Earthline Journal of Chemical Sciences
E-ISSN: 2581-9003; CODEN: EJCSB4
Volume 13, Number 1, February 2026, Pages 1-12
https://doi.org/10.34198/ejcs.13126.01.001012

Push-pull interactions in cis/trans diaminodinitro ethylenes – DFT treatment

Lemi Türker

Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey
e-mail: lturker@gmail.com; lturker@metu.edu.tr

Abstract

The *cis* and *trans* isomers of 1,2-diamino-1,2-dinitroethylene are even alternant systems and partly exist in structure of FOX-7 explosive. Presently, they have been investigated thoroughly within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). The collected data have revealed that the optimized structures of them have exothermic heats of formation and favorable Gibbs free energy of formation values. They are thermally favored and electronically stable at the standard states. Various structural and quantum chemical data have been collected and discussed, including IR and UV-VIS spectra.

1. Introduction

Cis and *trans*-isomers of 1,2-diamino-1,2-dinitroethylenes are structures which could be constructed from structure of FOX-7 (1,1-diamino-2,2-dinitroethylene) by certain structural modifications. FOX-7 is a novel insensitive high-energy material exhibiting good thermal stability and low sensitivity. In addition to that, it possesses excellent application performance among the solid propellants and insensitive ammunitions. It exhibits abundant chemical reactivity [1,2]. FOX-7 is much less sensitive than RDX in terms of impact, friction, and electrostatic discharge sensitivities.

FOX-7 is classified as a push-pull type alkene having two electron-donating substituents (NH_2) on one end of C=C double bond and with two electron-accepting substituents (NO_2) at the other end [3,4]. This push-pull effect is of decisive influence on both the dynamic behavior and the chemical reactivity of this class of compounds [3,5]. Through the decades various scientists have investigated different aspects of push-pull effect [6-13].

Presently considered isomeric aminonitroethylenes combine the effects of resonance-donating NH_2 (strongly electron donating) and the inductively and mesomerically electron-withdrawing NO_2 groups in a molecular framework containing polarizable electronic charge.

In the present density functional study, push-pull interactions in *cis*/*trans* diaminodinitro ethylenes have been investigated.

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [14-16]. Afterwards, the structure optimizations have been achieved within the

Received: October 17, 2025; Accepted: November 14, 2025; Published: November 18, 2025
Keywords and phrases: diaminodinitro ethylenes, push-pull, explosive, density functional.

framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-311++G(d,p) [17,18]. 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 [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]. 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 cleavages occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [22].

3. Results and Discussion

Figure 1 shows some resonance forms of the isomers considered. As seen in the figure the amino and the nitro groups on same carbon atom are crossly conjugated in contrast to the case in which the donor and the acceptor groups are at opposite ends of the ethylenic π-structure.

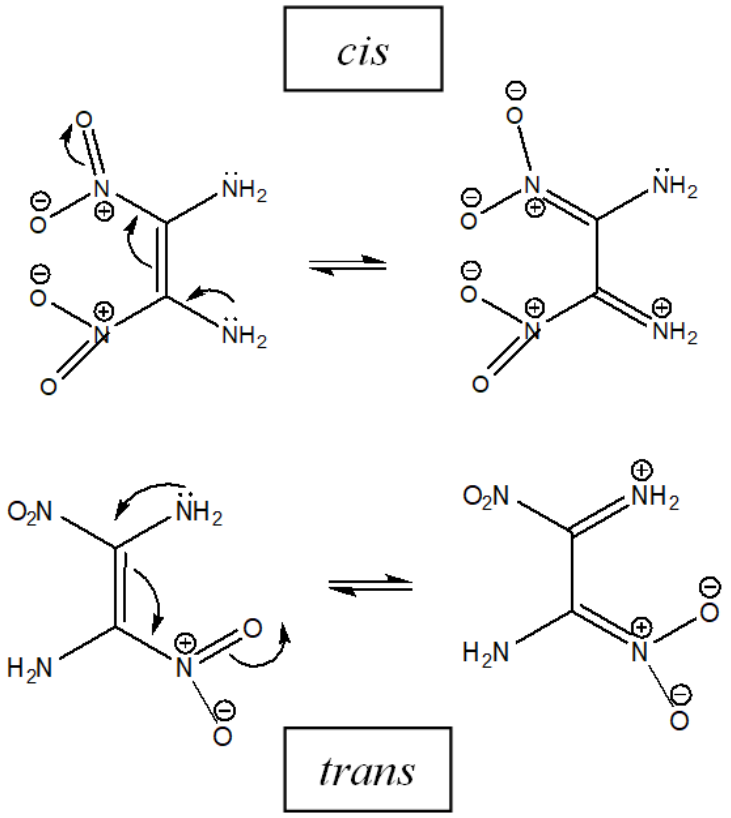

Figure 1. Some resonance forms of the isomers considered.

Optimized structures as well as the direction of the dipole moment vectors of the *cis* and *trans* isomers considered are shown in Figure 2. As seen in the figure the *cis* isomer possesses more effectively twisted/puckered groups compared to the *trans* isomer. Obviously this effect is expected to influence the conjugation in disfavorable manner (partly broken conjugation). Also note that the dipole moment vector of *cis* isomer lies in the molecular plane in contrast to the respective vector of the *trans* isomer which is perpendicular to the molecular plane. The donor and acceptor groups of the *trans* isomer form hydrogen bonds in between.

