1-Benzyl-3,5-dimethyl-4-nitrosopyrazole (Ib, $C_{12}H_{13}N_3O$). A. This was synthesized analogously to the nitrosopyrazole Ia by method A, but the mixture of N-benzyl-N-nitrosohydrazine [7] and acetylacetone was kept for 3 days. The reaction product was a green liquid, yield after purification on a column 60%; d_4^{20} 1.1218. R_f 0.86 (Silufol UV-254; eluent ethylacetate–chloroform, 1:4). UV spectrum, λ_{max}, nm (log ε): 205 (4.21), 304 (4.14), 670 (1.73).

B. This was synthesized with addition of urea analogously to Ia by method B, but the solvent was ethanol only. Treatment was done for three days. Urea was recovered quantitatively. Yield of nitrosopyrazole Ib, 57% (in the absence of urea, 60%).

C. The synthesis was done as described for Ia by method C, but the temperature during addition of the isonitrosoacetylacetone was kept below 30°C, and it was left for 1 day. From 6.1 g (50 mmole) benzylhydrazine and 6.45 g (50 mmole) isonitrosoacetylacetone, 8.8 g (82%) of green liquid were obtained after chromatographic separation.

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ELECTRON STRUCTURES OF AZOLOISOINDOLES WITH A NODAL NITROGEN ATOM.

2.* TRIAZOLO- AND TETRAZOLOISOINDOLES

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UDC 547.759.4'791'792'796:541.6:519.25

The electron structures of N-methyl-substituted triazolo- and tetrazoloisoindoles with a modal nitrogen atom were calculated by the Pariser–Parr–Pople (PPP) and CNDO/2 methods. On the basis of an analysis of the canonical and localized MO it was concluded that the examined compounds, to a first approximation, can be regarded as 1,2-disubstituted isoindoles, i.e., 10 π-electron systems rather than 14π-electron systems, as one should have expected on the basis of the structural formulas. It was also established that the degree of conjugation through the nitrogen atoms of the pyrrole type depends on their position. Equalization of the bonds and intensification of the interannular conjugation occur in the first singlet excited state of all of the investigated structures. The calculated data obtained are in good agreement with the known chemical properties and UV spectra of derivatives of triazolo- and tetrazoloisoindoles.

*See [1] for Communication 1.

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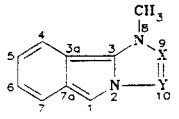
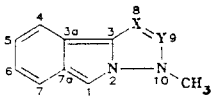
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 340-346, March, 1989. Original article submitted November 9, 1987.

We have previously described the electron structures of isoindole [2], various azinoisoindoles [3], and three azoloisoindoles obtained by annelation of the imidazole, benzimidazole, and pyrazole systems along the *a* side of isoindole [1]. In the present paper we will deal with condensed isoindoles that contain triazole (I-III) and tetrazole (IV and V)* rings. The calculations were made by the Pariser–Parr–Pople (PPP) and CNDO/2 methods, and the conclusions regarding the electron structures were based on an analysis of both the canonical and localized MO [4]. In view of the fact that N-methyl-substituted azoloisoindoles are more accessible than unsubstituted systems, in the calculations by the CNDO/2 method the methyl group in the 8 or 10 position (see the numbering in structural formulas I-V) was taken into account.



