EXPERIMENTAL

The ^1H NMR spectra of 5% (by volume) solutions of the compounds in CCl_4 were recorded with a Varian HA-100D spectrometer at 29°C with tetramethylsilane as the internal standard. The IR spectra of films of the compounds between NaCl plates were recorded with a Specord 71-IR spectrometer with an NaCl prism. The UV spectra of aqueous solutions of the compounds in 10-mm thick quartz cuvettes were recorded with a Specord UV-vis spectrophotometer.

2-Furyl-4-phenyl-1,3-dioxolane (VI). A mixture of 6.01 g (0.05 mole) of furylacrolein, 6.9 g (0.05 mole) of phenylethylene glycol, 1.5 g of KU-2 cation-exchange resin in the H^+ form, and 80 ml of benzene was refluxed for 3-4 h in a three-necked flask equipped with a stirrer, a Dean–Stark apparatus, and a reflux condenser. After decantation and removal of the solvent by distillation, the reaction product was isolated by vacuum frationation to give 8.5 g of dioxolane VI.

Compounds I-V were similarly obtained.

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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM. 5.* π-ELECTRON STRUCTURE OF THIAZOLO[3,2-*a*]PYRIDINIUM 3-OXIDE DERIVATIVES

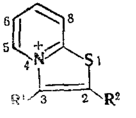
G. G. Dyadyusha, N. N. Romanov,
A. D. Kachkovskii, and A. I. Tolmachev

UDC 547.789.6'834.2:541.67

The π-electron structure of thiazolopyridinium derivatives was analyzed thoroughly by the methods of quantum chemistry in order to ascertain the reason for the development of colors in the case of mesoionic compounds.

Despite the fact that mesoionic compounds have been known for a relatively long time [2], the reasons responsible for their deep coloration have thus far remained unclear [3]. It therefore seemed of interest to thoroughly analyze the π-electron structures of such compounds by means of the methods of quantum chemistry. Such calculations of mesoionic compounds have already been made (see [2]); however, only certain properties of the ground state were discussed.

In the present research we performed quantum-chemical calculations of the model systems the thiazolo[3,2-*a*]pyridinium cation (I), thiazolo[3,2-*a*]pyridinium 3-oxide (II), and the 3-methoxythiazolo[3,2-*a*]pyridinium cation (III) in order to determine the electron distribution in both the ground and excited states and to ascertain the reasons for the development of coloration in compounds of the II type.



III

I $R^1=H$, $R^2=H$;
II $R^1=O^-$, $R^2=H$;
III $R^1=OCH_3$, $R^2=C_6H_5$.

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*See [1] for communication 4.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1618-1623, December, 1980. Original article submitted December 18, 1979.

0009-3122/80/1612-1221$07.50

TABLE 1. Parameters of the Atoms and Bonds*

Atom	Z_μ	I_μ, eV	$\gamma_{\mu\mu}$, eV	$\beta_{\mu\nu}$, eV
C	1	−11,42	10,83	−2,32
N	2	−23,13	12,98	−2,53
S	2	−20,27	9,80	−1,65
O	1; 2	−27,17	14,58	−2,53

*Symbols: Z_μ is the charge of the skeleton, I_μ is the ionization potential, $\gamma_{\mu\mu}$ is the one-center integral of interelectronic interaction, and $\beta_{\mu\nu}$ is the resonance integral ($I_{\ddot{O}} = I_O - \gamma_{OO}$).

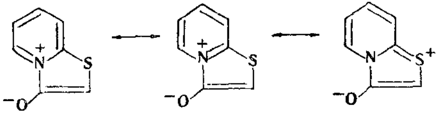
Computational Method and Parameters

In the present research we applied the self-consistent field (SCF) method within the Pariser—Parr—Pople (PPP) approximation [4] to the analysis of the electronic structures. The singly excited configurations were taken into account for the calculation of the excited states. Since we were interested primarily in the position of the long-wave absorption band that corresponds to the first transition of the π electrons, in the selection of the configurations we took into account only those for which the $\langle S_1|H|S_i\rangle$ matrix element exceeds a present value (0.01 eV). To construct the configuration interaction (CI) matrix we used a basis of orthonormalized vectors obtained by effecting self consistency of the ground state by the PPP method.

The parameters of the atoms and bonds necessary for the calculation were borrowed from [5], and their numerical values are presented in Table 1. The two-center integrals of electronic interaction were calculated from the Mataga—Nishimoto formula [6]. The dependence of the ionization potential on the magnitude of the charge on the atom $I_\mu = I_\mu^0 - \omega(Z_\mu - q_\mu)$, where q_μ is the electron density, Z_μ is the charge of the skeleton, and ω is an empirical coefficient (ω = 3.15 eV), was taken into account in the calculation of the skeletal integrals. The approximative interatomic distances and angles between the bonds used for the calculations were taken from [7] and are presented in Fig. 1.

