π ELECTRON STRUCTURE AND REACTIVITIES OF ISOMERIC PYRROLO-sym-TRIAZOLES

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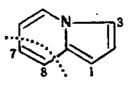
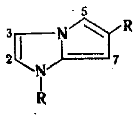
The π electron structures and energies of the singlet π→ π* transitions of a number of isoelectronic analogs of indolizine were calculated by the MO LCAO method within the semiempirical self-consistent field (SCF) approximation. In contrast to the calculations made by the simple MO LCAO method, the π electron density distribution obtained is in better agreement with the direction of electrophilic substitution. On the basis of an analysis of the electronic spectra, it was concluded that the 6-phenyl group is not coplanar.

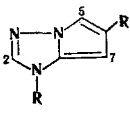
Replacement of the $-\dot{H}C_{(7)}=C_{(8)}H-$ group of indolizine (I) by the $-N(R)-$ grouping makes it possible to derive the formula of the isoelectronic compound – 1H-pyrrolo[1,2-*a*]imidazole (II) – in which a system of 10 electrons is provided by the joining of two five-membered rings. The electronic structure of indolizine (I) has been studied by methods of different accuracy [1-9], while 1H-pyrrolo[1,2-*a*]imidazole has been studied only by the simple MO method [8]. The empirical values of the coulombic (α) and resonance (β) integrals have been varied over wide limits by various investigators [1, 3, 8, 9]. The distribution of the π electron densities (q_r^π) in 1H-pyrrolo[1,2-*a*]imidazole [8] and in 4H-pyrrolo[1,2-*a*]benzimidazole (V) [9, 10] in calculations by the simple MO method does not correspond to the direction of electrophilic substitution. A distribution of the π electron density in accord with the direction of electrophilic substitution reactions was obtained for indolizine only in the calculation in [1] by the simple MO method. The conclusions relative to the role of the energies of electrophilic localization of the carbon atoms ($L_r^\oplus$) obtained in [3, 8] are contradictory, despite the identical methods of calculation. The $L_r^\oplus$ values obtained in [8] for indolizine (I) and pyrroloimidazole (II) correlate with the experimental data on electrophilic substitution, but correlation is absent in [3]. Only the distribution of the boundary electron densities (f_r^π) reflect the correct direction of the S_E reactions in all of the known calculations by the simple MO method [2, 8].



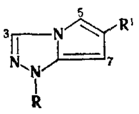
I



II



III



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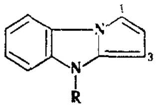

V

We have investigated the electronic structures of indolizine (I), 1H-pyrrolo[1,2-*a*]imidazole (II), and its aza derivatives – 1H-pyrrolo[1,2-b]-sym-triazole (III) [11] and 1H-pyrrolo[2,1-c]-sym-triazole (IV) [12]. It might have been hoped that the use of a more thorough method of calculation of the electronic structures and the spectra would make it possible to avoid the contradictory conclusions obtained by various authors within the framework of the simple MO method. We performed the calculations of the electronic structures and spectra of neutral molecules and protonated cations of indolizine (I) and a large group of its isoelectronic analogs by the MO LCAO method within the semiempirical self-consistent field (SCF) approximation. The ionization potentials of the valence orbitals of the atoms were taken from [13]. The ionization potential of the p_π orbital of the protonated nitrogen atom was taken to be −17.8 eV [14]. The calculations were made both without self-consistency of the ionization potentials with respect to the atomic charges (the programs in [16] were used) and with self-consistency with the aid of the program in [15]. The calculations were carried out with broad variation of the empirical values of the resonance integrals. Concrete examples of the effect of the selection of the values of the resonance integrals are presented in Table 2.

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TABLE 1. Bond Orders (p_{r-s}), and Charges on the Atoms (q_r^{π}) for Isomeric Pyrrolo-sym-triazoles *