I, II, IV



III, V

I, III—V X=N, II X=CH, I, III Y=CN; II, IV, V Y=N

The bond orders (p_{rs}) in the ground state of the I-V molecules are presented in Fig. 1. An analysis of the p_{rs} values in the investigated systems makes it possible to draw the following conclusions. Localization of the 4–5 and 6–7 bonds is noted in the benzene ring of all of the molecules. The bond orders in the pyrrole part are more equalized. In the case of I-III the greatest localization is characteristic for the multiple bond of the triazole ring. In tetrazoloisoindoles IV and V the localization of the 9–10 and 8–9 bonds, respectively, is expressed to a lesser extent. The valence activities (w) of the two-center fragments (Table 1, lines 1-14) that include the 4 and 5 and 6 and 7 atoms are smaller than the w values of the adjacent bonds, while the w values of the bonds in the pyrrole ring are close. The valence activities of the bonds of the triazole and tetrazole rings are much lower than the w values of the adjacent bonds. These bonds can be assumed to be isolated to a sufficient extent. An analysis of the valence activities of the fragments that contain three to five atoms each (Table 1, lines 15-19) shows that the pyrrole ring is conjugated to a greater extent with the remaining atoms of the benzene ring than those of the tri- or tetrazole ring. This is particularly true for compounds (II) and (IV). Thus w for the pyrrole ring is 1.3, of which 0.8 goes into conjugation with the fragment containing the 4-7 atoms and 0.5 goes into conjugation with the fragment containing the 8-10 atoms. The w value of the isoindole fragment (Table 1, line 22) in the triazolo- and tetrazoloisoindole structures is equal to the w value of the 8–9–10 fragment (since the w value of the molecule as a whole is equal to zero) and constitutes evidence for its substantial localization. The valence activities of the nitrogen atoms bonded to the methyl group calculated by means of a known formula [1, 4] for I-V are as follows: 0.60, 0.54, 0.45, 0.63, and 0.48, respectively. This constitutes evidence that the degree of participation of the free electron pair on conjugation depends on its position and decreases when it is adjacent to the isoindole nitrogen atom (structures III and V). It is interesting that in the same structures the conjugation through the isoindole nitrogen atom also decreases as compared with the position isomers (its w values in I-V are 0.73, 0.74, 0.68, 0.75, and 0.70, respectively).

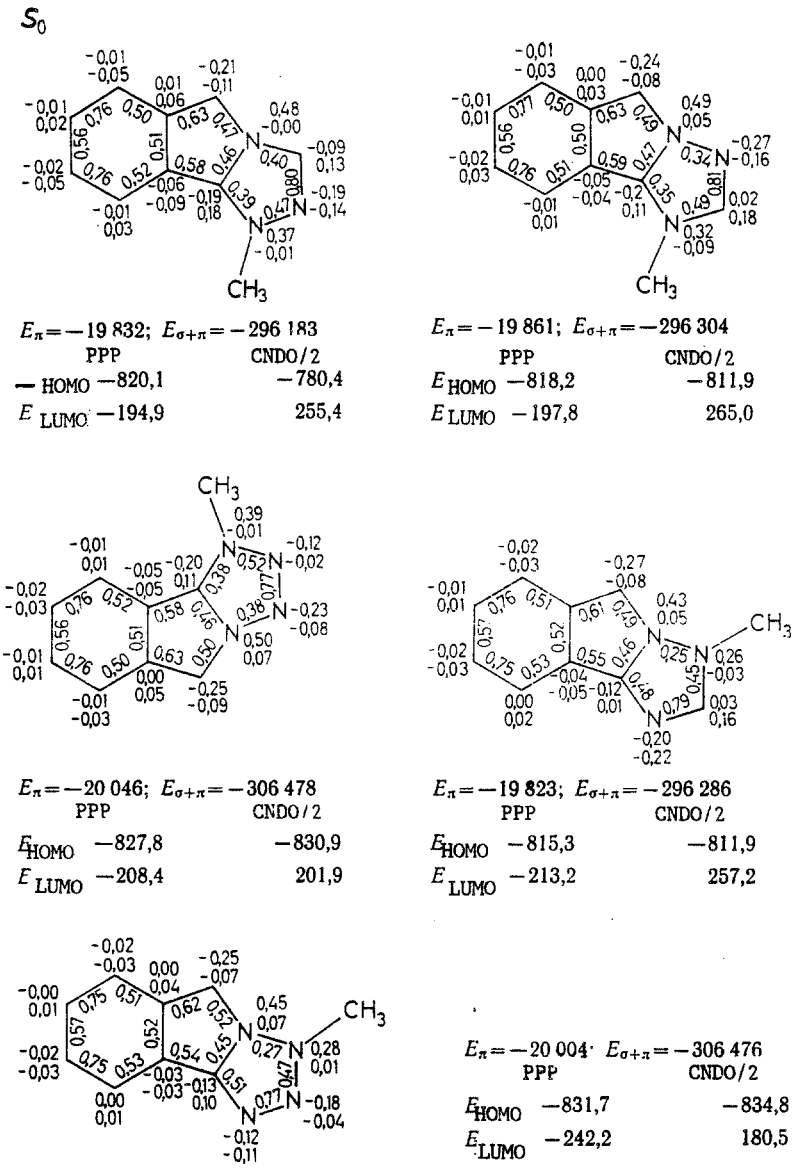
From the information set forth above one should draw the conclusion that, despite certain differences, the fragmentation of the π systems of the triazolo- and tetrazoloisoindoles with a nodal nitrogen atom is identical on the whole. To a first approximation I-V can be represented in the form of three π fragments, viz., the isoindole part, the free electron pair of the N-methyl nitrogen atom, and the multiple bond in the azole ring; this is reflected most accurately by structural representations Ia-Va (see scheme on page 284).

