Earthline Journal of Chemical Sciences
E-ISSN: 2581-9003; CODEN: EJCSB4
Volume 11, Number 4, 2024, Pages 489-514
https://doi.org/10.34198/ejcs.11424.489514

Isomers and tautomers of aminonitroethylenes – A DFT study

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Abstract

Aminonitroethylene isomers and their 1,3- and 1,5-proton tautomers are considered within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). Aminonitroethylene is a part of the well known explosive FOX-7 which is characterized with a pull-push type resonance. All the structures considered possess thermodynamically exothermic heat of formation values are, electronically stable, and have favorable Gibbs' free energy of formation values at the standard states. Various quantum chemical properties, including IR and UV-VIS spectra, the HOMO and LUMO energies etc., have been obtained and discussed.

1. Introduction

Push-pull alkenes are substituted alkenes with one or two electron-donating substituents (D) on one end of C=C double bond and with one or two electron-accepting substituents (A) at the other end [1,2]. Allowance for π-electron delocalization leads to the central C=C double bond becoming ever more polarized and with rising push-pull character, the π-bond order of this double bond is reduced and, conversely, the corresponding π-bond orders of the C-donor and C-acceptor bonds are accordingly increased. This push-pull effect is of decisive influence on both the dynamic behavior and the chemical reactivity of this class of compounds [1,3].

Different aspects of push-pull effect have been investigated by various scientists [4-11]. Yanai et al., studied the chemical bonding in polarized push-pull ethylenes [4]. Captodative aromaticity and push-pull systems were the interest of Shainyan and

Received: July 13, 2024; Accepted: August 11, 2024; Published: August 18, 2024

Keywords and phrases: aminonitroethylene; push-pull alkenes; explosives; density functional; donor-acceptor.

coworkers [5]. Pappalardo et al., studied theoretically simple push-pull ethylenes in solution [6]. Politzer et al., decades ago carried out computational investigation of the structures and relative stabilities of amino/nitro derivatives of ethylene (at the level of Perdew-86/6-31+G(d,p)) [7]. In recent years some studies (including NMR studies) have been performed experimentally and theoretically on the push-pull type systems [8-11].

Isomeric aminonitroethylenes presently considered are shown in Figure 1. They combine the effects of resonance-donating NH_2 and the inductively and mesomerically electron-withdrawing NO_2 groups in a molecular framework containing polarizable electronic charge. Note that of those structures the *cis* and *trans* forms are embedded in FOX-7 explosive.

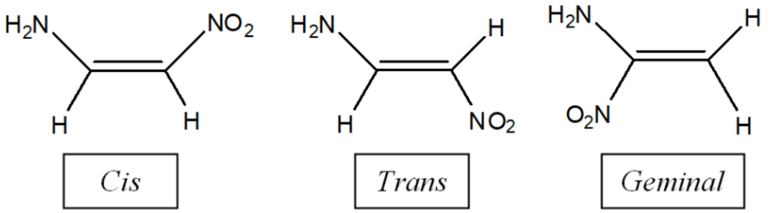


Figure 1. Structures of the isomers presently considered.

2. Method of Calculation

In the present study, the initial structural optimizations of all the structures leading to energy minima have been achieved by using molecular mechanics (MM2) method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [12,13] at the restricted level [14,15]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, the structural optimizations were managed within the framework of density functional theory (DFT) [16,17] at the level of B3LYP/6-311++G(d,p) [15,18]. Note that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [17,19]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [20] and Lee, Yang, Parr (LYP) correlation correction functional [21]. Also, the vibrational analyses have been carried out. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N–6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [22].

3. Results and Discussion

Structural and theoretical considerations

Presently considered isomeric ethylenes structurally are examples of pull-push type systems. The nitro and amino groups stand for acceptor and donor substituents, respectively. In general, acceptor substituents increase the pull-push character; electron releasing substituents are less influential, but the push-pull effect is still greater than the reference compound considered [5].

Structurally, a nitro group has an odd alternant conjugated system, containing three atoms and four π-electrons, thus it is isoconjugate with allyl anion. According to Dewar [23,24] it is not however, a -E substituent, because it is attached to adjacent system (R) through the central, inactive atom of the allylic system. Since there is no π-interaction between R and NBMO of allyl, R moiety lying on the nodal plane of the latter. Then the effect of allyl on R in R-allyl should be precisely analogous to the effect of the vinyl group on R in $R\text{-}CH=CH_2$. Thus, the 2-allyl group is to all intents and purposes is a ±E substituent. It follows that the corresponding isoconjugate of $-NO_2$ is a +E substituent. Thus $-NO_2$ group could be considered as -N=O group. Especially in the cases where push-pull type resonance predominantly occurs.

Figure 2 shows the isoconjugate alternant hydrocarbons of the presently considered isomers where allyl moiety stands for the nitro group. The differences of the number of starred and unstarred positions, $\Delta n=n^*-n^\circ$, are also shown in the figure. In the realm of perturbation molecular orbital theory (PMO) the *cis* and *trans* isomers presently considered are to be classified as non-Kekulé systems ($\Delta n\geq 2$), whereas the geminal isomer a Kekulé system (isoconjugate with en even alternant system $\Delta n=0$). However, if the nitro group is considered as the nitroso group (-N=O), the *cis*, *trans* and *geminal* isomers all turn out to be Kekulé compounds, isoconjugate with odd alternant hydrocarbon systems ($\Delta n=1$).

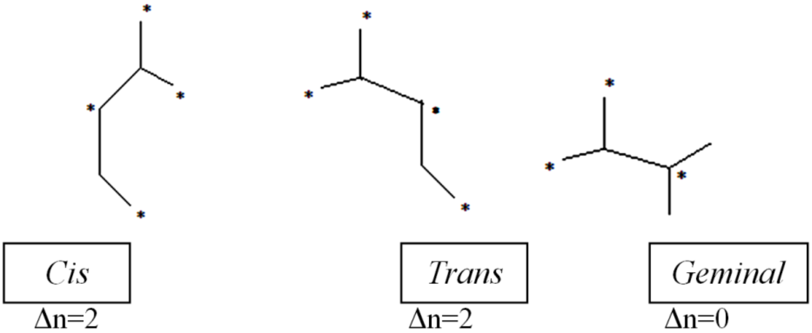


Figure 2. Isoconjugates of the isomers considered.