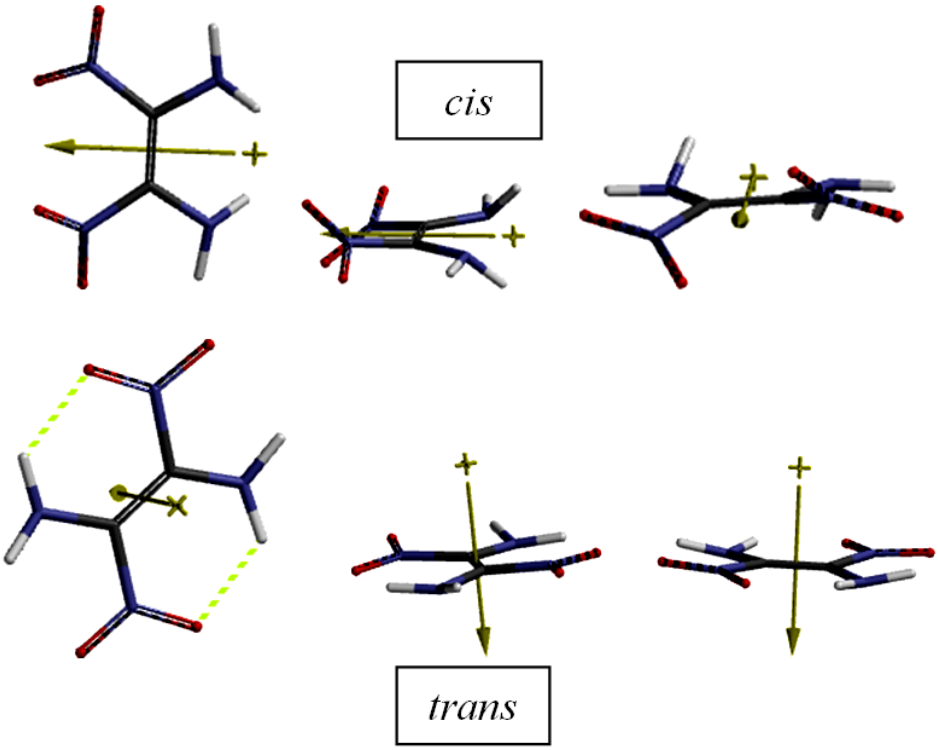

Figure 2. Optimized structures of the *cis* and *trans* isomers considered (three different views).

Figure 3 shows the ESP charges on atoms of the isomers considered. It is note worthy 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 [22].

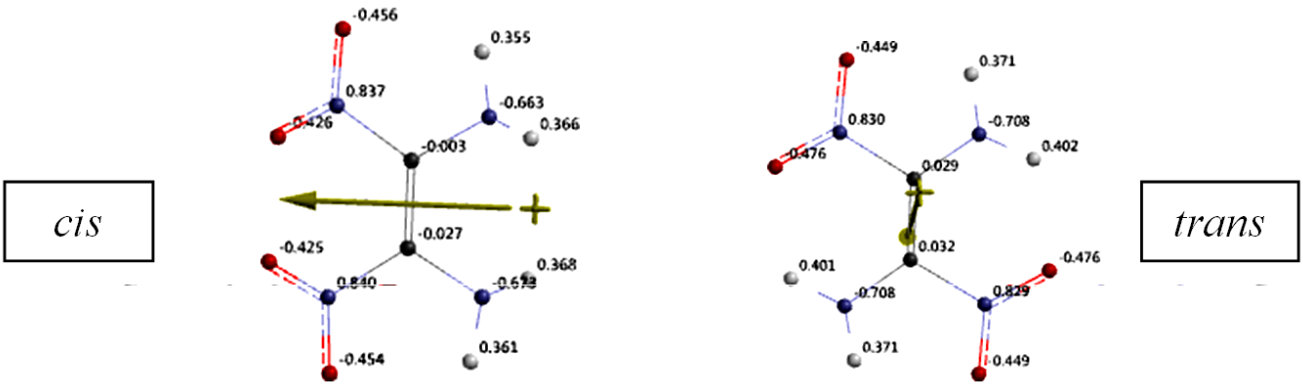

Figure 3. ESP charges on atoms of *cis* and *trans* isomers considered.

Figure 4 displays the electrostatic potential (ESP) maps of *cis* and *trans* isomers considered where negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps. In the *cis* isomer, one of the two NH_2 moieties is appreciably more positive compared to the other one. Whereas in the *trans* case the difference is not so pronounced.

