time with water, as a result of which light-brown crystals with a metallic luster and mp 140-142° [from aqueous alcohol (1:10)] formed. Found: C 55.4; H 4.5%. $C_{26}H_{24}IN_5O_3$. Calculated: C 54.7; H 4.1%. UV spectrum, λ_{max}: 265 (340 nm).

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QUANTUM-CHEMICAL ANALYSIS OF THE TAUTOMERISIM OF 1,2,4-TRIAZOLE AND ITS AMINO AND DIAMINO DERIVATIVES

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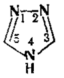
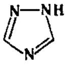
Calculation of the dipole moments and heats of formation for 1,2,4-triazole confirmed that it exists primarily in the unsymmetrical form, while similar calculations for 3-amino- and 3,5-diamino-1,2,4-triazoles showed that the amino tautomers with a hydrogen atom attached to the N–N bond are the preferred forms.

Despite the relatively large number of publications devoted to the tautomerism of 1,2,4-triazole (I), 3-amino-1,2,4-triazole (II), and 3,5-diamino-1,2,4-triazole (III), it is not completely clear which of the possible tautomeric forms of these compounds are actually realized. This is particularly true for the amino and diamino derivatives of 1,2,4-traiazole. This problem was studied in the present research by the methods of quantum chemistry.

X-ray diffraction analysis of 1,2,4-triazole (I) provides evidence [1, 2] that in the crystalline phase, of the two possible tautomeric forms, planar unsymmetrical form IA is realized. Dipole moments ranging from 2.7 to 3.27 D have been obtained [3-5] for 1,2,4-triazole. The quantum-chemically calculated [5] dipole moment for IA is 3.07 D and is close to the experimental value. For solutions of 1,2,4-triazole in hexamethylphosphoric triamide, both the NMR data [6] and the method of fixed structures [7] provide evidence that form IA predominates.



IS



IA

The situation is less definite for amino derivatives II and III (there are five tautomeric forms with amino and imino structures; see below). The research involving the establishment of the structure of triazole II is of qualitative character and indicates the high probability of an amino structure (IIA-S) [8, 9]. An amino–imino form (IIIC or IIID) has been proposed for guanazole III from the UV spectra [10]. It was later proposed that it has a diamino structure (IIIE) [11]. Infrared spectroscopy of guanazole before and after deuteration of the

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TABLE 1. Heats of Formation (H_{IA}) for Asymmetrical Form IA for Various Initial Structural Parameters (l, Å)

Characteristics of the initial structure*	Exptl. structure ($\angle N_2N_1C_5$ 102°, $\angle N_1N_2C_3$ 110.2°)		Valence angles the same as in the exptl. structure; the l_{C-N} bond lengths are increased		All l_{C-N} 1.33 Å, $\angle N_2N_1C_5 = \angle N_1N_2C_3$ = 106°	
	initial	final	initial	final	initial	final
$l_{C_5-N_1}$	1,319	1,320	1,36	1,322	1,33	1,320
$l_{C_3-N_2}$	1,326	1,356	1,32	1,351	1,33	1,353
$l_{N_4-C_5}$	1,352	1,368	1,38	1,369	1,33	1,367
$l_{N_4-C_3}$	1,320	1,320	1,36	1,331	1,33	1,321
H_{IA} cal/mole	94,4	79,2	98,7	80,4	94,0	79,1

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*In all of the variants, l_{N-N} = 1.354 Å before and after OPG.

TABLE 2. Heats of Formation (H_{IS}) for Symmetrical Form IS for Various Initial Structural Parameters (I, A)

Characteristics of the initial structure*	All l_{C-N} = 1.33 Å, $\angle N_2N_1C_5 = \angle N_1N_2C_3$ = 106°		l_{C-N} double bonds shortened to 1.30 Å; angles the same as in I		l_{C-N} double bonds shortened to 1.30 Å, l_{C-N} single bonds increased to 1.38 Å	
	initial	final	initial	final	initial	final
$l_{C_5-N_1}$	1,33	1,302	1,30	1,309	1,30	1,313
$l_{C_3-N_2}$	1,33	1,302	1,30	1,309	1,30	1,313
$l_{C_3-N_4}$	1,33	1,412	1,33	1,408	1,38	1,433
$l_{C_5-N_4}$	1,33	1,412	1,33	1,408	1,38	1,433
H_{IS}†	104,7	85,0	100,6	83,0	98,3	86,2

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*In all variants, l_{N-N} = 1.364 Å before and after OPG.