Compound	R	R₁		π-Electron charges (q_r^{π})									Bond orders (p_{r-s})									
				7	6	5	4	3	2	1	9	8	7–6	5–6	4–5	3–4	2–3	1–2	1–8	4–8	7–8	1–9
I	—	—	G	0,02	−0,01	−0,04	0,34	−0,10	−0,04	−0,08	−0,01	0,01	0,49	0,84	0,33	0,43	0,78	0,58	0,46 †	0,36 ‡	0,80	0,71
			F	−0,01	−0,10	−0,25	0,30	0,12	−0,02	0,08	0,06	−0,17	0,65	0,61	0,28	0,32	0,72	0,61	0,56	0,39	0,53	0,53
II	H	H	G	−0,11	−0,05	−0,12	0,32	−0,09	−0,05	0,19		−0,08	0,55	0,80	0,40	0,29	0,91	0,33	0,30	0,41	0,76	
			F	0,09	−0,02	−0,10	0,36	−0,16	−0,26	0,35		−0,16	0,58	0,66	0,27	0,40	0,62	0,28	0,36	0,38	0,56	
III	H	H	G	−0,11	−0,06	−0,10	0,34	−0,32	0,12	0,22		−0,10	0,55	0,79	0,43	0,25	0,86	0,42	0,28	0,42	0,76	
			F	0,12	−0,04	0,15	0,35	−0,58	−0,41	0,35		0,06	0,61	0,71	0,36	0,20	0,44	0,23	0,45	0,47	0,56	
IV	H	H	G	−0,11	−0,04	−0,13	0,33	0,08	−0,27	0,20		−0,07	0,54	0,80	0,38	0,35	0,87	0,30	0,32	0,38	0,76	
			F	0,12	−0,04	0,11	0,32	−0,37	−0,62	0,44		0,05	0,59	0,73	0,35	0,26	0,44	0,20	0,49	0,43	0,58	
V	H	—	G	−0,10	−0,05	−0,11	0,30	−0,05	−0,02	0,16		−0,08	0,53	0,81	0,39	0,25	0,65	0,29	0,28	0,40	0,77	
			F	0,00	−0,06	−0,05	0,31	−0,06	0,00	0,37		−0,09	0,56	0,76	0,35	0,31	0,55	0,41	0,35	0,40	0,68	
IIc	C_6H_5	C_6H_5	G	−0,10	−0,05	−0,11	0,33	−0,08	−0,05	0,24		−0,09	0,51	0,75	0,42	0,29	0,91	0,32	0,29	0,40	0,77	
			F	0,11	−0,10	−0,16	0,34	−0,04	−0,13	0,45		−0,14	0,53	0,66	0,28	0,39	0,76	0,37	0,37	0,39	0,61	
IIIa	H	C_6H_5	G	−0,10	−0,06	−0,10	0,35	−0,32	0,12	0,22		−0,10	0,52	0,75	0,44	0,25	0,86	0,43	0,28	0,41	0,77	
			F	0,09	−0,04	0,16	0,36	−0,54	−0,35	0,28		0,07	0,57	0,62	0,39	0,22	0,49	0,25	0,42	0,45	0,56	
IIIb	C_6H_5	H	G	−0,11	−0,04	−0,11	0,34	−0,30	0,12	0,27		−0,10	0,56	0,79	0,41	0,25	0,86	0,48	0,29	0,43	0,74	
			F	0,14	−0,04	0,12	0,37	−0,51	−0,34	0,36		0,04	0,61	0,72	0,33	0,26	0,50	0,28	0,40	0,50	0,53	
IIIc	C_6H_5	C_6H_5	G	−0,10	−0,06	−0,09	0,35	−0,31	0,12	0,27		−0,10	0,52	0,75	0,44	0,25	0,86	0,41	0,27	0,41	0,77	
			F	0,11	−0,05	0,14	0,36	−0,50	−0,33	0,39		0,04	0,57	0,66	0,38	0,24	0,51	0,29	0,41	0,47	0,59	
IVa	H	C_6H_5	G	−0,11	−0,04	−0,12	0,34	0,08	−0,27	0,21		−0,07	0,51	0,76	0,40	0,35	0,87	0,30	0,33	0,38	0,77	
			F	0,12	−0,06	0,09	0,34	−0,27	−0,57	0,34		0,06	0,56	0,63	0,36	0,32	0,50	0,20	0,47	0,42	0,57	
IVb	C_6H_5	H	G	−0,12	−0,03	−0,14	0,33	0,10	−0,27	0,26		−0,07	0,55	0,80	0,37	0,36	0,87	0,29	0,33	0,39	0,75	
			F	0,12	−0,05	0,05	0,34	−0,24	−0,55	0,42		0,00	0,60	0,72	0,32	0,35	0,52	0,22	0,44	0,44	0,55	
IVc	C_6H_5	C_6H_5	G	−0,10	−0,04	−0,12	0,34	0,09	−0,27	0,26		−0,08	0,51	0,76	0,40	0,35	0,87	0,29	0,31	0,38	0,77	
			F	0,10	−0,06	0,03	0,34	−0,21	−0,54	0,46		−0,02	0,56	0,67	0,36	0,35	0,53	0,24	0,43	0,42	0,62	

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* The calculation was carried out within variant A. Abbreviations: G is the ground state, and F is the first excited state.

