MESOIONIC COMPOUNDS WITH A BRIDGE NITROGEN ATOM.

11.* π-ELECTRON STRUCTURES AND ABSORPTION SPECTRA OF AZA ANALOGS OF THIAZOLO[3,2-a]PYRIDINIUM 3-OXIDE

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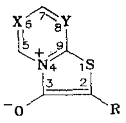
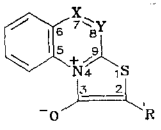
The π-electron structures and energies of the first electronic transitions of a number of mesoionic thiazoloazinium oxides were calculated by the Pariser—Parr—Pople method. An analysis of the data obtained showed that in the case of annelation of the heterorings and the introduction of a phenyl group in the 2 position the first absorption band should be shifted bathochromically, in agreement with the experimental data. In the case of replacement of the methylidyne groups by a trivalent nitrogen atom, however, one should have expected both bathochromic and hypsochromic effects, depending on the position into which the nitrogen atom was introduced. However, it was found experimentally that the first band is shifted to the long-wave region in all cases.

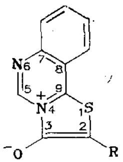
The quantum-chemical analysis of the π-electron structures of thiazolo[3,2-a]pyridinium 3-oxide (Ia) and its benzo homolog II enabled us to explain their unusually deep color [2]. In the present paper we present the results of an investigation of the effect of replacement of the methylidyne groups by a nitrogen atom, as well as the introduction of a phenyl substituent, on the absorption spectra of such compounds.



I,III,V



II,IV,VI



VII

I, II X=Y=CH; III, IV X=CH, Y=N; V, VI X=N, Y=CH; I—VII a R=H; б R=C_6H_5

For this purpose we used the methods described in [3-8] to synthesize I-VII,† for which we recorded the UV spectra and calculated the π-electron density distributions for the ground and excited states, as well as the energies of the first electronic transitions, within the framework of the Pariser—Parr—Pople (PPP) approximation [9]. The wave function of the p-th excited state (Ψ_p) was approximated by expansion with respect to the set of singly excited configurations:

$$\Psi_p = \sum_{i,j} T_{i\to j,p}\Phi_{i\to j}$$

No fewer than 20 of the lower-energy configurations were used in the calculations. The parameters for the calculation and the geometries of the model systems were the same as in [2]; the phenyl group was assumed to be located in the plane of the heteroring, and the C—N bond length for III-VII was assumed to be equal to the C—C bond length.

The π charges in the ground state are presented in Table 1 (only those atoms, the charges on which are discussed, are indicated). It is apparent that neither annelation nor the intro-

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*See [1] for communication 10.

†The numbering of the atoms was selected for convenience in comparing the data.

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TABLE 1. Charges on the Atoms in the Ground State of I-VII

Compound	Position					
	2	5	6	7	8	9
Ia	−0,132	+0,065	−0,010	+0,032	−0,021	−0,031
Ib	−0,119	+0,053	−0,003	+0,027	−0,014	−0,033
IIa	−0,124	+0,001	−0,025	+0,036	−0,042	−0,029
IIb	−0,114	−0,013	−0,022	+0,028	−0,028	−0,036
IIIa	−0,135	+0,106	−0,021	+0,126	−0,205	+0,037
IIIb	−0,120	+0,094	−0,015	+0,123	−0,200	+0,036
IVa	−0,129	+0,023	−0,035	+0,134	−0,223	+0,040
IVb	−0,118	+0,007	−0,033	+0,136	−0,211	+0,023
Va	−0,134	+0,168	−0,192	+0,100	−0,032	−0,010
Vb	−0,120	+0,155	−0,187	+0,098	−0,026	−0,012
VIa	−0,096	−0,011	+0,023	−0,167	+0,076	−0,053
VIb	−0,086	−0,022	+0,030	−0,175	+0,083	−0,056
VIIa	−0,141	+0,154	−0,208	+0,061	−0,031	−0,012
VIIb	−0,126	+0,153	−0,203	+0,058	−0,030	−0,015

duction of a phenyl group in the 2 position causes substantial changes in the π-electron densities on the atoms in the ground state; on the other hand, replacement of the methylidyne groups of the heterorings by a nitrogen atom leads to appreciable changes in these densities. Appreciable negative charge (−0.17...−0.22) is localized on the introduced nitrogen atom, and, correspondingly, positive charge appears on the carbon atoms in the ortho and para positions relative to the introduced nitrogen atom. Thus, for example, the charges in the 5 and 7 positions in IIIb are +0.094 and +0.123, respectively. The presence of such charges adjacent to nitrogen atoms, one of which is a quaternary nitrogen atom, should lead to weakening of the C−N bonds. In fact, 2-phenylthiazolo[3,2-a]pyrimidinium 3-oxide (IIIb) is attacked by nucleophilic reagents precisely at these carbon atoms with detachment of the trimethylidyne chain [3].

