Earthline Journal of Chemical Sciences
E-ISSN: 2581-9003; CODEN: EJCSB4
Volume 9, Number 1, 2023, Pages 1-16
https://doi.org/10.34198/ejcs.9123.116

Effect of Aluminum on 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) - A 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

DNNC is an explosive as well as an oxidant for propellants and pyrotechnics. It possesses C-NO_2 and N-NO_2 bonds. In the present study, DNNC and aluminum interaction has been investigated within the limitations of density functional theory at the level of unrestricted B3LYP/6-31++G(d,p). The composites having formula of DNNC+Al and DNNC+2Al are considered. Since aluminum has an unpaired electron in the ground state, various multiplicities arise for the composites of present interest. Some geometrical, physico chemical, quantum chemical and some spectral data have been obtained and discussed. The calculations within the constraints of the theory and the basis set employed have indicated that DNNC+Al (doublet) keeps its structural integrity but DNNC+2Al composite either in singlet or triplet case expels one of the geminally substituted NO_2 groups. However, the aluminum atom in each case acquires different kind of charge. The N-NO_2 bonds remain intact in the presence of aluminum.

1. Introduction

1,3,5,5-tetranitrohexahydropyrimidine (TNDA, French abbreviation is DNNC [1]) is relatively novel explosive which may also find some applications as an oxidant for propellants and pyrotechnics [2]. It can also be used as a filling material for warheads, shell and bombs. It was synthesized in 1982 and has the following properties; mp. 151-154°C [3,4,5], density: 1.82 g/cm^3, VOD: 8730 m/s, P_{CJ} : 34 Pa, OB: 6%. It has very low impact sensitivity [6]. The hybrid molecular structure of DNNC produces an energetic material with impact sensitivity much lower than RDX and more like that exhibited by TNT. It is an thermally stable and insensitive high-energy oxidizer that could have a

Received: August 16, 2022; Accepted: September 10, 2022; Published: September 15, 2022

Keywords and phrases: 1,3,5,5-tetranitrohexahydropyrimidine; DNNC; TNDA; explosive; aluminum; DFT.

potential candidate for replacement of RDX in explosive and propeller formulations [7]. Crystal structure of DNNC was studied by Oyumi et. al. [8]. Thermo chemical decomposition studies of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) have been published by Shackelford and Goldman [9,10]. They observed that unlike the cyclic RDX and HMX, symmetrical nitramine compounds which readily undergo thermo chemical decomposition during liquefaction, and an accurate heat of fusion can be determined for the thermally stable DNNC heterocyclic nitramine derivative. Hendrickson and Shackelford also performed thermo chemical decomposition studies on DNNC [11]. Pyrolysis of 5-substituted 1,3,5-trinitrohexahydropyrimidines was studied also by Roos and Brill [12]. The thermal stability of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC, TNDA) in liquid phase under isothermal conditions was studied [4]. The surface temperature and combustion mechanism of DNNC (TNDA) were established with the help of thermocouple studies.

Aluminum powder is one of the combustible high energy materials. Hence, it influences the explosive performance by increasing the heat of explosion and acts as intermediate sensitive agent [13]. As an overall effect it enhances reaction temperature and air blast, increases bubble energies in underwater weapons etc. Aluminum has been used for several decades in certain TNT/NH_4NO_3 commercial explosives (e.g., the Ammonals) as an additional fuel to increase the power and gas volume. Aluminized military explosives appeared as prominent charges in II World War [14].

Although, in the literature some work exists about aluminum compositions in certain ammunitions, the effect of aluminum on DNNC (TNDA) has not been published so far up to the best knowledge of the author. In the present study, interaction of DNNC with aluminum has been investigated at the molecular level within the limitations of density functional theory (DFT).

2. Method of Calculation

In the present study, all the initial geometry optimizations of the structures leading to energy minima were achieved by using MM2 method then followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [15,16] at the unrestricted level [17]. Afterwards, the structure optimizations have been managed within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the level of UB3LYP/6-31++G(d,p) [18,19]. Note that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with

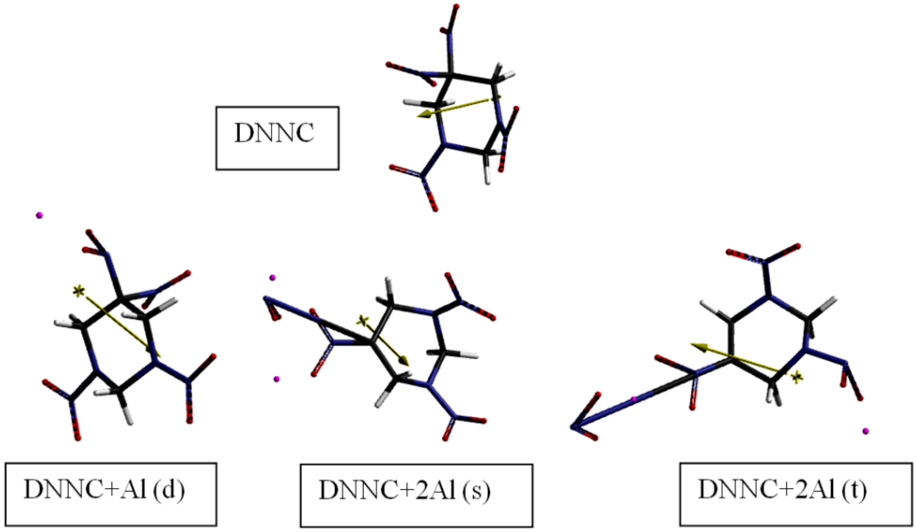
Becke's gradient correlation to LSD exchange [20]. Also note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [21] and Lee, Yang, Parr (LYP) correlation correction functional [22]. Presently, a rather high level of basis set has been employed in order to minimize the basis set superposition error [17,23]. 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 indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were 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 [24].

