

Ab initio and DFT studies on nitrosoguanidine tautomers

Lemi Türker*

Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey

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Abstract

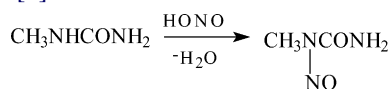
Isolated nitrosoguanidine tautomers have been subjected to 6-31G(d,p), 6-31G(d,p)/(MP2), B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) type quantum chemical analyses in the gas phase. The geometrical features and energetics of some conformers of the tautomers are reported. The nitrosimine form has the highest stability than the others and the diazoic acid form is the least stable one. The nitrosoimine form has the highest HOMO and LUMO energies. Whereas, the nitrosamine form possesses the lowest HOMO and the diazoic acid form has the lowest LUMO energies.

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Keywords: Nitrosoguanidine; Explosive; Nitroso compound; Tautomerism; Ab initio calculation; DFT calculation

1. Introduction

Secondary amines react with nitrous acid to yield nitroso derivatives. Secondary amides likewise yield nitroso derivatives, called nitrosamides (or nitroso amides). Nitrosomethylurea which is used in the preparation of diazomethane is such a nitrosamide. The nitrosation of *N*-methylurea or alkyldiazines is especially interesting since it illustrates the rule that the attack of nitrous acid occurs preferentially at the more basic of the two amino groups [1]:



Guanidine (**1**) which is the imine of urea also possesses nitroso derivative (**2**) conforming to the above rule. Nitrosoguanidine prepared by the reduction of nitroguanidine has been known for a long time [3,4]. It is an initiating explosive and has severe explosion risk [2,5]. Also nitrosoguanidine is an interesting ligand. Its Ni(II) complex is to be mentioned because of its extreme stability [6]. Nitrosoguanidine is an ampholyte and may exist in several neutral and ionic forms in solution [7]. Note that the tautomeric equilibria of guanidine yield the same structure.



However, in the case of its nitroso derivative, proton tautomerism yields different structures (see Scheme 1).

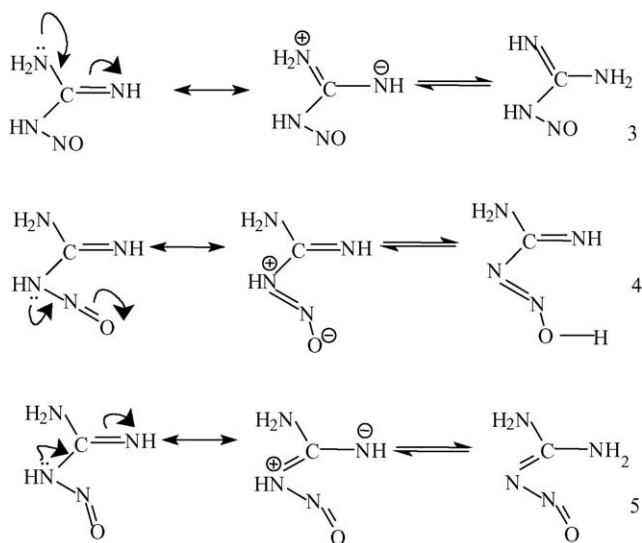
In the literature, of the various nitrosoguanidine derivatives only a few of them were subjected to some theoretical analysis. One of them is *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (MNNG) which is a tumor initiator in rats [8]. Molecular orbital studies at the level of INDO theory were reported on *N*-alkyl-*N'*-nitro-*N*-nitrosoguanidine [9]. *N*-Methyl-*N'*-nitro-*N*-nitrosoguanidine was the subject of MNDO and ab initio calculations [10,11]. In a recent study, Murmann et al., determined the X-ray structure of nitrosoguanidine and performed some ab initio calculations for the gaseous state of the most stable configurations of it [7].

In the present study, various nitrosoguanidine tautomers and some of their energetically favorable conformers have been subjected to ab initio and DFT type calculations.

2. Method

After the initial geometry optimizations of all the structures (MM+ method), conformational analyses were carried out (PM3 self consistent method [12–14]). Then various quantum chemical methods (ab initio and DFT [15,16]) at the restricted level (6-31G(d,p), B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p))

* Tel.: +90 312 2103244; fax: +90 312 2101280.
E-mail address: lturker@metu.edu.tr.