Ground State

The charges on the atoms and the bond orders for the ground state of I and II are presented in the molecular diagram (Fig. 2, diagrams a and b). It is apparent that the π-electron density in the thiazolopyridinium oxide molecule (Fig. 2b) is shifted primarily to the exocyclic oxygen atom. The pyridinium ring in both systems is electron deficient; however, the positive charge in this ring is concentrated mainly on the nitrogen atom, whereas the charges on the carbon atoms are one order of magnitude smaller. The multiplicity of the bonds in the pyridinium ring is close to the multiplicity of the bonds in the benzene molecule, except for the nitrogen—carbon bonds, the order of which is reduced because of the greater electronegativity of the nitrogen atom and the consequent disruption of the symmetry of the wave function. The order of the bond between the C_2 and C_3 atoms is increased markedly in the five-membered (thiazole) ring of the I and II systems, although it is somewhat less in oxide II than in cation I. Using the language of the valence bond theory one may say that three structures make the prevailing contribution to the electron distribution in the II molecule:



In contrast to cation I, there is considerable negative charge in the 2 position of mesoionic compound II, by virtue of which, as confirmed by the experiments in [8], it displays increased reactivity with respect to electrophilic reagents. We will not examine the reactivities of I and II in greater detail in this paper, since this requires a more rigorous analysis with an examination of the transition states.

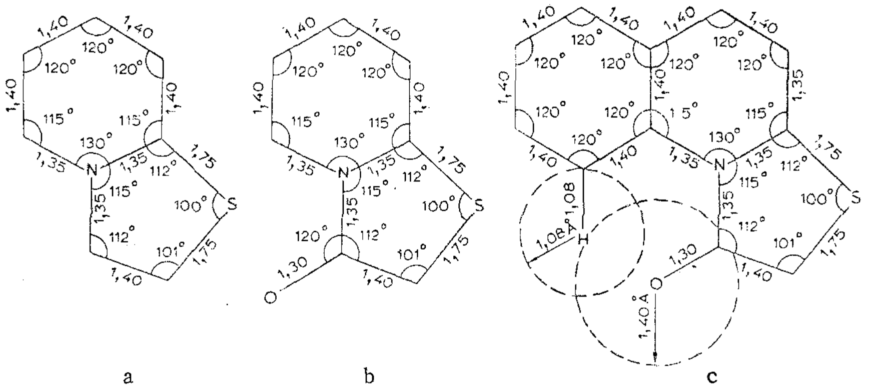


Fig. 1. Bond lengths and angles of model systems (see the text for an explanation of the designations).

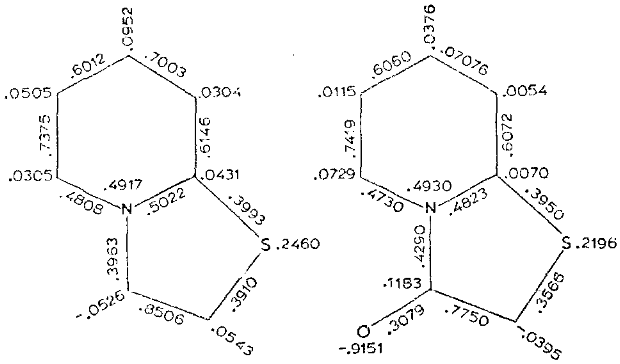


Fig. 2. Molecular diagrams of the ground state of the I and II systems (the charges on the atoms are given by $Z_\mu - q_\mu$, where q_μ is the π-electron density; see the text for an explanation of the designations).

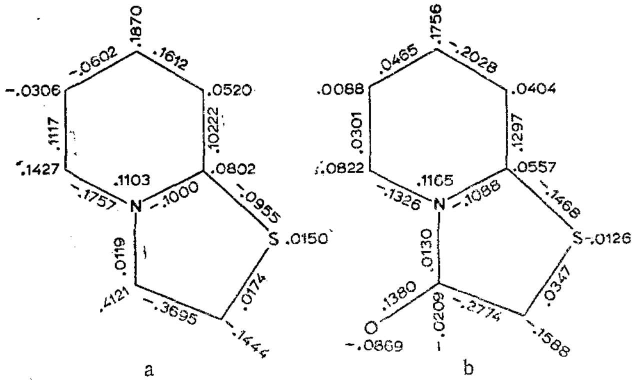


Fig. 3. Change in the electron distribution during conversion of the molecules to the first excited state ($q_\mu^{ex} - q_\mu^{gr}$; see the text for an explanation of the designations).