† p_{8-9}.

‡ p_{4-9}.

TABLE 2. Reactivity Indexes of I-V*

Compound	r	q_r^{π}			f_r^{π}	$L_r^{\oplus}$	$-E^{\pi}$, eV
		A	B	C			
I	3	−0,10	−0,14		0,21	12,37	137,93
	1	−0,08	−0,11		0,20	13,26	
II	5	−0,12	−0,17	−0,14	0,25	22,24	148,80
	7	−0,11	−0,16	−0,11	0,23	23,28	
III	5	−0,10	−0,15	−0,23	0,30	22,45	151,59
	7	−0,11	−0,15	−0,10	0,22	23,51	
IV	5	−0,13	−0,17	−0,25	0,26	22,35	151,46
	7	−0,11	−0,16	−0,11	0,22	23,42	
V	1	−0,11			0,25	22,09	200,24
	3	−0,10			0,19	23,11	

*The q_r^{π} values are the charges on atom r, f_r^{π} is the boundary π electron density on atom r, and $L_r^{\oplus}$ is the energy of electrophilic localization of atom r.

The π electron densities (q_r^{π}) and bond orders (p_{r-s}) in the ground and first excited states of the compounds that we investigated are presented in Table 1, while the reactivity indexes of the most active positions with respect to electrophilic attack are presented in Table 2.

A comparison of the data shows that the maximum π electron densities of all of the examined compounds (I-V) are localized on the $C_{(3)}$ and $C_{(1)}$ atoms for indolizine I and 4H-pyrrolo[1,2-*a*]benzimidazole (V) and on $C_{(5)}$ and $C_{(7)}$ for II-IV. An exception to this is III, in which the relative magnitude of the charges on $C_{(5)}$ and $C_{(7)}$ proved to be very sensitive to the selection of the values of the empirical parameters. In pyrrolo-sym-triazoles III and IV, the greater π electron densities are localized on the nitrogen atoms of the pyridine type. The character of the distribution of the π electron density is radically changed in the first excited state. The introduction of phenyl rings into the 1 and 6 positions of pyrrolo-sym-triazoles III and IV, just as in the case of introduction of two phenyl groups at once, has practically no effect on the q_r^{π} and p_{r-s} values of the two-ring compounds. Aza substitution in the imidazole portion of the 1H-pyrrolo[1,2-*a*]imidazole molecule (II) in the 2 position does not substantially change the distribution of π electron density and the bond orders of the two-ring system, but the introduction of a nitrogen atom of the pyridine type into the 3 position (II → III) leads to equalization of the charges in the 5 and 7 positions of the III molecule. In some variants of the calculation, q_7^{π} becomes somewhat greater than π_5^{π}. Three variants of the calculation of q_r^{π} with different values of the resonance integral (β) for the C−N and $\dot{N}-\dot{N}$: bonds are presented in Table 2: in variant A, the β values are calculated from the formulas in [15]; in variant B, the β values are −2.3 eV. In variant C, self-consistency of the coulombic integrals was not realized with respect to the charges [16]. The values of the remaining indexes are presented for variant A. A comparison of the total conjugation energies (E_{π}) of the isomeric pyrrolo-sym-triazoles (III and IV) shows relatively high stability of 1H-pyrrolo[1,2-b]-sym-triazoles (III). It follows from an analysis of the data in Table 2 that all of the most important reactivity indexes (q_r^{π}, f_r^{π}, and $L_r^{\oplus}$) of indolizine (I), 1H-pyrrolo[1,2-*a*]imidazole (II), and 4H-pyrrolo[1,2-*a*]benzimidazole (V) indicate that the $C_{3(5)1}$ atoms of I, II, and V will primarily undergo electrophilic attack, followed only by the $C_{1(7)3}$ atoms, respectively. These conclusions are in complete agreement with the experimental data for all of the compounds listed above [17-19]. In the case of pyrrolo-sym-triazoles (III, IV), the calculations predict the greatest reactivity of the carbon atoms in the 5 position in electrophilic substitution reactions. A comparison of the data in Table 2 on the reactivity indexes of the investigated compounds indicates an increase in reactivity on passing from I to II, which was previously noted in [8]. However, it is impossible to draw conclusions relative to the relative reactivities in the series of compounds II-IV from the calculations because of the closeness of the values of the reactivity indexes.