Scheme 1.

were used for the geometry optimizations of the energetically favorable structures obtained by prior conformational analyses. Also, single point MP2 calculations were performed on the geometry optimized structures (at the level of 6-31G(d,p)). All the optimized structures were subjected to vibrational analysis, using the same level of calculations as used in the geometry optimization of them, in order to judge their stabilities. Furthermore, all the bond lengths were thoroughly searched. All these computations were performed by using the Hyperchem (release 7.5) package program.

3. Results and discussion

Nitrosoguanidine like nitroguanidine is an explosive material [17]. It is isoconjugate with an even alternant hydrocarbon (6) which possesses four starred and two unstarred positions, thus a non-Kekule' type alternant conjugate system [18]. Hence, certain instability is expected even merely based on structural analysis [18]. However, nitrosoguanidine has a

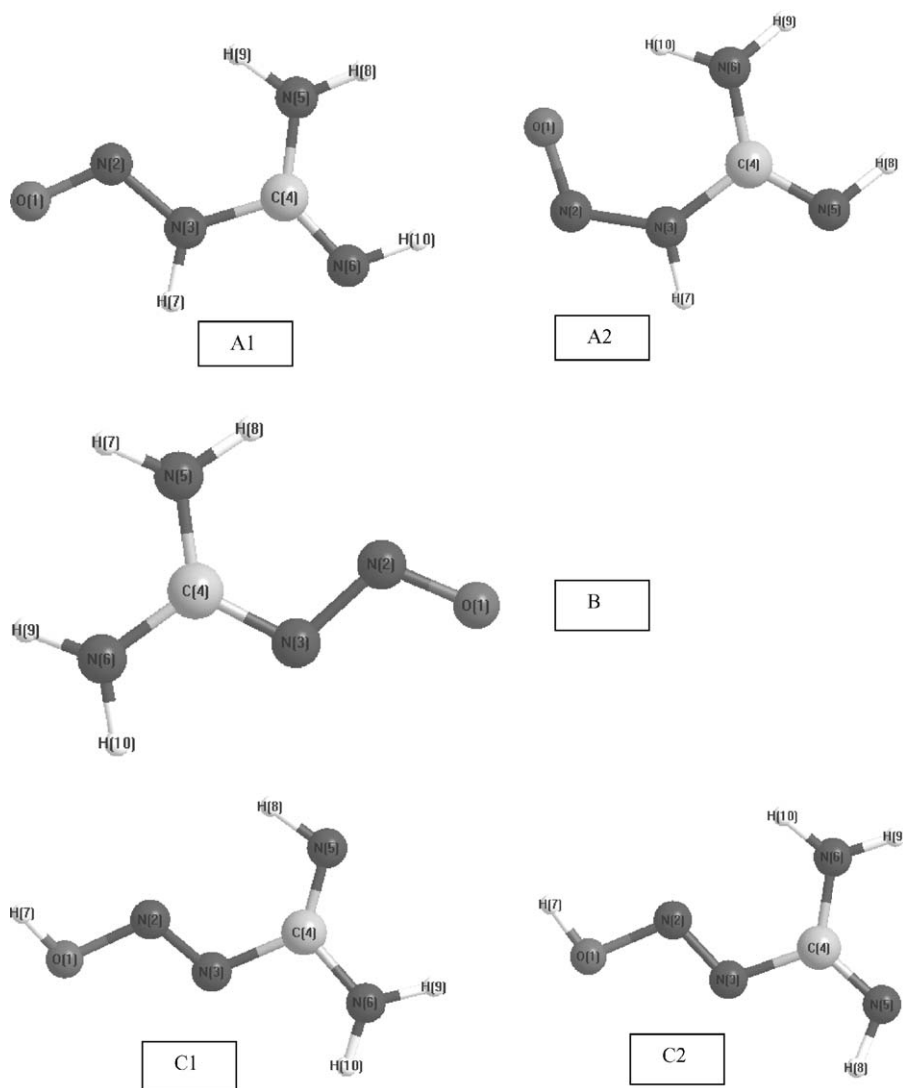
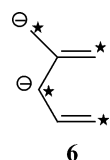


Fig. 1. The geometry optimized (B3LYP/6-311++G(d,p)) structures of the present concern.

