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QUANTUM CHEMICAL STUDY OF THE TAUTOMERISM, GEOMETRY, AND ELECTRONIC STRUCTURE OF 1,2,3- AND 1,2,4-TRIAZOLES

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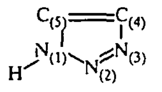
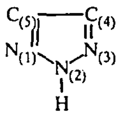
A systematic study was carried out on the tautomerism and geometry of 1,2,3- and 1,2,4-triazoles using the semiempirical AM1, PM3, MNDO, and MINDO/3 methods and nonempirical quantum chemical methods taking account of electronic correlation (MP2). The semiempirical methods were found to give incorrect results for the tautomerism of these triazoles, while the nonempirical methods correctly give the energy relationships and show enhanced stability for 2H-1,2,3- and 1H-1,2,4-triazoles attributed to the interaction of the unpaired electron pairs of the adjacent nitrogen atoms. Optimization of the geometry of 2H-1,2,3-triazole by the nonempirical methods showed that bases such as 6-21G and more expanded bases must be used and that electronic correlation should be taken into account. The use of updated calculation methods in the case of 1H-1,2,4-triazole did not give improved results.

Five-membered nitrogen heterocycles are structural fragments of a series of biologically active compounds [1], pesticides [2], corrosion inhibitors, pigments, and other industrial chemicals [3, 4]. The tautomerism of these compounds has been studied using ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy [5-7], vibrational and electronic spectroscopy [8], semiempirical quantum chemical methods [9, 10], and nonempirical quantum chemical methods [11-14]. Significant discrepancies exist between the results obtained [15, 16].

The tautomerism of 1,2,3-triazole (1,2,3-T) has been characterized as "the most confused case of ring tautomerism" [17]. This compound may exist in the 1H tautomeric form with C_s symmetry (Ia, 1H-1,2,3-T) or in the 2H-form with C_{2v} symmetry (Ib, 2H-1,2,3-T).



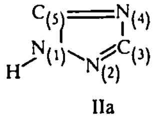
Ia



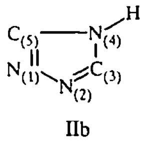
Ib

IR and microwave spectroscopy showed that 1,2,3-T exists in the gas phase as tautomer Ia [18, 19], while the photoelectronic spectra indicate only the 2H tautomer (Ib) [12]. The simultaneous presence of both tautomeric forms has been established for solutions. PMR spectroscopy has shown that form Ia exists at 175°K, while the fraction of tautomer Ib increases both with decreasing dipole moment of the solvent or concentration and increasing temperature. The Ia:Ib concentration ratio in methanol is $1:10^3$ [21], while it is 1:2 in aqueous solution [22]. The dipole moment of 1,2,3-T in benzene (1.85 D at 25°C and 2.08 D at 45°C [23]) suggests that the content of form Ib is 83%.

Two tautomers are possible for 1,2,4-triazole (1,2,4-T): the 1H-form with C_s symmetry (IIa) and 4H form with C_{2v} symmetry (IIb).



IIa



IIb

Prof. Asen Zlatarov University, 8010 Burgas, Bulgaria. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 645-651, May, 1998. Original article submitted October 13, 1997.

TABLE 1. Heats of Formation ΔH_f (kcal/mole) of Tautomers 1,2,3- and 1,2,4-T from Semiempirical Quantum Chemical Calculations

Method	1,2,3-T			1,2,4-T		
	1H	2H	$\Delta E_{(1H-2H)}$	1H	2H	$\Delta E_{(1H-4H)}$
AM1	86,4	92,4	-6,0	77,0	72,9	4,1
PM3	67,6	70,7	-3,1	51,8	51,8	0,0
MNDO	49,9	56,2	-6,3	43,7	40,1	3,6
MINDO/3	1,9	12,9	-11,0	17,8	9,2	8,6

TABLE 2. Energies of Tautomeric Forms of 1,2,3-T and 1,2,4-T (a. u.) Obtained by Nonempirical Methods

Base	1,2,3-T			1,2,4-T		
	1H-(Ia)	2H-(Ib)	$\Delta E_{(1H-2H)}$	1H-(IIa)	4H- (IIb)	$\Delta E_{(1H-4H)}$
3-21G	-239,393	-239,399	0,006	-239,428	-239,422	-0,006
4-31G	-240,203	-240,388	0,185	-240,414	-240,406	-0,008
6-21G	-240,435	-240,440	0,005	-240,469	-240,463	-0,006
6-31G	-240,639	-240,645	0,006	-240,670	-240,661	-0,009

Data have been published from two x-ray diffraction structural studies of 1,2,4-T [24, 25]. Denschl [24] carried out the study at room temperature but the hydrogen atom coordinates were not determined, such that discussion of the tautomerism is impossible. Goldstein et al. [25] found that tautomer IIa exists in the solid state as indicated by good accord between the calculated dipole moment (2.67 D) and the value found for the gas phase (2.72 D) [26]. About 20% tautomer IIb was found in dioxane [27]. The content of this tautomer was estimated at 5% by Wofford et al. [28], while this form was not detected in solutions in dimethylsulfoxide, acetone, and methanol in a ^{15}N NMR spectral study [7].