*For the most concise exposition of the material the numbering of the atoms does not coincide with the generally accepted numbering.

TABLE 1. π-Valence Activities of the Fragments Calculated by the Pariser–Parr–Pople (PPP) Method*

Line No.	Nos. of atoms that enter into the fragment	I		II		III		IV		V	
		S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
1	8,9	1,1 (1,28)	1,2	1,1 (1,07)	1,2	0,7 (0,69)	1,1	1,1 (1,12)	1,2	0,8 (0,75)	1,2
2	9,10	0,7 (0,60)	0,9	0,6 (0,50)	1,0	1,0 (0,99)	1,1	0,7 (0,69)	1,1	1,1 (1,07)	1,1
3	2,10	1,4 (1,38)	1,3	1,4 (1,57)	1,3	1,0 (1,15)	0,8	1,4 (1,47)	1,3	1,0 (1,14)	0,9
4	1,2	1,2 (1,34)	1,4	1,2 (1,24)	1,4	1,1 (1,22)	1,3	1,2 (1,28)	1,4	1,1 (1,20)	1,3
5	1,7*a*	1,1 (0,96)	1,2	1,1 (1,03)	1,3	1,2 (1,04)	1,2	1,2 (1,03)	1,3	1,2 (1,13)	1,2
6	7,7*a*	1,5	1,5	1,5 (1,53)	1,5	1,5 (1,52)	1,5	1,5 (1,51)	1,5	1,5 (1,48)	1,5
7	6,7	0,8 (0,81)	1,2	0,8 (0,80)	1,2	0,8 (0,81)	1,1	0,8 (0,82)	1,2	0,9 (0,84)	1,1
8	5,6	1,4 (1,39)	1,2	1,4 (1,41)	1,2	1,4 (1,39)	1,2	1,4 (1,39)	1,2	1,3 (1,36)	1,2
9	4,5	0,8 (0,85)	1,3	0,8 (0,82)	1,3	0,9 (0,84)	1,3	0,8 (0,84)	1,2	0,9 (0,87)	1,3
10	3*a*,4	1,5 (1,42)	1,4	1,5 (1,47)	1,4	1,4 (1,45)	1,3	1,5 (1,45)	1,4	1,4 (1,42)	1,3
11	3,3*a*	1,3 (1,34)	1,4	1,3 (1,23)	1,4	1,4 (1,30)	1,6	1,3 (1,29)	1,4	1,4 (1,36)	1,6
12	3,8	1,3 (1,06)	1,3	1,3 (1,27)	1,2	1,5 (1,57)	1,2	1,3 (1,26)	1,3	1,4 (1,47)	1,2
13	2,3	1,3 (1,32)	1,3	1,2 (1,18)	1,3	1,2 (1,17)	1,2	1,3 (1,27)	1,3	1,3 (1,28)	1,2
14	3*a*,7*a*	1,5 (1,54)	1,5	1,5 (1,55)	1,5	1,5 (1,53)	1,5	1,5 (1,54)	1,5	1,5 (1,50)	1,5
15	8,9,10	0,6		0,5		0,6		0,5		0,7	
16	4,5,6,7	0,8		0,8		0,8		0,8		0,8	
17	1,7*a*,3*a*,3	1,5		1,5		1,7		1,6		1,8	
18	8,9,10,2,3	1,0 (0,86)	1,7	1,0 (1,00)	1,8	1,0 (0,97)	1,5	1,0 (0,98)	1,9	1,1 (1,07)	1,6
19	1,2,3,3*a*,7*a*	1,3		1,2		1,3		1,3		1,4	
20	3*a*,4,5,6,7,7*a*	1,0 (1,12)	1,8	1,0 (1,15)	1,8	1,0 (1,10)	1,5	1,0 (1,11)	1,7	1,0 (1,04)	1,5
21	8,9,10,2,1,7*a*,3*a*,3	0,8		0,8		0,8		0,8		0,8	
22	1,2,3,3*a*,4,5,6,7,7*a*	0,6		0,5		0,6		0,5		0,7	