Although aliphatic or aromatic nitro compounds, aliphatic nitro esters, nitrogen halides, etc., all have topological assembly of various atoms, their explosophore groups (e.g., nitro group) have a common isoconjugate system, methylenepropenyl dianion. It is an odd alternant hydrocarbon anion [25,26]. The explosives in the completely coplanar form may display odd, even or non-Kekulé type alternant hydrocarbon characteristics depending on the overall structure of them [27]. Note that a non-Kekulé alternant hydrocarbon is much less stable than any isomeric Kekulé-type alternant hydrocarbon [23,24] and the characteristic feature of non-Kekulé systems is that the difference ($\Delta n = n^* - n$) between the number of starred and unstarred positions is either equal to two or far exceeds it [23,24]. Note that FOX-7 structure, in both way of treatment of nitro group (as nitro or nitroso) is a non-Kekulé structure having Δn value of 4 and 2, respectively. To be an explosive compound, non-Kekulé structure is necessary but not a sufficient condition. However, one should keep in mind that any compound which is a non-Kekulé type may get rid of that form if structurally certain rotations or twisting is possible. Thus, an explosive molecule isoconjugate with a non-Kekulé alternant hydrocarbon (AH) system may remain in metastable form at room temperature.

Computational treatment

Table 1 shows some of the standard thermo chemical formation data of the isomers considered. The data reveal that the standard heat of formation (H^o) values of all the isomers are exothermic and they are favored according to G^o values. The algebraic order of the heat of formation values is *Cis*< *Trans*< *Geminal*. The same order holds for G^o values because the entropies in the present cases contribute little in to the free energy of formation.

Table 1. Some thermo chemical values of the isomers considered.

Isomer	H°	S° (J/mol°)	G°
Cis	-888729.5708	311.83	-888822.5433
Trans	-888712.6703	321.15	-888808.4232
Geminal	-888690.9703	312.21	-888784.0557

Energies in kJ/mol.

Table 2 shows some energies of the isomers considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. As the data reveal, all of the structures are electronically stable and the relative stability order is *Cis*> *Trans*> *Geminal*.

Table 2. Some energies of the isomers considered.

Isomer	E	ZPE	E_C
Cis	-888928.96	190.60	-888738.36
Trans	-888911.21	188.97	-888722.24
Geminal	-888887.23	187.19	-888700.04

Energies in kJ/mol.

The calculated bond lengths of the isomers considered are shown in Figure 3. The order of C-NH_2 bonds lengths is *Geminal*< *Trans*< *Cis*. Whereas the order of C-NO_2 bond lengths is *Cis*< *Trans*< *Geminal*. Thus, the C-C bond has more double bond character in the geminal isomer (in terms of the bond length) compared to the others having the order of double bond character as *Geminal* >*Trans* >*Cis*. The order arises from the push-pull effect.

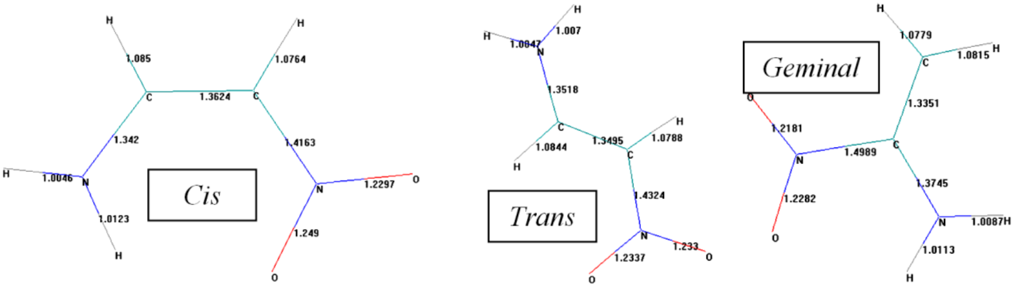
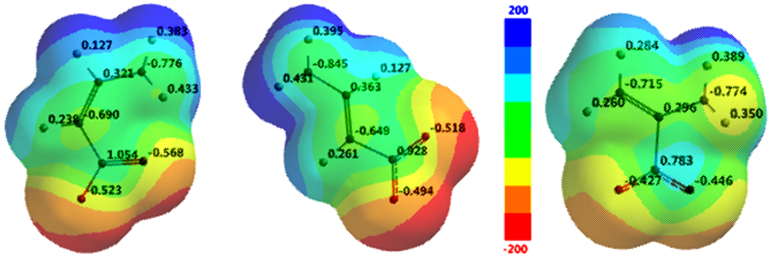


Figure 3. The calculated bond lengths of the isomers considered.

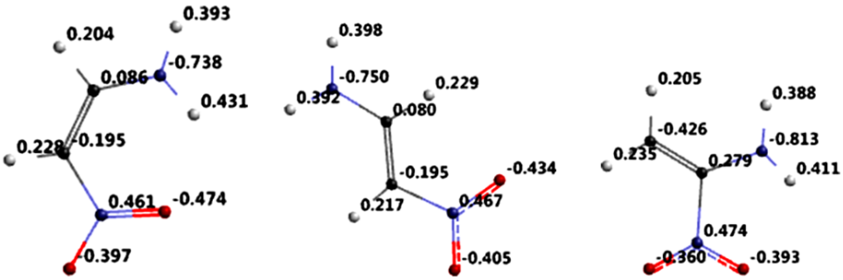
Figure 4 shows the electrostatic potential maps of the isomers considered where negative potential regions coincide with red/reddish and positive ones with blue/bluish parts of the maps. In the figure it is evident either from the charge distributions or from the spread of the positive and negative potential regions, the nitro group of the *geminal* isomer is less effective electron acceptor than the respective ones of the other isomers. The donor NH_2 group pushes electron population of the ethylenic group back by preventing the electron flow to the crossly conjugated nitro group.



Cis *Trans* *Geminal*

Figure 4. The ESP charges on atoms of the isomers considered and their ESP potential maps (overlapped form).