Microwave [26, 29] and photoelectronic spectral studies [12] showed that 1,2,4-T exists in the gas phase as IIa, while the content of tautomer IIb in tetrahydrofuran at −70°C is less than 1% [23]. Stabilization of the asymmetric form of 1,2,4-T is also indicated by the finding that the hydrogen atom at $N_{(1)}$ or $N_{(2)}$ is replaced upon alkylation, acetylation, and phosphorylation, while the hydrogen atom at $N_{(4)}$ is almost never replaced [30-32].

In the case of 1,2,3-T, the relative stabilities of the tautomers calculated by various semiempirical methods are in qualitative accord. The results given in Table 1 show high stability for 1H-1,2,3-T, which contradicts the experimental data. In the nonempirical calculations, the energy for 2H-1,2,3-T is always less, independently of the basis used. The tautomer concentration ratio in the equilibrium mixture may be determined using the following equation: $\Delta H = -RT\ln K$. Estimates show that the 1H form is virtually absent ($[2H]/[1H] = 3.5\cdot10^2$-$8.5\cdot10^2$).

The PM3 method in the case of 1,2,4-T predicts high stability for the 1H form, while the other semiempirical methods predict high stability for the 4H form. All the nonempirical calculations give a lower energy for 1H-1,2,4-T and the [1H]/[4H] concentration ratio falls in the range $5\cdot10^2$-$8\cdot10^3$.

The high stability of tautomers 2H-1,2,3-T and 1H-1,2,4-T may be attributed to the reduced repulsion of the unshared electron pairs of the nitrogen atoms in these species in comparison with 1H-1,2,3-T and 4H-1,2,4-T. This is seen in the electrostatic potential distribution shown in Fig. 1.

The results for optimization of the geometry of the stable tautomers for 1,2,3-T and 1,2,4-T obtained by semiempirical methods are given in Tables 3 and 4, while these data obtained by nonempirical methods are given in Tables 5 and 6.

The major conclusions may be given as follows:

1. Both molecules are planar.

2. The PM3 method best reproduces the bond lengths among the semiempirical approximations for 2H-1,2,3-T. Discrepancies of up to 0.05 Å are obtained by the other methods studied. However, the PM3 method gives a relatively high error for the $N_{(1)}-N_{(2)}-N_{(3)}$ bond angle.

The use of small bases up to 6-21G in the nonempirical calculations leads to overestimation of the N−N bond length. In these cases, $r_{N-N} > r_{C=N}$, which is not in accord with the experimental data. The C=N double bond in many bases is

TABLE 3. Geometrical Parameters of 2H-1,2,3-T Optimized by Semiempirical Methods

Method	Bond lengths (Å)							Bond angles (deg)					
	$N_{(1)}—N_{(2)}$	$N_{(3)}—N_{(2)}$	$C_{(4)}—N_{(3)}$	$C_{(5)}—C_{(4)}$	$H_{(6)}—C_{(5)}$	$H_{(7)}—N_{(2)}$	$H_{(8)}—C_{(4)}$	$N_{(1)}—N_{(2)}—N_{(3)}$	$C_{(4)}—N_{(3)}—N_{(2)}$	$C_{(5)}—C_{(4)}—N_{(3)}$	$H_{(6)}—C_{(5)}—C_{(4)}$	$H_{(7)}—N_{(2)}—N_{(3)}$	$H_{(8)}—C_{(4)}—N_{(3)}$
AM1	1,338	1,338	1,358	1,459	1,088	1,000	1,088	115,6	105,0	107,2	128,7	122,2	124,0
PM3	1,339	1,339	1,364	1,414	1,089	0,987	1,089	111,8	107,0	107,1	130,4	124,1	122,5
MNDO	1,330	1,330	1,355	1,443	1,081	1,013	1,081	115,6	104,9	107,3	129,4	122,2	123,2
MINDO/3	1,279	1,279	1,350	1,413	1,103	1,041	1,103	119,4	103,2	107,1	130,5	120,3	122,4

