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Ab-initio Study of Structural, Spectroscopic and Electronic Properties of High Energy Explosive Molecules: DFT/TD-DFT Calculations

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Abstract

This research explores the ground state geometry and molecular properties of FOX-7 and nitroguanidine molecules, with a focus on their spectroscopic and electronic characteristics. Initially, the conformational space of each molecule was systematically scanned using molecular mechanic calculations and the most probable conformer structure was obtained for each molecule. Subsequently, geometry optimizations of molecules were conducted by using ab initio density functional theory (DFT) with Becke's three-parameter hybrid-exchange functional, which combines the Lee–Yang–Parr correlation functional (B3LYP) method, and the standard 6-311++G(d,p) basis set. The theoretically determined geometrical parameters from optimized structure and experimental values available in the literature were compared, providing validation for the structural properties of both molecules. Furthermore, the stability and reactivity properties of both molecules are estimated in terms of HOMO-LUMO energies. Overall, this study contributes to a comprehensive understanding of the ground state geometry, molecular structure, and spectroscopic behavior of FOX-7 and nitroguanidine, paving the way for potential applications in various fields of science and technology.

Keywords: DFT, Molecular Structures, HOMO, LUMO, Spectroscopic Properties, FOX-7, Nitroguanidine.

Yüksek Enerjili Patlayıcı Moleküllerin Yapısal, Spektroskopik ve Elektronik Özelliklerinin Ab-initio Çalışması: YFT/TD-YFT Hesaplamaları

Öz

Bu araştırma, FOX-7 ve nitroguanidin moleküllerinin temel durum geometrisini ve moleküler özelliklerini incelemekte olup özellikle spektroskopik ve elektronik karakteristiklerine odaklanmaktadır. İlk olarak, her molekülün konformasyonel uzayı moleküler mekanik hesaplamalar kullanılarak sistemli bir şekilde tarandı ve her molekül için en olası konformer yapı elde edildi. Daha sonra, moleküllerin geometri optimizasyonları, Becke'nin üç parametreli hibrid-değişim fonksiyonu içeren ab initio yoğunluk fonksiyonel teorisi (DFT) kullanılarak gerçekleştirildi. Bu, Lee–Yang–Parr korelasyon fonksiyonelini (B3LYP) içeren yöntem ve standart 6-311++G(d,p) baz setini içermektedir. Teorik olarak belirlenen geometrik parametreler, optimize edilmiş yapıdan elde edilen deneysel değerlerle karşılaştırılarak, her iki molekülün yapısal özelliklerinin doğrulanmasını sağlamıştır. Ayrıca, her iki molekülün kararlılık ve reaktivite özellikleri HOMO-LUMO enerjileri açısından tahmin edilmiştir. Genel olarak, bu çalışma, FOX-7 ve nitroguanidin'in temel durum geometrisi, moleküler yapısı ve spektroskopik davranışının kapsamlı bir anlayışına katkıda bulunmakta olup, bilim ve teknolojinin çeşitli alanlarında potansiyel uygulamalar için yol açmaktadır.

Anahtar Kelimeler: YFT, Moleküler Yapı, HOMO, LUMO, Spektroskopik Özellikler, FOX-7, Nitroguanidin.

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1. Introduction

High energy explosives have been the topic of theoretical and experimental research (Chavez, Hill, Hiskey, & Kinkead, 2000; Chu et al., 2023; Ghanta, 2016, 2023; He et al., 2015; Manna, Das, & Ghanta, 2021; Mondal et al., 2009; Östmark et al., 1998). Owing to their capacity to store substantial quantities of chemical energy, these explosive materials pose significant challenges in handling and storage due to their exceptionally high reactivity. Furthermore, these chemical compounds find applications in both military and civilian sectors, serving roles in explosives, pyrotechnics, and propellants (Agrawal, 2010). This chemical group can be particularly dangerous to study experimentally since it can release a lot of energy in reaction to certain events including heat, collision, and friction. In this instance, theoretical studies are an excellent choice in terms of danger, time, and cost.

Nitroguanidine and FOX-7 molecules are very high-energy explosives. Especially, nitroguanidine can lower propellant flash and flame temperatures without lowering chamber pressure (Klapötke, 2022). Due to their simple molecular structure, these compounds can be easily manufactured and potentially employed in terrorist acts. The literature has many theoretical and experimental investigations for both molecules. These investigations have been used a variety of method to examine the structural, electrical, spectroscopic, and thermodynamic properties of both molecules (Agrawal, 2010; Jeong, Jeon, & Kwon, 2017; Kuklja, Rashkeev, & Zerilli, 2004; Pravica et al., 2012; Prendergast, 2018; Sorescu, Boatz, & Thompson, 2001, 2003; Sun et al., 2015; Taylor, Rob, Rice, Podeszwa, & Szalewicz, 2011).

To the best of our knowledge, the vertical ionization energy (VE) and adiabatic ionization energy (AE), as well as the nonlinear optical (NLO) characteristics of both molecules, have not been explored theoretically or experimentally. This work includes a theoretical examination of the VE, AE, and NLO properties in addition to the calculation of the structural, electronic, and spectroscopic properties were also compared with the previously estimated by various methods in the literature. The objective of this study is to develop a theoretical model applicable for uncovering the fundamental behavior and characteristics of high-energy explosives.

