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Charged forms of amminonitroethylene isomers – A DFT study

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Abstract

1-Amino-2-nitroethylene is a push-pull type π-structure which may be embedded some potential systems such as FOX-7 explosive. The extent of push-pull effect may be different in the constitutional isomers of aminonitroethylene. Presently, mono and diions of *cis*, *trans* and *geminal* aminonitroethylenes have been investigated within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). The collected data have revealed that all the structures considered possess exothermic heat of formation and favorable Gibbs free energy of formation values at the standard states. They are thermally favored and electronically stable with some exceptions, such as *cis*$^{+2}$ case in which the initial dication turns into *trans*$^{+2}$ during the repeated trials of structure optimization process. Various structural and quantum chemical data have been collected and discussed, including UV-VIS spectra.

1. Introduction

Aminonitroethylene isomers, as some forms of subunits, are embedded in various explosives, such as 1,1-diamino-2,2-dinitroethylene (FOX-7) which is also known as DADE or DADNE [1-3] and it is a push-pull type explosive system.

Monoaminomononitroethylenes in the form of *cis*, *trans* and *geminal* (constitutional isomers) isomers have different extents of push-pull resonance effects which dictate various structural and potential properties [4]. Amino and nitro groups have donor and acceptor properties, respectively in terms of classical resonance theory. When they are attached to a double or a triple bond, a polar system may arise depending on the positions of the donor and acceptor groups.

Spark sensitivity of explosives is an important subject. One of the causes of accidental explosion of explosives is due to static electricity. The last couple of decades have evidenced various experimental and/or theoretical publications about the spark sensitivity of explosives [5-9].

It has long been known that most of explosives are non-conductors, easily accumulate charge when contacting with and separating from other materials, and are sensitive to electrostatic discharge. Thus, explosives can be ignited by electric sparks due to local charge accumulation. Compounds such as lead styphnate are particularly sensitive, and electric discharges, rarely visible to the naked eye, are capable of igniting them. However, electrostatic discharge (ESD) sensitivity measurements show scatter [10].

The electrostatic discharge ignition of explosives, pyrotechnics, or propellants is considered to be mainly dependent upon various physical characteristics of those energetic materials. In general, all explosives, under all conditions must be considered vulnerable to generation, accumulation and discharge of static electric charge.

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The work by Skinner and coworker, shows that ESD ignition of secondary explosives tested in powdered form is primarily dependent upon the chemical characteristics of the energetic material (i.e., the decomposition rate kinetics of the materials) [11]. Explosives can be ignited by electric sparks due to local charge accumulation.

It was proposed that ignition occurs when a spark raises the temperature of the explosive particles to the point where thermal runaway occurs. Static or electrostatic discharge may supply enough energy to initiate ignition/detonation in a number of materials under some, most of the time unpredictable, circumstances. Some researches have tried to investigate the effect of ESD energy as a thermal source capable of raising the temperature of a flammable/explosable substance. However, it remains obscure how the spark heats the materials, what portion of the spark energy is being transferred and by which mechanism. How electrostatic charging affects the response of the material to thermal effects is to be contemplated in the light of further investigations and theoretical approaches.

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved by using MM2 method first which is then followed by semi empirical PM3 self consistent fields molecular orbital method [12-14]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) (restricted or unrestricted forms) [15,16]. 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]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [18] and Lee, Yang, Parr (LYP) correlation correction functional [19]. For mono anions and cations doublet state whereas the dianions and dications singlet state calculations have been performed. In the present study, 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 search has indicated that the structure of each molecule considered corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [20].

3. Results and Discussion

In the present study, monoaminomononitroethylene constitutional isomers are subjected to electrostatic (ES) charging to engender their respective mono and di ions to investigate their responses.

Figure 1 shows the optimized structures of the monoanions considered. The figure also displays the direction of the dipole moment vectors. Since their neutral analogs are push-pull type structures, mono ions of them exhibit similar behavior in many respects.

Optimized structures of the dianions considered and the ESP charges on the atoms are shown in Figure 2. Note that this time direction of the dipole moment vectors reversed compared to monoanions considered. It is worth mentioning that the ESP charges are obtained by the program which uses a numerical method that generates charges thus reproducing the electrostatic potential field from the entire wavefunction [20].