3. Results and Discussion

Aluminum has the ground state electronic configurations of $1s^2 2s^2 2p^6 3s^2 3p^1$ [25]. Certain metals are added in to composition of explosives for certain purposes. One of the most important one is to increase the heat produced in the explosion process. Those metals are oxidized, such as aluminum forms Al_2O_3 which is accompanied by the liberation of 1669 kJ/mol energy [26].

In the present study, composite structures, DNNC+Al and DNNC+2Al, have been investigated within the constraints of the theory and the basis set employed (UB3LYP/6-31G++(d,p)). Structurally DNNC molecule has two geminally located C-NO_2 bonds and two nitramine type bonds. Since aluminum atom has an unpaired electron various multiplicity states emerge. The investigated composite systems are DNNC+Al(d), DNNC+2Al(s) and DNNC+2Al(t). The letters d, s and t stand for doublet, singlet and triplet states, respectively.

Figure 1 shows the optimized structures as well as the directions of the dipole moment vectors of DNNC and the composite systems considered. As seen in the figure, in the doublet state DNNC undergoes some torsions and bendings in the bonds as compared to DNNC structure. Whereas, in the cases of DNNC+2Al(s) and DNNC+2Al(t) great perturbations occur leading to rupture of one of the C-NO_2 bonds, resulting in N-C distances of 5.14 Å in the singlet and 5.84 Å in the triplet case. A different behavior is exhibited by TNAZ (1,3,3-trinitroazetedine) molecule although it also has geminally substituted NO_2 groups (C-NO_2) and a nitramine bond (N-NO_2). Selenium and TNAZ interact at different extents and the systems are electronically stable, but TNAZ+2Se (singlet) structurally decomposes by the elongation of one of the N-O bonds of the geminally substituted nitro groups [27]. On the other hand, TNAZ+3Al (doublet), contrary to DNNC singlet and triplet cases, keeps the C-NO_2 bond(s) (also the nitramine bonds) intact but bond cleavage of N-O bond occurs in one of the geminally substituted NO_2 groups [28]. This behavioral variation between TNAZ and DNNC molecules can be attributed to ring system of TNAZ, thus to different orbital interactions happening in 4-membered ring as compared to the 6-membered ring of DNNC.



DNNC

DNNC+Al (d)

DNNC+2Al (s)

DNNC+2Al (t)

Figure 1. Optimized structures and directions of the dipole moment vectors of the systems considered.

Table 1 lists some properties of the systems considered. Note that DNNC+Al (d) system is stable structurally but DNNC+2Al systems singlet or triplet undergo decomposition which have % Al content greater than 10 %.

Table 1. Some properties of the systems considered.

Systems	Formula	Dipole moment	MW (amu)	% Al
DNNC	$C_4H_6N_6O_8$	5.06	266.126	-
DNNC+Al (d)	Al.$C_4H_6N_6O_8$	5.53	293.108	9.2055
DNNC+2Al (s)	2Al.$C_4H_6N_6O_8$	4.03	320.090	16.859
DNNC+2Al (t)	2Al.$C_4H_6N_6O_8$	10.73	320.090	16.859

Dipole moments in debye units.

Figure 2 displays the calculated IR spectra of the systems considered. The calculated