*The π-valence activities calculated by the CNDO/2 method are presented in parentheses.



	PPP	CNDO/2
$E_\pi = -19\,832$; $E_{\sigma+\pi} = -296\,183$		
E_{HOMO}	−820,1	−780,4
E_{LUMO}	−194,9	255,4

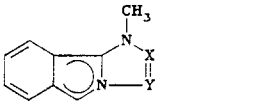
	PPP	CNDO/2
$E_\pi = -19\,861$; $E_{\sigma+\pi} = -296\,304$		
E_{HOMO}	−818,2	−811,9
E_{LUMO}	−197,8	265,0

	PPP	CNDO/2
$E_\pi = -20\,046$; $E_{\sigma+\pi} = -306\,478$		
E_{HOMO}	−827,8	−830,9
E_{LUMO}	−208,4	201,9

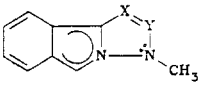
	PPP	CNDO/2
$E_\pi = -19\,823$; $E_{\sigma+\pi} = -296\,286$		
E_{HOMO}	−815,3	−811,9
E_{LUMO}	−213,2	257,2

	PPP	CNDO/2
$E_\pi = -20\,004$; $E_{\sigma+\pi} = -306\,476$		
E_{HOMO}	−831,7	−834,8
E_{LUMO}	−242,2	180,5

Fig. 1. Orders of the bonds calculated by the Pariser–Parr–Pople (PPP) method and charges on the atoms (upper number) and ($\sigma + \pi$) charges (lower number) in the ground state of I-V. The energies of the lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO), the π energies (PPP), and the overall electron energies (CNDO/2) are given in kilojoules per mole.



Ia, IIa, IVa



IIIa, Va

It hence follows that I-V can be regarded, like diazoloisoindoles [3], as 1,2-disubstituted isoindoles, i.e., 10π-electron systems rather than 14π-electron systems, as is predicted on the basis of structural formulas I-V. According to our observations, the synthesized (by us) pyrido[2,1-*a*]isoindole [3], the system of which, according to the calculated data, is a 14π-electron system, is more stable than 1,2-dimethyl-1,3,5-triazolo[2,1-*a*]isoindole (the latter undergoes oxidation in air in 15 min). This means that in this case the greater interannular conjugation in the three-ring system promotes greater stability.