TABLE 4. Geometrical Parameters of 2H-1,2,4-T Optimized by Semiempirical Methods

Method	Bond lengths (Å)							Bond lengths (Å)					
	$N_{(1)}—N_{(2)}$	$N_{(2)}—C_{(3)}$	$C_{(3)}—N_{(4)}$	$N_{(4)}—C_{(5)}$	$H_{(6)}—C_{(5)}$	$H_{(7)}—N_{(1)}$	$H_{(8)}—C_{(3)}$	$C_{(3)}—N_{(2)}—N_{(1)}$	$N_{(4)}—C_{(3)}—N_{(2)}$	$C_{(5)}—N_{(4)}—C_{(3)}$	$H_{(6)}—C_{(5)}—N_{(4)}$	$H_{(7)}—N_{(1)}—N_{(2)}$	$H_{(8)}—C_{(3)}—N_{(2)}$
AM1	1,335	1,365	1,407	1,351	1,095	0,992	1,094	104,6	112,7	103,5	127,2	121,0	124,4
PM3	1,360	1,351	1,387	1,353	1,093	0,987	1,092	106,6	108,8	108,4	125,7	120,4	125,8
MNDO	1,335	1,353	1,395	1,342	1,084	1,003	1,085	104,5	112,2	104,7	127,6	120,8	124,8
MINDO/3	1,304	1,334	1,368	1,334	1,003	1,033	1,112	102,4	113,1	104,2	127,6	120,5	123,4

TABLE 5. Geometrical Parameters of 2H-1,2,3-T Optimized by Nonempirical Methods

Base	Bond lengths (Å)				Bond lengths (Å)		
	$N_{(1)}$—$N_{(2)}$	$N_{(3)}$—$C_{(4)}$	$C_{(4)}$—$C_{(5)}$	H—$N_{(2)}$	$C_{(5)}$—$N_{(1)}$—$N_{(2)}$	$N_{(1)}$—$N_{(2)}$—$N_{(3)}$	H—$N_{(2)}$—$N_{(3)}$
3-21G	1,354	1,314	1,415	0,992	104,1	113,8	123,1
4-31G	1,328	1,314	1,409	0,986	104,6	114,4	122,8
6-21G	1,355	1,317	1,415	0,992	104,0	114,0	123,0
6-31G(d)	1,327	1,318	1,411	0,987	104,5	114,6	122,7
6-31 + G(d)	1,303	1,309	1,405	0,994	104,0	116,1	122,0
6-31 + G(d,p)	1,303	1,309	1,405	0,993	104,1	116,0	122,0
6-31 ++ G(d)	1,303	1,309	1,405	0,994	104,0	116,1	122,0
6-31 ++G(d,p)	1,303	1,309	1,405	0,993	104,1	116,0	122,0
6-311	1,326	1,319	1,408	0,984	104,4	114,8	122,6
6-311 + G(d)	1,301	1,306	1,405	0,990	104,1	116,0	122,0
6-311 + G(d,p)	1,301	1,306	1,405	0,993	104,2	116,0	122,0
6-311 ++ G(d)	1,301	1,306	1,405	0,990	104,1	116,0	122,0
6-311 ++ G(d,p)	1,301	1,306	1,405	0,993	104,2	116,0	122,0
MP2/6-31G(d) [13]	1,332	1,351	1,394	1,014	102,0	117,7	121,1
Experimental [13]	1,323	1,346	1,405	1,017		117,1	

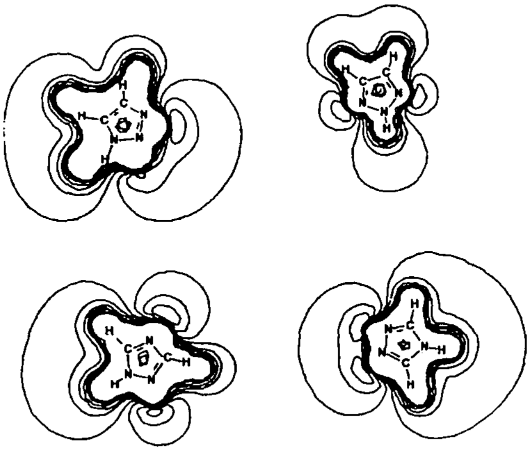


Fig. 1. Distribution of electrostatic potential in the ring plane for tautomeric forms of 1,2,3-T and 1,2,4-T found in an AM1 calculation.

much shorter than the experimental value (by up to 0.05 Å). These inadequacies are eliminated if electronic correlation is taken into account.

3. A tendency of these methods to overestimate the C=N bond length by up to 0.05-0.07 Å and underestimate the N−N bond length by up to 0.02-0.05 Å is seen for 1H-1,2,4-T by comparison of the results of the semiempirical calculations with the microwave spectroscopy data [29]. In the nonempirical calculations with basis 6-31 + G(d) and less extensive bases, the $C_{(2)}=N_{(3)}$ bond is underestimated by up to 0.04 Å and the C−N and N−N bond lengths are overestimated. Using more extensive bases, the results for the single bonds are slightly improved but the C=N is still underestimated. Taking account of electronic correlation does not give a significant improvement. Kassimi et al. [14] argued that the accuracy of the parameters determined by Bolton et al. [29] is unsatisfactory. Thus, neutron diffraction [37] and x-ray diffraction data [25] are also given in Table 6. In this case, the calculation results are closer to the experimental data.