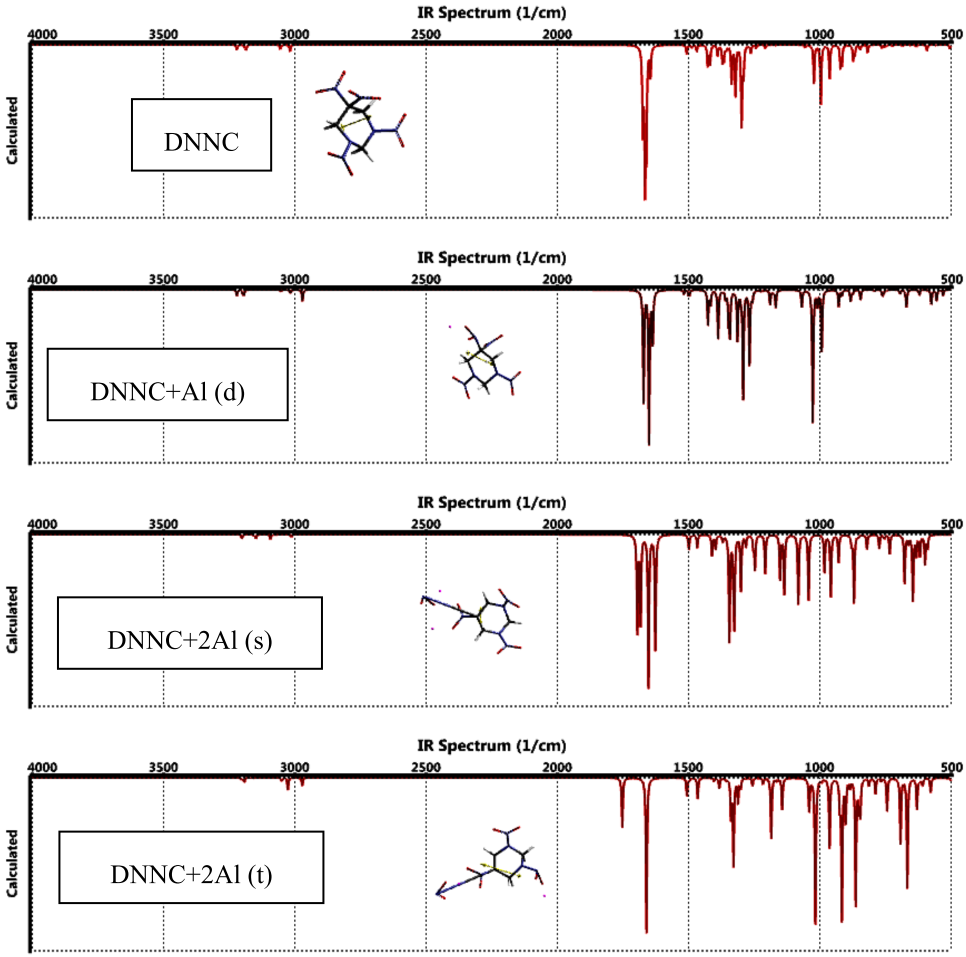


Figure 2. The calculated IR spectra of the systems considered.

IR spectrum of DNNC exhibits asymmetrical N-O stretchings at 1674-1664 cm^{-1} belonging to nitro groups of $C-NO_2$ and $N-NO_2$ types. In the case of DNNC+Al (d), N-O stretchings happen at 1671-1636 cm^{-1}. In the case of DNNC+2Al (s) the N-O stretching of the expelled nitro moiety occurs at 1695 cm^{-1}. The $C-NO_2$ stretching of the geminal nitro group is at 1683 cm^{-1}. On the other hand, asymmetrical nitramine N-O stretchings take place at 1653-1626 cm^{-1}. As for the DNNC+2Al (t) case, the vibration at 1752 cm^{-1} stands for $C-NO_2$ stretching of the geminal nitro group. The asymmetrical nitramine N-O stretching happens at 1660 cm^{-1}. Various IR modes of C-H bonds in DNNC occur in the region of 1427-1298 cm^{-1}, whereas they happen at 1416-1268 cm^{-1} in DNNC+Al (d), 1396-1208 cm^{-1} in DNNC+2Al (s) and 1507-1164 cm^{-1} in DNNC+2Al (t). In general IR spectra of DNNC and DNNC(d) resemble each other except the intensities of some of the peaks. Note that DNNC(d) system preserves its structural integrity. The decomposed systems exhibit greater variations as compared to DNNC. Changes of IR frequencies in the presence of aluminum atoms and the present spin states should be due to the structure-dependent variations of the bond constants which is one of the factors dictating the vibrational frequencies [29,30].

Table 2 shows some energies of the systems 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 seen in the table, DNNC+2Al (t) system is electronically more stable than DNNC+2Al(s), although both of them undergo a similar type of structural perturbations leading to decompositions.

Table 2. Some energies of the systems considered.

Systems	E	ZPE	E_C
DNNC	-2851100.98	408.27	-2850692.71
DNNC+Al (d)	-3487699.93	406.76	-3487293.17
DNNC+2Al (s)	-4124450.43	402.58	-4124047.85
DNNC+2Al (t)	-4124544.47	401.23	-4124143.24

Energies in kJ/mol.

Figure 3 shows the electrostatic potential charges (ESP) on the atoms of the systems considered. It is worth noting that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [24]. The figure reveals a striking difference among the aluminum composites of present interest. The aluminum atom in DNNC+Al (d) (structurally stable) has some positive partial charge in contrast to DNNC+2Al (s) in which both of the aluminum atoms present possess some partial negative but unequal charges in magnitude. The NO_2 moiety departing the DNNC molecule (DNNC+2Al (s) case) has positive overall charge (0.209 esu). As for the DNNC+2Al (t) case, both of the aluminum atoms acquire positive charge even the one next to the departing NO_2 moiety possess some charge greater than unity and the NO_2 group of the broken bond has negative over all charge (-1.00 esu).