Table 1
Some calculated (6-31G(d,p), B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p)) and experimental [7] bond lengths of the structures (bond lengths in 10^{-10} m, see also Fig. 1 for kind and numbering of the atoms)

Bond		6-31G(d,p)				
		A ₁	A ₂	B	C ₁	C ₂
R(3, 4)	C3–N4	1.397	1.397	1.302	1.441	1.436
R(4, 5)	C4–N5	1.363	1.363	1.350	1.250	1.250
R(4, 6)	C4–N6	1.255	1.255	1.350	1.361	1.367
R(2, 3)	N2–N3	1.312	1.313	1.347	1.202	1.203
R(3, 7)	N3–H7	1.000	1.000	0.993	–	1.002
R(5, 8)	N5–H8	0.992	0.992	0.993	1.001	0.992
R(5, 9)	N5–H9	0.993	0.993	0.994	–	0.994
R(6, 10)	N6–H10	1.001	1.001	0.995	0.993	–
R(1, 2)	N1–O2	1.183	1.183	1.178	1.341	1.341
R(1, 7)	O1–H7	–	–	–	0.945	0.945

Bond	B3LYP/6-311G(d,p)					Experimental	B3LYP/6-311++G(d,p)				
	A ₁	A ₂	B	C ₁	C ₂		A ₁	A ₂	B	C ₁	C ₂
R(1, 2)	1.213	1.220	1.207	1.381	1.383	1.260	1.214	1.220	1.211	1.383	1.383
R(1, 7)	–	–	–	0.965	0.965	–	–	–	–	0.967	0.967
R(2, 3)	1.335	1.339	1.375	1.225	1.229	1.302	1.333	1.338	1.364	1.223	1.227
R(3, 4)	1.413	1.431	1.324	1.464	1.444	1–391	1.412	1.431	1.328	1.460	1.446
R(3, 7)	1.019	1.011	–	–	–	–	1.020	1.012	–	–	–
R(4, 5)	1.372	1.275	1.359	1.269	1.272	1.309	1.371	1.277	1.357	1.270	1.273
R(4, 6)	1.273	1.362	1.359	1.366	1.369	1.315	1.275	1.362	1.357	1.367	1.369
R(5, 7)	–	–	1.007	–	–	–	–	–	1.008	–	–
R(5, 8)	1.006	1.017	1.012	1.017	1.018	0.93	1.006	1.017	1.012	1.017	1.018
R(5, 9)	1.000	–	–	–	–	–	1.009	–	–	–	–
R(6, 9)	–	1.006	1.007	1.006	1.007	0.91	–	1.007	1.008	1.008	1.008
R(6, 10)	1.017	1.011	1.008	1.006	1.006	0.91	1.017	1.011	1.009	1.007	1.007



couple of tautomeric forms and some of stability differences are expected among them. Presently, following the conformational analysis, five tautomeric forms (two of them are a pair of conformers energetically close to each other) of nitrosoguanidine have been considered. These are A₁, A₂, B, C₁ and C₂ (see Fig. 1). Note that in A_i and C_j series, subscripts stand for different conformers of the same tautomeric forms.

One of the present methodologies involves 6-31G(d,p) basis set that is a polarized set adding d-type functions to heavy atoms and p-type functions to light atoms (hydrogen atoms presently) [15,16]. Note that it has been empirically determined that adding polarization functions to the heavy atoms is more important than adding polarization functions to hydrogen. Also note that 6-31G(d,p) level of calculations provide in many cases, quantitative results considerably superior to some others. The 6-311G(d,p) basis set is a single zeta for the core and triple zeta for the valence orbitals and contains five d-type Gaussian polarization functions on each nonhydrogen atom and three p-type polarization function on each hydrogen atom [15]. Since the tautomeric structures possess lone-pairs and due to the hydrogen bonding have significant electron density at large distances from the nuclei, 6-311++G(d,p) diffuse basis set [15] has also