Figure 5 shows the natural charges on atoms of the isomers considered. Note that the carbon atom bearing the nitro group possesses positive partial charge in contrast to the respective charge in the other isomers. In that sense there exist parallelism between the ESP and natural charges.



Cis *Trans* *Geminal*

Figure 5. The natural charges on atoms of the isomers considered.

Table 3 displays some of the calculated properties of the isomers considered. The order of dipole moments is *Geminal*< *Cis*< *Trans*. One should keep in mind that a net dipole moment which is the vector sum of individual bond dipoles are a function of bond charges (charges on the atoms linked by the bond considered) and the bond distance.

The polarizability is defined according to a multivariable formula [22] which are the functions of van der Waals volume and hardness, respectively. Hardness is defined as,

$$\text{Hardness} = -(\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}})/2$$

where $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ are the molecular orbital energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital energies, respectively.

Table 3. Some calculated properties of the isomers considered.

Isomer	Dipole Moment	Polarizability	Area (Å²)	Volume (Å³)	PSA (Å²)	Ovality	Log P
Cis	6.35	46.65	104.50	78.99	60.273	1.17	-1.97
Trans	7.45	46.68	107.58	79.65	64.246	1.20	-0.22
Geminal	4.19	46.89	106.16	79.70	62.263	1.19	0.40

Dipole Moments in Debye units. Polarizabilities in 10^{-30} m^3 units.

It is worth mentioning that the polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N,O) together with their attached hydrogen atoms. Although these compounds are isomeric, their PSA values differ from each other meaning that the same kind of atoms might be influenced by electronic factors differently at different positions.

Note that the *cis* and *trans* isomers considered have negative log P values. It is worth mentioning that a negative value for log P means the compound has a higher affinity for the aqueous phase (it is more hydrophilic); when log P = 0 the compound is equally partitioned between the lipid and aqueous phases; whereas a positive value for log P denotes a higher concentration in the lipid phase (i.e., the compound is more lipophilic). Thus, the geminal isomer distinctly differs from the others. In that compound orientation of the acceptor and donor moieties are not in conjugated form (crossly conjugated). Hence, any electron flow between the acceptor and donor groups is prevented which affects the polar character of the structure. It has the smallest dipole moment value but the largest polarizability which is the tendency of matter, when subjected to an electric field, to acquire an electric dipole moment in proportion to that applied field.

Figure 6 shows chemical function descriptors (CFDs) of the isomers considered. Note that CFDs are attributes given to a molecule in order to characterize or anticipate its chemical behavior. In the figure purple spheres stand for hydrogen bond donor, acceptor and + ionizable moieties whereas green ones hydrogen bond acceptors.

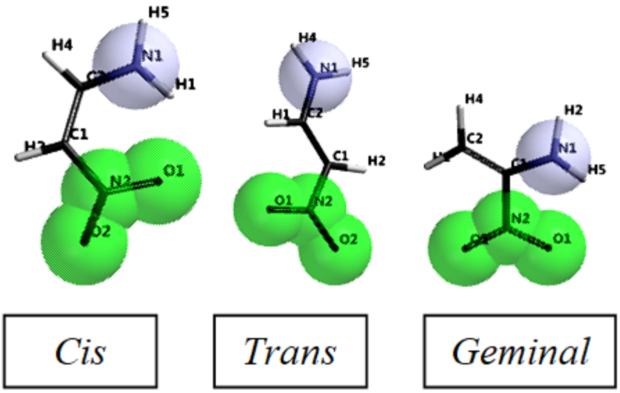


Figure 6. CFDs of the isomers considered.

Table 4 shows aqueous and solvation energies of the isomers considered. The solvation energy data are based on SM5.4/A model [22]. The algebraic order of aqueous energies is *Cis*< *Trans*< *Geminal*. The solvation energies follow the order of *Trans*< *Cis*< *Geminal*. The energy of solvation is the amount of energy associated with dissolving a solute in a solvent. If it is a positive number, the dissolving process is endothermic; if it is negative, it is exothermic.

Table 4. Aqueous (E_{aq}) and solvation energies of the isomers.

Isomer	E_{aq}	Solvation E
Cis	-888976.32	-47.356
Trans	-888958.66	-47.448
Geminal	-888907.94	-20.714

Energies in kJ/mol.

In the Ir spectrum of *Cis* isomer, the unsymmetrical and symmetrical N-H stretchings occur at 3710 cm^{-1} and 3529 cm^{-1}, respectively. The peaks at 3270 cm^{-1} and 3183 cm^{-1} are ethylenic C-H stretchings. The C-NO_2 stretching happens at 1311 cm^{-1}. The skeletal stretchings and bendings (overlapped) occur at 1693-1510 cm^{-1}.

In the case of *Trans* isomer unsymmetrical and symmetrical N-H stretchings happen at 3730 cm^{-1} and 3609 cm^{-1} respectively,. The peaks 3244 cm^{-1} and 3198 cm^{-1} are C-H stretchings. They are quite weak compared to N-H stretchings. Various skeletal bendings and C-C stretching are at 1702 cm^{-1}. The N=O stretchings happen at 1510 cm^{-1}. The C-NO_2 stretching is at 1367 cm^{-1} and as strong as the various peaks overlapped at 1702 cm^{-1}.

As for the *geminal* isomer, unsymmetrical and symmetrical N-H stretchings are at 3673 cm^{-1} and 3562 cm^{-1}, respectively. At 1723 cm^{-1} C=C and C-NH_2 stretchings occur. At 1586 cm^{-1} N=O stretchings and N-H bendings overlapped. The peak at 1363 cm^{-1} is due to C-NO_2 stretching and is moderately strong.

To help the inspection of data presented in Tables 5-13, the atom labels for the isomers considered are shown in Figure 7.

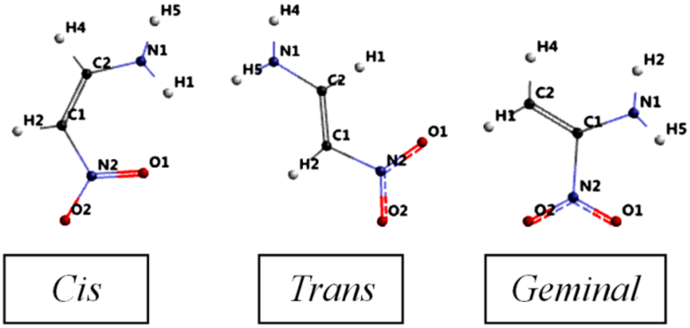


Figure 7. The atom labels for the isomers considered.

