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AB INITIO CALCULATION OF THE STRUCTURE OF 5-CHLORO-1,2,4-TRIAZOLE

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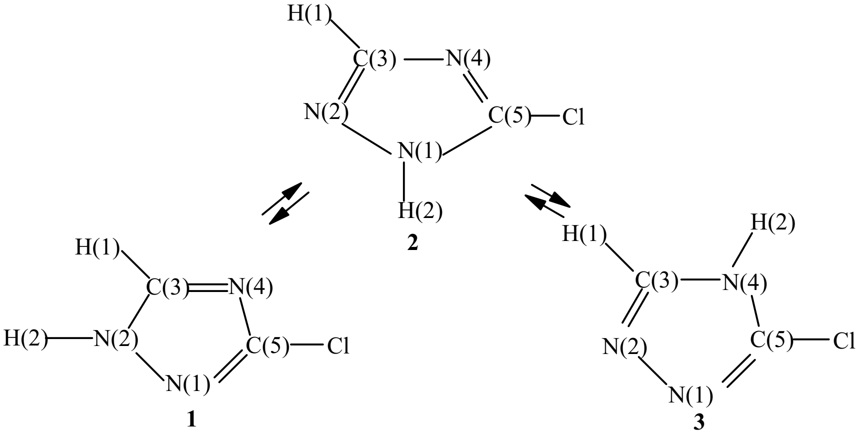
Three tautomeric forms of 5-chloro-1,2,4-triazole were calculated using the Hartree–Fock (ab initio) and Meller–Plesset methods in the 6-31G(d) basis. The ^{35}Cl NQR parameters were calculated using the occupancies of the 3p-components of the valence p-orbitals of the chlorine atom. The structure of this triazole was derived from the data obtained.

Keywords: 5-chloro-1,2,4-triazole, *ab initio* calculations, ^{35}Cl NQR.

The prospective practical use of *exo*-halo derivatives of 1,2,4-triazole and the special features of the electronic structure of these compounds have stimulated their multifaceted study [1-6]. Three tautomeric forms, analogs of **1**, **2**, and **3**, may exist for 3-substituted 5-chloro-1,2,4-triazoles in solution.



The dipole moment data indicated that 3-nitro-1,2,4-triazole and its derivatives in dioxane are similar to **1** [3]. PMR spectra [4] and X-ray diffraction structural analysis showed that structure **3** does not exist at low temperatures in the case of 1,2,4-triazole. These data along with the ^{35}Cl NQR spectra of 3-substituted 5-chloro-1,2,4-triazole suggested that tautomer **2** is energetically most favorable for 1,2,4-triazole and its 5-chloro-3-substituted derivatives [2].

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The three tautomeric forms of 5-chloro-1,2,4-triazole were subjected to *ab initio* calculations in a further study of the electronic and three-dimensional structure of these compounds. The calculations were carried out using the Hartree-Fock (HF) and Meller–Plesset (MP2) methods in the 6-31G(d) basis with total optimization of the molecular geometry using the Gaussian 94W program [7]. The origin of the coordinate system in all cases was taken as the site of the chlorine nucleus such that the ^{35}Cl NQR frequencies (ν) of these forms could be calculated using the occupancies (*Np*) of the 3*p*-components of the chlorine valence *p*-orbitals and these frequencies could be compared to the experimental values obtained in our previous work [2]. The *Z*-axis of this coordinate system is in the direction of the Cl–C(5) bond, the *X*-axis lies in the plane of the 1,2,4-triazole ring, while the *Y*-axis is perpendicular the *X*- and *Z*-axes.

The value of $e^2Qq_{\text{at}}/2h$ in calculation the NQR frequencies was taken equal to 93.093 or 91.626 MHz when using the results of the HF/6-31G(d) or MP2/6-31G(d) calculations, respectively [8, 9]. These values were found in calculations of the Cl_2 molecule by the two indicated methods:

$$\nu = (e^2Qq_{\text{at}}/2h)[(Np_x + Np_y)/2 - Np_z](1 + \eta^2/3)^{1/2} \qquad (1)$$

The HF/6-31G(d) results for the geometry optimization of each of these tautomers are given in Table 1. All the dihedral angles in forms **1-3** are equal to 0.0°±0.01° or 180.0°±0.1°, i.e., all the atoms, including the sp^3-hybridized nitrogen atom, lie in a single plane. The total energies of these tautomers are similar. Form **1** is more stable than **2** by about 0.5 kcal/mole, while **3** is less stable than **2** by ~7.4 kcal/mole.