been used. It has been reported that B3LYP/6-31++G(d,p) level of calculations are sufficiently accurate for tautomeric studies [18]. The presently used correlation term of B3LYP consists of the VWN3 (Vosko, Wilk, Nusair) local correlation functional [19] and LYP (Lee, Yang, Parr) correlation correction functional [20]. The BLYP method gives a better improvements over the SCF-HF results. Its predictions are in qualitative agreement with experiment. Fig. 1 shows the geometry optimized structures of the present concern. Note that of the various conformers only the ones having comparable energies have been taken into account. Tables 1 and 2 show some geometrical features of the tautomers. As seen in Table 1, the level of calculations do not yield very different bond lengths. However, 6-31G(d,p) method generally predicts shorter bond lengths than the DFT methods do. The calculated N=O bond in all the tautomers (A₁, A₂ and B) is shorter than the experimentally found one. The N–O bond in C₁ and C₂ is longer than the experimental one. On the other hand, the experimental bond length R(1, 2) is shorter than the calculated one in A₁, A₂ and B (N–N bond), but longer than the one in C₁ and C₂ (N=N bond). Fig. 2 shows the charges and 3D-charge density plots for the tautomers.

Table 3 shows the total energies of the tautomers calculated at different levels of theory.

When the energetics of A₁ and A₂ are compared, the former is characterized with more negative total energy in all the calculations. The total energy with MP2 correlation is in the favor of A₁ (more negative). Also the nuclear energy for A₁ is