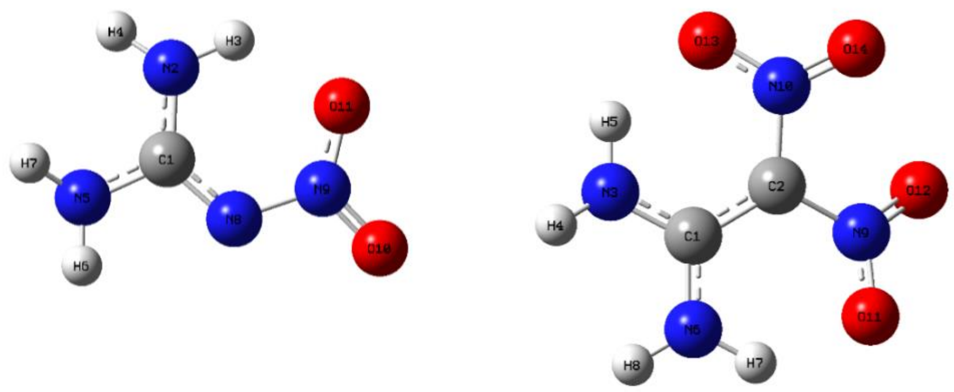
2. Computational Methods

In this study, the conformational analysis of FOX-7 and Nitroguanidine molecules were performed using the Spartan08 program with Merck molecular force field (MMFF) in the molecular mechanic method (Shao et al., 2006). The quantum chemical calculations for both molecules were carried out using the GAUSSIAN 09 program with density functional theory using the Becke three-parameter Lee–Yang–Parr exchange correlation functional (B3LYP) with the standard 6-311++G (d,p) basis set (Frisch et al., 2009). The UV–vis spectra for both molecules were calculated using time-dependent density functional theory (TD-DFT) (Improta & Barone, 2004). The computations utilized an identical basis set and exchange correlation functional.

3. Results and Discussion

3.1. Structural Geometry Analysis

In the structural geometry analysis, it is critical to discover all possible conformations of molecules. The conformational space of each molecule was systematically scanned using molecular mechanic calculations using the Spartan08 program (Shao et al., 2006) and the Merck molecular force field (MMFF) (Halgren, 1996) method. The most probable conformer structure was obtained for each molecule. As a result, just one conformer was obtained for both molecules. The findings of conformational analysis indicated that the FOX-7 and nitroguanidine molecules lack a conformational distribution. There is only one stable conformer with a DFT energy of -598.507687 Hartree for FOX-7 and -409.996269 Hartree for nitroguanidine according to molecular mechanic method calculations. These structures were optimized using the DFT//B3LYP/6-311++G(d,p) method. The optimized molecules structures and structural properties are shown in Figure 1. and Table 1., respectively.



NITROGUANIDINE **FOX-7**

Figure 1. The optimized molecular structure obtained for **FOX-7** and **nitroguanidine** molecules.

Table 1. Comparative analysis of calculated bond lengths, bond angles and dihedral angles for FOX-7 and Nitroguanidine molecules.

Molecules					
NITROGUANIDINE			**FOX-7**		
Parameters			**Parameters**		
Bond Lengths (Å)	**Calculated**	**Experimental (Koch, 2019)**	**Bond Lengths (Å)**	**Calculated**	**Experimental (Sorescu et al., 2001)**
C1-N2	1.34	1.34	C1-C2	1.42	1.46
C1-N5	1.36	1.34	C2-N9	1.43	1.39
C1-N8	1.33	1.35	C2-N10	1.43	1.42
N8- N9	1.38	1.35	N9-O12	1.22	1.23
N9-O10	1.22	1.22	N10-O13	1.25	1.26
N9-O11	1.24	1.23	C1-N3	1.34	1.32
Bond angles (°)			**Bond angles (°)**		
N5-C1-N2	117.04	118	O12-N9-C2	119.36805	120
N5-C1-N8	113.96	112	O13-N10-C2	117.69497	118
N2-C1-N8	128.99	129	N9-C2-N10	116.44066	116
C1-N8-N9	119.35	118	N9-C2-C1	121.77967	123
N8-N9-O11	121.86	-	C2-C1-N6	121.48531	121
N8-N9-O10	115.09	124	N6-C1-N3	117.02937	118
O11-N9-O10	123.03	121	H5-N3-C1	117.29306	122
Dihedral angles (°)			**Dihedral angles (°)**		
H6-N5-C1-N2	-172.14206	-	O11-N9-C2-N10	156.13465	-148
N5-C1-N2-H3	-174.12730	-	O11-N9-C2-C1	-23.86535	6.34
H4-N2-C1-N8	164.04647	-	O12-N9-C2-C1	153.75423	-170
H6-N5-C1-N8	151.87073	-	O14-N10-C2-N9	-26.24577	33
N5-C1-N8-N9	173.42129	-	N10-C2-C1-N6	-166.15266	172
N2-C1-N8-N9	-6.36510	-	N9-C2-C1-N6	13.84734	-
C1-N8-N9-O11	6.23282	-	C2-C1-N3-H4	-162.89913	178
C1-N8-N9-O10	-174.68108	-			

