General Method for the Synthesis of IV-IX (Table 1). An alcohol solution of 5.6 mmole of α- or γ-chloroacetoacetic ester was added at 18-20° to a solution of 5.65 mmole of the appropriate mercaptan I-III in 50 ml of ethanol containing 5.65 mmole of KOH, and the mixture was stirred for 3-4 h, after which the solvent was removed by distillation, and the residue was triturated with water. The solid material was removed by filtration, washed with water, dried, and recrystallized.

General Method for the Synthesis of X-XIII (Table 1). The reaction mixture from the preparation of VI-IX (or the corresponding hydroxyamino compounds VI-IX) was treated with an alcohol solution of hydrogen chloride, and the mixture was allowed to stand for 15 h. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized.

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CALCULATION OF THE ELECTRON STRUCTURES AND ELECTRONIC SPECTRA OF 3-CHLORO- AND 3-AMINO-1,2,4-TRIAZOLE DERIVATIVES

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3-Chloro- and 3-amino-1,2,4-triazole derivatives were subjected to a theoretical study by means of quantum-chemical calculation by the Pariser—Parr—Pople method. The experimentally observed electron transitions were assigned. The Cl atom and the NH_2 group in the 3 position of 1,2,4-triazole subject the electron system of the heteroring to substantial perturbation.

The 1,2,4-triazole molecule has previously been studied with the application of an improved MO LCAO method [1]. In addition, the π-electron densities, bond orders, and π-electron interaction energies of 1,2,4-triazole and its 3-Cl, 3-Br, 3-amino-, and 3,5-dichloro derivatives and 3-amino-1,2,4-triazole have been calculated within the Hückel approximation [2].

We have calculated several 3-chloro- and 3-amino-1,2,4-triazole derivatives within the Pariser—Parr—Pople (PPP) π-electron approximation. The calculated energies of the electron transitions were compared with the experimentally found values [3] (Table 1). The peculiar-

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TABLE 1. Energies (E), Extinctions (ε), and Oscillator Forces (f) of the Electron Transitions of 3,5-Disubstituted Triazoles

Compound	Name	E, eV (f), calc.	E, eV (ε), exptl. (C_2H_5OH solvent)
I	1,2,4-Triazole	6,67 (0,098)	6,14 (2680)
II	3-Cl-1,2,4-Triazole	6,43 (0,153)	6,31 (2540)
III	3-Cl-5-Carbamido-1,2,4-triazole	6,03 (0,102), 5,70 (0,234)	6,21 (6480), 5,60 (7260)
IV	3-Cl-5-Carbomethoxy-1,2,4-triazole	6,24 (0,355), 5,97 (0,220)	6,24 (5940), 5,33 (5300)
V	3-Cl-5-Phenyl-1,2,4-triazole	6,37 (1,319), 5,83 (0,885), 5,36 (0,038), 4,80 (0,512)	6,21 (23070), 5,94 sh 5,80 sh 4,94 (16960), 4,74 sh 4,52 sh
VI	3-Amino-1,2,4-triazole	6,57 (0,190), 5,57 (0,170)	6,00 (6060)
VII	3,5-Diamino-1,2,4-triazole	6,54 (0,395), 6,18 (0,389), 5,67 (0,359)	6,34 sh 5,97 (6320)
VIII	3-Amino-5-carbamido-1,2,4-triazole	6,47 (0,172), 5,75 (0,229), 5,14 (0,131)	6,34 (15850), 6,15 sh 5,24 (2350)
IX	3-Amino-5-carbomethoxy-1,2,4-triazole	6,21 (0,451), 5,03 (0,136)	6,21, 4,93
X	3-Amino-5-phenyl-1,2,4-triazole	6,34, 6,09, 5,50, 5,45, 4,78, 4,66	6,26 (43180), 5,65 sh 4,80 (12880)

TABLE 2. Coefficients of Expansion ($L^N_{\mu\to\nu^*}$) with Respect to the Principal Interacting Configurations of the First Electron-Excited States

Compound	Electron transitions		
	first	second	third
1,2,4-Triazole	$L^1_{1\to1^*}=0{,}858$ $L^1_{1\to2^*}=0{,}463$	$L^2_{1\to1^*}=0{,}223$ $L^2_{3\to2^*}=0{,}247$ $L^2_{2\to2^*}=0{,}938$	
3-Chloro-1,2,4-triazole	$L^1_{2\to2^*}=0{,}878$ $L^1_{3\to2^*}=0{,}349$ $L^1_{4\to2^*}=0{,}254$	$L^2_{1\to2^*}=0{,}365$ $L^2_{2\to2^*}=0{,}298$ $L^2_{4\to2^*}=0{,}873$	
3-Chloro-5-carbamido-1,2,4-triazole	$L^1_{3\to3^*}=0{,}977$	$L^2_{2\to2^*}=0{,}262$ $L^2_{6\to3^*}=0{,}914$	
3-Amino-1,2,4-triazole	$L^1_{3\to2^*}=0{,}222$ $L^1_{2\to2^*}=0{,}968$	$L^2_{4\to2^*}=0{,}219$ $L^2_{1\to2^*}=0{,}916$	
3,5-Diamino-1,2,4-triazole	$L^1_{3\to2^*}=0{,}225$ $L^1_{2\to2^*}=0{,}943$	$L^2_{4\to2^*}=0{,}968$	$L^3_{1\to1^*}=0{,}237$ $L^3_{1\to2^*}=0{,}936$
3-Amino-5-carbamido-1,2,4-triazole	$L^1_{3\to3^*}=0{,}944$	$L^2_{6\to3^*}=0{,}964$	$L^3_{3\to2^*}=0{,}261$ $L^3_{2\to3^*}=0{,}843$

ities of the computational scheme employed and the semiempirical parameters [the resonance integrals of the bonds (β_{X-Y}) and the ionization potentials of the atoms (W_X)] have been previously described [4, 5].