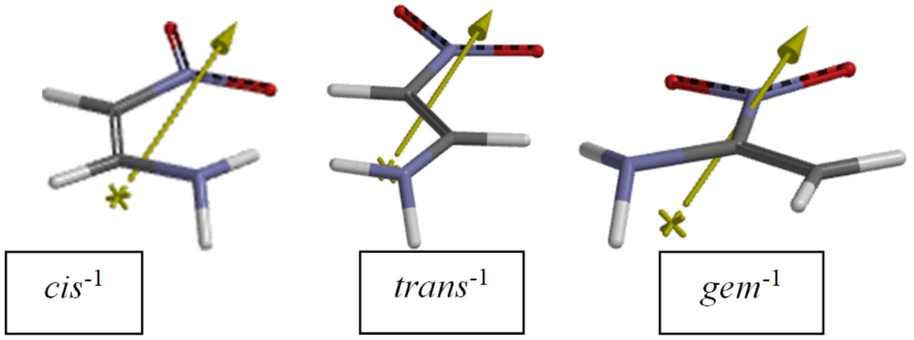


Figure 1. Optimized structures of the monoanions considered.

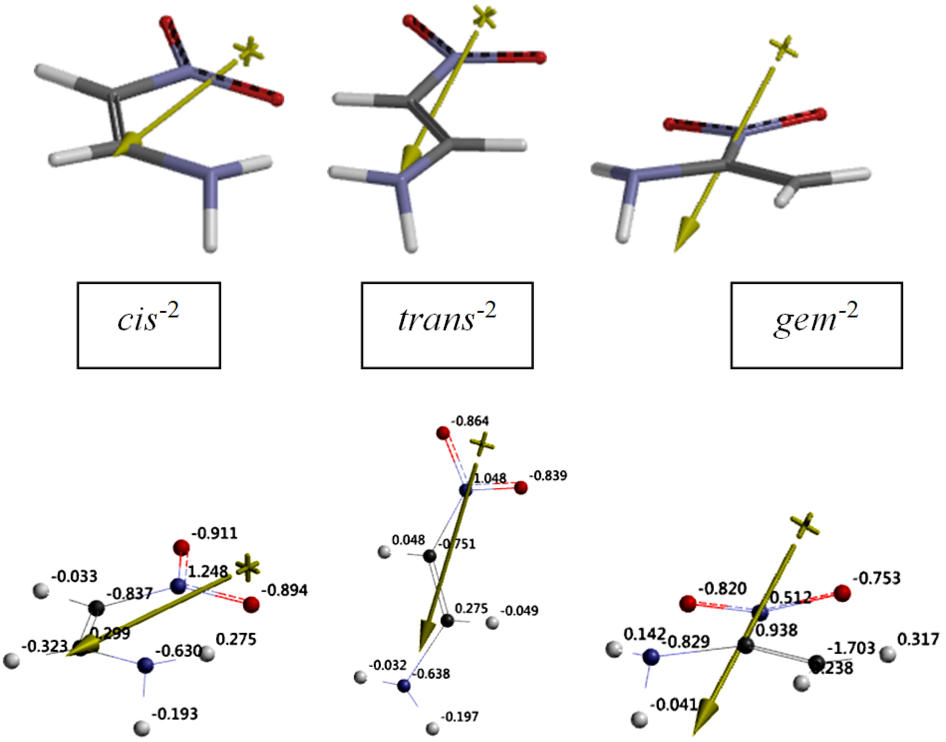


Figure 2. Optimized structures of the dianions considered and the ESP charges on the atoms of them.

Figure 3 displays the optimized structures of the monocations considered. Note that the directions of the dipole moment vectors mimic the direction of the monoanions.

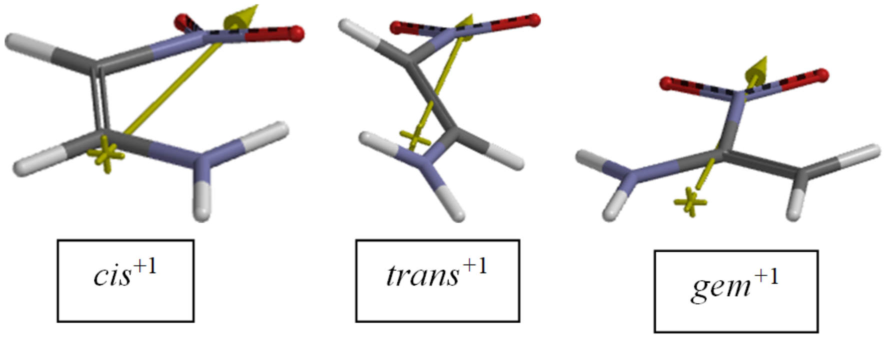


Figure 3. Optimized structures of the monocations considered.