As a result, the computed molecular structure and properties align closely with the experimental data documented in the literature. The measured C1-N2, N9-O10, and N9-O11 bond lengths for the nitroguanidine molecule are 1.34 Å, 1.22 Å, and 1.23 Å, respectively. These values closely match the theoretical predictions of 1.34 Å, 1.22 Å, and 1.24 Å. Likewise, the experimental C2-N10, N10-O13, and C1-N3 bond lengths for the FOX-7 molecule are 1.43 Å, 1.25 Å, and 1.34 Å, demonstrating notable agreement with the corresponding theoretical data of 1.42 Å, 1.26 Å, and 1.32 Å.

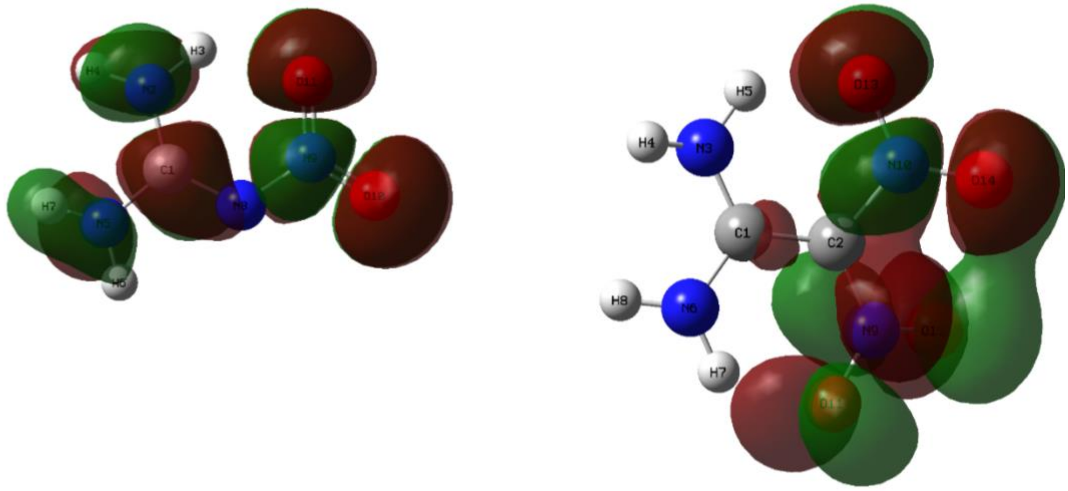
For the hydrogen bond interaction of a molecule, it must be in the range of < 3.0 Å (Jeffrey & Jeffrey, 1997). In this study, the calculated bond length and bond angle of H3-O11 and N9-O11...H3 for Nitroguanidine are 1.85 Å and 108.17˚ respectively. The calculated bond lengths of H5-O13 and H7-O11 for FOX-7 are 1.82 and 1.81 Å respectively, and the calculated bond angles of N10-O13...H5 and N9-O11...H7 for FOX-7 are obtained as 108.24˚ and 108.24˚ respectively. According to our calculations, there is a possibility of an intramolecular N-H-O hydrogen bond between the -NO2 and -NH2 groups for the molecules studied.

The calculated bond angles for both molecules are in good agreement with the experimental values. However, it is noteworthy that the dihedral angles, particularly for the FOX-7 molecule, exhibit slight deviations from the experimental measurements.