Tables 5-7 show the Mulliken bond order matrix for the isomers considered. It is to be kept in mind that Mulliken population analysis is a charge partitioning scheme which electrons are shared equally between different basis set functions [18]. In Mulliken population analysis, the overlap population can be zero by symmetry or negative, indicating antibonding interactions whereas a large positive overlaps between basis functions on different atoms are one indication of chemical bond.

Table 5. Mulliken bond order matrix for the *Cis* isomer.

Bond	Bond order	Bond length (Å)	Remark
C1 H2	0.955	1.0766	Sing-H
C1 C2	1.675	1.3624	Deloc
C1 N2	0.898	1.4164	Single
C2 H4	0.936	1.0849	Sing-H
C2 N1	1.239	1.3410	Single
N1 H1	0.858	1.0129	Sing-H
N1 H5	0.891	1.0048	Sing-H
H1 O1	0.076	1.9956	Hbond
N2 O1	1.558	1.2493	Deloc
N2 O2	1.799	1.2301	Double

Table 6. Mulliken bond order matrix for the *Trans* isomer.

Bond	Bond order	Bond length (Å)	Remark
C1 H2	0.929	1.0787	Sing-H
C1 C2	2.076	1.3502	Double
C1 H1	0.201	2.0903	Hbond
C1 N2	0.865	1.4319	Single
C2 H1	0.757	1.0842	Sing-H
C2 N1	1.170	1.3516	Single
N1 H4	0.912	1.0045	Sing-H
N1 H5	0.912	1.0069	Sing-H
N2 O1	1.669	1.2347	Deloc
N2 O2	1.803	1.2327	Double

Table 7. Mulliken bond order matrix for the *Geminal* (Å) isomer.

Bond	**Bond order**	**Bond length (Å)**	**Remark**
C1 C2	1.806	1.3352	Double
C1 H1	0.070	2.0966	Hbond
C1 N1	1.156	1.3749	Single
C1 N2	0.707	1.4988	Single
C2 H1	0.903	1.0777	Sing-H
C2 H4	1.040	1.0818	Sing-H
N1 H2	0.908	1.0083	Sing-H
N1 H5	0.894	1.0108	Sing-H
H5 O1	0.066	2.1339	Hbond
N2 O1	1.757	1.2282	Double
N2 O2	1.838	1.2186	Double

Tables 8-10 show the Lowdin bond order matrix for the isomers considered. Note that Lowdin population analysis scheme was created to circumvent some of the unreasonable orbital populations predicted by the Mulliken scheme which it does.

Table 8. Lowdin bond order matrix for the *Cis* isomer.

Bond	Bond order	Bond length (Å)	Remark
C1 H2	0.871	1.0766	Sing-H
C1 C2	1.626	1.3624	Deloc
C1 H4	0.094	2.0836	Hbond
C1 N2	1.160	1.4164	Single
H2 C2	0.091	2.1436	Hbond
H2 N2	0.070	2.1017	Hbond
C2 H4	0.868	1.0849	Sing-H
C2 N1	1.498	1.3410	Deloc

C2 H1	0.074	2.0277	Hbond
C2 H5	0.084	2.0458	Hbond
H4 N1	0.074	2.0570	Hbond
N1 H1	0.939	1.0129	Sing-H
N1 H5	0.982	1.0048	Sing-H
H1 O1	0.075	1.9956	Hbond
N2 O1	1.864	1.2493	Double
N2 O2	1.971	1.2301	double

Table 9. Lowdin bond order matrix for the *Trans* isomer.

Bond	Bond order	Bond length (Å)	Remark
C1 H2	0.867	1.0787	Sing-H
C1 C2	1.668	1.3502	Deloc
C1 H1	0.084	2.0903	Hbond
C1 N2	1.120	1.4319	Single
H2 C2	0.081	2.1729	Hbond
H2 N2	0.068	2.1119	Hbond
C2 H1	0.847	1.0842	Sing-H
C2 N1	1.457	1.3516	Deloc
C2 H4	0.080	2.0539	Hbond
C2 H5	0.076	2.0683	Hbond
H1 N1	0.071	2.0719	Hbond
N1 H4	0.988	1.0045	Sing-H
N1 H5	0.980	1.0069	Sing-H
N2 O1	1.941	1.2347	Double
N2 O2	1.964	1.2327	Double

Table 10. Lowdin bond order matrix for the *Geminal* isomer.

Bond	Bond order	Bond length (Å)	Remark
C1 C2	1.810	1.3352	Double
C1 H1	0.099	2.0966	Hbond
C1 H4	0.101	2.1012	Hbond
C1 N1	1.325	1.3749	Deloc
C1 H2	0.077	2.0317	Hbond
C1 H5	0.075	2.0222	Hbond
C1 N2	0.956	1.4988	Single
C2 H1	0.898	1.0777	Sing-H
C2 H4	0.910	1.0818	Sing-H
N1 H2	0.983	1.0083	Sing-H
N1 H5	0.959	1.0108	Sing-H
N2 O1	1.974	1.2282	Double
N2 O2	2.022	1.2186	Double

Natural atomic populations and charges for the isomers considered are displayed in Tables 11-13. Note that NBO is used to analyze the charge density between atoms, not centered on each atom.

Table 11. Natural atomic populations and charges for the *Cis* isomer.

Atom	Occupancy	Charge
C1	6.19512	-0.19513
H2	0.77191	0.22809
C2	5.91369	0.08630
H4	0.79549	0.20451

N1	7.73774	-0.73775
H1	0.56861	0.43138
H5	0.60708	0.39291
N2	6.53909	0.46090
O1	8.47434	-0.47434
O2	8.39689	-0.39690

Table 12. Natural atomic populations and charges for the *Trans* isomer.