Figure 4 shows the optimized structures of the dications considered. In this case, the initial structure of *cis*$^{+2}$ cation underwent a transformation to *trans* isomer(s) (*cis*$^{+2t}$ or *cis*$^{+2l}$). Therefore, in the figure it is labeled as *cis*$^{+2t}$ and *cis*$^{+2l}$. However, as it will be mentioned in the following paragraphs that *cis*$^{+2t}$ and *cis*$^{+2l}$ are not exactly *trans*$^{+2}$ structure. It has to be mentioned that structure initially designed as *cis*$^{+2}$ having a locked dihedral angle, in order to keep the π-bond intact, turned out to be *cis*$^{+2l}$ while the structure optimization process. Dications *cis*$^{+2t}$ and *cis*$^{+2l}$ are conformers of each other. Many properties of them are the same but some are different.

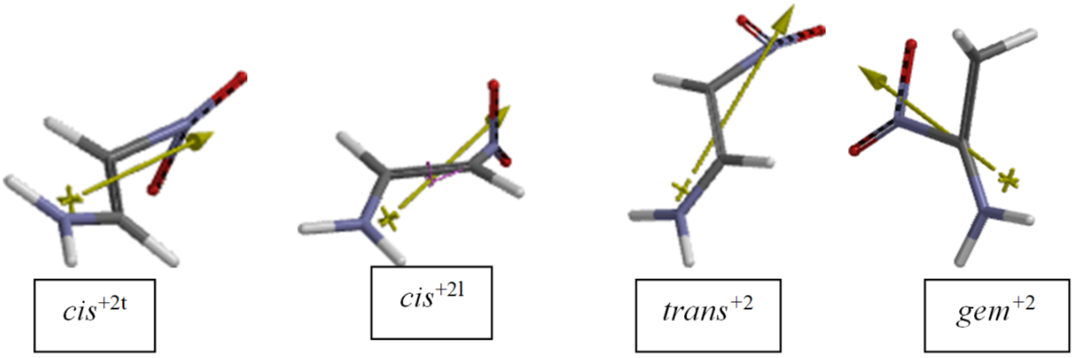


Figure 4. Optimized structures of the dications considered.

Some thermo chemical values for the monoanions considered are shown in Table 1. As seen in the table all these monoanions considered possess exothermic H^{o} and favorable G^{o} values (standard heat of formation and Gibbs free energy of formation values, respectively).

Table 1. Some thermo chemical values for the monoanions considered.

Ions	**H^{o}**	**S^{o} (J/mol^{o})**	**G^{o}**
cis^{-1}	-888793.224	313.51	-888886.698
trans^{-1}	-888772.947	324.36	-888869.656
gem^{-1}	-8888040.561	314.72	-888898.397

Energies in kJ/mol.

Table 2 shows some energy values for the monoanions considered. The data in the table shows that they are electronically stable structures. The stability order is *gem*$^{-1}$> *cis*$^{-1}$> *trans*$^{-1}$.

Table 2. Some energy values for the monoanions considered.

Ions	**E**	**ZPE**	**E$_{C}$**
cis^{-1}	-888984.71	182.31	-888802.40
trans^{-1}	-888962.66	179.62	-888783.04
gem^{-1}	-888994.67	180.56	-888814.11

Energies in kJ/mol.

Table 3 lists some thermo chemical values for the cations considered. The cations considered, as seen in the table, possess exothermic H^{o} (standard heat of formation) and favorable G^{o} (Gibbs free energy of formation) values. The algebrical order of H^{o} and G^{o} values for the monocations is *cis*$^{+1}$< *trans*$^{+1}$< *gem*$^{+1}$ whereas the dications exhibit the order of *gem*$^{+2}$< *trans*$^{+2}$< *cis*$^{+2t}$. The conformers *cis*$^{+2t}$ and *cis*$^{+2l}$ show mostly identical values.

Table 3. Some thermo chemical values for the cations considered.

Ions	**H^{o}**	**S^{o} (J/mol^{o})**	**G^{o}**
cis^{+1}	-887841.8594	311.14	-887934.6271
trans^{+1}	-887836.1988	317.06	-887930.7308
gem^{+1}	-887827.5818	310.53	-887920.1657
cis^{+2t}	-886416.1961	311.35	-886509.0268
cis^{+2l}	-886416.1987	311.35	-886509.0268
trans^{+2}	-886416.2013	311.35	-886509.0321
gem^{+2}	-886436.3102	305.10	-886527.2768

Energies in kJ/mol.