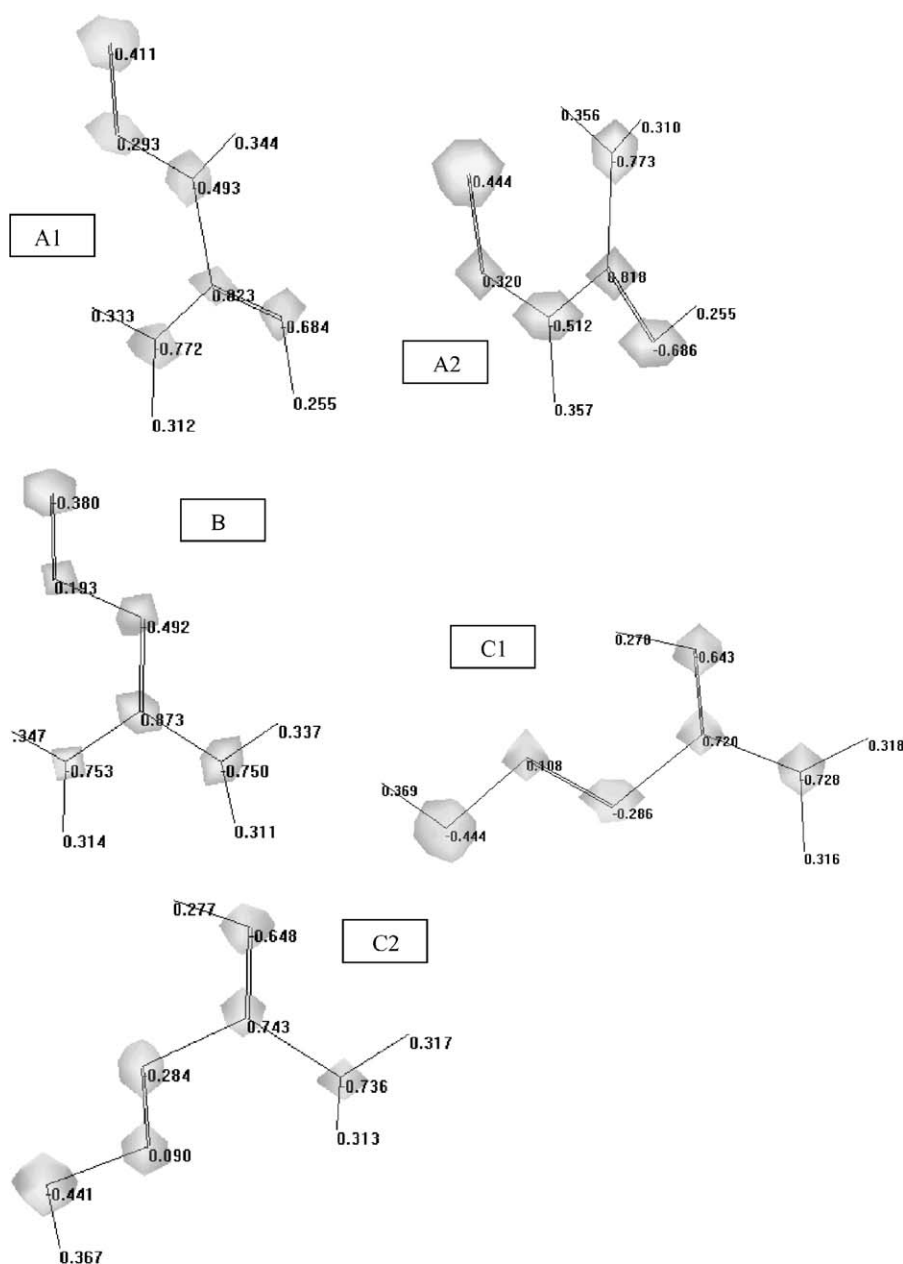


Fig. 2. The charges and 3D-charge density plots for the structures (6-31G(d,p)).

more favorable (less positive, see Table 4). The total energy for C_1 with or without MP2 correlation energy is less favored as compared to C_2 (note that C_1 and C_2 are different conformers of the same tautomeric form). Also, B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) calculations favor C_2 over C_1 .

As for the tautomeric form B, the total energy is the most favorable of all the tautomeric forms (in all the four levels of theory). However, with MP2 correlation, its total energy becomes the same with the respective energy of A_1 . Also, DFT calculations at the level of B3LYP/6-311G(d,p) predicts the same result. On the other hand, interestingly enough, 6-31G(d,p) level of ab initio calculations and the highly elaborate B3LYP/6-311++G(d,p) type DFT calculations yield parallel results in estimating the stability order of these

tautomers as $B > A_1 > A_2 > C_2 > C_1$ (Table 3). Murmann et al., also found B (nitrosamine form) as the most stable tautomer of nitrosoguanidine [7] at the MP2 (full)/6-31G* level. Also their X-ray studies and ab initio molecular orbital calculations predicted the same geometry in the gas state for the individual molecule as that found in the crystal state by single crystal X-ray diffraction.

Structures A, B and C (see Fig. 1) stand for *N*-nitrosamine, *N*-nitrosimine and diazoic acid forms of nitrosoguanidine, respectively. As mentioned above, the nitrosimine form (structure B) is the most favorable tautomer among the others. Whereas, the diazoic acid forms (structures C_1 and C_2) are the least stable of all. The stability of B over the others can also be justified within the valence-bond formalism by writing series of

Table 2

Some calculated (B3LYP/6-311G(d,p)) bond angles of the structures (angles (°), see Fig. 1 for kind and numbering of the atoms)

Angles	A ₁	A ₂	B	C ₁	C ₂
A(1, 2, 3)	114.7	117.1	113.9	109.9	109.9
A(2, 3, 4)	122.1	133.2	109.8	112.4	113.5
A(2, 3, 7)	119.6	113.2	–	–	–
A(4, 3, 7)	118.2	113.4	–	–	–
A(3, 4, 5)	113.7	113.7	125.6	128.7	119.2
A(3, 4, 6)	115.8	115.5	117.2	107.8	117.8
A(5, 4, 6)	130.5	130.8	117.2	123.5	122.9
A(4, 5, 7)	–	–	118.4	–	–
A(4, 5, 8)	116.9	111.8	113.3	110.6	109.1
A(4, 5, 9)	117.5	117.9	–	–	–
A(4, 6, 9)	–	–	119.2	116.8	115.0
A(7, 5, 8)	–	–	117.1	–	–
A(8, 5, 9)	116.9	118.2	–	–	–
A(4, 6, 10)	111.8	119.8	114.6	117.7	117.7
A(9, 6, 10)	–	–	114.6	118.4	117.5
D(1, 2, 3, 4)	–178.9	–2.4	–177.6	–178.8	–179.1
D(1, 2, 3, 7)	–1.3	–177.9	–	–	–
D(2, 3, 4, 5)	–7.3	–172.6	9.5	10.3	172.1
D(2, 3, 4, 6)	175.0	9.4	–171.5	–169.1	–9.9
D(7, 3, 4, 5)	175.0	2.8	–	–	1.8
D(7, 3, 4, 6)	–2.8	–175.2	–	–	–
D(3, 4, 5, 7)	–	–	–153.7	–	–
D(3, 4, 5, 8)	161.9	–179.0	–10.9	–2.9	1.8
D(3, 4, 5, 9)	15.1	–1.4	–	–	–
D(3, 4, 6, 9)	–	–169.4	–153.3	–168.7	167.7
D(6, 4, 5, 7)	–	–	27.3	–	–
D(6, 4, 5, 8)	–20.7	–	170.1	176.5	–175.9
D(6, 4, 5, 9)	–167.5	–	–	–	–
D(3, 4, 6, 10)	178.6	–12.2	–7.8	–18.4	22.5
D(5, 4, 6, 9)	–	13.0	25.7	11.8	–14.5
D(5, 4, 6, 10)	1.3	–	171.3	162.1	–159.6