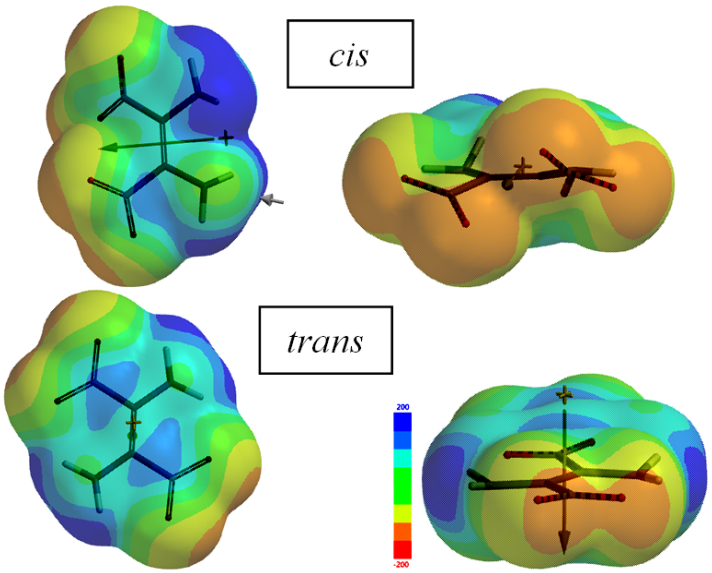

Figure 4. Electrostatic potential maps of *cis* and *trans* isomers considered (two different views).

Figure 5 displays the calculated bond lengths (Å) of the isomers considered. The *trans* isomer possesses a longer C-C bond length as compared to the *cis* isomer. The difference arises from the fact that ease of flow of electrons from donor group(s) to the acceptor(s) groups which is due to the configurational and conformational factors associated with the respective groups.

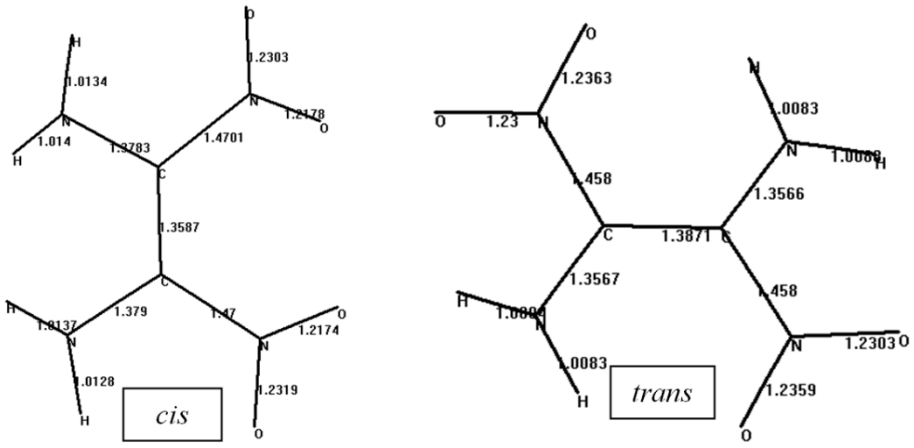

Figure 5. Calculated bond lengths (Å) of the isomers considered.

Table 1 contains some thermo chemical properties of the isomers considered. Whereas, Table 2 includes some energies of them. The data in Table 1 reveal that the standard heat of formation (H°) values of the isomers are exothermic and they are favored according to their G° (Gibbs free energy of formation) values. The algebraic order of H° and G° values are *trans*< *cis*. Whereas S° values follow the order of *cis*> *trans*.

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

Isomer	H° (au)	S° (J/mol°)	G° (au)
cis	-1571065.516	379.27	-1571178.598
trans	-1571114.529	373.16	-1571225.789

Energies in kJ/mol.

The data in Table 2 reveal that they are all electronically stable structures. The stability order is *trans*> *cis*. Probably favorable steric factors and the hydrogen bondings possible between the donor and acceptor groups make the *trans* isomer more stable than the *cis* isomer. Note that E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively [22].

Table 2. Some energies of the isomers considered.

Isomer	E	ZPE	E_C
cis	-1571315.38	239.45	-1571075.93
trans	-1571363.57	238.95	-1571124.62

Energies in kJ/mol.

Calculated IR spectrums of the isomers considered are displayed in Figure 6. The asymmetric and symmetric N-H bond stretches of the *cis* isomer occur at 3614 cm^{-1} and 3511 cm^{-1}, respectively whereas they are at 3681 cm^{-1} and 3550 cm^{-1} in case of the trans isomer. The carbon-carbon bond stretching of the *cis* isomer happens at 1690 cm^{-1}. The peak at 1598 cm^{-1} is the coupled vibrations of asymmetric NO_2 stretching and NH_2 scissoring of the *cis* isomer. Whereas the symmetric stretchings of NO_2 and scissoring of NH_2 occur at 1575 cm^{-1}. The spectrum of the *trans* isomer is relatively simple, various vibrations occur, in coupled manner, at 1512, 1293 and 1157 cm^{-1}.