3.2. Frontier Molecular orbitals and Chemical Reactivity Descriptors

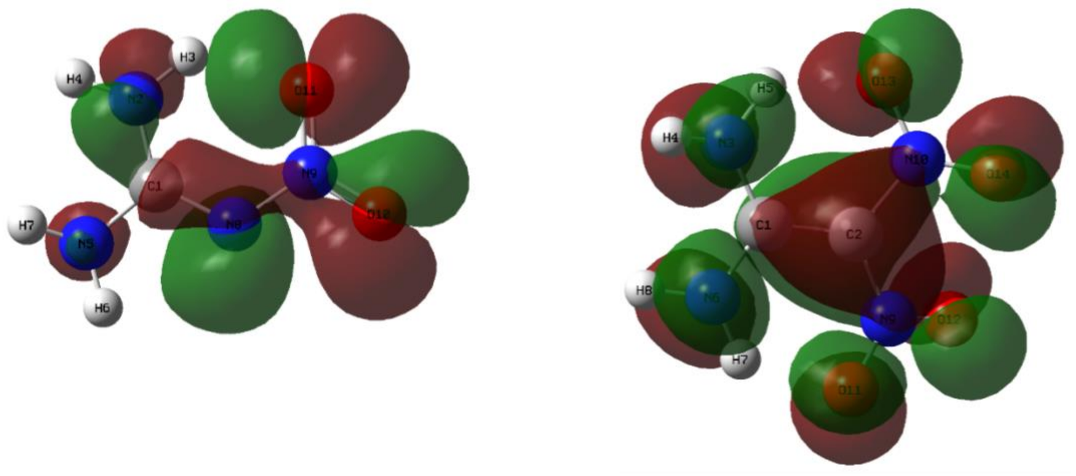
The frontier molecular orbitals (FMOs), namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), exert a significant influence on the electrical, electronic, and optical properties within the realm of physics (Fleming, 1976). The LUMO, or Lowest Unoccupied Molecular Orbital, represents the orbital with the minimal energy capable of accepting electrons. Consequently, it serves as an electron acceptor, delineating the molecule's susceptibility to nucleophilic attacks. Conversely, the HOMO, or Highest Occupied Molecular Orbital, designates the outermost orbital with higher energy containing electrons. Functioning as an electron donor, it defines the molecule's susceptibility to attacks by electrophiles (Karelson, Lobanov, & Katritzky, 1996). The energy gap, denoting the disparity between the energy levels of the LUMO and the HOMO, serves as a pivotal descriptor for elucidating the chemical reactivity and kinetic stability of the molecular system under consideration. In this context, the colors red and green symbolize the positive and negative phases, respectively. All compounds exhibit strong $\pi \rightarrow \pi*$ and $\sigma \rightarrow \sigma*$ transitions in the UV-vis range (Cotton, Wilkinson, Murillo, & Bochmann, 1999). The energies, oscillator strengths and major contributions of the transitions are given in Tables 4-5. The calculated absorption maxima values for FOX-7 and nitroguanidine molecules have been obtained as 341.874 nm and 318.438 nm, respectively. The maximum absorption at 341.874 nm and 318.438 nm corresponds to the transition from the HOMO to LUMO molecular orbitals (H→L (61%) and H→L (92%)). These transitions are predicted to be of $\pi \rightarrow \pi^*$ nature for FOX-7 and $n \rightarrow \pi^*$ nature for nitroguanidine molecules (see Figure.3).

NITROGUANIDINE	**FOX-7**



$\mathbf{E_{LUMO} = -2.047\ eV}$ ⇧

$\mathbf{E_{LUMO} = -2.864\ eV}$ ⇧



$\mathbf{E_{HOMO}} = -\mathbf{7.604\ eV}$ $\mathbf{E_{HOMO}} = -\mathbf{7.507\ eV}$

Figure 2. Localizations of the FMOs of **nitroguanidine** and **FOX-7** molecules.

The global chemical reactivity descriptors are defined utilizing Koopman's theorem (Koopmans, 1934). Ionization potential (I) and electron affinity (A) values are computed based on the energies of HOMO and LUMO through the equations $\mathrm{I} = -\mathbf{E_{HOMO}}$ and $A = -\mathbf{E_{LUMO}}$. Additionally, expressions for chemical potential (μ), global hardness (η), global softness (S), electrophilicity index (ω) and the electronegativity (χ) are provided by the following equations. These quantum chemical parameters, described by equations 1-5 (Ekincioğlu, Kılıç, & Dereli, 2021; Vijayaraj, Subramanian, & Chattaraj, 2009) were employed to calculate the global reactivity descriptors. The resulting values are presented in Table 2.

$$\mu = -\frac{(I+A)}{2} \tag{1}$$

$$\eta = \frac{(I-A)}{2} \tag{2}$$

$$S = \frac{1}{\eta} \tag{3}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{4}$$

$$\chi = \frac{(I+A)}{2} \tag{5}$$

Table 2. Chemical reactivity descriptors of **nitroguanidine** and **FOX-7** molecules.

Compounds	$\mathbf{E_{gap}}$ **(eV)**	**I (eV)**	**A (eV)**	**μ (eV)**	**η (eV)**	**S (eV)**	**ω (eV)**	**χ (eV)**
NITROGUANIDINE	5.557	7.604	2.047	-4.825	2.778	0.359	4.190	4.825
FOX-7	4.643	7.507	2.864	-5.185	2.321	0.430	5.791	5.185

Soft molecules have a smaller $\mathbf{E_{gap}}$ energy gap and are more reactive and less stable than hard molecules, which have a larger $\mathbf{E_{gap}}$ energy gap. According to the results, FOX-7 molecule is softer but less reactive and stable than nitroguanidine molecule. In the nitroguanidine molecule, the LUMO exhibits significant localization across the entire molecular moiety, while the region of the HOMO extends approximately over the entire molecule, excluding hydrogen atoms bonded to N5-N3 atoms. For the FOX-7 molecule, the HOMO is prominently localized almost entirely across the molecular moiety, whereas the localization of the LUMO extends approximately over the entire molecule, with the exception of N5-N2 atoms and hydrogen atoms bonded to these atoms.

3.3. Nonlinear Optical Properties

The nonlinear optical parameters, namely dipole moment (D), polarizability (α) (measured in atomic units and electrostatic units), and first-order hyperpolarizability (β) (expressed in atomic units and electrostatic units), were determined through computational simulations employing the DFT/B3LYP/6-311++G(d,p) level of theory.