†In kilocalories per mole.

N–H bond made it possible to conclude that it has a diamino structure [12], it was found to be impossible to choose between forms IIIA or IIIS.

Quantum-chemical methods (for example, see [13-15]) have recently begun to be used for the analysis of the relative stabilities of the tautomeric forms. In the present study we calculated the heats of formation and the dipole moments for all of the tautomeric foms of I-III.

The dipole moments were calculated by the CNDO/2 method (complete neglect of differential overlap) [16], and the geometry of the molecules was found experimentally. In our case x-ray diffraction data are known only for IA, and the standard values of the bond lengths and valence angles, which may vary over a wide range (for example, values ranging from 1.32 to 1.40 Å are known for l_{C-N} in cyclic compounds), were adopted for the remaining forms.

The heats of formation were calculated by the MINDO/2 method [17] with optimization of the geometry (OPG) by the method in [18]. In the program used for the OPG, the accuracy in the determination of the equilibrium bond lengths is 0.01 Å, and this leads to a certain dependence of the calculated heat of formation on the choice of the initial geometry. However, as we will show below, the ambiguity in this case is much less than in calculations without OPG. One cannot use an optimized geometry for the calculation of the dipole moments, since the OPG with respect to MINDO/2 is not the OPG of the CNDO/2 approximation.

Tautomerism of 1,2,4-Triazole

In calculations of the heats of formation with OPG the bond length between the heteroatoms (in our case, l_{N-N}) should remain unchanged and be equal to its experimental value [2]. This is due to the fact that the MINDO/2 method leads to equilibrium values of the lengths of these bonds that are too short (frequently 0.15-0.20 Å less than the experimental values) [17].

Experimental l_{N-N} values are known only for unsymmetrical form IA. To find l_{N-N} for symmetrical form IS we calculated the equilibrium l_{N-N} values for IA and IS with fixed values of the remaining ring bonds

TABLE 3. Dipole Moment μ (in Debye units) and its Components μ_1 and μ_2 along the Major Axes of Inertia for I

	Calc. (CNDO/2)				Found	
	IA[a]	IA[b]	IA[c]	IS[d]	in the gas phase	in dioxane
μ	3,04	3,00	3,07	6,12	2,72[5]	3,27[3]
μ_1	2,85	2,83	2,93	6,12	2,59	—
μ_2	0,93	0,92	0,92	0	0,82	—

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[a] For the experimental geometry in [1, 2] (initial data of variant 2 from Table 1).

[b] For a symmerical geometry (Initial data of variant 3 from (Table 1).

[c] Data from [5].

[d] For the geometry of variant 1 from Table 2.

(1.33 Å) by the CNDO/2 method; this satisfactorily predicts the lengths of the bonds between the heteroatoms. The calculated values were found to be 1.32 and 1.33 Å, respectively, for IA and IS. Since the experimental l_{N-N} value in IA was 1.354 Å, we assumed that l_{N-N} in IA is equal to this value and that it is 0.01 Å higher in IS (1.364 Å) in the subsequent calculations.

The selection, within reasonable limits, of the initial l_{N-N} values and the valence angles does not have a substantial effect on the final result – the scatter in the calculated heats of formation does not exceed 1 kcal/mole. Of greater importance is the selection of the initial lengths of the four C–N bonds. Some of the characterstics of the variants are presented in Tables 1 and 2.

It follows from the data for IA (Table 1) that the heats of formation found after optimization (H_{IA}^{OPG}) lie in the narrow interval 79.1-80.4 kcal/mole (ΔH_{IA}^{OPG} 1.3 kcal/mole), whereas the interval of the heats of formation prior to OPG (H_{IA}^{in}) is broader and ranges from 94.0 to 98.7 kcal/mole) (ΔH_{IN}^{in} 4.7 kcal/mole). This attests to the advantages of calculations with OPG.

A change in the initial l_{C-N} bond lengths of 0.03-0.04 Å has little effect on H_{IA}^{OPG}, and the l_{C-N} values obtained after optimization for the different variants differ only in the third digit and, except for $l_{C_3-N_2}$, are close to the experimental values.

