HETEROCYCLIC NITRO COMPOUNDS

X.* APPLICATION OF THE MO LCAO METHOD FOR THE CALCULATION OF THE ELECTRONIC PARAMETERS OF 1,2,4-TRIAZOLE DERIVATIVES

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The MO LCAO method with the Hückel approximation was used to calculate the π-electron densities, the bond orders, and the energies of the π-electron interaction of a number of 1,2,4-triazole derivatives. The results obtained agree satisfactorily with the chemical and physicochemical properties of the triazoles.

For a preliminary estimate of the structures and reactivities of nitro derivatives of 1,2,4-triazole [2,3] we undertook calculations of the electronic structures of these compounds. The literature contains individual examples of calculations of 1,2,4-triazole and several of its derivatives [4-8], but nitro derivatives of 1,2,4-triazole have not yet been investigated by this method.

The calculations were made by the MO LCAO method with the Hückel approximation with a "BÉSM-3M" computer with the program of Gribov [9].

The following optimum values [10] were used as the starting parameters for the calculations:

$\alpha_C = \alpha$
$\alpha_{(-N=)} = \alpha + 0.5\beta$
$\alpha_{(-N<)} = \alpha + 1.5\beta$
$\alpha_{(\overset{+}{N})} = \alpha + 2\beta$
$\alpha_O = \alpha + \beta$
$\alpha_{Cl} = \alpha + 2\beta$
$\alpha_{Br} = \alpha + 1.5\beta$

$\beta_{C-C} = \beta$
$\beta_{C-N} = 0.8\beta$
$\beta_{NO} = 0.7\beta$
$\beta_{CCl} = 0.4\beta$
$\beta_{CBr} = 0.3\beta$
$\beta_{NN} = 0.8\beta$.

In calculating the C- and N-methyl derivatives we used two sets of parameters for the methyl group, viz., the Pauling induction model and the heteroatom model [10].

No correction was made for the induction effect exerted by the heteroatom on the adjacent carbon atom.

The molecular diagrams of nitro derivatives of 1,2,4-triazole are presented in Fig. 1.

As seen from the molecular diagrams, the introduction of a nitro group into the 3- and 5-positions leads to a substantial change in the charges on the ring atoms and a change in the bond orders; the most sensitive atom was the N_2 atom, which considerably decreases the effective negative charge. The overall distribution of electron density is such that the ring as a whole turns out to be positively charged, while the nitro group is negatively charged; consequently, the triazole ring is an electron donor with respect to the nitro group.

When electron-donating groups (Cl, Br, NH_2) are introduced into the 3- and 5-positions, the negative charges of the N_2 and N_4 atoms increase, and this results in localization of the partial negative charge on the ring. On the basis of the results obtained with respect to the bond orders, we estimated the bond lengths

*See [1] for communication IX.