The dipole moment, polarizability, and first-order hyperpolarizability components of both molecules are expressed by the equations provided below and summarized in Table 3. The obtained values, given in atomic units (a.u.), were converted to statcoulomb (esu) units using the following conversion factors: for μ, 1 a.u. = 2.5412 Debye; for α, 1 a.u. = 0.1482×10^{-24} esu; and for β, 1a.u. = 8.6393×10^{-33} esu (de Silva, de Silva, & De Silva, 2005; Ekincioğlu et al., 2021; Prasad & Williams, 1991) he transformed data facilitates a consistent comparison and analysis within the context of electrodynamic properties.

Total dipole moment (μ_{tot}) for molecule is defined as in Equation 6

$$\mu_{tot} = \left(\mu_x + \mu_y + \mu_z\right)^{1/2} \tag{6}$$

Total polarizability (α_{tot}) for molecule can be evaluated by Equation 7

$$\alpha_{tot} = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \tag{7}$$

The total first order hyper polarizability (β_{tot}) can be calculated by Equation 8

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{8}$$

were β_x, β_y and β_z are defined to be

$$\beta_x = \left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right) \tag{9}$$

$$\beta_y = \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right) \tag{10}$$

$$\beta_z = \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right) \tag{11}$$

Total first order hyper polarizability from Gaussian 09 output is given in Equation 12.

$$\beta_{tot} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \tag{12}$$

Table 3. The values of calculated dipole moment (μ), polarizability (α), first order hyperpolarizability (β) components of **nitroguanidine** and **FOX-7** molecules

Parameters	**NITROGUANIDINE**	**FOX-7**
Dipole moment (Debye)		
$\boldsymbol{\mu_x}$	-7.3946	0.0000
$\boldsymbol{\mu_y}$	1.2972	0.0000
$\boldsymbol{\mu_z}$	0.2076	8.5441
$\boldsymbol{\mu_{tot}}$	7.5104	8.5441
Polarizability (a.u)		
$\boldsymbol{\alpha_{xx}}$	83.533	58.281
$\boldsymbol{\alpha_{yy}}$	60.241	81.534
$\boldsymbol{\alpha_{zz}}$	60.241	105.047
$\boldsymbol{\alpha_{tot}}$ **(a.u)**	58.935	81.621
$\boldsymbol{\alpha_{tot}}$ **(esu)**	8.734×10^{-24}	12.096×10^{-24}
Hyperpolarizability (a.u)		
$\boldsymbol{\beta_{xxx}}$	67.429	7074.8×10^{-7}
$\boldsymbol{\beta_{xxy}}$	184.791	-10.087×10^{-7}
$\boldsymbol{\beta_{xyy}}$	8.884	16.616×10^{-7}
$\boldsymbol{\beta_{yyy}}$	-71.960	237.00×10^{-7}
$\boldsymbol{\beta_{xxz}}$	2.080	-20.694
$\boldsymbol{\beta_{xyz}}$	6.712	156.912
$\boldsymbol{\beta_{yyz}}$	2.465	-294.278
$\boldsymbol{\beta_{xzz}}$	-56.985	34.978×10^{-7}
$\boldsymbol{\beta_{yzz}}$	2.971	18.384×10^{-7}
$\boldsymbol{\beta_{zzz}}$	1.965	344.995
$\boldsymbol{\beta_{tot}}$ **(a.u)**	117.585	29.022
$\boldsymbol{\beta_{tot}}$ **(esu)**	1015.85×10^{-33}	250.73×10^{-33}

The investigation revealed that a comparative analysis of the dipole moment and first-order hyperpolarizability values of the molecules under scrutiny with those of urea, serving as a reference molecule, proves instrumental in elucidating the behavior of nonlinear optical materials. The outcomes indicated that the overall dipole moments of nitroguanidine and FOX-7 molecules were 7.5104 and 8.5441 Debye, respectively. Notably, both molecules exhibited higher dipole moments compared to urea (1.3732 Debye) (Dixon & Matsuzawa, 1994). The dipole moment of urea was determined to be 5.47 times smaller than that of nitroguanidine and 6.22 times smaller than that of FOX-7.

The polarizability assessments indicate that the polarizability tensor along the x-axis exhibits greater dominance for the nitroguanidine molecule compared to its counterparts along the y and z directions. Conversely, the polarizability tensor along the z-axis displays heightened dominance for the FOX-7 molecule relative to the x and y directions. Consequently, it is evident that the contribution of the x-axis to the polarizability of the nitroguanidine molecule surpasses that of the other axes, while the z-axis holds greater influence on the polarizability of the FOX-7 molecule.

The first-order hyperpolarizability of urea, as documented in the literature, stands at 0.1947 $\times10^{-30}$ esu (Dixon & Matsuzawa, 1994). Calculations reveal that the first-order hyperpolarizability values for nitroguanidine and FOX-7 molecules are approximately 5.21 times and 1.28 times greater, respectively, than the magnitude reported for urea.