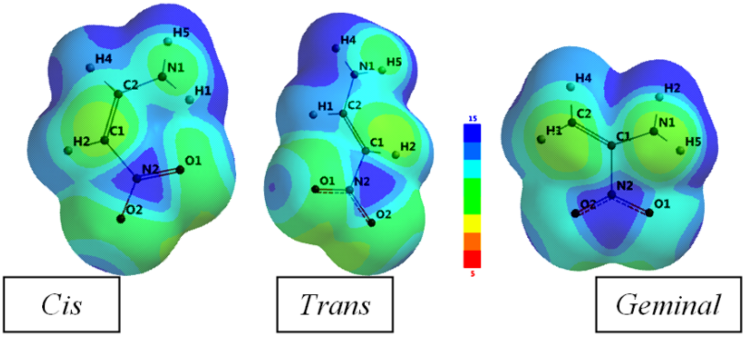
Atom	Occupancy	Charge
C1	6.19462	-0.19463
H2	0.78284	0.21715
C2	5.92021	0.07978
H1	0.77140	0.22859
N1	7.74964	-0.74964
H4	0.60200	0.39799
H5	0.60817	0.39182
N2	6.53293	0.46706
O1	8.43363	-0.43364
O2	8.40450	-0.40450

Table 13. Natural atomic populations and charges for the *Geminal* isomer.

Atom	Occupancy	Charge
C1	5.72062	0.27937
C2	6.42641	-0.42641

H1	0.76470	0.23529
H4	0.79549	0.20450
N1	7.81304	-0.81305
H2	0.61194	0.38805
H5	0.58877	0.41122
N2	6.52575	0.47424
O1	8.39279	-0.39279
O2	8.36043	-0.36044

Figure 8 shows the local ionization potential maps of the isomers considered where conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. It is worth remembering that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.



Cis *Trans* *Geminal*

Figure 8. The local ionization potential maps of the isomers.

Figure 9 displays the LUMO maps of the isomers considered. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value. Note that the LUMO and NEXTLUMO are the major orbitals directing the molecule towards of the attack of nucleophiles. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.

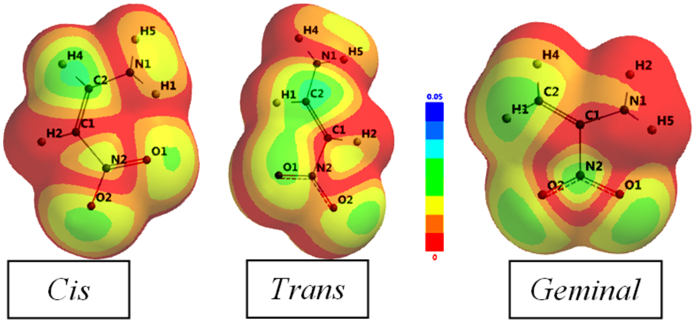


Figure 9. The LUMO maps of the isomers.

Figure 10 displays some of the molecular orbital energy levels of the isomers considered.

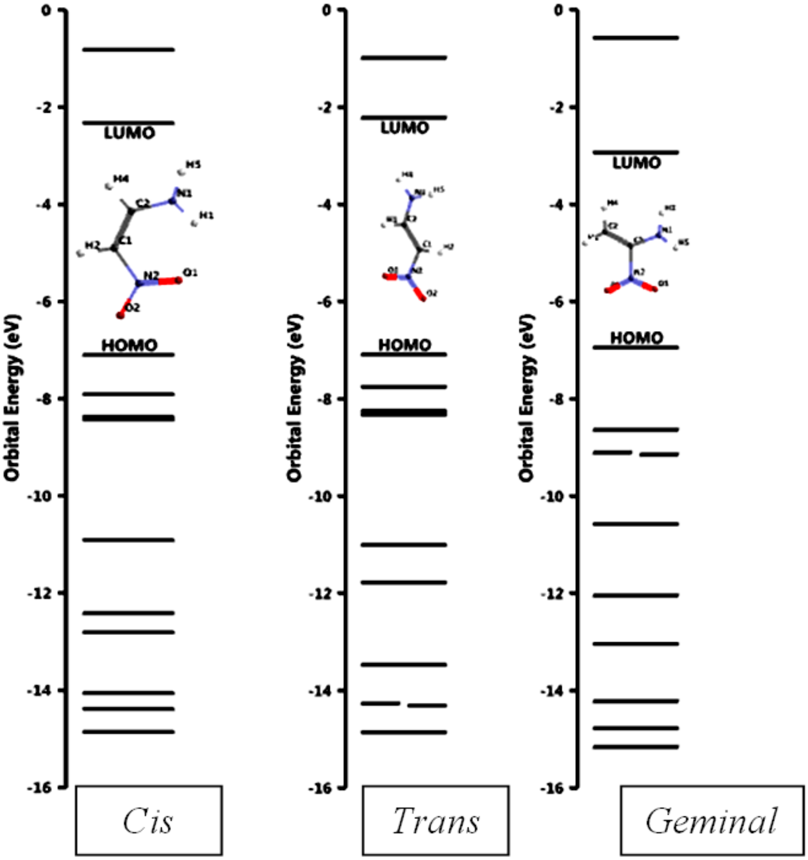


Figure 10. Some of the molecular orbital energy levels of the isomers considered.

Table 14 shows the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps (Δε) of the isomers considered, where $\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$. The algebraic orders of the HOMO and LUMO energies are *Cis*< *Trans*< *Geminal* and *Geminal*< *Cis*< *Trans*, respectively. Thus, going from *Cis* to *Trans* isomer the HOMO and LUMO energy levels raise.

Table 14. The HOMO, LUMO energies and Δε values of the isomers considered.

Isomer	HOMO	LUMO	Δε
Cis	-684.58	-224.17	460.41
Trans	-683.86	-213.82	470.04
Geminal	-669.62	-283.41	386.21

Energies in kJ/mol.