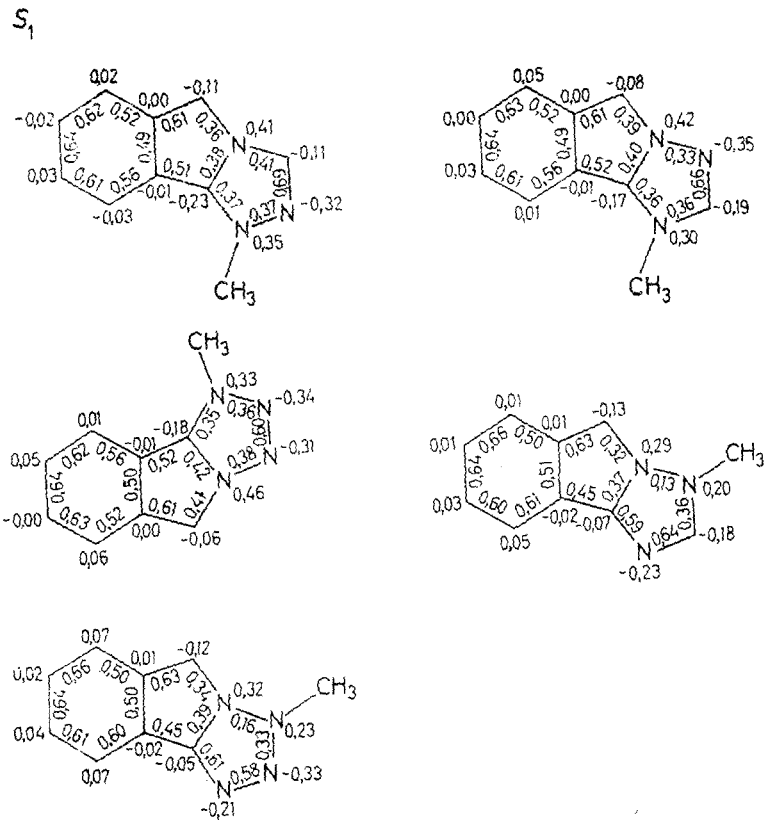


Fig. 2. Order of the π bonds calculated by the PPP method, the π charges on the atoms (upper number), and the (σ + π) charges (lower number) in the first singlet excited state of I-V. The energies of the LUMO and HOMO and the π energies (PPP) are given in kilojoules per mole.

TABLE 2. Boundary Electron Densities on the HOMO Calculated by the PPP Method

Compound No.	Atom No.											
	8	9	10	2	1	7a	7	6	5	4	3a	3
I	0,16	0,00	0,14	0,00	0,60	0,00	0,28	0,06	0,20	0,20	0,08	0,26
II	0,12	0,00	0,08	0,00	0,58	0,00	0,30	0,08	0,20	0,24	0,06	0,34
III	0,04	0,16	0,10	0,00	0,56	0,00	0,30	0,06	0,20	0,22	0,06	0,28
IV	0,12	0,00	0,12	0,00	0,58	0,00	0,30	0,08	0,20	0,24	0,06	0,30
V	0,02	0,18	0,14	0,00	0,54	0,00	0,30	0,06	0,20	0,22	0,06	0,32

A comparison of the E_π and $E_{\sigma+\pi}$ values of the isomeric structures of I-V shows that II and IV should be the most stable (Fig. 1). Judging from the values of the energies of the highest occupied molecular orbitals (HOMO) calculated by the PPP method, in accordance with Koopman's theorem, one can assume an increase in the ionization potentials in the order III < II < I < IV < V. The investigated compounds can be arranged in the same order with respect to the degree of resistance to oxidation. The order changes appreciably for triazoloisoindoles when one compares the energies of the HOMO calculated by the CNDO/2 method: I < II = III < IV < V.

According to the charges on the atoms calculated by the PPP and CNDO/2 methods (Fig. 1) in triazolo- and tetrazoloisoindoles, the most likely sites of electrophilic attack are the α position of the pyrrole ring and then the nitrogen atom of the pyridine type of the adjacent azole ring. The boundary electron densities (see Table 2) in I-V confirm the high activity of the 1 position. The experimental data on electrophilic substitution in 1-methyl-1,2,4-triazolo[2,1-a]isoindole [5] and 1-methyltetrazolo[2,1-a]isoindole [6] are in agreement with these conclusions. A comparison of the charges on the atoms of the

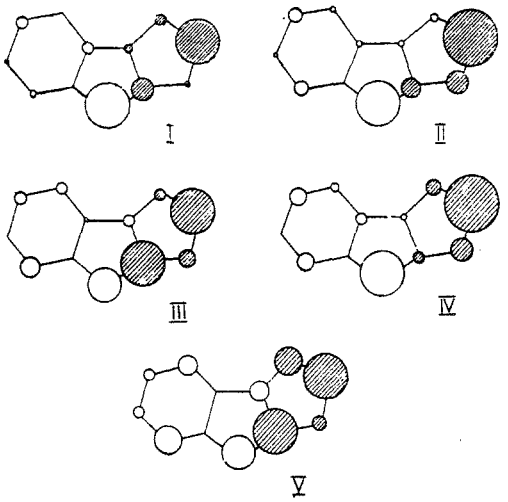


Fig. 3. Change in the π-electron density on the atoms on passing from the ground state to the first singlet exited state.