The discrepancies between the theoretical and experimental bond angles are 1-3° for the semiempirical methods, 1° for the nonempirical methods, and 1-2° for the MP2 method. The greatest errors up to 4° are found for the $C_{(3)}-N_{(4)}-C_{(5)}$ bond angle and the angles between the bonds involving hydrogen atoms without regard to the calculation method employed.

TABLE 6. Geometrical Parameters of 1H-1,2,4-T Optimized by Nonempirical Methods

Base	Bond lengths (Å)						Bond angles (deg)					
	$N_{(1)}—N_{(2)}$	$N_{(2)}—C_{(3)}$	$C_{(3)}—N_{(4)}$	$N_{(4)}—C_{(5)}$	$C_{(5)}—N_{(1)}$	$H—N_{(1)}$	$C_{(5)}—N_{(1)}—N_{(2)}$	$N_{(1)}—N_{(2)}—C_{(3)}$	$N_{(2)}—C_{(3)}—N_{(4)}$	$C_{(3)}—N_{(4)}—C_{(5)}$	$N_{(4)}—C_{(5)}—N_{(1)}$	$H—N_{(1)}—N_{(2)}$
3-21G	1,395	1,305	1,379	1,308	1,348	0,993	109,2	102,6	114,1	104,2	110,0	120,0
4-31G	1,367	1,303	1,370	1,308	1,341	0,987	109,6	103,1	113,5	104,2	109,5	120,3
6-21G	1,396	1,307	1,380	1,310	1,348	0,993	109,3	102,4	114,2	104,1	110,0	110,0
6-31G	1,363	1,307	1,371	1,311	1,343	0,988	109,8	103,2	113,5	104,2	109,4	120,4
6-31 + G(d)	1,340	1,295	1,355	1,299	1,330	0,994	109,9	102,5	114,9	102,6	110,2	120,5
6-31 + G(d,p)	1,340	1,295	1,355	1,299	1,330	0,993	109,8	102,6	114,8	102,7	110,2	120,7
6-31 ++ G(d)	1,340	1,295	1,355	1,299	1,330	0,994	109,9	102,5	114,8	102,7	110,2	120,7
6-31 ++ G(d,p)	1,340	1,295	1,355	1,299	1,330	0,993	109,8	102,6	114,8	102,7	110,2	120,7
6-311	1,361	1,307	1,370	1,310	1,341	0,985	109,8	103,1	113,6	104,0	109,4	120,2
6-311 + G(d)	1,340	1,292	1,355	1,296	1,329	0,990	109,7	102,6	114,8	102,6	110,3	120,7
6-311 + G(d,p)	1,339	1,292	1,356	1,296	1,330	0,992	109,7	102,6	114,7	102,7	110,2	120,8
6-311 ++ G(d)	1,340	1,292	1,355	1,296	1,329	0,990	109,7	102,6	114,8	102,6	110,2	120,7
6-311 ++ G(d,p)	1,339	1,292	1,356	1,296	1,330	0,992	109,7	102,6	114,7	102,7	110,2	120,8
MP2/6-31G(d) [14]	1,351	1,338	1,361	1,328	1,353	1,013	111,0	101,2	115,5	102,6	109,6	119,4
MP2/6-311 + G(d,p) [14]	1,344	1,337	1,360	1,326	1,354	1,009	111,0	101,4	115,5	102,5	109,6	119,5
Experimental· [29]	1,381	1,328	1,354	1,280	1,375	0,998	108,5	102,7	113,0	106,8	109,0	127,5
[36]	1,363			1,338								
[25]	1,359	1,323	1,359	1,324		1,03		101,8	114,5	104,1		124,0

Thus, our calculations show that use of updated quantum chemical methods for 1H-1,2,4-T leads to only a slight improvement in the results but requires much more machine time. Taking account of electronic correlation does not guarantee the usual accuracy of about 1% [8, 38].

EXPERIMENTAL

The semiempirical PM3, AM1, MNDO, and MINDO/3 methods were carried out using the MOPAC 6.0 program package [33], while the nonempirical methods were carried out using the GAUSSIAN-92 program [34]. The dependence of the results on the atomic orbital basis was studied by using valence split (3-21G−6-21G), polarized (6-31G(d)), and diffuse bases (6-31+G(d)−6-311++G(d)), and the effect of electronic correlation was taken into account using perturbation theory in MP2 [35].

In order to obtain information on the relative stability of the tautomeric forms of 1,2,3- and 1,2,4-T, we carried out total optimization using semiempirical and nonempirical methods. The total energies E_0 (a. u.) and heats of formation ΔH_f (kcal/mole) are given in Tables 1 and 2.

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