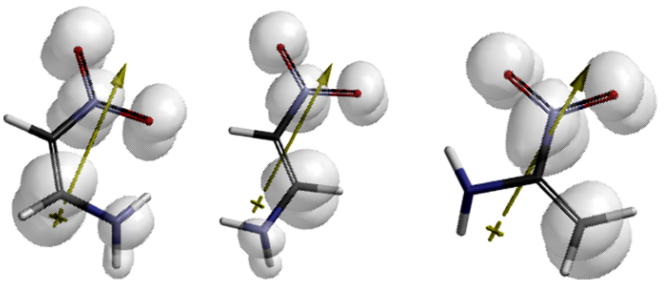
Table 4 shows some energy values for the cations considered. The data in the table reveal that the stability order for the monocations is *cis*$^{+1}$ > *trans*$^{+1}$ > *gem*$^{+1}$. On the other hand, the dications possess the order of *gem*$^{+2}$ > *trans*$^{+2}$ > *cis*$^{+2}$. It is worth mentioning that cations *cis*$^{+2t}$ and *cis*$^{+2l}$ are conformers of each other.

Table 4. Some energy values for the cations considered.

Ions	E	ZPE	E$_{C}$
cis^{+1}	-888038.71	188.19	-887850.52
trans^{+1}	-888033.10	187.84	-887845.26
gem^{+1}	-888021.71	185.32	-887836.39
cis^{+2t}	-886616.38	191.85	-886424.53
cis^{+2l}	-886616.39	191.86	-886424.53
trans^{+2}	-886616.39	191.85	-886424.54
gem^{+2}	-886635.92	191.93	-886443.99

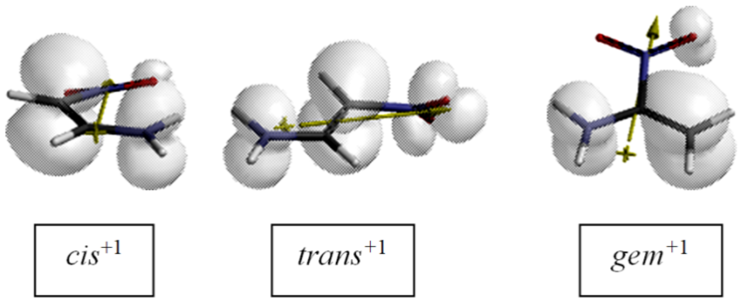
Energies in kJ/mol.

The monoanions and monocations are open-shell systems, thus certain spin density accompanies their structures. Spin densities of the monoanions and monocations considered are shown in Figures 5 and 6, respectively. As seen in the figures certain atoms do not have any spin densities, for instance in the case of *gem*$^{-1}$, atoms of the amino group do not have any spin density.



cis^{-1} *trans*$^{-1}$ *gem*$^{-1}$

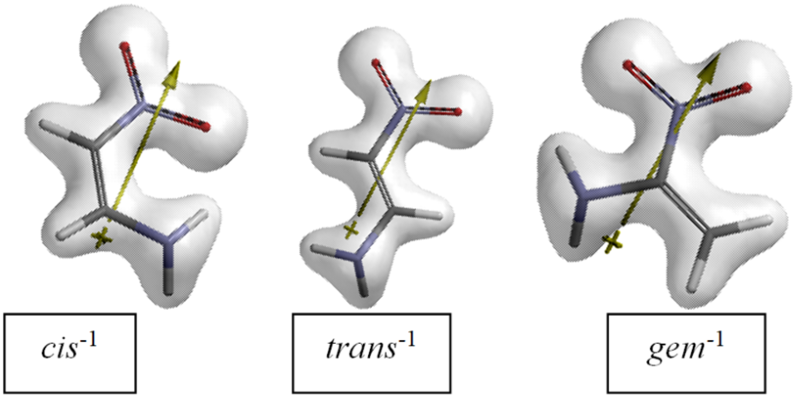
Figure 5. Spin densities of the mono anions considered.