Figure 11 shows the time-dependent density functional UV-VIS spectra of the isomers. As seen in the figure, *cis* /*trans* configurational change has some slight influence on the spectra. A very weak absorption of the *Cis* isomer at 192.29 nm disappears in the spectrum of the *Trans* isomer. The λ_{max} values of the *Cis* and *Trans* isomers are at 253.14 nm and 252.18 nm, respectively. The λ_{max} values of the *Geminal* isomer occur at 191.75 nm and 342.74 nm, respectively. All these values are in accord with the calculated Δε values of the isomers considered. The *Geminal* isomer possesses a more narrow interfrontier energy gap compared to the others. In the *Cis* and *Trans* isomers the effects of amino and nitro groups operate in parallel to enforce the push-pull action whereas in the case of the *Geminal* isomer the effects of the substituents on the conjugation with the ethylenic double bond occur independently but in opposite directions.

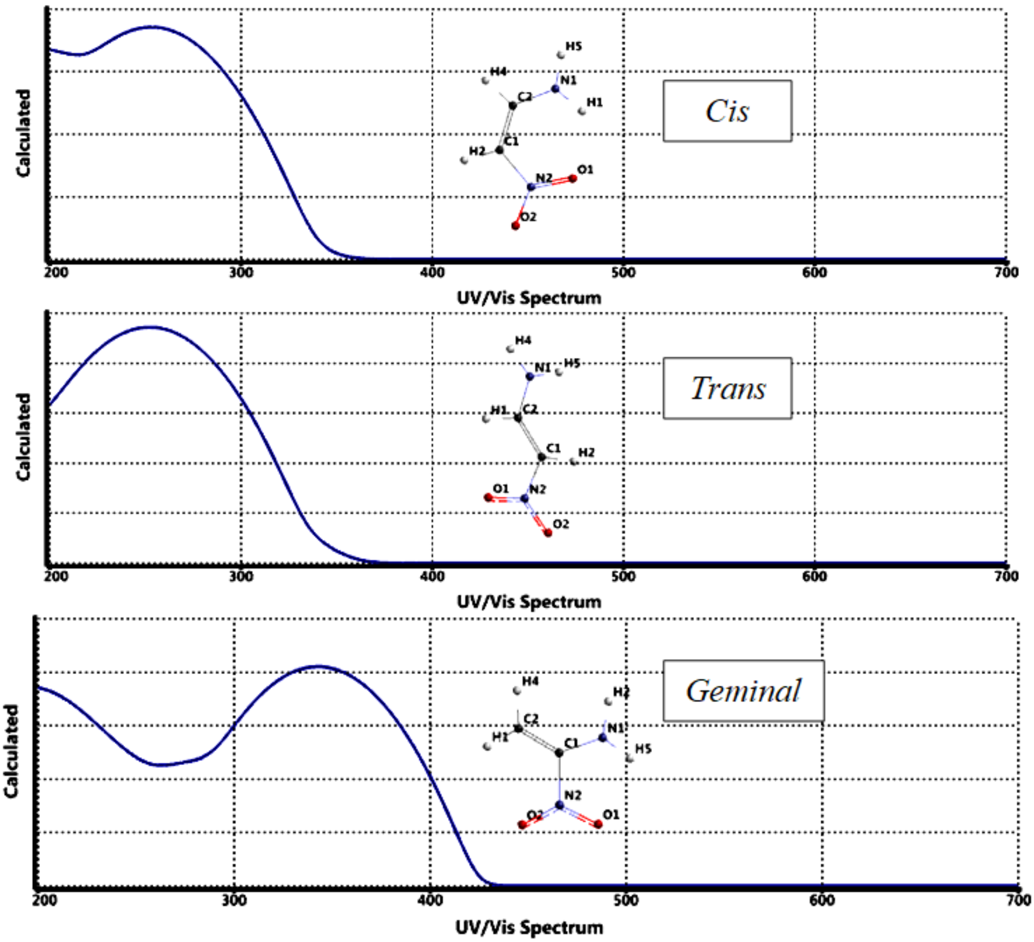


Figure 11. The time-dependent density functional UV-VIS spectra of the isomers.

The tautomers

The isomers presently considered may exhibit 1,3- and 1,5-type proton tautomerism. Figure 12 shows optimized structures of these tautomers. The first type (1,3) is N-H to carbon and the second one (1,5) N-H to oxygen proton tautomerism, respectively. Note that tautomers having different structures possess dual reactivity, therefore it is anticipated that a material which is potent to exhibit tautomerism should display variable properties depending on its tautomer content (allelotropic mixture [28]). It is worth noting that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [28].

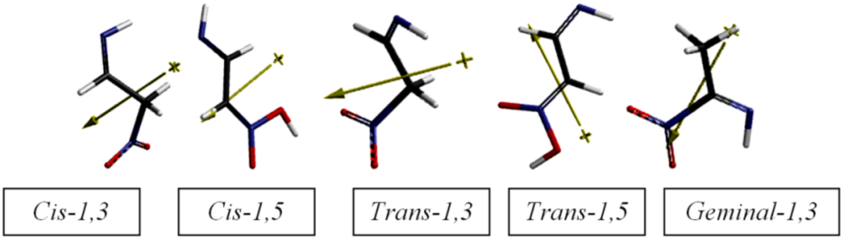


Figure 12. The optimized structures of the tautomers considered.

Figure 13 shows the chemical function descriptors (CFDs) of the tautomers considered. In the figure green spheres stand hydrogen bond acceptors. The yellowish ones indicate hydrogen bond acceptors and donors in character. As seen in the figure, 1,3- and 1,5-tautomerism causes some CFD variations.

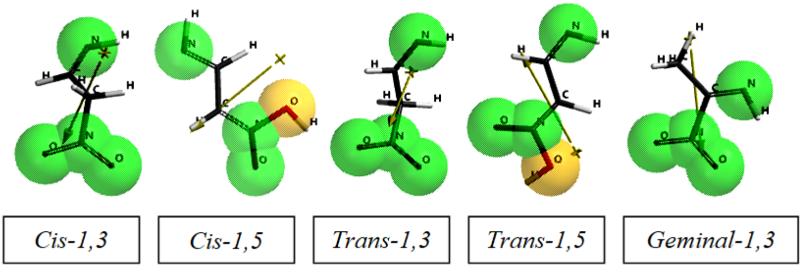


Figure 13. CFDs of the tautomers considered.