In the case of symmetrical tautomer IS the effect of the bond lengths in the initial geometry on the result is manifested to a greater degree than in the unsymmetrical form (Table 2). The interval of heats of formation of the optimized structures lies over a broader range than in the case of IA (ΔH_{IS}^{OPG} 3.6 kcal/mole). Taking into account the appreciably expressed dependence of the properties of the optimized structures on the choice of the initial geometry, we calculated a large number of IS structures with different initial parameters, but in all cases the heats of formation were higher than 83 kcal/mole (variant 2 from Table 2).

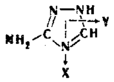
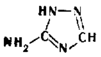
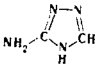
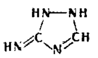
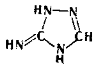
It follows from Table 2 that the $l_{N_1=C_5}$ and $l_{N_2=C_3}$ double bond lengths obtained as a result of optimization are appreciably shorter than the $l_{N_4-C_5}$ and $l_{N_4-C_3}$ single bond lengths (1.30 and 1.41 Å, respectively). This difference is less (1.32 Å compared to 1.36-1.37 Å) in unsymmetrical tautomer IA. This difference between forms IA and IS is evidently due to the fact that the C_5-N_4 bond in IA is found between alternating C=N bonds and is therefore, shorter than ordinary C–N bonds. Unfortunately, because of the lack of experimental data on the structure of symmetrical tautomer IS, one cannot verify the predicted values.

The lowest calculated values of the heats of formation of the unsymmetrical (H_{IA}^{OPG}) and symmetrical (H_{IS}^{OPG}) forms are, respectively, 79.1 and 83.0 kcal/mole, i.e., the unsymmetrical tautomeric form is more favorable by 4 kcal/mole. Hence the tautomeric equilibrium constant (K_T) at room temperature (RT = 0.6 kcal/mole) is 0.001. Of course, this value may be different in solution due to, for example, solvation effects.

The data from the calculation of the dipole moments for IA and IS by the CNDO/2 method are presented in Table 3. The μ_1 and μ_2 components of the dipole moments along the major axes are known from microwave spectroscopic data [5], and we also presented their calculated values. There is only one axis of inertia in IS (C_{2v} symmetry).

A comparison of the calculated and experimental data clearly indicates the existence of unsymmetrical form IA. Although variation of the geometry leads to a change of ~1% in μ_{calc}, this change is much less than the difference between the dipole moments of the IA and IS forms.

TABLE 4. Heats of Formation H^{OPG} (kcal/mole) and Dipole Moments (in Debye units) in 3-Amino-1,2,4-Triazole

	 IIA	 IIA′	 IIS	 IIC	 IID
l_{N-N}*	1,36	1,36	1,363	1,385	1,380
HOPG	57,38	57,41	65,9	69,8	66,4
μ†	1,70	4,08	6,80	6,45	5,03
μ_X	−0,84	−3,96	6,67	4,96	3,54
μ_Y	1,47	−1,01	−1,33	−4,12	3,57

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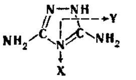
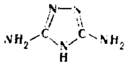
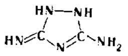
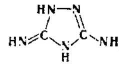
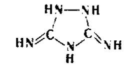
*No change for OPG.

†Calculated by the CNDO/2 method for the initial geometry.

TABLE 5. Heats of Formation H^{OPG} (kcal/mole) and Dipole Moments (in Debye units) in 3,5-Diamino-1,2,4-triazole III

	 IIIA	 IIIS	 IIIC	 IIID	 IIIE
l_{N-N}*	1,37	1,37	1,385	1,385	1,405
HOPG	35,4	43,2	45,5	44,0	46,33
μ†	2,91	7,36	7,76	6,96	0,48
μ_X	2,90	7,36	6,73	4,49	0,48
μ_Y	−0,20	0	−3,86	5,32	0

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*No change for OPG.

†Calculated by the CNDO/2 method for the initial geometry.