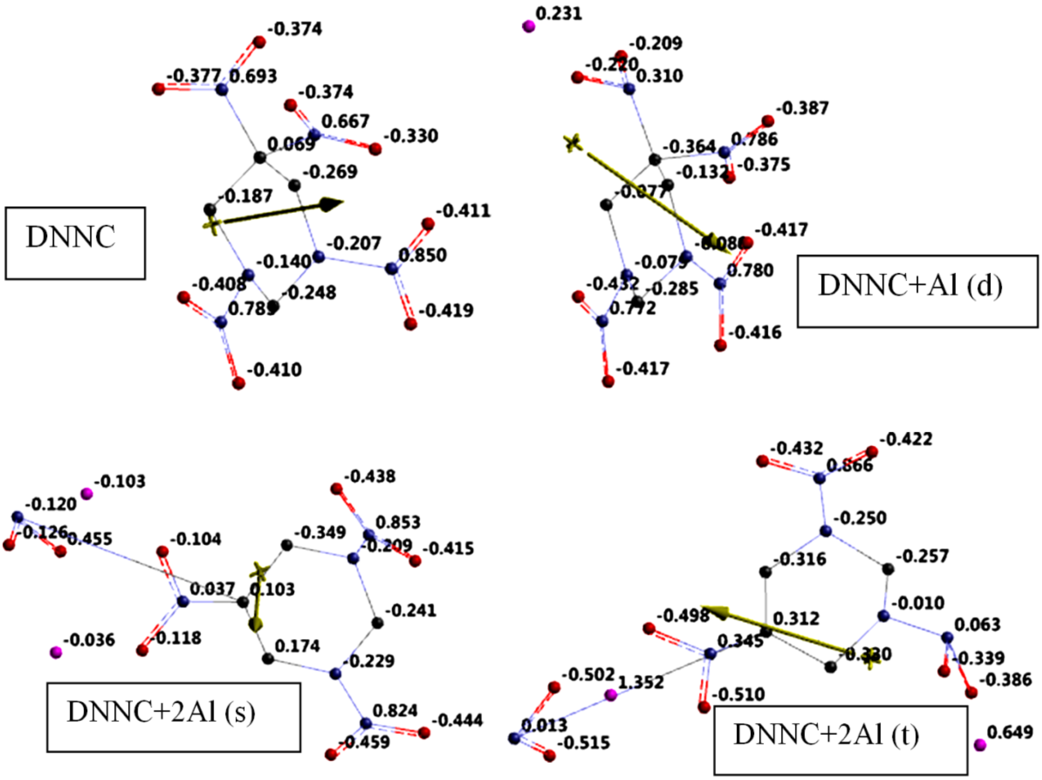


Figure 3. The ESP charges on the atoms of the systems considered (Hydrogens omitted).

Figure 4 contains the electrostatic potential maps of the systems considered where negative potential regions coincides with red/reddish and positive ones with blue/bluish parts of the maps.

Figure 5 displays some of the molecular orbital energy levels of the systems considered. Since the calculations were performed at the unrestricted level, for the open shell systems α- and β-type orbitals arise. In the figure they are indicated as a- and b-types. It is evident from the figure that the presence of aluminum atom raises up the LUMO energy levels as compared to DNNC molecule, and the highest one occurs in DNNC+2Al (t) case. A similar raise happens for the HOMO energy levels again compared to DNNC HOMO energy level. The highest raise arises for DNNC+2Al (s) case. Also note that HOMO-α of DNNC+2Al (t) is higher than the HOMO level of DNNC+2Al (s) but the LUMO-β level of DNNC+2Al (t) is much lower than the LUMO of DNNC+2Al (s). Consequently, DNNC+2Al (t) should be much willingly to accept electrons whereas DNNC+2Al (s) should prefer to donate some electron population. Also the presence of two unpaired electrons in the triplet case should enhance eagerness of DNNC+2Al (t) to accept electrons. That is why aluminum atoms in the singlet case possess some negative partial charges whereas they acquire positive charges in the triplet case namely in DNNC+2Al (t) composite.

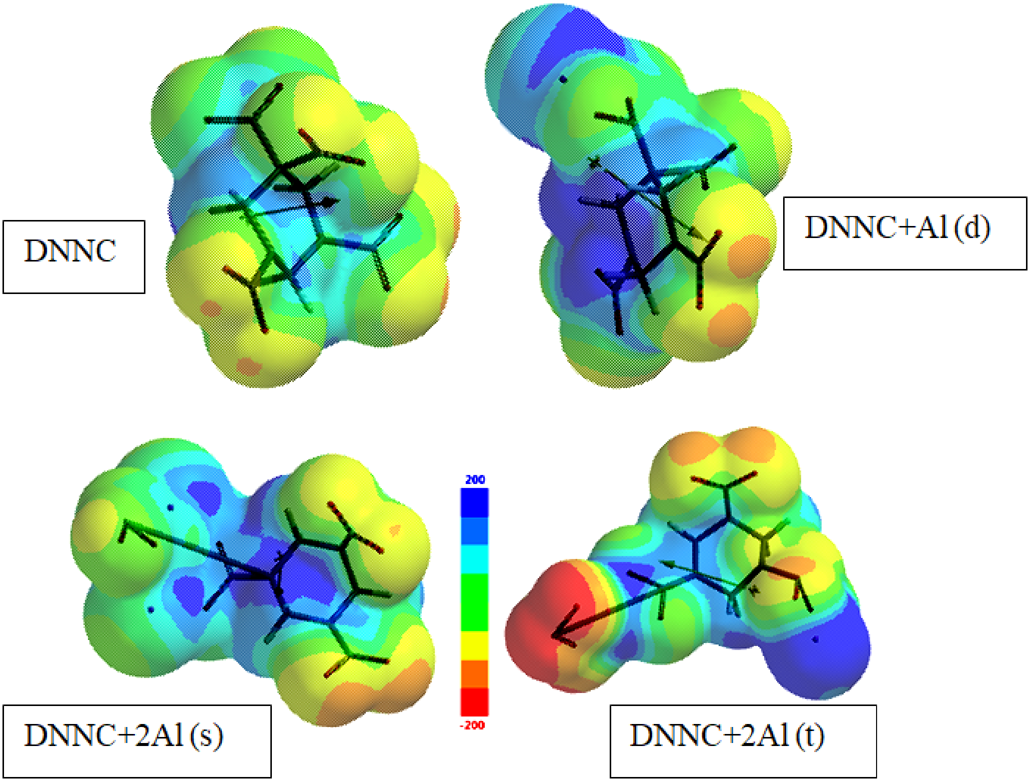


Figure 4. Electrostatic potential maps of the systems considered.