canonical structures in which both of the NH₂ groups may participate electron donation one at a time (Scheme 2). Such kind of extended conjugation does not exist in the other tautomeric forms in which the nitroso group and the unsubstituted amino group behave as crossly conjugated moieties of nitrosoguanidine molecule. The extended conjugation existing in B (the most favorable tautomeric form) raises up the HOMO and LUMO (the

Table 3

Calculated total energies (kJ/mol) of the structures

Method	Structure					Stability order
	A ₁	A ₂	B	C ₁	C ₂	
6-31G(d,p)	–873703	–873691	–873712	–873679	–873680	B > A ₁ > A ₂ > C ₂ > C ₁
6-31G(d,p)/MP2(sp)	–876299	–876292	–876299	–876274	–876275	B = A ₁ > A ₂ > C ₂ > C ₁
B3LYP/6-311G(d,p)	–878928	–878922	–878928	–878999	–878902	B = A ₁ > A ₂ > C ₂ > C ₁
B3LYP/6-311++G(d,p)	–878963	–878955	–878969	–878939	–878942	B > A ₁ > A ₂ > C ₂ > C ₁

Table 4

Some calculated (6-31G(d,p)) energies (kJ/mol) of the structures

Energy	A ₁	A ₂	B	C ₁	C ₂
Electronic kinetic	871909	871856	871970	871962	871981
EK, ee, and eN	–1487829	–1498729	–1487736	–1480922	–1482846
Nuclear repulsion	614126	625038	614024	607243	609167
MP2	–2596.2	–2601.2	–2587.0	–2595.4	–2595.5

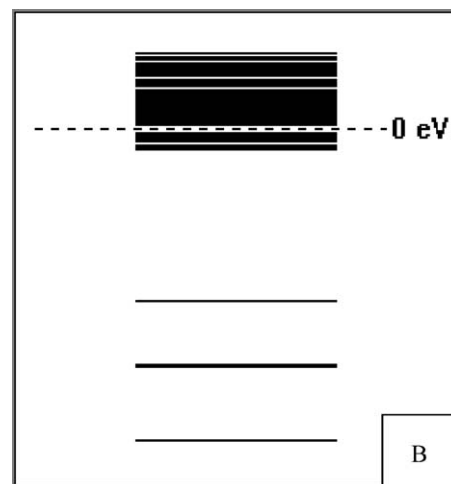
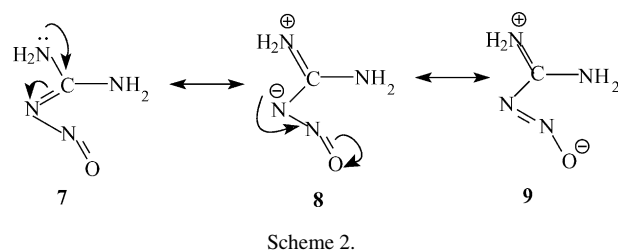


Fig. 3. A typical distribution of molecular orbital energies (6-31G(d,p)).

frontier molecular orbitals) energies compared to A and C forms. This foresight within VB formalism is theoretically supported by all the ab initio and DFT calculations presently performed.