Thus, in contrast to the results calculated previously by the simple MO LCAO method, we have obtained self-consistent conclusions relative to the preferred direction of electrophilic substitution both with respect to the q_r^{π} values and the $L_r^{\oplus}$ values for I, II, and V.

TABLE 3. Charges on the Atoms (q_r^π) of the Monocations of Pyrrolo-sym-triazoles

Proton added to	r	Monocations of pyrrolo-sym-triazoles							
		III	IIIa	IIIb	IIIc	IV	IVa	IVb	IVc
$N_{(3)}$ or $N_{(2)}$	2 (3)	+0,13	+0,13	+0,12	+0,01	+0,07	+0,06		+0,07
	5	−0,21	−0,10	−0,21	−0,21	−0,25	−0,15		−0,25
	7	−0,10	−0,09	−0,10	−0,09	−0,12	−0,11		−0,10
$C_{(5)}$	2	+0,06	+0,05		+0,03	−0,17	−0,18	−0,19	−0,20
	3	−0,18	−0,20		−0,20	+0,05	+0,04	+0,04	+0,03
	7	−0,01	−0,06		−0,05	−0,01	−0,06	−0,13	−0,05
$C_{(7)}$	2	+0,07	+0,06	+0,04	+0,03	−0,16	−0,17	−0,20	−0,19
	3	−0,19	−0,21	−0,19	−0,21	+0,04	+0,02	+0,05	+0,02
	5	−0,13	−0,09	−0,13	−0,19	−0,13	−0,10	0,00	−0,20

TABLE 4. Calculated Positions of the Absorption Band Maxima in the UV Spectra of Pyrrolo-sym-triazoles (III, IV)

Compound	Base		λ_{max}^{theor} for the cations, nm					λ_{max}^{exp} of the cations, nm
			monocations			dications		
	theory λ_{max}	λ_{max}^{exp}	5-H	7-H	$>\overset{\oplus}{N}$-H	5-H+$\overset{\oplus}{N}$H	7-H+$\overset{\oplus}{N}$H	
III	307 234		302 220	297 234	321 248 220	323 244	296 232	
IIIa	288 270 262		407 358 250	425 349 287	332 281	404 364 276	435 363 304	
IIIb	328 272		322 269 248	323 319 271	342 266 256	339 321 289		
III	333 273	sh 300— —340 264	426 350 316	408 336 306	341 292 266	419 356 312	440 353 309	315
IV	316 240		300 218	296 237	346 251	320	289	
IVa	311 262	308 266	405 357 253	426 344 297	355 280	399 362 283	436 348 341	306
IVb	340 275 258	319 242	329 324 270	344 340 279	370 264 262	363 356 273	349 334 277	325 272
IVc	343 273	328 270	430 351 327	404 330 316	376 288 272			319

The calculations of the electronic structures of the 5-H and 7-H monocations of pyrrolo-sym-triazoles show that significant negative charges are localized on the nitrogen atoms of the pyridine type in the monocations. This indicates the possibility of the formation of the corresponding dications. The π electron charges on the atoms in the monocations of the investigated compounds, which were obtained within variant C, are presented in Table 3. It is apparent from Table 3 that there are considerable negative charges on the $C_{(5)}$ and $C_{(7)}$ atoms in the N-cations and that these charges differ little from the charges in the molecules of the bases. The high negative charge on the pyridine nitrogen atom of the sym-triazole ring is retained in the C-cations during protonation of the $5_{(7)}$ carbon atoms, and is reduced considerably on the $7_{(5)}$ carbon atoms. The π-electron density on $C_{(7)}$ in the 5-H cations is particularly reduced; this also indicates the preferred character of the formation of the 5-H cations. The calculated positions of the absorption band maxima (λ_{max}^{theor}) together with the experimental values (λ_{max}^{exp}) for isomeric pyrrolo-sym-triazoles (III, IV) and their protonated cations are presented in Table 4. In agreement with the experimental results, the calculation shows a considerably lower integral intensity of the long-wave band as compared with the short-wave band in the spectra of the neutral molecules. In the observed spectra, this leads to the fact that the long-wave band is often observed only as a shoulder. A comparison of the calculated and experimental positions of the absorption band maxima of the neutral molecules shows that they coincide satisfactorily.