Excited States and Color of the Mesoionic Compounds

Diagrams of the changes in the electron densities and bond orders during conversion of the molecules to the first singlet excited state for model systems I and II are presented in Fig. 3. It is apparent that a pronounced change in the electron densities in the 2, 3, 4, and 7 positions with electron transfer from the thiazole ring to the pyridinium ring occurs in both cases. It is interesting to note that the change in the charge on the oxygen atom is considerably greater than in the positions indicated above. Consequently, the introduction

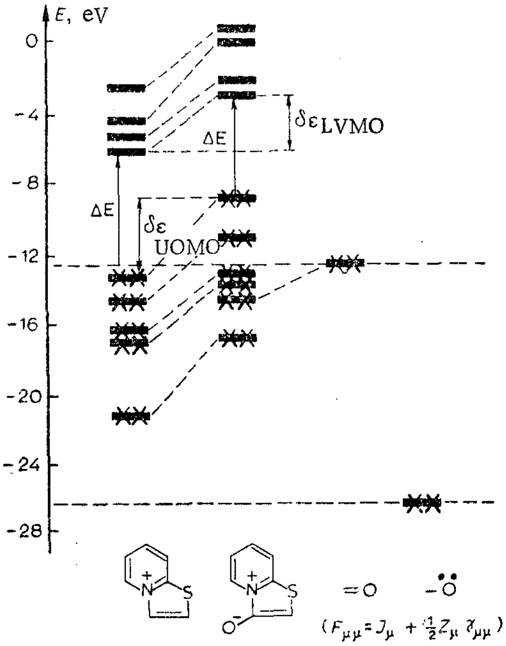
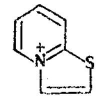
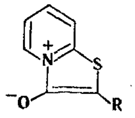
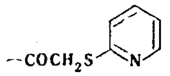
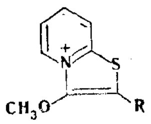
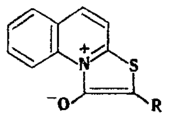
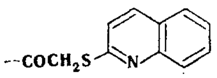


Fig. 4. Spacing of the boundary levels (within the PPP aproximation) of model systems I-III.

of an oxygen atom with an additional pair of electrons (and with skeletal charge $Z_\mu = 1$) in cation I, i.e., conversion to mesoionic compound II, does not lead to fundamental changes in the electron distribution either in the ground state or in the excited states. However, I is colorless, whereas II absorbs intensely in the visible region of the spectrum. Quantum-chemical calculations give estimates of the position of the maxima of the first absorption bands, which coincide closely with the experimentally measured values (Table 2).

TABLE 2. Absorption Maxima of Thiazolopyridinium and Thiazoloquinolinium Derivatives

Compound	Formula	R	Absorption maximum, nm theor.	Absorption maximum, nm exptl. (CH_3OH)
I		—	320	316*
II		—H	390	390
IIa		—C_6H_5	456	435
V			405	416
III		—H	326	—
IIIa		—C_6H_5	397	330
IV		—H	425	462
VI			427	455
VII		—$COCH_3$	427	452

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*The 5-methyl-substituted analog.

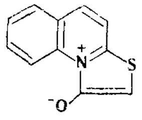
An analysis of the spacing of the electron levels makes it possible to explain the pronounced bathochromic shift of the long-wave band on passing from thiazolopyridinium cation I to thiazolopyridinium oxide II in analogy with the explanation of the shift of the absorption to the long-wave side on passing from pyridine to its N-oxide [9]. In our case the introduction of an oxygen atom with skeletal charge $Z_\mu = 1$ and with an additional pair of electrons into the π system of cation I leads to the appearance in the electronic spectrum of another π level (Fig. 4). This level turns out to be close to the boundary levels of cation I (in our model it even lies within the range of the energy gap), and this leads to a pronounced shift of the remaining levels. The wave function corresponding to this level in system II (φ_2 in Fig. 4) is delocalized from the oxygen atom to the remaining atoms:

$$\varphi_2 = -0{,}0852\chi_1 + 0{,}0858\chi_2 + 0{,}2914\chi_3 - 0{,}1699\chi_4 - 0{,}1432\chi_5 - 0{,}1255\chi_6 - \\ -0{,}1348\chi_7 - 0{,}1596\chi_8 - 0{,}2071\chi_9 + 0{,}8653\chi_0.$$

As a consequence of the shift of the boundary levels, the first absorption band of thiazolopyridinium 3-oxide II is shifted to the long-wave region as compared with the position of the absorption maximum of cation I.