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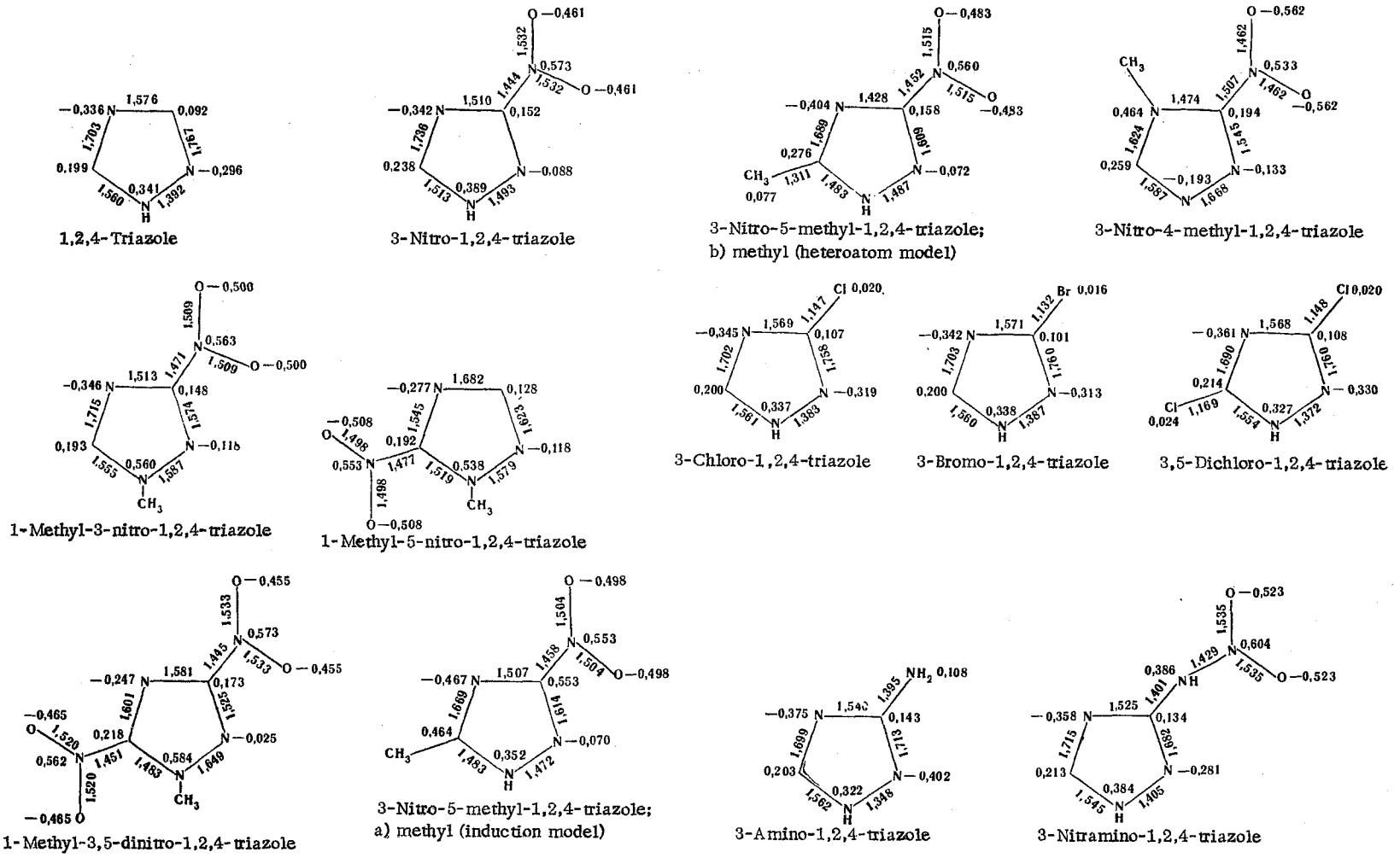

Fig. 1. π-Electron charges and bond orders of 1,2,4-triazole derivatives.

TABLE 1. Ring Charges, π-Electron Energies, and Energies of Interaction of the Substituents with the Triazole Ring*

Compound	Name	q_{ring}	E^{π}	E^{π}_{exp}	E^{π}_{int}
I	3-Nitro-1,2,4-triazole	0,349	16,058	15,821	0,237
II	1-Methyl-3-nitro-1,2,4-triazole	0,436	15,435	15,023	0,412
III	1-Methyl-5-nitro-1,2,4-triazole	0,464	15,442	15,023	0,419
IV	1-Methyl-3,5-dinitro-1,2,4-triazole	0,706	23,040	22,241	0,799
V	3-Nitro-5-methyl-1,2,4-triazole	0,442	15,879	15,479	0,400
VI	3-Nitro-4-methyl-1,2,4-triazole	0,591	15,497	15,033	0,464
VII	3-Chloro-1,2,4-triazole	−0,019	12,662	12,603	0,059
VIII	3-Bromo-1,2,4-triazole	−0,016	11,643	11,603	0,040
IX	3,5-Dichloro-1,2,4-triazole	−0,044	16,729	16,603	0,126
X	3-Amino-1,2,4-triazole	−0,107	11,883	11,603	0,280

*E^{π}, E^{π}_{exp}, and E^{π}_{int} are given in β units.