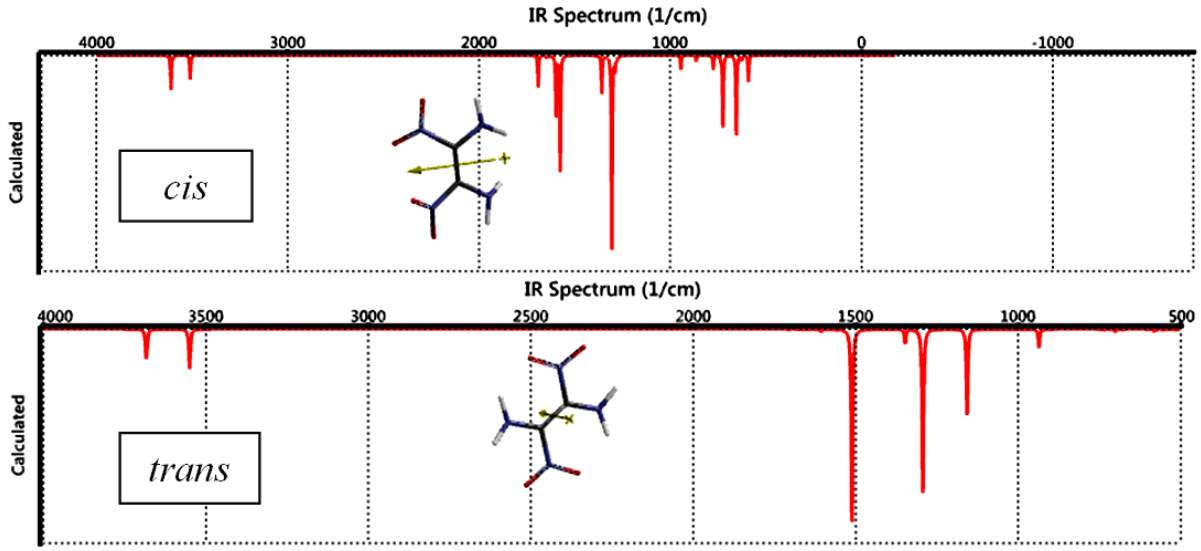

Figure 6. Calculated IR spectrums of the isomers considered.

Table 3 includes some properties of the isomers of interest. As expected, the *trans* isomer has much less value for the dipole moment. The polarizability is defined according to a multivariable formula which is a function of Van der Waals volume and hardness [22]. The later one is dictated by molecular orbital energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital energies. 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. On the other hand, a negative value for log P means the compound has a higher affinity for the aqueous phase (it is more hydrophilic).

Table 3. Some properties of the isomers of interest.

Isomer	Dipole moment	Polarizability	Cv (J/mol°)	Area (Å²)	Volume (Å³)	PSA (Å²)	Ovality
cis	6.50	49.68	108.48	144.23	111.66	123.344	1.29
trans	0.51	49.65	111.03	137.60	109.67	114.559	1.24

Dipole moments in debye units. Polarizabilities in 10^{-30} m^3 units. Log P: -0.31 for the both.

Figure 7 shows the bond densities of the isomers considered. The bond density contains fewer electrons in total and demarks atomic connectivity.

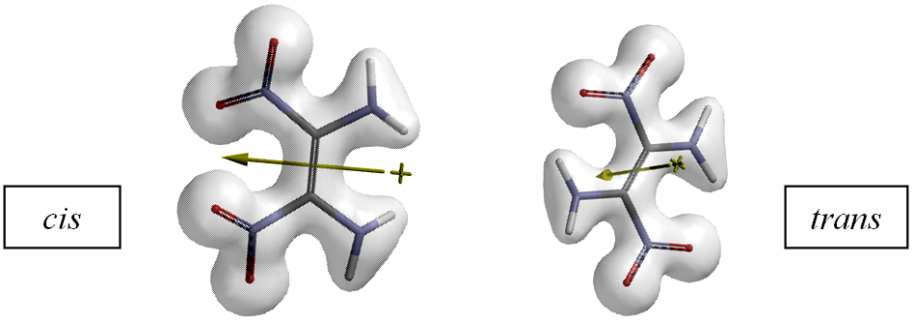

Figure 7. Bond densities of the isomers considered.

Figure 8 shows the local ionization 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. Note 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.

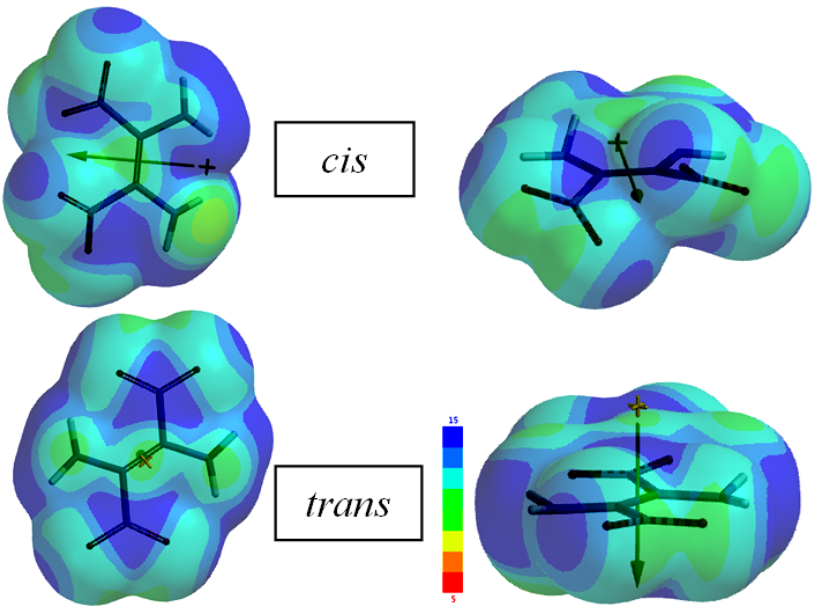

Figure 8. Local ionization maps of the isomers considered (two different views).

The LUMO maps of the isomers presently considered are shown in Figure 9. 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. It is to be

noted that the LUMO and NEXTLUMO (LUMO+1) are the major orbitals directing the molecule towards the attack of nucleophiles [22]. Positions where the greatest LUMO coefficient exists is the most vulnerable site in nucleophilic reactions.