3.4. TD-DFT Results: UV-Vis Spectra and Ionization Energies

The ultraviolet-visible (UV-Vis) spectra of FOX-7 and nitroguanidine were investigated using the TD-DFT approach, employing the B3LYP/6-311++G(d,p) functional and basis set. Figure 3 illustrates the computed spectra, revealing prominent absorption bands at approximately 245 nm and 270 nm for nitroguanidine and FOX-7, respectively. Additionally, weaker absorption bands are observed around 200 nm for nitroguanidine and at 300 nm and 340 nm for FOX-7. The key features of the UV-Vis spectra, along with their associated transitions, are summarized in Tables 4 and 5. Furthermore, we explored the ionization of nitroguanidine and FOX-7 molecules by calculating adiabatic and vertical transitions, and the obtained results are presented in Table 6.

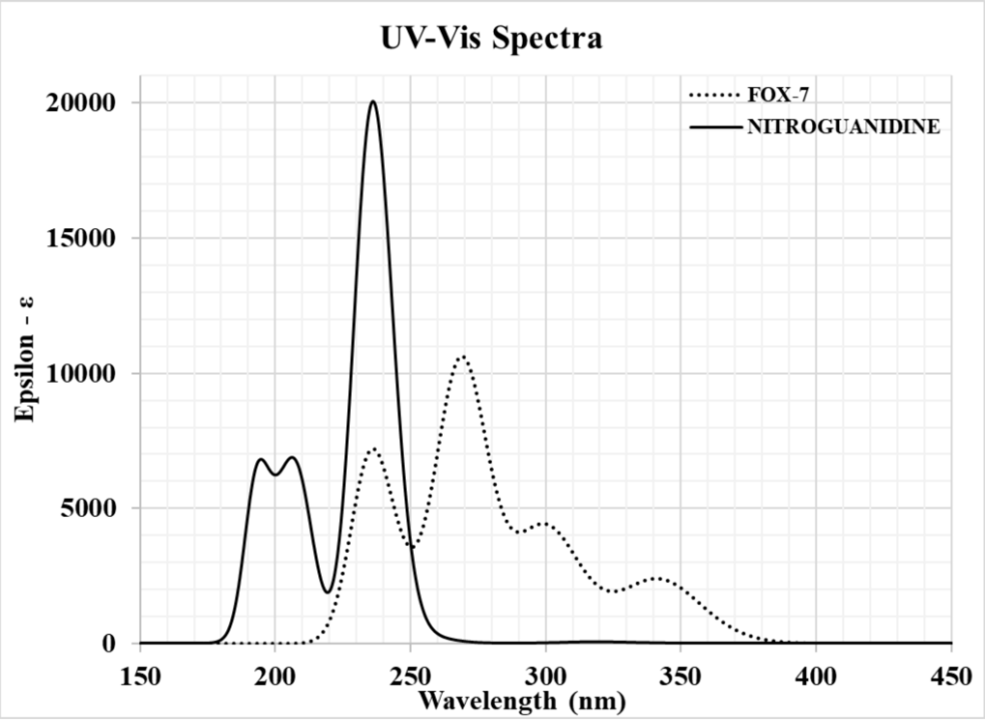


Figure 3. Calculated UV-Vis spectra of the FOX-7 and nitroguanidine molecules (GaussSum program (O'boyle, Tenderholt, & Langner, 2008) was used to plot spectra)

Table 4. TD-DFT results for the excited states of the neutral nitroguanidine (f is the oscillator strength)

Excited State	ΔE (nm)	f	Major Contributions to the Transitions (percentage)
1	318.438	0.0007	H->L (92%)
2	257.543	0.0024	H-3->L (81%)
3	235.872	0.2769	H-1->L (83%)
4	209.826	0.0224	H-4->L (15%), H-2->L (13%), H-1->L+1 (15%), H->L+1 (50%)
5	208.601	0.038	H-5->L (20%), H-4->L (30%), H-2->L (16%), H->L+1 (24%)
6	205.074	0.0196	H-1->L+1 (75%), H->L+1 (21%)
7	201.521	0.0299	H-5->L (70%), H-4->L (10%), H-2->L (15%)
8	193.106	0.0816	H-4->L (38%), H-2->L (39%)
9	189.827	0.0015	H-4->L+1 (28%), H-2->L+1 (63%)
10	185.299	0.0021	H->L+2 (68%), H->L+3 (11%), H->L+4 (10%)

The calculated absorption maximum value for the nitroguanidine molecule is 318.438 nm (f = 0.0007). This value is corresponding to the excited state S0→S1, which includes the transition from HOMO to LUMO (n → π* in nature). The absorption value of the excited state S0→S2 is the transition HOMO-3→LUMO with the absorption value 257.543 nm (f = 0.0024), which is n → π* in nature. The transition HOMO-1→LUMO has a wavelength of 235.872 nm. This transition corresponds to the excited state S0→S3 and is π→π* in nature. Furthermore, the absorption of the excited state S0 →S4 is 209.826 nm (f = 0.0224), corresponding to n→π*, and involving four configurations (HOMO-4→LUMO), HOMO-2→LUMO, HOMO-1→LUMO+1, and HOMO→LUMO+1). The excited state S0→S5 has a wavelength of 208.601 nm (f = 0.038), corresponding to π→π* transition, and involving four configurations (HOMO-5→LUMO, HOMO-4→LUMO, HOMO-2→LUMO, HOMO→LUMO+1). The excited state S0→S6 has a wavelength of 205.074 nm (f= 0.0196). This transition corresponds to n→π* and involving two configurations (HOMO-1→LUMO+1, HOMO→LUMO+1). The excited state S0→S7 transition and involves three configurations (HOMO-5→LUMO, HOMO-4→LUMO, HOMO-2→LUMO) with an absorption value of 201.521nm (f = 0.0299), corresponds to π → π* transition in nature. The excited state S0 →S8 with a wavelength of 193.106 nm (f = 0.0816) corresponds to n → σ* transition and involves two configurations (HOMO-4→LUMO, HOMO-2→LUMO). The absorption of the excited state S0 →S9 is 189.827nm (f = 0.0015) and corresponding to n → π^* transition and involving three configurations (HOMO-4→LUMO+1, HOMO-2→LUMO+1, HOMO-1→LUMO+1). Finally, the excited state S0 →S10, with a wavelength of 185.299 nm (f = 0.0021), corresponds to n → π^* transition and involves three configurations (HOMO→LUMO+2, HOMO→LUMO+3, HOMO→LUMO+4).