Table 15 lists some thermo chemical values of the tautomers considered. The data reveal that formations of all the isomers are exothermic and favored. The orders of Hº and Gº values are the same and follows the algebraic order of *Geminal-1,3*< *Trans-1,3*< *Cis-1,3*< *Cis-1,5*< *Trans-1,5* and *Geminal-1,3*< *Trans-1,3*= *Cis-1,3*< *Cis-1,5*< *Trans-1,5*, respectively.

Table 15. Some thermo chemical values of the tautomers considered.

Tautomer	Hº	Sº (J/molº)	Gº
Cis-1,3	-888671.6832	312.48	-888764.8500
Cis-1,5	-888654.6829	318.99	-888749.7926
Trans-1,3	-888671.6937	312.44	-888764.8500
Trans-1,5	-888651.5401	318.89	-888746.6209
Geminal-1,3	-888709.8977	314.34	-888803.6159

Energies in kJ/mol.

Table 16 shows some energies of the tautomers considered. According to E_C data included in the table the stability of the tautomers follow the order of *Geminal-1,3> Trans-1,3= Cis-1,3> Cis-1,5> Trans-1,5.*

Table 16. Some energies of the tautomers considered.

Tautomer	E	ZPE	E_C
Cis-1,3	-888869.14	189.21	-888679.93
Cis-1,5	-888850.86	186.73	-888664.13
Trans-1,3	-888869.17	189.24	-888679.93
Trans-1,5	-888848.15	187.27	-888660.88
Geminal-1,3	-888905.13	186.26	-888718.87

Energies in kJ/mol.

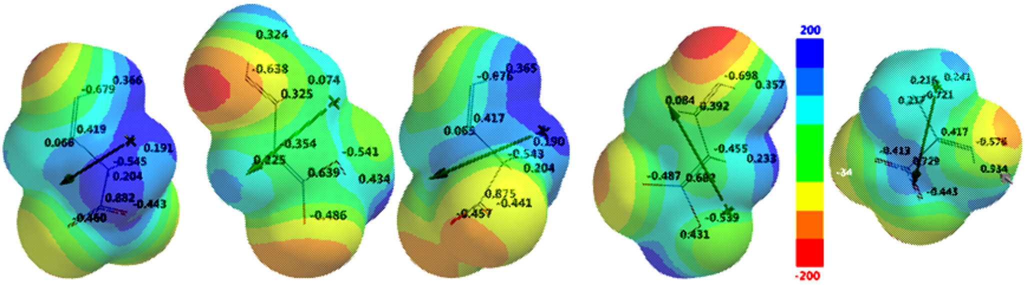
Table 17 displays various properties of the tautomers considered. In the table dipole moments in debye units and the polarizabilities in 10^{-30} m^3 units. As seen in the table aqueous energies follow the algebraic order of *Geminal-1,3< Trans-1,3< Cis-1,3< Cis-1,5< Trans-1,5*. On the other hand, the solvation energy order is *Cis-1,5< Trans-1,3< Cis-1,3< Trans-1,5< Geminal-1,3*. The data reveal that 1,3-type tautomers are hydrophilic whereas 1,5- types and the *Geminal-1,3* tautomer tend to be lipophilic. The determining factors are numerous, including the hydrogen bonding possibilities, charge-charge, charge-dipole and dipole-dipole interactions, ovality etc., which are also dictating on the solvation of molecules. In the table one observes that the dipole moment values of the tautomers are less compared to the respective values of the parent structures (see Table 3). The bond dipoles which are dictated by the bond lengths and charges are the responsible factors.

Table 17. Various properties of the tautomers considered.

Tautomer	E_{aq}	Solvation Energy	Log P	Dipole moment	Polarizability
Cis-1,3	-888902.09	-32.944	-0.40	3.23	46.55
Cis-1,5	-888886.00	-35.132	1.03	2.66	46.78
Trans-1,3	-888902.16	-32.994	-0.40	3.23	46.55
Trans-1,5	-888880.68	-32.532	1.03	3.10	46.78
Geminal-1,3	-888922.26	-17.130	0.31	2.22	46.61

Energies in kJ/mol. The solvation energy data based on SM5.4/A model.

Figure 14 shows the ESP charges on atoms of the tautomers considered and their ESP potential maps.



Cis 1,3 *Cis 1,5* *Trans 1,3* *Trans 1,5* *Geminal 1,3*

Figure 14. The ESP charges on atoms of the tautomers considered and their ESP potential maps (overlapped form).

Table 18 shows the HOMO, LUMO energies and Δε values of the tautomers considered. The data in the table reveal that going from 1,3- to 1,5-tautomer both of the HOMO and LUMO energies raise up. The algebraic order of HOMO energies is *Trans-1,3< Cis-1,3< Trans-1,5< Cis-1,5< Geminal-1,3* whereas the LUMO energies follow the order of *Geminal-1,3< Trans-1,3< Cis-1,3< Trans-1,5< Cis-1,5.*

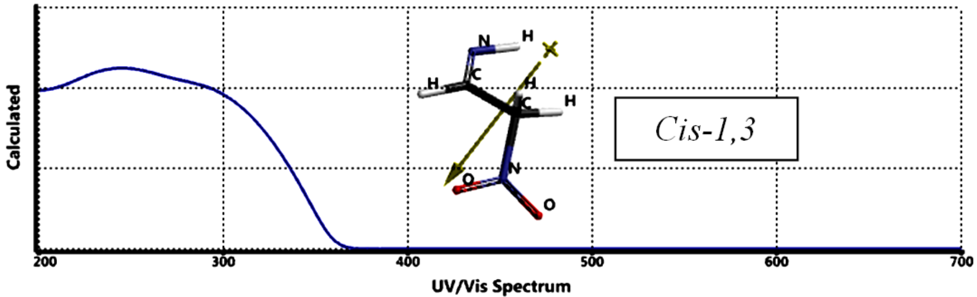
Table 18. The HOMO, LUMO energies and Δε values of the tautomers considered.