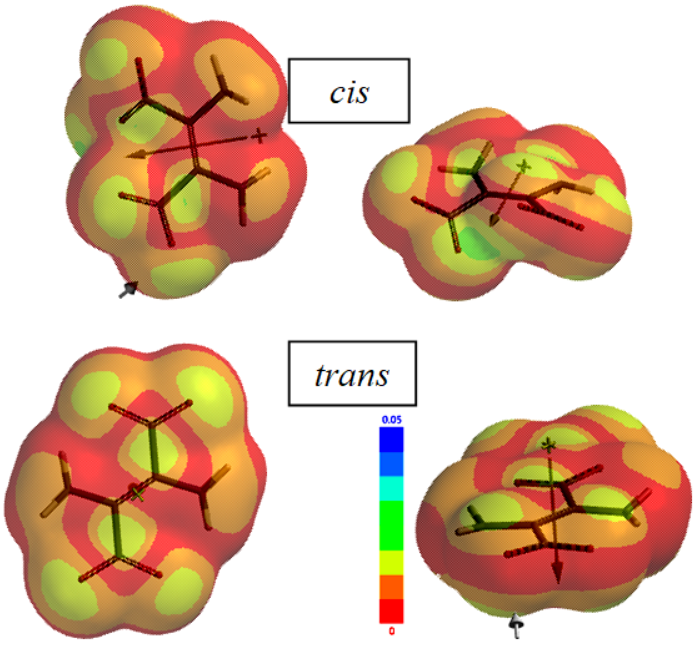

Figure 9. The LUMO maps of the isomers considered (two different views).

Some of the molecular orbital energy levels of the isomers considered are displayed in Figure 10. Note that that the inner lying occupied molecular orbitals are assumed to be responsible for the thermal stability of the compound.

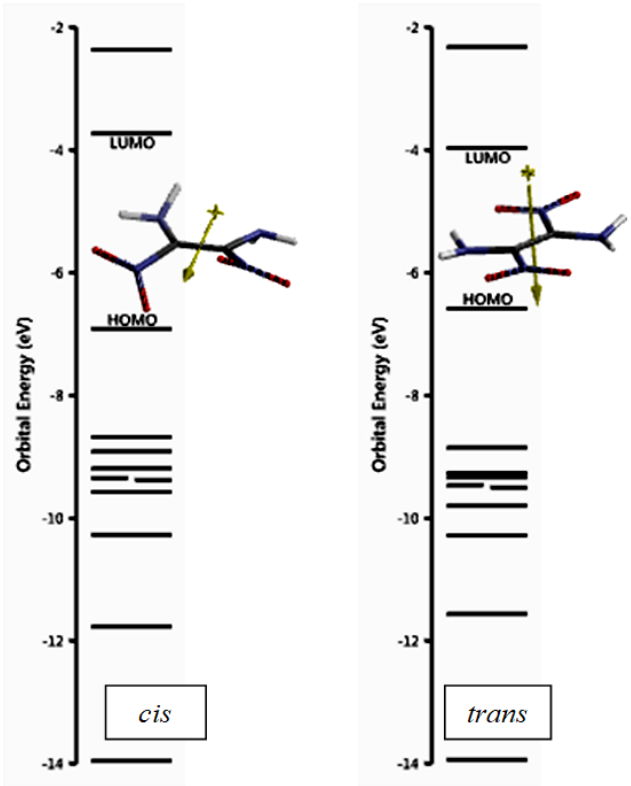

Figure 10. Some of the molecular orbital energy levels of the isomers considered.

The HOMO and LUMO energies and interfrontier molecular orbital energy gap, Δε (Δε = ε_{LUMO}-ε_{HOMO}) values of the isomers considered are included in Table 4.

Table 4. The HOMO and LUMO energies and Δε values of the isomers considered.

Isomer	HOMO	LUMO	Δε
cis	-667.24	-359.31	307.93
trans	-634.79	-382.67	252.12

Energies in kJ/mol.

The algebraic orders of the HOMO and LUMO energies are *cis* < *trans* and *trans* < *cis*, respectively. Whereas, the interfrontier molecular orbital energy gap values, Δε, possess the order of *cis*> *trans.* Thus, the configuration and conformation of the donor and acceptor groups highly affect the extended conjugation which is responsible for the HOMO-LUMO energy separation. The *trans* isomer has smaller interfrontier molecular energy gap value. Thus, any ballistic property which correlates with the narrowness of it should have the highest value between the isomers considered. An example is the impact sensitivity, that is narrower the gap, the explosive becomes more sensitive to an impact stimulus [23,24].

Figures 11 and 12 stand respectively for the HOMO and LUMO patterns of the isomers considered. As seen in the figures a π-symmetry exists in both types of the orbitals. As seen in the figure, the amino groups in the *cis* and *trans* isomers have larger contribution into the HOMO orbital than the nitro groups.