A similar result was reported in the case of *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine [10,11] that is the nitrimine tautomers were found to be the most stable in agreement with the experimental data. Namely, in nitrimine type structures there exist an extended conjugation involving amino groups and the NO₂ moiety. Note that a NO₂ group, according to Dewar, can be considered as a NO group when in conjugation with another π-system because one of the oxygen atoms present in NO₂ group is crossly conjugated with the rest of π-skeleton of

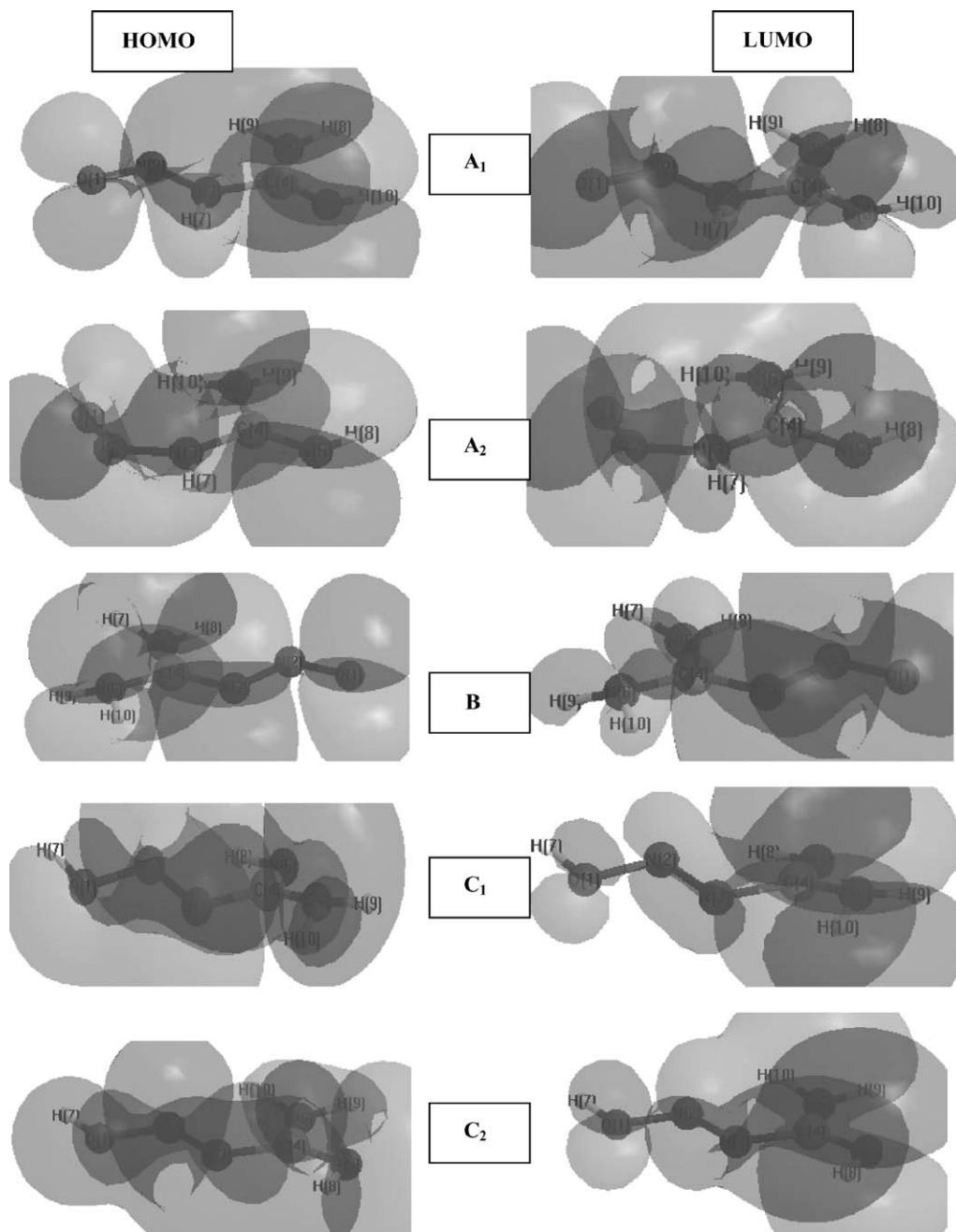


Fig. 4. The frontier molecular orbitals of the tautomers considered (B3LYP/6-311++G(d,p)).