TABLE 3. Electronic Spectra of I-V

Compound*	Calc. data			Exptl. data, λ_{max}, nm
	λ_{max}, nm	configuration interaction	polarization** (M_x/M_y)	
I	344	$F_7^8=73\%$	−0,07	
II	205		2,97	
	226		0,52	224
	230		−3,03	230*3
	234	$F_7^{11}: F_5^8=23:23$	−1,96	241; 262*3
	276	$F_7^{10}=55\%$	−14,34	277
	316	$F_7^9: F_6^8=35:58$	−0,58	325; 356
	343	$F_7^8: F_7^9=59:29$	0,28	374*4; 393
III	351	$F_7^8=94\%$	−1,17	
IV	364	$F_7^8=69\%$	0,76	
V	360	$F_7^8=92\%$	−1,41	

*For the compounds the close derivatives of which have not been obtained or literature data on their spectra are not available only the longest-wave transition is indicated.
**The x axis was selected in the direction of the 3a–7a bond, and the y axis was selected as perpendicular to it in a direction opposite to the azole ring.
***The inflection of the absorption band is indicated.
****The fine structure.

benzene and tri- or tetrazole rings shows that the latter should be more reactive also with respect to nucleophilic reagents.

On the basis of the concept of the π-surplus character of heterocycles [7] with allowance for the carbon atoms of only the isoindole fragment the investigated compounds can be arranged in the following order with respect to an increase in this characteristic: V < III < II < IV < I. In the case of isomeric triazoloisoindoles taking into account all of the carbon atoms suggests greater π-surplus character of the I molecule as compared with the II and III molecules.

Let us pass to an examination of the excited states of the investigated molecules. An analysis of the first singlet excited states (S_1) carried out in the same way as the analysis of the ground states shows that a tendency for equalization of the bond orders and intensification of conjugation is observed on the whole in the case of excitation (Fig. 2, Table 1). This equalization occurs most appreciably in the benzene ring of the isoindole

fragment. The distribution of the p_{rs} values in the S_1 state of I-V is very close to that in the corresponding diazoloisoindoles that have a similar orientation of the nitrogen atom bonded to the methyl group [1]. The azole ring in I-V is polar. The nitrogen atom bonded to the methyl group always has a positive charge in the S_1 state; this charge is quite high but does not exceed the positive charge on the isoindole nitrogen atom. The nitrogen atoms of the pyridine type bear a negative charge.

The nature of the first singlet transition in I is determined by migration of the electron density from the free α position of the pyrrole ring and, to a lesser extent, from the ortho and para positions of the benzene ring relative to it to the nitrogen atoms of the pyridine and, to a lesser extent, the isoindole type (Fig. 3). A similar pattern is also observed for triazoloisoindole II. In III migration of electron density is realized from the I position primarily to the isoindole nitrogen atom in the 9 position. The same is also characteristic for tetrazoloisoindoles, the difference being that in IV the transition is localized to a greater extent than in V.

The data for the first electron transition of I and III-V were calculated (Table 3). A completely theoretical electronic spectrum, a comparison of which with the spectrum of 1,2-dimethyltriazolo[2,1-*a*]isoindole shows, on the whole, good agreement between the calculated and experimental data, is presented for II.

EXPERIMENTAL

The calculations were made by the PPP [8] and CNDO/2 [9] methods with the standard parametrization [10]. The geometrical parameters of the molecules were borrowed from studies of related compounds [11, 12]. The localization of the MO was determined by means of the valence activities [4]. The UV spectrum was recorded with a Specord UV-vis spectrophotometer. The melting points were measured with a Boetius stage (East Germany). The results of elementary analysis were in agreement with the calculated values.

1,2-Dimethyl-1,3,5-triazolo[2,1-*a*]isoindole ($C_{11}H_{11}N_3$). A mixture of 0.6 g of 1,2-dimethyl-5H-triazolo[2,1-*a*]isoindolium metasulfate [5] and a threefold excess of potassium hydroxide was triturated and introduced into a sublimator. Sublimation was carried out in vacuo at 100-115°C. The substance isolated was purified by repeated sublimation to give lemon-yellow crystals with mp 101-102°C. The yield was 0.26 g (70%).

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