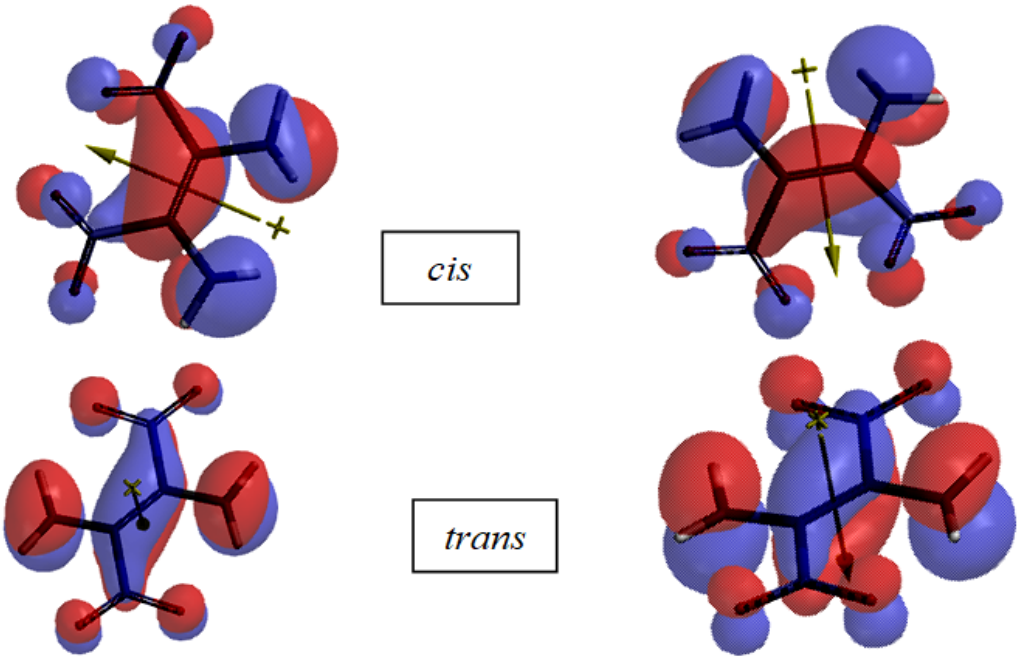

Figure 11. The HOMO pattern of the isomers considered (two different views).

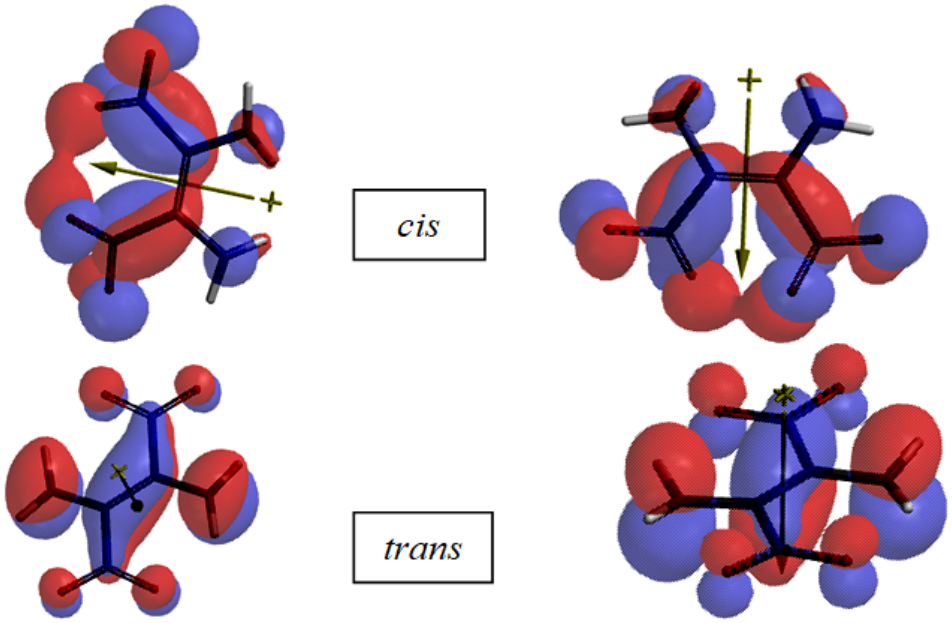

Figure 12. The LUMO pattern of the isomers considered (two different views).

As for the LUMO orbitals, the amino groups again contribute more than the nitro groups in the case of *trans* isomer whereas the contributions are quite comparable in the *cis* isomer.

Figure 13 stands for the NEXTHOMO (HOMO-1) and NEXTLUMO (LUMO+1) patterns of the isomers considered. In each case the contribution coming from the amino groups is comparably less than the contribution of the nitro groups.