Table 3 lists the HOMO, LUMO energies and the interfrontier molecular orbital (FMO) energy gap values (Δε) of the systems considered. Note that Δε is the LUMO-HOMO energy difference. The orders of the HOMO and LUMO energy levels are the same; DNNC < DNNC+Al (d) < DNNC+2Al (s) < DNNC+2Al (t). Consequently, Δε values follow the order of DNNC+2Al(t) < DNNC+2Al(s) < DNNC+Al(d) < DNNC. So, structurally stable DNNC+Al (d) system should be more susceptible to impact stimulus compared to DNNC, because the impact sensitivity is correlated with the inter frontier molecular orbital (FMO) energy gap reversely [31,32]. Namely, as the FMO energy gap (Δε) becomes less and less the impact sensitivity increases more and more.

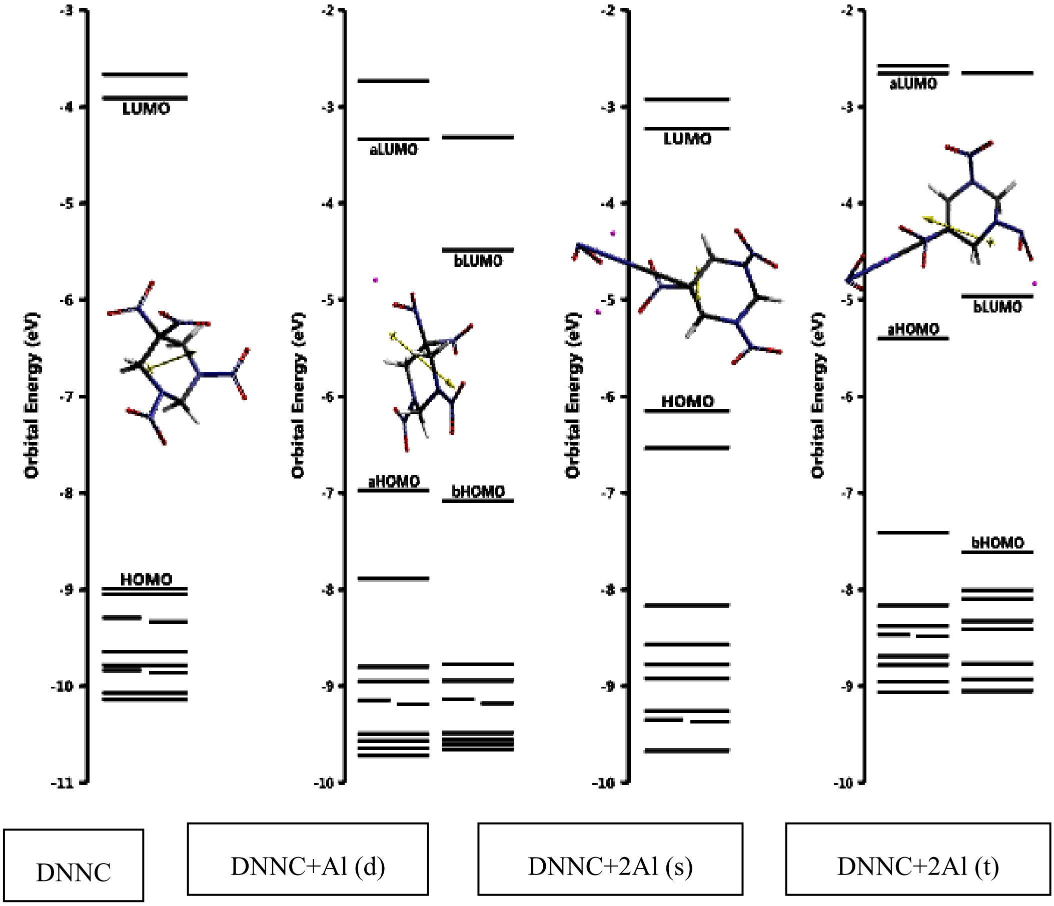


Figure 5. Some of the molecular orbital energy levels of the systems considered.

Table 3. The HOMO, LUMO energies and Δε values of the systems considered.

Systems	HOMO	LUMO	Δε
DNNC	-867.73	-377.56	490.17
DNNC+Al (d)	-673.04	-321.98	351.06
DNNC+2Al (s)	-593.23	-311.56	281.67
DNNC+2Al (t)	-520.78	-256.36	264.42

Energies in kJ/mol.