the whole system [21,22]. Table 5 shows the lowest occupied and the highest unoccupied molecular orbital energies (LOMO and HUMO, respectively) of the structures. As seen there, C-type tautomers have lower LOMO energy values than the others. Whereas A types have higher HUMO energy values (A₂ possesses the highest of all). Fig. 3 shows a typical distribution of the molecular orbital energy levels of these structures.

Fig. 4 shows the frontier molecular orbitals of the tautomers. As seen there, most of these frontier molecular orbitals mainly possess π -type symmetry. Table 6 tabulates the HOMO and LUMO energies of the structures considered.

Table 7 shows various calculated geometrical and physicochemical properties of the structures (based on 6-31G(d,p)

optimized geometry) but some data in the table is obtained (such as the refractivities and polarizabilities) based on group additivities and independent of the geometry optimization. Thus, A₁ and A₂, also C₁ and C₂ pair wise possess the same

Table 5
The LOMO and HUMO energies ($\times 10^{-19}$ J, 6-31G(d,p)) of the structures

	LOMO	HUMO
A ₁	-898.68	213.51
A ₂	-898.70	214.76
B	-897.22	211.99
C ₁	-899.89	210.83
C ₂	-899.96	209.88

Table 6
The calculated HOMO and LUMO energies (in Hartree) of the structures considered

	B3LYP/6-311++G(d,p)		B3LYP/6-311G(d,p)		6-31G(d,p)		6-31G(d,p)/MP2(sp)	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
A ₁	-0.26621	-0.08482	-0.25504	-0.07113	-0.3771	0.1181	-0.3771	0.1181
A ₂	-0.26461	-0.08501	-0.25360	-0.07244	-0.3719	0.1149	-0.3720	0.1149
B	-0.21777	-0.06951	-0.20586	-0.05561	-0.3645	0.1286	-0.3645	0.1286
C ₁	-0.26170	-0.08493	-0.24862	-0.07407	-0.3718	0.1095	-0.3718	0.1095
C ₂	-0.26519	-0.08829	-0.25407	-0.07587	-0.3732	0.1031	-0.3732	0.1031

Table 7
Some calculated geometrical and physicochemical properties of the structures (based on 6-31G(d,p) geometry optimized structures)

	Area	Volume	Hydration energy	log <i>P</i>	Refractivity	Polarizability
A ₁	223.57	294.63	-100.37	-0.08	20.68	7.46
A ₂	217.03	289.97	-101.46	-0.08	20.68	7.46
B	223.25	294.82	-105.98	-0.24	20.80	7.46
C ₁	229.36	301.20	-131.58	1.05	22.93	7.59
C ₂	226.37	299.68	-129.41	1.05	22.93	7.59

Area, volume, refractivity and polarizability values are in the order of 10⁻²⁰ m², 10⁻³⁰ m³, 10⁻³⁰ m³, 10⁻³⁰ m³, respectively. Hydration energy is in kJ/mol.

log *P*, polarizability and refractivity values. Trend of the data indicates that within the limitation of the method, C-series of tautomers are better hydrated than the others. Of course, this fact has to be taken into account when the stabilities are considered in aqueous systems. In Table 7, the trends rather than absolute values are to be considered.

4. Conclusion

Within the limitations of restricted 6-31G(d,p) and the more elaborate B3LYP/6-311++G(d,p) (restricted) calculations, nitrosoguanidine in vacuum conditions prefers the nitroso imine (B) form. However, 6-31G(d,p) method with MP2 correlation energy and B3LYP/6-311G(d,p) methods predict that B and A₁ (nitrosamine) forms are characterized with the same total energy. In the absence of any water, such as in explosive conditions, the present values obtained for the tautomers in the gas form may be valuable, although the calculations were performed for single isolated molecule(s) and the behavior in the bulk might be different.

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