TABLE 2. π-Dipole and Total Dipole Moments of Nitrotriazoles

Compound	μ_{π}, D	$\mu_{\sigma+\pi}$, D	μ_{exp}, D
I	5,38	7,08	6,74
II	6,82	7,55	6,78
III	3,91	3,99	3,30
IV	5,13	5,37	4,96
V*	*a*—6,93	8,67	7,19
	b —5,45	7,28	
VI	5,37	5,23	5,96

*a indicates methyl (induction model), b indicates methyl (heteroatom model).

and then used them in a subsequent investigation of the vibrational spectra, since there are currently no x-ray diffraction data on the bond lengths of nitro derivatives of 1,2,4-triazole. To substantiate this sort of approach we calculated the bond lengths from "bond order-bond length" graphs [11], and the results obtained were compared with the experimental values of the bond lengths [12]. The deviations for the theoretically calculated CN bond lengths and the experimental values do not exceed 0.02 Å.

The effective ring charges, π-electron energies, and π-electron energies of interaction of the substituents with the triazole ring are presented in Table 1.

The π-electron interaction energy, calculated using the induction model of the methyl group (Table 1), is 0.237β for I and about 0.43β for the remaining mononitrotriazoles. The interaction energy for 1-methyl-3,5-dinitrotriazole (IV) is 0.799β, i.e., about twice the value obtained for mononitrotriazoles. The use of the model of the methyl group within the framework of the heteroatom model leads to a considerably larger value of the π-electron interaction energy ($7.0-7.6\beta$).*

A comparison of these values with the energies calculated from the data of the UV spectra of nitrotriazoles [1] ($0.7-1.5\beta$) indicates that in the pseudoheteroatom model the contribution of the methyl group to the conjugation energy is markedly overstated, and the induction model is apparently more real.

On the basis of the results obtained we calculated the π-electron and total dipole moments of the nitrotriazoles, and their values were compared with the experimentally found values [13] (Table 2).

The bond moments presented in [8, 14] were used to estimate the σ components of the dipole moments.

As seen from Table 2, the π components make a major contribution to the values of the dipole moments of nitrotriazoles. The agreement between the calculated moments and the experimental values (allow-

*The β value was taken as 20 kcal/mole.

ing for the assumption adopted in the calculation of the electron charges on the atoms and the vector calculation of the σ components) can be considered to be satisfactory.

For 3-nitro-5-methyl-1,2,4-triazole (V) the dipole moment calculated for the heteroatom model of the methyl group was close to the experimental value, while the dipole moment for the induction model was markedly high. The real structure of 3-nitro-5-methyl-1,2,4-triazole apparently does not correspond to any of the selected models.

The chemical behavior of nitrotriazoles agrees in general with the assumptions which can be made during an analysis of the molecular diagrams. If the π-electron charges of the atoms are taken as indexes of the reactivity, one should expect that the nitro groups in the nitrotriazoles will enter into nucleophilic substitution reactions. The experimental data confirm this conclusion [2, 3].

The chemical properties of 1-methyl-3,5-dinitro-1,2,4-triazole (IV) are of particular interest. For it one might expect that the nitro group in the 5-position will be more active in nucleophilic substitution; this is experimentally confirmed [2-3]. The rate of reaction with nucleophilic reagents for IV is considerably higher than in mononitrotriazoles, despite the fact that the delocalization energies due to one π electron for mono- and dinitrotriazoles are quite close (1.54 and 1.64β, respectively, for planar configurations).

The possibility of the deviation of the nitro group in the 5-position of these compounds from the plane of the ring probably cannot be excluded in an examination of the structure of 1-methyl-3,5-dinitro- and 1-methyl-5-nitro-1,2,4-triazoles.

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