Figure 6 shows the calculated (time dependent density functional spectra) UV-VIS

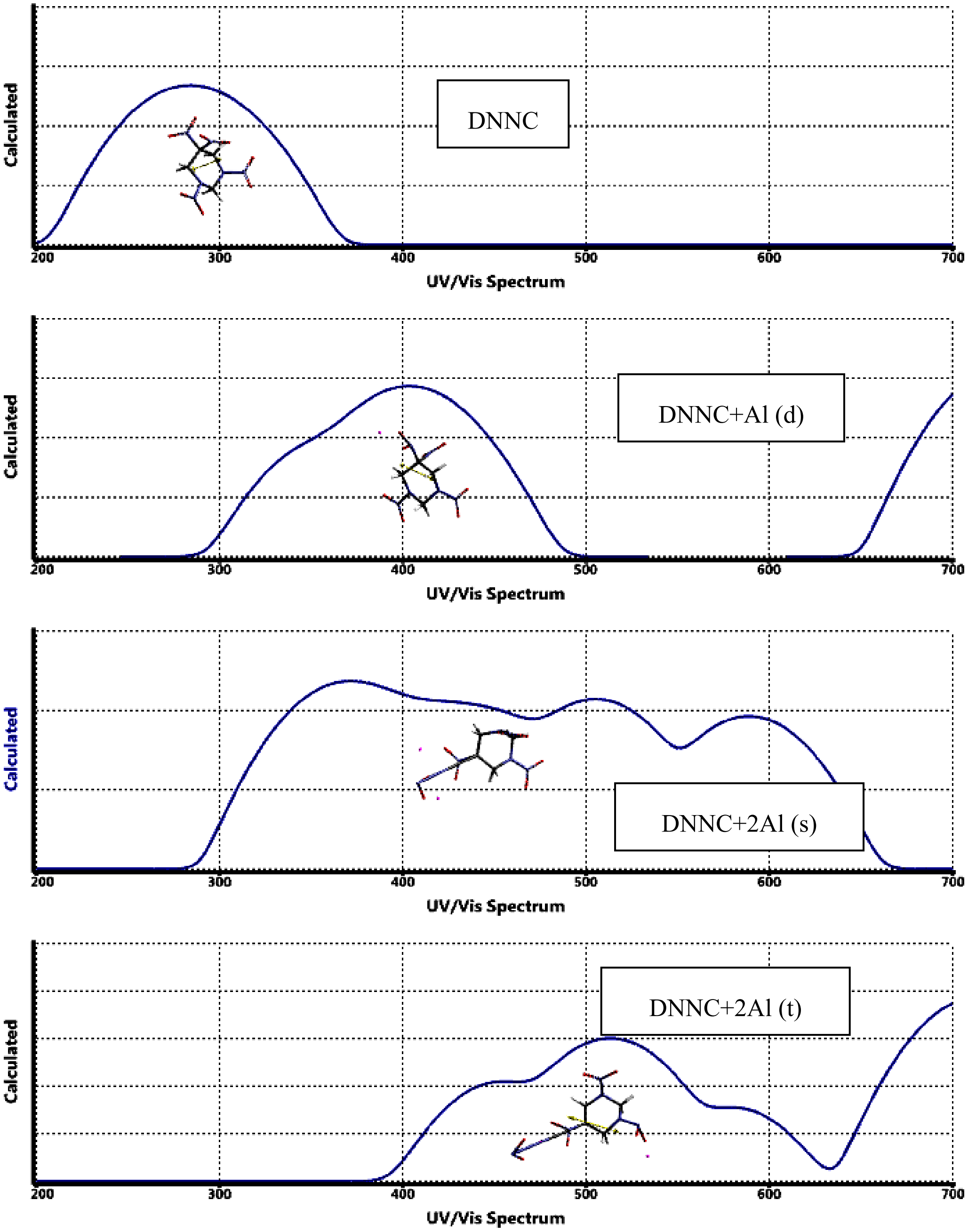


Figure 6. The calculated UV-VIS spectra of the systems considered.

spectra of the systems considered. As seen in the figure the presence of aluminum atom(s) causes considerable degree of bathochromic effect towards the visible region as compared to DNNC. However keep in mind that the singlet and triplet states of DNNC are actually decomposed systems, whereas the doublet is structurally intact. The bathochromic effect shows that in those systems a better conjugated paths should have been developed especially in the triplet case. Note that the doublet and triplet cases are open-shell systems having an unpaired electron. Figure 7 shows the spin density maps of the open-shell systems considered. The blue regions stand for high spin density possessing regions of the systems where an aluminum atom resides.

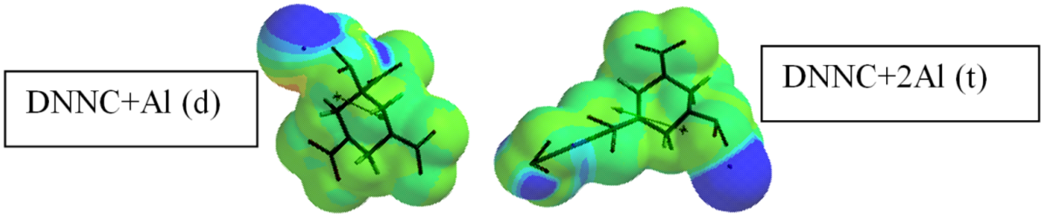


Figure 7. The spin density maps of the open-shell systems considered.

Figure 8 shows the HOMO and LUMO patterns of the systems considered. As seen in the figure, the LUMO of DNNC consists of orbitals supplied by the geminally substituted nitro groups and the rest of the molecule, including the nitramine groups, contributes nil. When aluminum atom(s) is/are incorporated in to the systems the HOMO is confined to one or two of the geminally substituted nitro groups with the exception of DNNC+2Al (t) in which the nitramine moiety is the main contributor of the HOMO-β, whereas the HOMO-α is provided by the departing NO_2 moiety only. The LUMO-β is spread over the nitramine moiety solely. Note that it is a decomposed composite. In rest of the systems nitramine moieties either contribute nothing or they have very small contribution to the LUMOs.

Figure 9 shows the local ionization potential maps of the systems considered. In the local ionization potential map, 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. As seen in the figure, the presence of aluminum atom(s) highly affect the ease of electron distribution depending on the multiplicity of the systems and all the systems are in general electron deficient although in some of them aluminum atom provides some electron population into DNNC component and itself acquires some positive partial charge.