The calculated energy of the first electron transition of 1,2,4-triazole is 6.67 eV (186 nm), which is in good agreement with the experimental value of 190-206 nm. According to an analysis of the configuration interaction (Table 2), the MO 1 → 1* interaction makes the principal contribution to it. The atomic orbitals (AO) of the N_2 and C_3 atoms and the AO* of the N_1 atom participate almost equally in the transition.

The introduction of a chlorine atom (3-chloro-1,2,4-triazole) leads to a small bathochromic shift of the band; this is reflected in the calculation: the energy of the first electron transition is 6.38 eV (193 nm). The first electron transition is primarily a transition of the 2 → 2* type with the maximum contribution of the AO of the N_1 atoms and the AO* of the C_3 atom. The calculated value of the electron affinity of the 3-chloro-1,2,4-triazole molecule is elevated, and the energy of its lower vacant orbital is increased by 1.5 eV as compared with unsubstituted 1,2,4-triazole.

Substituents in the 5 position (alkyl groups and halogen atoms) of 3-chloro-1,2,4-triazole do not give rise to changes in the electron density distribution and the character of the electron transition.

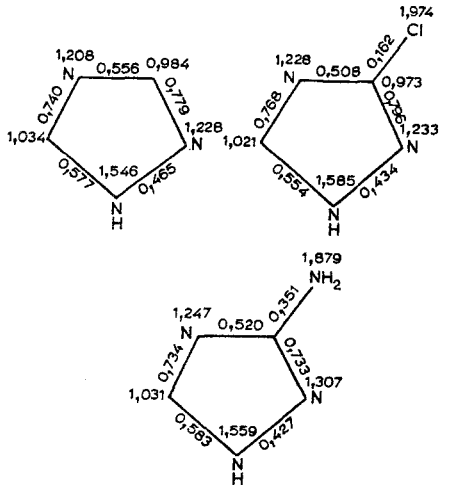

Fig. 1. Molecular diagrams of 1,2,4-triazole and its derivatives.

The long-wave band of 3-chloro-5-carbamido-1,2,4-triazole (III) is due to the first electron transition (5.70 eV), in which the AO of the C_7, O_8, and N_9 atoms participate. In addition to the AO of the heteroring atoms, the AO of the carbamido group also make a definite contribution to the second electron transition. Similar effects are observed for the first and second electron transitions of 3-chloro-5-carbomethoxy-1,2,4-triazole (IV).

The calculation of the 5-phenyl derivatives of 3-chloro-1,2,4-triazole are also in good agreement with the experimental data, and this makes it possible to assign the electron transitions (Table 1).

The calculation of 3-amino-1,2,4-triazole indicates the existence of, in addition to the 6.57 eV (189 nm) electron transition, of a longer-wave 5.57 eV (223 nm) transition, which is not experimentally observed in the spectrum of an alcohol solution of this compound. However, the spectrum of 3-amino-1,2,4-triazole in the gas phase contains an intense band at λ_{max} 207 nm and a band of weak intensity at λ_{max} 227 nm; this is in complete agreement with the calculated data. The maximum contribution of the AO of the nitrogen atom of the NH_2 group is made to the first MO. The first and second electron transitions in diaminotriazole are associated with the AO of the atoms of both NH_2 groups and the AO* of the atoms of the heteroring. As in the case of 3-chloro-1,2,4-triazole derivatives, there is a contribution of the AO of the carbomethoxy and carbamido groups to the longest-wave electron transition of 3-amino-1,2,4-triazoles VIII and IX. Good agreement between the experimental and calculated values was obtained for 5-phenyl-3-amino-1,2,4-triazoles. The assignment of the absorption bands to the electron transitions of X is given in Table 1.

Thus the Cl atom and the NH_2 group in the 3 position of 1,2,4-triazole substantially "perturb" the electronic system of the ring, leading in the case of the amino group to the appearance of additional electron transitions. The Cl and NH_2 substituents have electron-donor capacity, as evidenced by an increase in the negative electronic charge on the N_2 and N_4 atoms (Fig. 1). The increased basicities of aminotriazoles [6] are in complete agreement with this. However, halo-substituted triazoles display acidic rather than basic properties [7]; this is clearly associated with predominance of the inductive effect of the Cl and Br atoms. The sensitivity of the extinction coefficient of the absorption band of 3-amino-1,2,4-triazoles to ionization of the compounds [3] can be explained both by an increase in the basicity of the triazole when an amino group is present and by the increase in its capacity for dipole–dipole interactions.

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