Table 5. TD-DFT results for the excited states of the neutral FOX-7 (f is the oscillator strength)

Excited State	ΔE (nm)	f	Major Contributions to the Transitions (percentage)
1	341.874	0.0323	H-1->L (28%), H->L (61%)
2	307.104	0.0187	H-4->L (16%), H-2->L (30%), H-1->L+1 (20%), H->L+1 (28%)
3	297.688	0.0445	H-3->L (12%), H-1->L (51%), HOMO->L (25%)
4	269.361	0.0875	H-2->L (25%), H->L+1 (57%)
5	269.115	0.0523	H-3->L (69%), H->L (12%)
6	256.383	0.0161	H-7->L (24%), H-6->L (21%), H-3->L+1 (31%)
7	241.529	0.0331	H-4->L (39%), H-1->L+1 (51%)
8	234.286	0.0734	H-4->L (32%), H-2->L (27%), H-1->L+1 (15%)
9	233.242	0.001	H-4->L+1 (20%), H-2->L+1 (68%)
10	225.102	0.0068	H-5->L (50%), H-4->L+1 (27%)

The calculated absorption maximum value for the FOX-7 molecule is 341.874nm (f = 0.0323). This value is equal to the excited state S0→S1, including the transition from HOMO to LUMO and from HOMO-1 to LUMO corresponding to a π → π* transition in nature. The absorption value of the excited state S0→S2 is 307.104 nm (f = 0.0187), and corresponds to π →π* transition and involves four configurations (HOMO-4→LUMO), HOMO-2→LUMO, HOMO-1→LUMO+1, HOMO→LUMO+1). The absorption value of the excited state S0→S3 is 297.688 nm (f = 0.0445), and this transition corresponds to π →π*, and involves three configurations (HOMO-3→LUMO), HOMO-1→LUMO, HOMO→LUMO,) Furthermore, the absorption of the excited state S0 →S4 is 269.361 nm (f = 0.0875), and this transition corresponds to π →π* and involves two configurations (HOMO-2→LUMO), HOMO→LUMO+1). The excited state S0→S5 is equal to 269.115 nm (f = 0.0523), and this transition corresponds to π→π*, and involves two configurations (HOMO-3→LUMO), HOMO→LUMO). The excited state S0→S6 has a wavelength of 256.383 nm (f = 0.0161). This transition corresponds to π→π* nature and involves three configurations (HOMO-7→LUMO, HOMO-6→LUMO, HOMO-3→LUMO+1). The excited state S0→S7 is the transition and involves two configurations (HOMO-4→LUMO, HOMO-1→LUMO+1) with the absorption wavelength of 241.529 nm (f = 0.0331), which is π → π* in nature. The excited state S0 →S8 is with a wavelength of 234.286nm (f = 0.0734) corresponding to n → π* transition and involves three configurations (HOMO-4→LUMO, HOMO-2→LUMO, HOMO-1→LUMO+1). The absorption of the excited state S0 →S9 is 189.827 nm (f = 0.001) and this transition is corresponded to π →π* and involves two configurations (HOMO-4→LUMO+1), HOMO-2→LUMO+1). The excited state S0 →S10 is 225.102 nm (f = 0.0068) and this transition is corresponded to n →π* and involves two configurations (HOMO-5→LUMO+1), HOMO-4→LUMO+1).

Table 6. Molecular energies (relative to its neutrals) and dipole moments of the FOX-7 and nitroguanidine (AI: Adiabatic Ionization, VI: Vertical Ionization)

Isomers	Energy (Hartree)	Relative Energy (Hartree)	Relative Energy (kcal/mol)	Relative Energy (cm^{-1})	Relative Energy (eV)	Dipole Moment (D)
FOX-7	-598.374	0.000	0.000	0.000	0.000	8.544
FOX-7 (AI)	-598.172	0.203	532.018	127.155	5.514	9.775
FOX-7 (VI)	-598.157	0.217	570.219	136.286	5.910	8.975
NITROGUANIDINE	-409.853	0.000	0.000	0.000	0.000	7.510
NITROGUANIDINE (AI)	-409.656	0.197	518.400	123.901	5.373	8.016
NITROGUANIDINE (VI)	-409.631	0.222	583.646	139.495	6.049	7.190

The ionization of FOX-7 was studied through adiabatic and vertical ionization methods. The resulting minimum energies were found to be -598.174, and -598.157 Hartree for the adiabatic and vertical ionized states. These energies correspond to 0.203, and 0.217 Hartree relative to their respective neutrals. Adiabatic and vertical ionization energies were calculated as 5.514 eV and 5.910 eV.