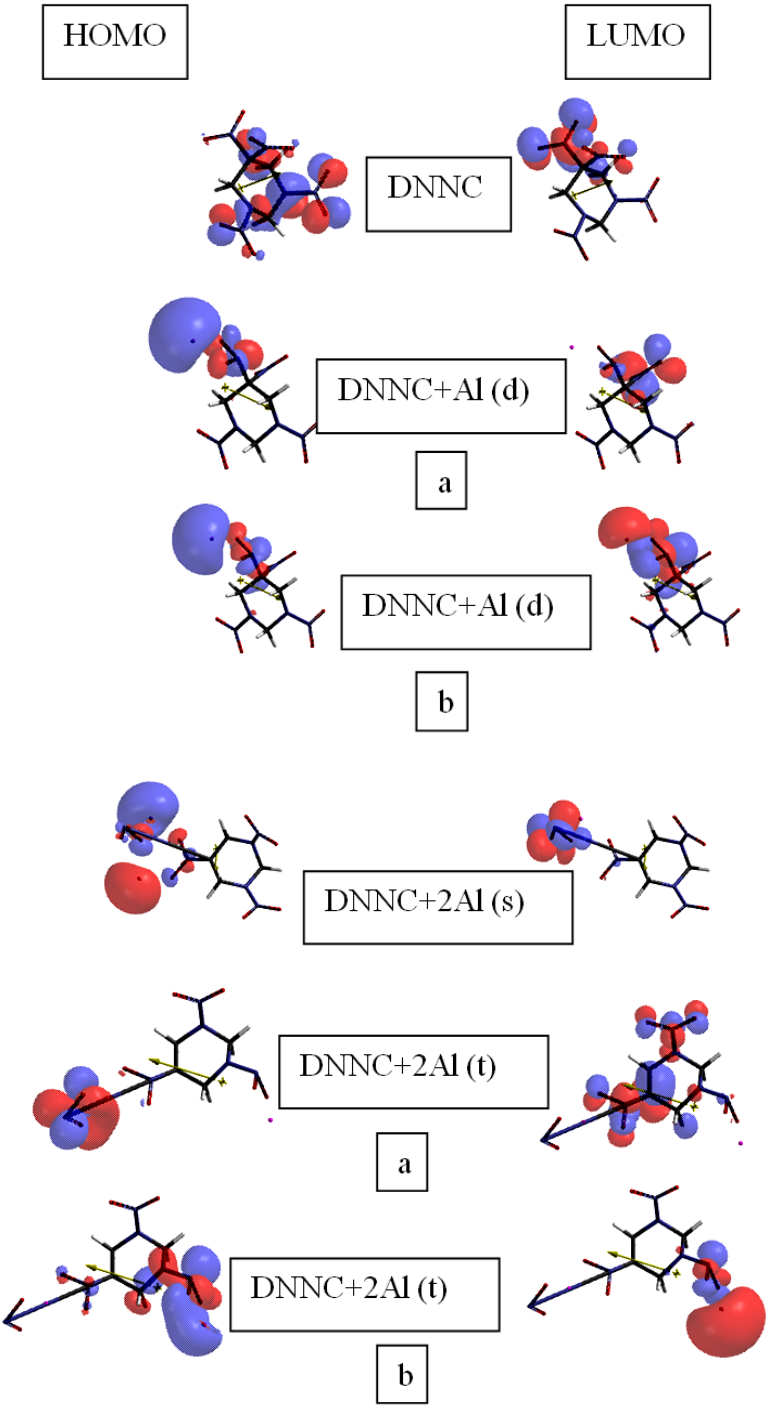


Figure 8. The HOMO and LUMO patterns of the systems considered.

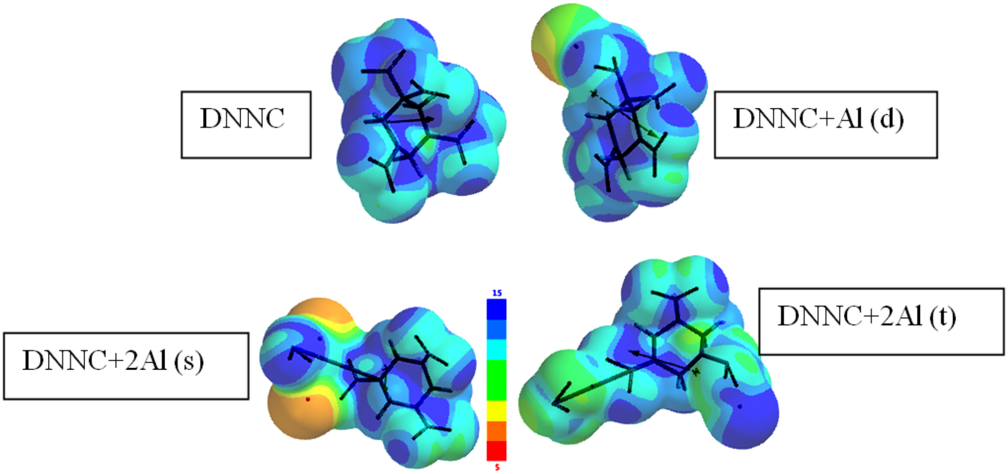


Figure 9. The local ionization potential maps of the systems considered.

4. Conclusion

The present DFT treatment of aluminum and DNNC interaction (within the constraints of the theory and basis set employed) has revealed that aluminum may be compatible or not with DNNC molecule depending on the percent of aluminum in the composite as well as the multiplicity state of the composite. The DNNC+Al(d) composite is structurally stable but DNNC+2Al is stable neither in the singlet nor in the triplet state. In all the cases, except DNNC+2Al (s) case, aluminum atom(s) possesses some partial positive charge whereas in the exceptional case some negative partial charge accumulates on the aluminum atoms. The decomposed systems eliminate NO_2 group but in different kind of overall charge appears on them (positive and negative in the cases of DNNC+2Al (s) and DNNC+2Al (t), respectively).