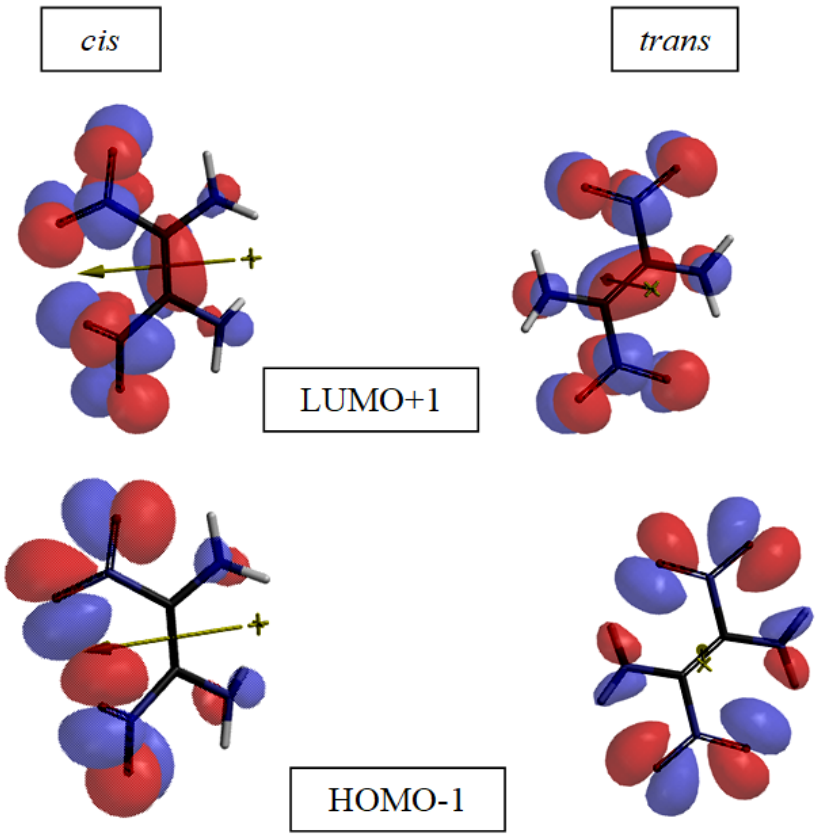

Figure 13. The NEXTHOMO and NEXTLUMO patterns of the isomers considered.

Time dependent density functional UV-VIS spectra of the isomers of interest are shown in Figure 14. The λ_{max} values of them are listed in Table 5.

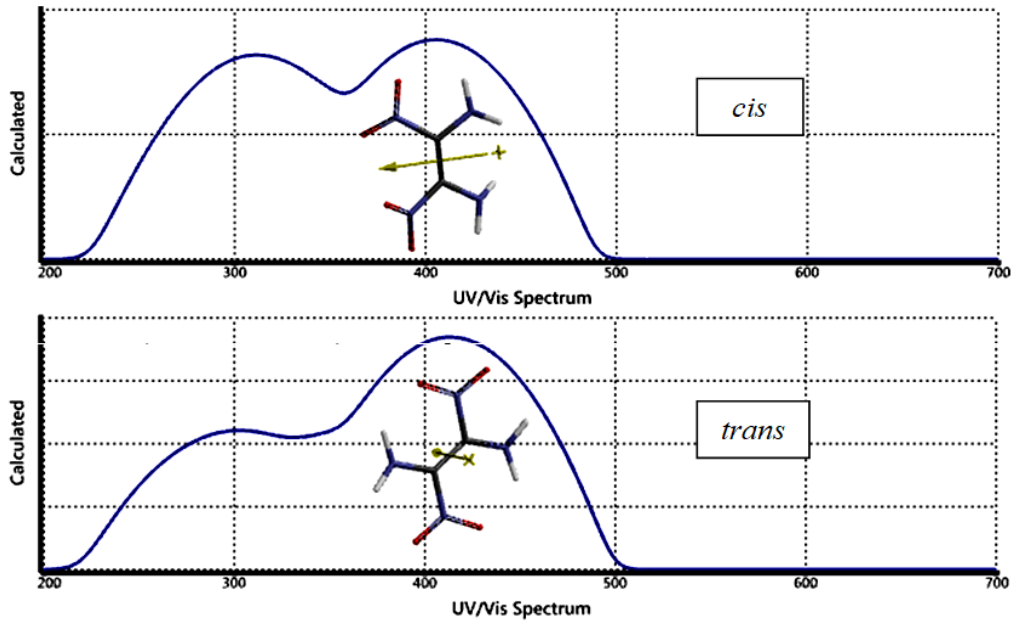

Figure 14. Time dependent density functional UV-VIS spectra of the isomers of interest.

Table 5. The calculated λ_{max} values of the isomers.

Isomers	λ_{max}
cis	310.73, 405.49
trans	298.01, 412.24

λ_{max} values in nm.

The *cis-trans* isomerism affects both of the peaks of the *cis* isomer, although there is no appreciable bathochromic effect, the intensities are greatly vary. The calculated intensities of the peaks are related to magnitudes of the transition moments between the orbitals involved which vary from isomer to isomer [4,25].

4. Conclusion

The present computational study considered *cis* and *trans* isomers of 1,2-diamino-1,2-dinitroethylene within the restrictions of DFT study at the level of B3LYP/6-311++G(d,p). Both of the isomers possess exothermic H^o and favorable G^o values. They are electronically stable. The *trans* isomer is found to be more stable than the *cis,* probably due to favorable steric factors and the hydrogen bondings which is possible between the donor and acceptor groups. In spite of the fact that these are isomeric structures, the configuration and conformation of the donor and acceptor groups affect the push-pull interactions which cause various differences to arise when some properties are considered, such as IR and UV-VIS spectra.