Tautomerism of Aminotriazole II and Diaminotriazole III

To simplify the calculation of 10 tautomeric forms we used the results obtained for 1,2,4-triazole. As the initial geometry, the lengths of all of the bonds (except l_{N-N}) were assumed to be 1.38 Å and the angles formed by the N_1 and N_2 atoms were each assumed to be 106° (the same geometry was used for the calculation of the dipole moments by the CNDO/2 method). Even in the case of the application of other than the optimum initial parameters the possible error hardly exceeds 1-2 kcal/mole for many of the examined tautomers (Tables 1 and 2). As in the case of 1,2,4-triazole, we determined the equilibrium l_{N-N} values by means of the CNDO/2 method (with allowance for the fact that the experimental l_{N-N} value for IA is 1.35 Å, whereas the calculated value is 1.32 Å) and assumed the N−N bond lengths presented in Tables 4 and 5 for tautomers II and III. The hydrogen atoms of the amino and imino groups were assumed to lie in the plane of the ring.

Two groups of tautomers − amino IIA, IIA′, IIS, IIIA, and IIIS and imino IIC, IID, IIIC, IIID, and IIIE − can be isolated.

As in the case of 1,2,4-triazole, the forms with a hydrogen attached to N_1 and N_2 rather than to N_4 are energically favorable for the amino tautomers (Table 4 and 5).

The heats of formation of imine tautomeric forms for II and III are 10-12 kcal/mole higher than for the tautomers with a hydrogen attached to N_1 or N_2. This is in agreement with data on the preferableness of amino over imino tautomers [8, 9, 12]. It is interesting that the heats of formation of the imino tautomers are extremely close to the heats of formation of the amino forms that have a hydrogen attached to N_4. For example, the IIIS → D transition requires almost no energy expenditures, in contrast to the monotypic IIIA → C transition. It is possible that the unfavorableness of tautomers with a hydrogen attached to N_4 is associated with the presence in them of two unshared electron pairs of adjacent N_1 and N_2 atoms lying in the same plane. Their dipole−dipole and exchange intereaction also leads to a decrease in stability, but when hydrogen is present at N_1 or N_2 these unshared pairs are mutually perpendicular and the intereaction is reduced.

The calculated H^{OPG} values make it possible to estimate the probability of the existence of various tautomers:

$$[X]=\exp[-H_x^{OPG}/RT]/\sum_{i=1}^{5}\exp[-H_i^{OPG}/RT];$$

$$IIA : IIA' : IIS : IIC : IID \sim 1 : 1 : 8\cdot10^{-8} : 3\cdot10^{-8} : 8\cdot10^{-10};$$

$$IIIA : IIIS : IIIC : IIID : IIIE \sim 1 : 2\cdot10^{-6} : 4\cdot10^{-8} : 8\cdot10^{-8} : 1\cdot10^{-8}.$$

The known value of the dipole moment for 3-amino-1,2,4-triazole II is 3.38 D [4]. Since the probability of the existence of the most favorable tautomers IIA and IIA' is practically the same, it follows from the calculation that

$$\mu_{II}=\sqrt{\frac{\mu_{IIA}{}^2+\mu_{IIA'}{}^2}{2}}=3{,}12D.$$

This is in satisfactory agreement with the experimental data. If the other tautomeric forms were realizable, the dipole moment would be larger than the observed value. Unfortunately, because of the low solubility of triazole II in nonpolar solvents, its dipole moment could not be determined.

In conclusion, let us compare the calculated and experimental heats of formation of I and II. The heats of formation for I (62.1 kcal/mole) and II (39.4 kcal/mole) were calculated from data for the heats of combustion of I and II (336.9 and 343.1 kcal/mole, respectively) by means of the Hess principle. The calculation gave higher values −79.1 kcal/mole for IA and 57.4 kcal/mole for IIA. The reason for the deviation between the calculated and experimental values is possibly associated with certain inadequacies in the MINDO/2 method, which include, in addition to the poor description of the bonds between the heteroatoms, overestimation of the strain energy in the cyclic systems (thus H_{exp} in cyclobutane is +6.4 kcal/mole and H_{calc} is +18.7 kcal/mole [17]). However, we emphasize that the indicated inadequacies should not affect the calculation for the establishment of the relative stabilities of the tautomeric forms. One should also bear in mind that partial formation of nitrogen oxides is possible during combustion; this was not taken into account in the calculation of the heats of formation.

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