The data presented in Table 4 make it possible to make the following observations:

1. The positions of the $\lambda_{\max}^{\text{theor}}$ values of the monocations formed by protonation of a nitrogen of the pyridine type do not correspond at all to the experimentally observed values. Consequently, monocations of this type are not formed on protonation.

2. According to the calculations, any variants of the formation of the monocations of 6-phenyl- or 1,6-diphenylpyrrolo-sym-triazoles (III, IV) lead to long-wave bands with $\lambda_{\max}^{\text{theor}} > 400$ nm; this contradicts the experimental data (a deviation of more than 100 nm). The accuracy in the calculation of the position of $\lambda_{\max}^{\text{theor}}$ can be estimated at 20-30 nm. The assumption regarding disruption of the planarity of the system on passing from the base to the cation may serve as a possible explanation of this contradiction; the 6-phenyl group deviates from the plane, since the calculated $\lambda_{\max}^{\text{theor}}$ values for the monocations of phenylpyrrolo-sym-triazoles are in satisfactory agreement with the experimentally observed values. In these cases, the observed absorption bands are due to the π system of IIIb, IV, and IVb.

3. The calculated $\lambda_{\max}^{\text{theor}}$ values for the 5-H and 7-H cations are very close; this does not enable one to draw a conclusion regarding the direction of protonation from the position of $\lambda_{\max}^{\text{exp}}$.

4. Closeness of the calculated $\lambda_{\max}^{\text{theor}}$ values for the dications formed by protonation at the carbon atoms and the nitrogen atoms of the pyridine type and of the 5-H and 7-H monocations and the experimental $\lambda_{\max}^{\text{exp}}$ values is observed in most cases. This does not make it possible to form a judgment regarding the formation of the corresponding dications from the experimentally observed spectra, although the $\lambda_{\max}^{\text{theor}}$ values for dications are somewhat closer to the experimental values.

LITERATURE CITED

1. C. A. Coulson and H. C. Longuet-Higgins, Trans. Faraday Soc., 43, 87 (1947).
2. K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, J. Chem. Phys., 22, 1433 (1954).
3. A. Galbraith, T. Small, R. A. Barnes, and V. Boekelheide, J. Am. Chem. Soc., 83, 453 (1961).
4. A. Streitwieser, J. Am. Chem. Soc., 82, 4132 (1960).
5. A. Gamba and G. Favini, Gazz. Chim. Ital., 98, 167 (1968).
6. V. Galasso, G. de Alti, and A. Bigoto, Theor. Chim. Acta, 9, 222 (1968).
7. V. Galasso, Gazz. Chim. Ital., 99, 1078 (1969).
8. L. M. Alekseeva, G. G. Dvoryantseva, I. V. Persianova, Yu. N. Sheinker, A. A. Druzhinina, and P. M. Kochergin, Khim. Geterotsikl. Soedin., 492 (1972).
9. L. M. Alekseeva, G. G. Dvoryantseva, I. V. Persianova, Yu. N. Sheinker, R. M. Palei, and P. M. Kochergin, Khim. Geterotsikl. Soedin., 1132 (1972).
10. M. Yu. Kornilov, G. G. Dyadyusha, and F. S. Babichev, Khim. Geterotsikl. Soedin., 905 (1968).
11. V. A. Kovtunenko and F. S. Babichev, Ukr. Khim. Zh., 38, 1142 (1972).
12. F. S. Babichev, V. A. Kovtunenko, and L. N. Didenko, Ukr. Khim. Zh., 40, No. 2 (1974).
13. J. Hinze and H. H. Jaffe, J. Am. Chem. Soc., 84, 545 (1962).
14. L. I. Savranskii, Zh. Prirodn. Soedin., 13, 1084 (1970).
15. G. I. Kagan, I. N. Fundyler, and G. M. Kagan, Teor. i Éksperim. Khim., 2, 589 (1966).
16. Yu. A. Kurglyak, G. G. Dyadyusha, V. A. Kuprievich, L. M. Podol'skaya, and G. I. Kagan, Methods for the Calculation of the Electronic Structures and Spectra of Molecules [in Russian], Naukova Dumka, Kiev (1969), p. 175.
17. W. L. Mosby, Heterocyclic Systems with Bridgehead Nitrogen Atoms, Vol. 1, New York-London (1961), p. 239.
18. A. A. Druzhinina, P. M. Kochergin, and L. M. Alekseeva, Khim. Geterotsikl. Soedin., 405 (1972).
19. F. S. Babichev, G. P. Kutrov, and M. Yu. Kornilov, Ukr. Khim. Zh., 34, 1020 (1968).