References

[1] Zhang, Y., Sun, Q., Xu, K., Song, J., & Zhao, F. (2016). Review on the reactivity of 1,1-diamino-2,2-dinitroethylene (FOX-7). *Propellants Explos. Pyrotech., 41*, 35–52. https://doi.org/10.1002/prep.201500065

[2] Baum, K., Nguyen, N.V., Gilardi, R., Flippen-Anderson, J.L., & George, C. (1992). Nitration of 1,1-diamino-2,2-dinitroethylenes. *Journal of Organic Chemistry, 57*, 3026-3030. https://doi.org/10.1021/jo00037a015

[3] Kleinpeter, E. (2006). Push-pull alkenes: Structure and π-electron distribution. *Journal of the Serbian Chemical Society*, *71*(1), 1-17. https://doi.org/10.2298/JSC0601001K

[4] Anslyn, E.V., & Dougherty, D.A. (2006). *Modern physical organic chemistry*. Sausalito, California: University Science Books.

[5] Dykstra, C.E., Frenking, G., Kim, K., & Scuseria, G. (2015). *Theory and applications of computational chemistry: The first forty years*. New York: Elsevier.

[6] Yanai, H., Suzuki, T., Kleemiss, F., Fukaya, H., Malaspina, L.A., Grabowsky, S., & Matsumoto, T. (2019). Chemical bonding in polarized push-pull ethylenes. *Angewandte Chemie International Edition*, *58*(26), 8839-8844. https://doi.org/10.1002/anie.201904176

[7] Shainyan, B.A., Fettke, A., & Kleinpeter, E. (2008). Push-pull vs captodative aromaticity. *J. Phys. Chem. A*, *112*(43), 10895-10903. https://doi.org/10.1021/jp804999m

[8] Pappalardo, R.R., Marcos, E.S., Ruiz-Lóapez, M.F., & Rinaldi, D. (1991). Theoretical study of simple push-pull ethylenes in solution. *Journal of Physical Organic Chemistry*, *4*(3), 41-148. https://doi.org/10.1002/poc.610040304

[9] Politzer, P., Concha, M.C., Grice, M.E., Murray J.S., Lane, P., & Habibollazadeh, D. (1998). Computational investigation of the structures and relative stabilities of amino/nitro derivatives of ethylene. *Journal of Molecular Structure* (*Theochem*), *452*, 75- 83. https://doi.org/10.1016/S0166-1280(98)00136-5

[10] Kleinpeter, E., Klod, S., & Rudorf, Wolf-Dieter. (2004). Electronic state of push-pull alkenes: An experimental dynamic NMR and theoretical *ab ınitio* MO study. *J. Org. Chem.*, *69*(13), 4317-4329. https://doi.org/10.1021/jo0496345

[11] Ababneh-Khasawneh, M., Fortier-McGill, B.E., Occhionorelli, M.E., & Bain, A.D. (2011). Solvent effects on chemical exchange in a push-pull ethylene as studied by NMR and electronic structure calculations. *J. Phys. Chem. A*, *115*(26), 7531-7537. https://doi.org/10.1021/jp201885q

[12] Türker, L., Bayar, Ç.Ç., & Balaban, A.T. (2010). A DFT study on push-pull (aminonitro) fulminenes and hexahelicenes. *Polycyclic Aromatic Compounds*, *30*(2), 91-111. https://doi.org/10.1080/10406631003756005

[13] Türker, L., & Bayar, Ç.Ç. (2010). A DFT study on disubstituted R-hexahelicenes having donor/acceptor groups. *Procedia Computer Science*, *1*(1), 1155-1164. https://doi.org/10.1016/j.procs.2010.04.129

[14] Stewart, J.J.P. (1989). Optimization of parameters for semi-empirical methods I. *J. Comput. Chem.*, *10*, 209-220. https://doi.org/10.1002/jcc.540100208

[15] Stewart, J.J.P. (1989). Optimization of parameters for semi-empirical methods II. *J. Comput. Chem., 10*, 221-264. https://doi.org/10.1002/jcc.540100209

[16] Leach, A.R. (1997). *Molecular modeling*. Essex: Longman.

[17] Kohn, W., & Sham, L.J. (1965). Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, *140*, 1133-1138. https://doi.org/10.1103/PhysRev.140.A1133

[18] Parr, R.G., & Yang, W. (1989). *Density functional theory of atoms and molecules*. London: Oxford University Press.

[19] Becke, A.D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys.Rev. A*, *38*, 3098-3100. https://doi.org/10.1103/PhysRevA.38.3098

[20] Vosko, S.H., Wilk, L., & Nusair, M. (1980). Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys*., *58*, 1200-1211. https://doi.org/10.1139/p80-159

[21] Lee, C., Yang, W., & Parr, R.G. (1988). Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B*, *37*, 785-789. https://doi.org/10.1103/PhysRevB.37.785

[22] SPARTAN 06 (2006). Wavefunction Inc. Irvine CA, USA.

[23] Anbu, V., Vijayalakshmi, K.A., Karunathan, R., Stephen, A.D., & Nidhin, P.V. (2019). Explosives properties of high energetic trinitrophenyl nitramide molecules: A DFT and AIM analysis. *Arabian Journal of Chemistry*, *12*(5), 621-632. https://doi.org/10.1016/j.arabjc.2016.09.023

[24] Badders, N.R., Wei, C., Aldeeb, A.A., Rogers, W.J., & Mannan, M.S. (2006). Predicting the impact sensitivities of polynitro compounds using quantum chemical descriptors. *Journal of Energetic Materials*, *24*, 17-33. https://doi.org/10.1080/07370650500374326

[25] Turro, N.J. (1991). *Modern molecular photochemistry.* Sausalito: University Science Books.