However, the introduction of an oxygen atom with skeletal charge $Z_\mu = 2$ into the π system leads to the appearance of an additional level with a considerably lower energy, and this level should interact to a considerably lesser extent with the boundary levels of cation I. The 3-methoxythiazolo[3,2-*a*]pyridinium cation III should therefore be colorless, and this is actually observed (Table 2).

The introduction of a phenyl group in the 2 position of the thiazolopyridinium cation leads to a lengthening of the conjugated system and additionally shifts the absorption band to the long-wave region (Table 2).

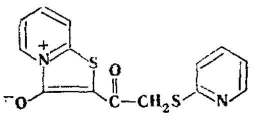


IV

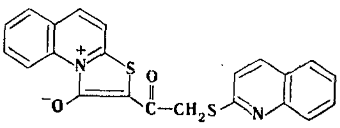
It was demonstrated by quantum-chemical analysis that the transition from mesoionic compound II to thiazoloquinolinium 1-oxide IV should not lead to a considerable shift of the long-wave absorption band. The substantially greater bathochromic shift of the band obtained experimentally (72 nm) [1] as compared with that obtained by a theoretical estimate (35 nm) (Table 2) should probably be ascribed primarily to the steric hindrance that arises in IV between the oxygen atom and the hydrogen atom in the 9 position of the quinoline ring (Fig. 1c). If it is assumed that steric hindrance deflects the oxygen atom from the plane of the molecule and thereby decreases overlapping of the atomic orbitals between the carbon atoms in the thiazole ring, this should lead to a considerable bathochromic effect, since the order of this bond decreases markedly ($\Delta p_{1,2} = -0.2774$) on passing to the excited state.

The deeper coloration of the 5-methyl-substituted derivatives of thiazolo[3,2-*a*]pyridinium 3-oxides as compared with the unsubstituted analogs [10] is possibly due to similar interaction of the oxygen atom with the methyl group. For example, the introduction of a methyl group in the 5 position of IIa leads to a bathochromic shift (16 nm).

It has been previously shown [1, 11] that mesoionic heterocycles II and IV readily undergo dimerization to give derivatives V and VI:



V



VI

In these compounds one can isolate two mutually unconjugated π-electron systems, of which the 2-substituted mesoionic fragments are responsible for the long-wave absorption bands, since 2-alkylthio derivatives of pyridine and quinoline absorb in the UV portion of the spectrum. In fact, the experimental values of the absorption maxima of VI and 2-acetylthiazolo[3,2-*a*]quinolinium 1-oxide (VII) are close [1]. The corresponding 2-acyl derivatives were therefore calculated for a theoretical estimate of the long-wave absorption bands of V and VI (Table 2). It is apparent from the data presented above that the acylation of thiazolopyridinium and thiazoloquinolinium oxides II and IV leads to deepening of their coloration. As in the case of the starting compounds, a greater bathochromic shift of the band obtained experimentally as compared with the theoretical estimate (Δλ 28 nm) is observed for product VI; the latter value is somewhat lower than in the case of oxide IV (Δλ 37 nm), which can probably be explained by the smaller decrease in the order of the C_1—C_2 bond on passing to the excited state for VI ($\Delta p_{1,2} = -0.2031$).

Thus the quantum-chemical analysis of thiazolopyridinium derivatives carried out in this paper makes it possible to explain the difference in their coloration and reactivities with respect to electrophilic reagents.

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FORMATION OF IMIDAZOLE SYSTEMS IN THE REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH AMIDINES, ETHYL CARBAMATE, AND RHODANAMINE

A. V. Eremeev, R. S. El'kinson
É. É. Liepin'sh, and V. A. Imuns

UDC 547.298.5.495.1:546.268.5

The reactions of 2,2-dimethyl-3-phenylazirine with guanidine, guanylurea, formamidinium acetate, ethyl carbamate, and rhodanamine lead to substituted imidazoles, 2-imidazolidone, and imidazolidine-2-thione. It was established experimentally that the initial process is nucleophilic addition of alcohol to the azirine, after which the resulting 3-alkoxy-2,2-dimethyl-3-phenylaziridine reacts with the amine component to give the corresponding imidazole derivative.

It is known the ethyl ester of carbazic acid reacts with 3-dimethylamino-2,2-dimethyl-2H-azirine to give 4,5-dihydro-1,2,4-triazine-3(2H)-one [1]. No information regarding the reaction of 2H-azirine with amines, ethyl carbamate, and rhodanamine is available in the literature.

We have investigated the reactions of 2,2-dimethyl-3-phenylazirine (I) with ethyl carbamate (urethane), formamidinium acetate, guanylurea, guanidine, and rhodanamine.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenni, No. 12, pp. 1624-1626, December, 1980. Original article submitted March 20, 1980.

0009-3122/80/1612-1226$07.50