We have already shown that the ^{35}Cl NQR frequencies (ν_{cal}) and electric field gradient asymmetry parameters on the ^{35}Cl nuclei (η_{cal}) calculated using the occupancies of the 3*p*-components of the valence *p*-orbitals of the chlorine atoms obtained by the HF/6-31G(d) method for organic and elementorganic molecules are in satisfactory accord with the experimental values for ν_{exp} and η_{exp}. Satisfactory linear correlations are observed between the calculated and experimental values of ν and η [8, 9]. In accord with recent data, the correlation equation for NQR frequencies has the form

$$\nu_{\text{cal}} = 1.006(\pm0.035)\nu_{\text{exp}} - 0.300(\pm1.120),\ r = 0.996,\ n = 28 \qquad (2)$$

TABLE 1. Bond Lengths (*d*) and Angles (α) in Tautomers **1-3** Calculated by the HF/6-31G(d) and MP2/6-31G(d) Methods

Bond	*d*, Å					
	1		**2**		**3**	
	HF	MP2	HF	MP2	HF	MP2
Cl–C(5)	1.709	1.708	1.704	1.705	1.704	1.704
N(4)–C(5)	1.347	1.356	1.289	1.322	1.352	1.363
C(3)–N(4)	1.299	1.330	1.358	1.363	1.358	1.366
N(2)–C(3)	1.327	1.352	1.292	1.340	1.280	1.323
N(1)–N(2)	1.342	1.353	1.343	1.353	1.367	1.388
N(1)–C(5)	1.290	1.340	1.327	1.353	—	1.319
Angle*	α, deg.					
N(1)N(2)C(3)	110.0	111.2	102.4	101.3	107.8	107.5
N(2)C(3)N(4)	110.3	109.7	115.1	115.8	110.4	110.4
C(3)N(4)C(5)	102.1	102.1	102.0	101.9	103.5	104.4
N(4)C(5)N(1)	115.9	116.4	111.3	110.6	—	111.4
N(4)C(5)Cl	122.1	122.6	126.5	127.0	122.1	122.3

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* In **1** ∠H(2)N(2)C(4) = 129.8°, ∠H(1)C(3)N(4) = 126.1°, in **2** ∠H(2)N(1)N(2) = 121.5°, ∠H(1)C(3)N(4) = 122.6°, in **3** ∠H(1)C(3)N(4) = = 123.6°, ∠H(2)N(4)C(3) = 129.0°.

The occupancies of the valence *p*-orbitals and their 3*p*- and 4*p*-components found for the chlorine atoms in tautomers **1-3** by the HF/6-31G(d) method are given in Table 2. The ^{35}Cl NQR frequencies calculated using the occupancies of the 3*p*-components (Table 3) are close to the experimental values, especially for forms **2** and **3**. The experimental ^{35}Cl NQR spectrum of 5-chloro-1,2,4-triazole at 77°K consists of lines at ν^{77} = 37.007 and 37.111 MHz with intensity ratio 1:5 [2].

This spectrum presumably corresponds either to crystallographically nonequivalent molecules in the crystal unit cell or two tautomers present in 1:5 ratio. The difference between the NQR frequencies of forms **2** and **3** ($\Delta\nu_{\text{cal}}$ = 0.103 MHz) is virtually equal to the line splitting in the experimental spectrum ($\Delta\nu_{\text{exp}}$ = 0.104 MHz). The NQR frequency calculated for tautomer **1** (Table 3) is much lower than the experimental values although the difference between them is in the standard error range due to approximation by correlation equation (2) and the contribution of the crystal effect to the ^{35}Cl NQR frequency. Thus, comparison of the NQR frequencies evaluated using the occupancies of the 3*p*-components of the valence *p*-orbitals of the chlorine atoms in forms **1-3** with the experimental values found for 5-chloro-1,2,4-triazole does not provide an unequivocal conclusion concerning the structure of this compound. However, in light of the calculated total energies of tautomers **1-3** and ^{35}Cl NQR frequencies for these forms, we may confidently conclude that form **2** is characteristic for 5-chloro-1,2,4-triazole.

For a further investigation of the structure of this compound, we carried out *ab initio* calculations taking account of electron correlation using the MP2/6-31G(d) method with complete geometry optimization of tautomers **1-3**. The optimized geometrical parameters found by this method and by the HF/6-31G(d) method differ only slightly (Table 1). All the dihedral angles obtained by optimization using the MP2/6-31G(d) method

TABLE 2. Occupancies of the Valence *p*-Orbitals (ΣNp) and Their 3*p*- and 4*p*-Components in the Chlorine Atoms of Tautomers **1-3** Calculated by the HF/6-31G(d) and MP2/6-31-G(d) Methods

Form	Contri-bution	HF			MP2		
		Np_x	Np_y	Np_z	Np_x	Np_y	Np_z
1	$N3p$	1.333	1.310	0.930	1.333	1.311	0.927
	$N4p$	0.622	0.640	0.160	0.622	0.638	0.160
	ΣNp	1.955	1.950	1.090	1.955	1.949	1.087
2	$N3p$	1.331	1.315	0.924	1.332	1.316	0.919
	$N4p$	0.619	0.631	0.150	0.617	0.629	0.149
	ΣNp	1.950	1.946	1.074	1.949	1.945	1.068
3	$N3p$	1.329	1.317	0.923	1.329	1.318	0.820
	$N4p$	0.620	0.634	0.153	0.619	0.632	0.153
	ΣNp	1.949	1.951	1.076	1.948	1.950	1.073