cis^{+1} $trans^{+1}$ gem^{+1}

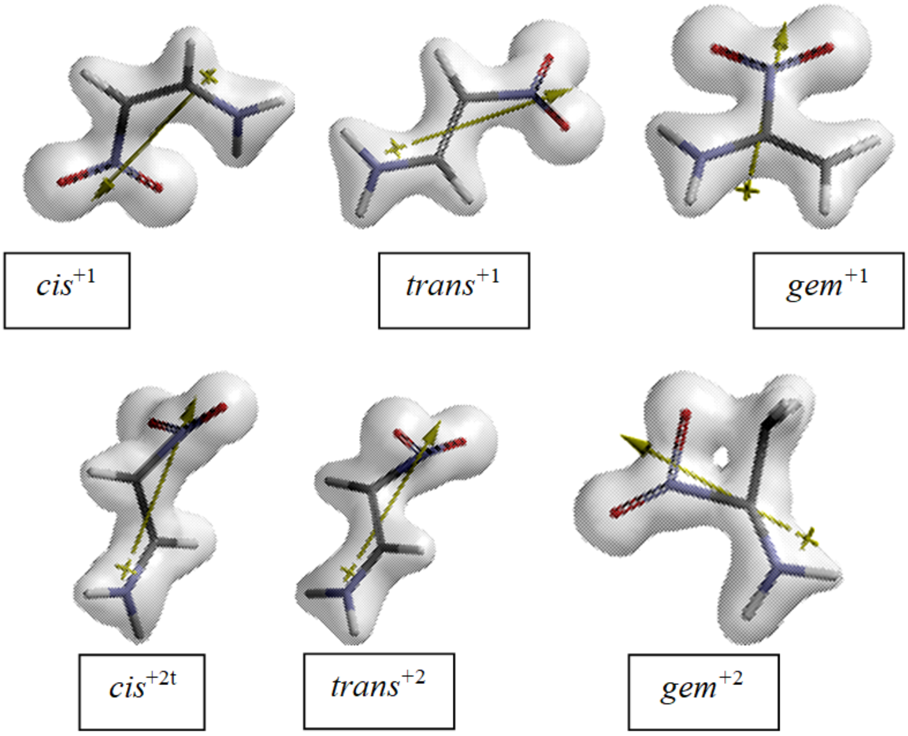
Figure 6. Spin densities of the monocations considered.

Figure 7 shows the bond densities of some of the monoanions considered whereas bond densities of the cations considered are included in Figure 8. Note that in the case of *gem*$^{+2}$ considerable amount of density exists between the nitro and methylene groups.



cis^{-1} $trans^{-1}$ gem^{-1}

Figure 7. Bond densities of some of the monoanions considered.



cis^{+1} $trans^{+1}$ gem^{+1}

cis^{+2t} $trans^{+2}$ gem^{+2}

Figure 8. Bond densities of the cations considered.

Some properties of the monoanions considered are listed in Table 5. Note 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 [20]. Their PSA values differ from each other, meaning that the same kind of atoms might be influenced by electronic factors differently at different positions. 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). Extending the log P notion/calculations to ions, as seen in Tables 6 and 7, *gem*$^{-1}$ and *gem*$^{+1}$ possess positive log P values in contrast to other anions and cations considered. As for the Cv values, generally the anions considered have greater values compared to the cations of the respective structures.

Table 5. Some properties of the monoanions considered.

Ions	Dipole (debye)	Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality	Log P	Cv (J/molº)
cis^{-1}	5.47	105.79	80.04	61.668	1.18	-0.22	73.09
trans^{-1}	6.85	109.30	80.88	66.058	1.21	-0.22	73.96
gem^{-1}	4.52	106.92	80.29	62.947	1.19	0.40	77.10

Some properties of the cations considered are listed in Table 6.

Table 6. Some properties of the cations considered.

Ions	Dipole (debye)	Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality	Log P	Cv (J/molº)
cis^{+1}	8.23	104.85	79.35	60.033	1.17	-0.22	69.87
trans^{+1}	9.37	108.09	79.89	64.226	1.20	-0.22	70.17
gem^{+1}	7.85	106.43	79.93	61.784	1.19	0.40	73.72
cis^{+2t}	7.75	106.34	78.39	63.387	1.20	-0.22	66.91
cis^{+2l}	7.75	106.34	78.39	63.386	1.20	-0.22	66.90
trans^{+2}	7.75	106.34	78.39	63.388	1.20	-0.22	66.90
gem^{+2}	7.54	103.33	77.13	59.766	1.18	0.40	67.18

Table 7 lists the HOMO, LUMO energies and Δε values for the anions considered. Note that all the anions have positive HOMO and LUMO energies. The order of HOMO energies is *gem*$^{-1}$< *cis*$^{-1}$< *trans*$^{-1}$< *trans*$^{-2}$ < *cis*$^{-2}$ < *gem*$^{-2}$, whereas the LUMO energies follow the order of *trans*$^{-1}$< *cis*$^{-1}$< *gem*$^{-1}$ < *cis*$^{-2}$ < *trans*$^{-2}$< *gem*$^{-2}$. The orders reveal that the doubly charged anions have more positive energies as compared to the singly charged anions. As a consequence of the HOMO and LUMO energies the order of interfrontier molecular orbital energy gap, Δε, ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) values exhibit the order of *cis*$^{-2}$< *trans*$^{-2}$< *gem*$^{-2}$< *trans*$^{-1}$< *cis*$^{-1}$< *gem*$^{-1}$. Namely doubly charged anions have much narrower Δε values compared to the singly charged anions.