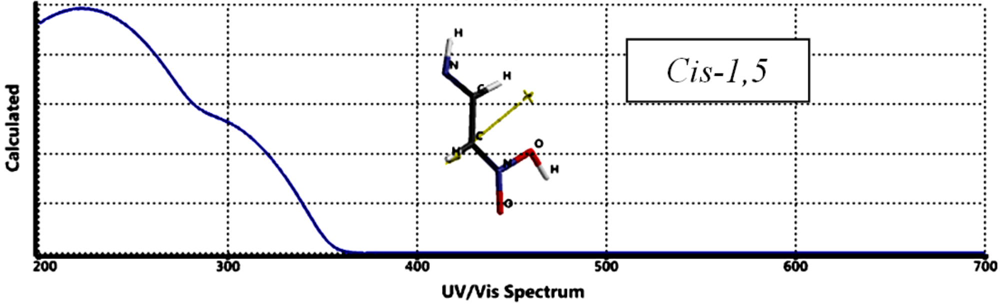
Isomer	HOMO	LUMO	Δε
Cis-1,3	-795.91	-266.54	529.37
Cis-1,5	-682.63	-233.41	449.22
Trans-1,3	-796.23	-266.66	529.57
Trans-1,5	-698.17	-244.78	453.39
Geminal-1,3	-669.62	-283.41	386.21

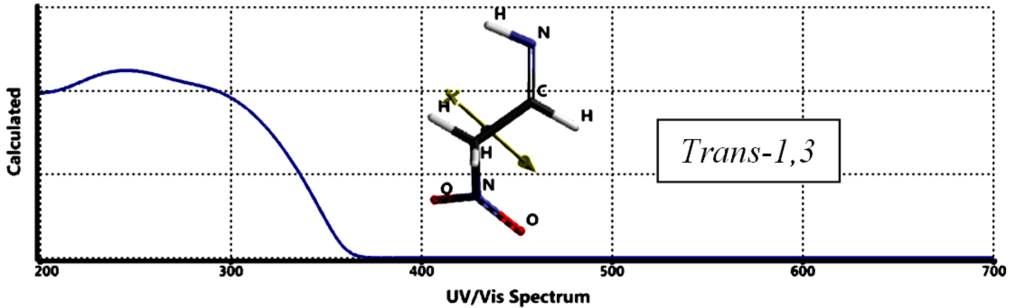
Energies in kJ/mol.

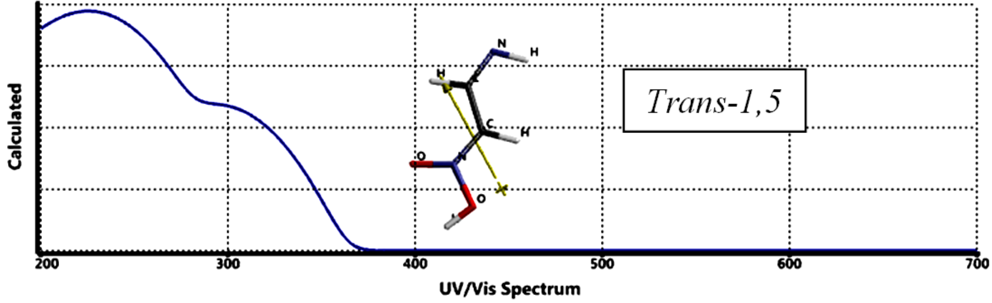
Figure 15 displays the time-dependent density functional UV-VIS spectra of the tautomers considered. All of the tautomers absorb in the UV region except the geminal spectrum which has a weak absorption in the visible region. The 1,5-type tautomers have better discernable shoulders as compared to the 1,3-types. In general, the spectra of 1,3-

types whether they are *cis* or *trans* resemble each other. So do the spectra of 1,5-types. Note that in 1,5-types there exist an extended conjugation as well as two C=N chromophores of different kind and a nitro chromophore is present whereas in the 1-3-types only a single imino and the nitro chromophores exist. So many absorption possibilities arise to yield shoulders in the spectra of these tautomers.









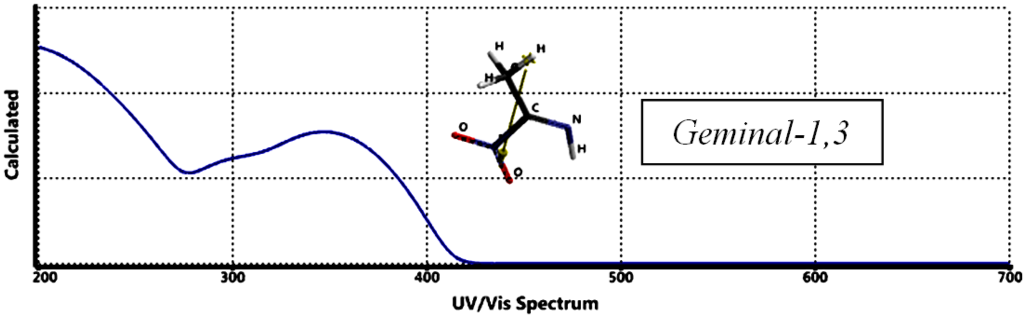


Figure 15. The time-dependent density functional UV-VIS spectra of the tautomers.

4. Conclusion

In the present study, some aminonitroethylenes and their 1,3- and 1,5-tautomers have been studied within the restrictions of density functional theory at the level of B3LYP/6-311++G(d,p). The results have revealed that all the structures considered possess thermo chemically favorable formation values at the standard states and they are electronically stable. The formation values indicate that the *Cis* isomer is the most exothermic, most favorable and most stable whereas the *Geminal* one possesses the least of those values. As for the tautomers, the *Geminal* 1,3-tautomer precedes the others in terms of the above mentioned properties. The calculated Log P values reveal that the *Cis* and *Trans* isomers are hydrophilic but the *Geminal* tends to be lipophilic.

As for the frontier molecular orbital energies, they are highly under the influence of isomerization. The *Geminal* isomer has the highest HOMO but lowest LUMO energy levels thus it has the smallest Δε value. Consequently, its UV-VIS spectrum does not resemble the others. The same arguments are also valid for the 1,3-tautomer of the *Geminal* one.

Overall, the present study considers *cis* and *trans* aminonitroethylenes which are pull-push type structures and embedded in the structure of FOX-7. Also, an isomer of them. *Geminal* isomer has been the focus of present interest, to gather with various tautomers of them in order to analyze the pull-push effect on various properties associated.

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