References

[1] Boileau, J., Piteau, M., & Jacob, G. (1990). Short communication – notice. Synthèse de la 1,3,5,5-tetranitrohexahydropyrimidine, *Propellants Explos. Pyrotech.*, *15*(1), 38-38. https://doi.org/10.1002/prep.19900150111

[2] Agrawal, J.P. (2010). *High energy materials*, Weinheim: Wiley-VCH. https://doi.org/10.1002/9783527628803

[3] Dorothy, A.C., & Horst, G.A. (1982). Nitrolysis of dialkyl tert-butylamines. *J. Org. Chem.*, *47*(12), 2474-2476. https://doi.org/10.1021/jo00133a047

[4] Sinditskii, V.P., Smirnova, A.D., Vu, T.Q., Filatov, S.A., Serushkin, V.V., & Rudakov, G.F. (2020). Thermal decomposition of 1,3,5,5-tetranitrohexahydropyrimidine: a new type of autocatalysis that persists at high temperatures. *Propellants Explos. Pyrotech*., *45*, 1-10. https://doi.org/10.1002/prep.202000259

[5] Zhang, L.-J., Ji, Y.-P., Chen, B., Ding, F., Li, D.-P., & Liu, W.-X. (2012). Synthesis of 1,3,5,5-tetranitrohexahydropyrimidine with high yield. *Chinese J. Energ. Mater*., *20*, 441-444.

[6] Levins, D.L., Bedford, C.D., & Coon, C.L. (1982). 1,3,5,5-Tetranitrohexahydro-pyrimidine (DNNC), U.S. Patent 4,346,222 (1982), SRI International, USA (24 Aug. 1982), SRI International, Menlo Park, California, US.

[7] Shackelford, S.A., & Goldman, J.F. (1995). Heat of fusion for 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) and its DNNC-d_6 deuterium labeled analogue. *Propellants Explos. Pyrotech*., *20*(1), 1-4. https://doi.org/10.1002/prep.19950200102

[8] Oyumi, Y., Brill, T.B., Rheingold, A.L., & Haller, T.M. (1985). Crystal structure and molecular dynamics of the energetic nitramine 1,3,5,5-tetranitrohexahydropyrimidine and a comparison with 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane and 1,3,3-trinitroazetidine. *J. Phys. Chem*., *89*, 4317-4324

[9] Shackelford, S.A., & Goldman, J.F. (1992). Intramolecular mechanistic thermochemical decomposition studies of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) and its deuterium labeled analogues, 203rd National American Chemical Society Meeting, San Francisco, CA, 5-10 April, [Abstract, 1992] American Chemical Society, 1155 16th St. N.W., Washington, D.C. 20036 (USA).

[10] Shackelford, S.A., Menapace, J.A., & Goldman, J.F. (2007). Liquid state thermo chemical decomposition of neat 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) and its DNNC-*d*2, DNNC-*d*4, DNNC-*d*6 structural isotopomers: Mechanistic entrance into the DNNC molecule. *Thermochimica Acta*, *464*(1-2), 42-58. https://doi.org/10.1016/j.tca.2007.08.005

[11] Hendrickson, S.A. & Shackelford, S.A. (2006). Solid state thermo chemical decomposition of neat 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) and its DNNC-d_6 perdeuterio-labeled analogue. *Thermochimica Acta*, *440*(2), 146-155. https://doi.org/10.1016/j.tca.2005.11.007

[12] Roos, B.D., & Brill, T.B. (2003). Thermal decomposition of energetic materials 84: pyrolysis of 5-substituted 1,3,5-trinitrohexahydropyrimidines. *Propellants Explos. Pyrotech*., *28*(2), 65-71. https://doi.org/10.1002/prep.200390010

[13] Keshavarz, M.H. (2005). New method for predicting detonation velocities of aluminized explosives. *Combustion Flame*, *142*, 303-307. https://doi.org/10.1016/j.combustflame.2005.03.011

[14] Taylor, J. (1959). *Solid propellant and exothermic compositions*, London: George Newnes Ltd.

[15] 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

[16] 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

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

[18] 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

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

[20] 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

[21] 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

[22] 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

[23] Cramer, C.J. (2004). *Essentials of computational chemistry*. Chichester, West Sussex: Wiley.

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

[25] Durant, P.J., & Durant, B. (1972). *Introduction to advanced inorganic chemistry*. London: Longman.

[26] Stark, J.G., & Wallace, H.G. (1982). *Chemistry data book* (2nd ed.). London: John Murray Pub.

[27] Türker, L. (2021). Effect of selenium on TNAZ molecule - A DFT treatment. *Earthline Journal of Chemical Sciences*, *6*(1), 119-135. https://doi.org/10.34198/ejcs.6121.119135

[28] Türker, L. (2020). A DFT treatment of some aluminized 1,3,3-trinitroazetidine (TNAZ) systems-A deeper look. *Earthline Journal of Chemical Sciences*, *3*(2), 121-140. https://doi.org/10.34198/ejcs.3220.121140

[29] Barrow, G.M. (1962). *Introduction to molecular spectroscopy*. Tokyo: McGraw-Hill (Int. Student Ed.).

[30] Harris, D.C., & Bertolucci, M.D. (1978). *Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy*. New York: Oxford University Press.

[31] 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

[32] 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/10.1080/07370650500374321