Table 7. The HOMO, LUMO energies and Δε values for the anions considered.

Ions	HOMO	LUMO	Δε
cis^{-1}	102.73	262.10	159.37
$trans^{-1}$	103.97	230.36	126.39
gem^{-1}	63.07	270.36	207.29
cis^{-2}	427.53	492.71	65.18
$trans^{-2}$	425.65	494.13	68.48
gem^{-2}	464.22	536.73	72.51

Energies in kJ/mol.

Calculated (time dependent DFT) UV-VIS spectra of the anions considered are displayed in Figure 9. In general, as the absolute value of negative charge increases from 1 to 2, the spectra shift to visible region. Also note that direction of the dipole moment vectors are reversed as the absolute value of negative charge increases (see Figure 2). Pay attention to resemblance between the spectrums of cis^{-2} and $trans^{-2}$ anions.

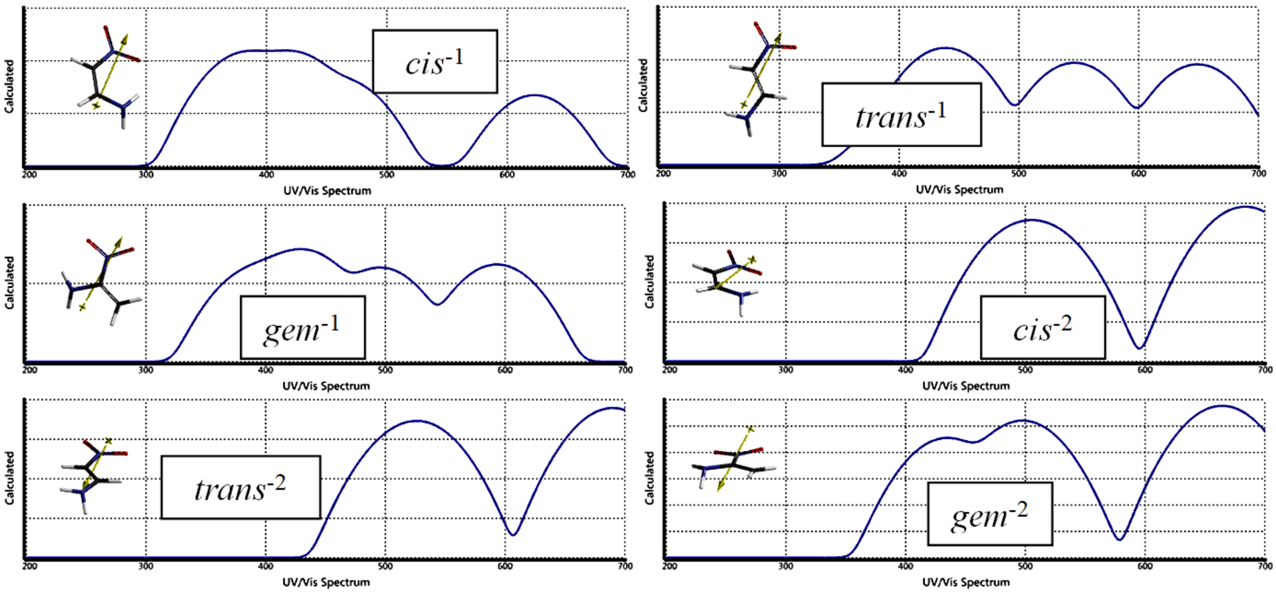


Figure 9. Calculated UV-VIS spectra of the anions considered.

Table 8 lists the HOMO, LUMO energies and Δε values for the cations considered. The algebrical orders of the HOMO and the LUMO energies are $trans^{+1} < cis^{+1} < gem^{+1} < trans^{+2} < cis^{+2t} < cis^{+2l} < gem^{+2}$. Consequently, Δε values follow the order of $gem^{+2} < gem^{+1} < trans^{+1} < cis^{+1} < cis^{+2t} < cis^{+2l} < trans^{+2}$.