TABLE 3. ^{35}Cl NQR Frequencies (ν_{cal}, MHz) and Asymmetry Parameters (η_{cal}, %) of the Electric Field Gradient for ^{35}Cl Nuclei Calculated Using the Occupancies of the 3*p*-Components of the Chlorine *p*-Orbitals

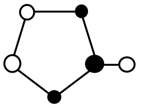
Form	HF		MP2	
	$\nu^{\text{в}}$	$\eta^{\text{в}}$	$\nu^{\text{в}}$	$\eta^{\text{в}}$
1	36.497	8.44	36.238	8.59
2	37.097	6.08	37.072	5.90
3	37.211	4.40	37.005	4.23

are equal to 0.0°±0.04° or 180.0°±0.02°. The total energies of forms **1**, **2**, and **3** lie in the same order as in the HF/6-31G(d) approximation. However, the total energy of tautomer **1** calculated by the MP2/6-31G(d) method differs even less from that for form **2** (by ~0.4 kcal/mole), while the difference between the total energies of systems **2** and **3** is ~7.5 kcal/mole.

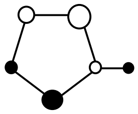
The ^{35}Cl NQR frequency of tautomer **1** found using the occupancies of the 3*p*-components of the valence *p*-orbitals of the chlorine atom obtained by the MP2/6-31G(d) method (Table 2), as in the HF/6-31G(d) approximation, is considerably lower than the experimental value. Analogously, calculated NQR frequencies of systems **2** and **3** are similar to the experimental values. However, the ratio of the NQR frequencies found for these two tautomers in the framework of the MP2/6-31G(d) method is opposite to the ratio found in the HF/6-31G(d) calculation (Table 3). The calculated ^{35}Cl NQR frequency for form **3** coincides with the less intense line in the spectrum of 5-chloro-1,2,4-triazole, while the calculated frequency for tautomer **2** is close to the frequency of the more intense line. These MP2/6-31G(d) results suggest that the experimental ^{35}Cl NQR spectrum of 5-chloro-1,2,4-triazole at 77°K corresponds to a 5:1 mixture of isomers **2** and **3**.

The predominance of energetically favored form **2** may be explained. However, the following questions remain unanswered. 1. Why doesn't the even more stable tautomer **1** appear in the ^{35}Cl NQR spectrum of the polycrystalline sample at 77°K? 2. If the ^{35}Cl NQR spectrum at 77°K indicates the presence of some amount of the energetically less favorable form **3**, why is this form not detected in the X-ray crystallographic structural analysis? This may occur because one of structures **1-3** may predominate at given temperatures. A check this proposal required a study of the temperature dependence of the NQR frequencies of this compound.

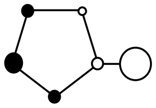
Table 4 gives the occupancies of the p_y-orbitals and their 2*p*- and 3*p*-components of the carbon and nitrogen atoms of the 1,2,4-triazole ring obtained in an MP2/6-31G(d) calculation of isomer **2**, which show that these occupancies differ only slightly from the values obtained in the HF/6-31G(d) calculation. Judging from the occupancies, the p_y-orbitals of the chlorine atom, N(1), C(3), and C(5) are electron-deficient (Table 4). The electrons in these orbitals are transferred to the p_y-orbitals of N(2) and N(4) and to other atomic orbitals. As a result of this transfer, the excess of p_y-electrons on N(2) and N(4) (~0.5 e) is significantly less than the electron deficiency on the other ring atoms and the chlorine atom (~0.6 e). The π-bonding MO with *E* = 18.0 eV is found in the π-system of tautomer **2**, while the p_y-orbitals of the chlorine atom and 1,2,4-triazole ring form three MO with *E* = 14.2, 11.8, and 10.1 eV. The latter MO is the HOMO. These MO may be clearly represented as follows:



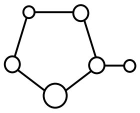
10.1 eV



11.8 eV



14.2 eV



18.0 eV

TABLE 4. Occupancies of the p_y-Orbitals and Their 2*p*- and 3*p*-Components for the Carbon and Nitrogen Atoms in the 1,2,4-Triazole Ring in Form **2** Calculated by the MP2/6-31G(d) Method

Contribution	N(1)	N(2)	C(3)	N(4)	C(5)
$N2p$	0.918	0.702	0.520	0.685	0.563
$N3p$	0.680	0.552	0.395	0.565	0.367
$\sum Np$	1.598	1.254	0.915	1.250	0.930

We note that the p_y-AO participate somewhat in the formation of other MO. The energies (eV) of the highest occupied MO in structure **2** calculated by the MP2/6-31G(d) method are as follows: -20.5, -18.0, -17.5, -16.5, -14.2, -13.4, -12.7, -11.8, and -10.1 eV.

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