As shown in [2], significant redistribution of the π electron density on the atoms of thiazolo[3,2-a]pyridinium oxide (Ia) occurs during excitation. Since, according to perturbation theory [10], the spectral sensitivity to substitution, which is characterized by a shift in the absorption maximum (Δλ), is proportional to the change in the electron density during excitation, the introduction of substituents into the Ia molecule should be accompanied by substantial changes in the absorption spectra. From the molecular diagrams for Ia [2], one should have expected that substituents in the 2 position would give rise to significant shifts of the absorption band. In our research this was modeled by introduction of a phenyl group into the indicated position. An analysis of the experimental data and the results of calculations within the PPP approximation (Table 2) confirms the conclusion drawn above. For example, on passing from IIa to IIb the position of the absorption maximum is shifted +36 nm in CH_3CN and +50 nm in the slightly polar CCl_4 ($\Delta\lambda^{calc}$ = +42 nm), as compared with +59 nm in CH_3CN and +70 nm in CCl_4 ($\Delta\lambda^{calc}$ = 52 nm) for VIa and VIb. It must also be noted that the position of the absorption bands depends markedly on the nature of the solvent, and this constitutes evidence for the existence of significant solvation effects.

Annelation of thiazolopyridinium oxide and its aza analogs — both linear and angular — also leads to significant changes in the UV spectra, and these effects are similar to one another. However, calculations within the framework of the PPP method with allowance for only the singly excited configurations lead to markedly depressed shifts of the absorption band. For example, in comparing Ib and IIb the calculated shift is +16 nm ($\Delta\lambda^{exp}$ +46 nm in CH_3CN), and calculation gives +7 nm ($\Delta\lambda^{exp}$ = +40 nm) for IIIb and IVb, whereas the shift is +5 nm ($\Delta\lambda^{exp}$ = +47 nm) for Vb and VIIb. The doubly excited configurations evidently must be taken into account for the best agreement.

Finally, let us examine the changes in the spectra that arise when the methylidyne groups are replaced by a trivalent nitrogen atom. It follows from the molecular diagrams of Ia [2] that replacement of a methylidyne group by a nitrogen atom in the 8 position should lead to a comparatively large shift of the absorption band, whereas replacement in the 6 position should lead to a slight shift. This prediction is in qualitative agreement with both the results of the calculations and with the experimental data. In addition to this, it may be noted that the calculated Δλ values are appreciably smaller than the experimentally observed values. For example, for the Ib and IIIb pair the difference in the wavelengths of the maxima of the absorption bands is +40 nm in CH_3CN and +45 nm in CCl_4 ($\Delta\lambda^{calc}$ = +27 nm), whereas it is only +12 nm in CH_3CN and +5 nm in CCl_4 ($\Delta\lambda^{calc}$ = −6 nm) for Ib and Vb. According-

TABLE 2. Position of the Long-Wave Absorption Maximum in the UV Spectra of Thiazoloazinium Oxides*

Compound	λ_{max}, nm		
	calc.	CH_3CN	CCl_4
Ia	461	424	450
Ib	503	470	513
IIa	477	480	507
IIb	519	516	557
IIIa	497	—	—
IIIb	530	510	558
IVa	483	—	—
IVb	537	550†	618†
Va	460	425†	451†
Vb	497	482	518
VIa	476	477	498
VIb	528	536	568
VIIa	462	474	500
VIIb	502	529	572

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*The UV spectra were recorded with an SF-10 spectrophotometer.

†The absorption maxima are presented for 7-methyl-substituted compounds (in accordance with the numbering adopted in this paper).

ing to perturbation theory, the maximum bathochromic shift of the absorption band should be expected when the methylidyne group in the 7 position is replaced [2]. However, for the benzo homologs both the calculations and experiments in the case of this sort of substitution lead to a hypsochromic shift and to only a small bathochromic effect in the case of phenyl derivatives. Thus $\Delta\lambda = -3$ nm in CH_3CN and -9 nm in CCl_4 ($\Delta\lambda^{calc} = -1$ nm) for IIa and VIa and $\Delta\lambda = +20$ nm in CH_3CN and +11 nm in CCl_4 ($\Delta\lambda^{calc} = +9$ nm) for IIb and VIb. This result is evidently associated with the large contribution of higher configurations to the expansion of the state functions and with the inapplicability of one-configuration perturbation theory. For example, in the case of Ia and IIa the coefficients of the chief configuration that describes the first excited state ($T_{i\to j,1}$) are, respectively, 0.9468 and 0.9866, as a consequence of which relative agreement in different approaches to the analysis of the effect of a second nitrogen atom was observed. However, in the case of VIa the second configuration [in an electron passed from the highest occupied molecular orbital (HOMO) to the second vacant MO: $\Psi_1 = 0.7325\Phi_1 + 0.6598\Phi_2 + \ldots$] also makes a large contribution. Multiconfiguration perturbation theory evidently must therefore be used for such transitions.

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