Table 8. The HOMO, LUMO energies and Δε values for the cations considered.

Ions	HOMO	LUMO	Δε
cis^{+1}	-1351.40	-810.73	540.67
$trans^{+1}$	-1314.42	-780.51	533.91
gem^{+1}	-1377.10	-846.34	530.76
cis^{+2t}	-2045.30	-1477.18	568.12
cis^{+2l}	-2045.21	-1477.01	568.20
$trans^{+2}$	-2045.23	-1477.09	568.14
gem^{+2}	-2093.56	-1590.46	503.10

Energies in kJ/mol.

Figure 10 shows the calculated (TDDFT) UV-VIS spectra of the cations considered. Note that structures labeled as cis^{+2t} or cis^{+2l} have the same spectra as $trans^{+2}$ because while the optimization process, initially cis^{+2} cation has been converted to cis^{+2t} (or cis^{+2l}) which eventually seemed $trans^{+2}$.

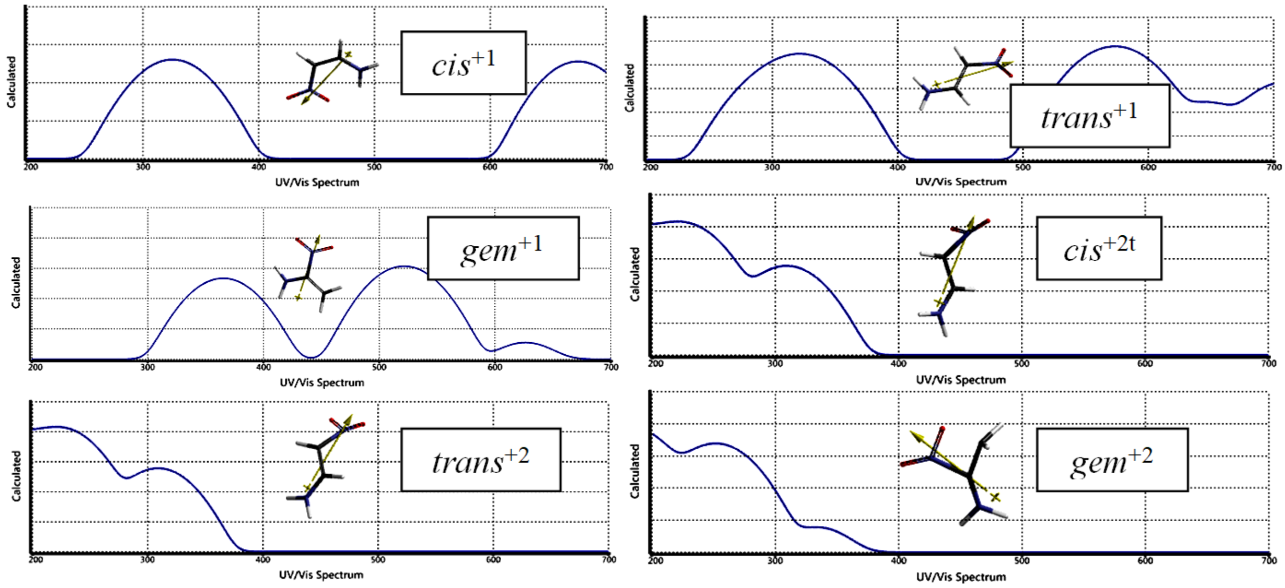


Figure 10. Calculated UV-VIS spectra of the cations considered.

Figure 11 shows some of the molecular orbital energy levels of certain anions and cations considered. Of them, cis^{-2} and $trans^{-2}$ possess almost identical molecular energy spectra for unoccupied and high occupied molecular orbital energies but they greatly differ below HOMO-6 level downwards. As seen in the figure structures labeled as cis^{+2t}, cis^{+2l} and $trans^{+2}$ exhibit identical energy spectrums, so although optimization initially starts with different structures (as cis^{+2} and $trans^{+2}$) during the process as the consequence of positive charge the π-bond of cis^{+2} ruptures then it isomerizes to $trans^{+2}$ structure.

