

It follows directly from the structure of the boundary MO of molecules of the IV, VII, X, and XII types that the unpaired electrons in the S^*_1 and T^*_1 excited states of these molecules are localized to a considerable extent on the close-to-double bonds in the ground state. In fact, the photoaddition of benzophenone to IVa proceeds via the close-to-double 4–5 bond in the ground state [32], the multiplicity of which is reduced appreciably during excitation of an electron from the UOMO to the LVMO. The increase in the multiplicity of the 5–6 bond and the decrease in the multiplicity of the 6–7 bond that occurs during excitation of an electron from the UOMO to the LVMO in X corresponds to the photochemical dimerization of α-pyridone described in [33, 34], which occurs at the 4 and 7 atoms† and also includes the formation of the σ bond of the photochemical isomerization of this molecule (Fig. 5). The unpaired electrons in mesoionic molecules of the V and VI types are localized to an appreciable degree, judging from the structure of the UOMO and LVMO of these molecules, respectively, on the 3,5 and 3,6 atoms. The electron structure of the S^*_1 and T^*_1 states of molecules of the V type, judging from the composition of the UOMO and LVMO, correlates to a greater degree than the structure of the ground states with the depiction of the classical formula with a 3–5 crosslink. It has been assumed [35] that elimination of CO_2 during the photochemical isomerization of sydnones (Vb) to isosydnones (Vc) proceeds through the formation of such structures. The photochemically initiated conversion VII → IV was described in [36, 37]. This isomerization and the possible subsequent radiationally or thermally initiated conversion of IV [38], as in the case of sydnones, include elimination of CO_2 or RNCO in one of the steps. Judging from the structure of the MO, the splitting out of the latter should promote a decrease in the multiplicity of the 2–3 and 2–6 bonds in IV and VI, of the 2–3 bond in V, and of the 2–6 bond in VII and promote excitation of an electron from the F_3 and F_4 MO to the F_5 and F_6 MO (Fig. 4). The excitation energies of these molecules in the S^*_2 and S^*_3 states are high as compared with the irradiation energies. For example, the isomerization Vb → Vc occurs on irradiation with light of wavelength 300 nm [35]. However, in analyzing the mechanisms of such reactions one should obviously take into account the probability of intercombination transitions from the lower singlet to the close-in-energy triplets T^*_2 and T^*_3, which correspond to the excited states of molecules with weakened 2–3 and 2–6 bonds. Excitation of the electron in the N-oxides weakens the N → O bond (Fig. 5), and this corresponds to the formation of pyridine from pyridine N-oxide observed on irradiation with light of wavelength 326 or 254 nm in the gas phase [39].

The above analysis shows that mesoionic heterocycles are characterized by a number of peculiarities with respect to the isomeric nonmesoionic systems. These peculiarities are manifested in quantitative form for some of the collective and one-electron properties that characterize these molecules.‡ The further development of this research presupposes quantitative refinement of the results of calculations of the π-electron shells of the systems under consideration by a search for a less empirical method of parametrization (see [40]), by bringing the models closer to real molecules, and by transition to calculations within the valence approximations of the SCF MO LCAO method [41, 42]. The latter and, particularly, sufficiently reliable nonempirical calculations will make it possible to evaluate the effect of the σ skeleton and the π–σ-electron interaction, to ascertain the role of the vacant AO in each concrete case, and thereby to more precisely refine or reject the very concept of mesoionicity.

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† See Fig. 4 for the symbols.

‡ It might be supposed that the conclusions of this paper will prove to be useful in the specific search for compounds with certain properties, the investigation of the electronic spectra of large conjugated systems (dyes), and physicochemical analysis. In particular, the use of mesoionic molecules as fragments of superconducting systems of the Little marcomolecule type (see [43]), in photosynthesis, etc., seems extremely attractive.

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