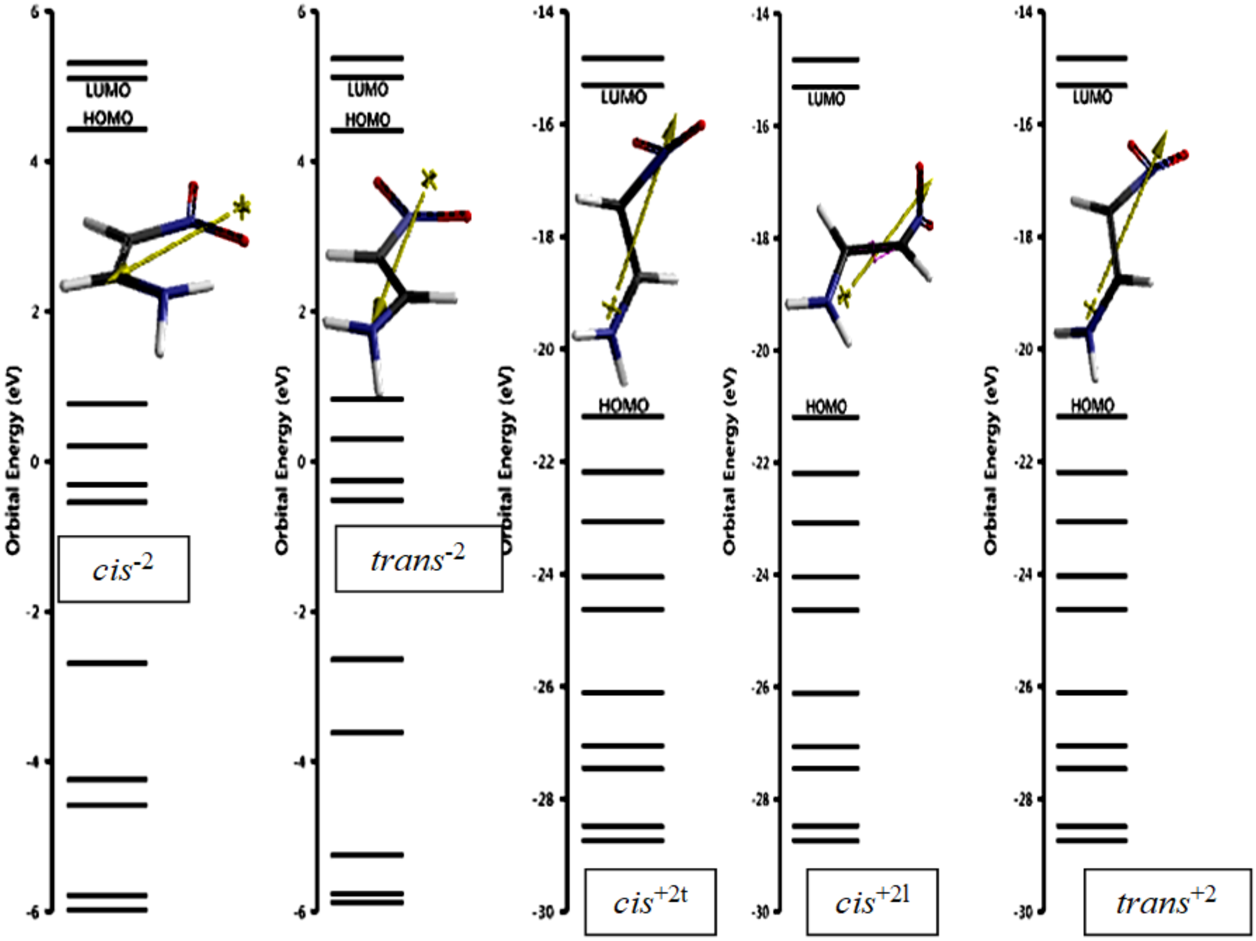


Figure 11. Some of the molecular orbital energy levels of certain anions and cations considered.

4. Conclusion

The present computational study considered mono and di anions and cations of aminonitroethylene constitutional isomers within the restrictions of DFT study at the level of B3LYP/6-311++G(d,p). All the ionic structures considered possess exothermic H° and favorable G° values. They are electronically stable with the exception of *cis*$^{+2}$ which during the optimization process it isomerizes to *trans*$^{+2}$ structure. Although, *cis*$^{-2}$ and *trans*$^{-2}$ spectra greatly resemble each other their inner lying molecular orbital energy levels have quite different spacing. In general, aminonitroethylene isomers are resistive to charging thus the monoanions and cations are stable. However, direction of the dipole moments of the dianions is opposite to dipole moment of the respective monoionic structure. Mono cations are also stable but dication of *cis* isomer undergoes to dication of *trans* aminonitroethylene during the optimization.

The present study shows the influence of electrostatic effects on the constitutional isomers of aminonitroethylene in the absence of any thermal effect of a spark.

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