Similarly, the ionization of nitroguanidine molecule was studied, and the resulting minimum energies were -409.656, and -409.631 Hartree, corresponding to 0.197, and 0.222 Hartree relative to their respective neutrals. Adiabatic and vertical ionization energies were calculated as 5.373 eV and 6.049 eV.

4. Conclusions and Recommendations

In this study, the structural, electronic, spectroscopic, adiabatic and vertical ionization energy values, and NLO properties of nitroguanidine and FOX-7 molecules, which are high energy explosives were studied using density functional theory. Every molecule underwent conformational analysis, these structures were optimized, and the results were consistent with previous research. The HOMO and LUMO energies of the titled molecules were then used to compute the ionization potential and electron affinity values. Furthermore, the chemical potential (μ), electronegativity (χ), global softness (S), global hardness (η), and electrophilicity index (ω) values were attained. The results showed that FOX-7 molecule is softer but less reactive and stable than nitroguanidine molecule. The dipole moment, polarizability, and first-order hyperpolarizability were used to examine the nonlinear optical properties of these compounds. According to the obtained results, the dipole moment of urea was found 5.47 times smaller than of nitroguanidine and 6.22 times smaller than of FOX-7. Furthermore, the calculated first-order hyper polarizability values for nitroguanidine and FOX-7 molecules were founded be approximately 5.21 times and 1.28 times greater than the magnitude of urea respectively. Additionally, the vertical ionization energy (VE) and adiabatic ionization energy (AE) parameters were calculated through the construction of the singly charged cation radicals. AE of the nitroguanidine calculated as 5.373 eV and 5.514 eV for the FOX-7 molecule. VE of the of the nitroguanidine calculated as 6.049 eV and 5.910 eV for the FOX-7 molecule.

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Statement of Conflicts of Interest

The authors affirm that they do not possess any conflicting interests to disclose.

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Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

References

Agrawal, J. P., (2010). High energy materials: propellants, explosives and pyrotechnics: J*ohn Wiley & Sons.*

Chavez, D., Hill, L., Hiskey, M., and Kinkead, S., (2000). Preparation and explosive properties of azo-and azoxy-furazans. *Journal of Energetic Materials, 18*(2-3), 219-236.

Chu, G.-b., Xi, T., Wang, S.-y., Shui, M., Yan, Y.-h., Lv, G.-q., and Tan, F., (2023). Recent progress in research on the dynamic process of high-energy explosives through pump-probe experiments at high-intensity laser facilities. *Energetic Materials Frontiers*.

Cotton, F. A., Wilkinson, G., Murillo, C. A., and Bochmann, M. (1999). *Advanced inorganic chemistry*: *John Wiley & Sons*.

De Silva, I. C., De Silva, R. M., and De Silva, K. N., (2005). Investigations of nonlinear optical (NLO) properties of Fe, Ru and Os organometallic complexes using high accuracy density functional theory (DFT) calculations. *Journal of Molecular Structure: THEOCHEM, 728*(1-3), 141-145.

Dixon, D. A., and Matsuzawa, N., (1994). Density functional study of the structures and nonlinear optical properties of urea. *The Journal of Physical Chemistry, 98*(15), 3967-3977.

Ekincioğlu, Y., Kılıç, H. Ş., and Dereli, Ö., (2021). DFT Study of Conformational Analysis, Molecular Structure and Properties of para-, meta-and ortho 4-Methoxyphenyl Piperazine Isomers. *Brazilian Journal of Physics, 51*(4), 958-968.

Fleming, I. (1976). Frontier orbitals and organic chemical reactions. *(No Title)*.

Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., and Petersson, G., (2009). 09, Revision D. 01, Gaussian. *Inc., Wallingford, CT.*

Ghanta, S. (2016). Theoretically predicted Fox-7 based new high energy density molecules. *Journal of Molecular Structure, 1118*, 28-33.

Ghanta, S., (2023). Design of derivatives of FOX-7-based new four-member heterocyclic insensitive high energy density molecules: a theoretical prospectives. *Journal of Molecular Modeling, 29*(1), 18.

Halgren, T. A., (1996). Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94. *Journal of computational chemistry, 17*(5-6), 490-519.

He, P. Zhang, J.-G., Wang, K., Yin, X., Jin, X., and Zhang, T.-L., (2015). Extensive theoretical studies on two new members of the FOX-7 family: 5-(dinitromethylene)-1, 4-dinitramino-tetrazole and 1, 1′-dinitro-4, 4′-diamino-5, 5′-bitetrazole as energetic compounds. *Physical Chemistry Chemical Physics, 17*(8), 5840-5848.

Improta, R., and Barone, V., (2004). Absorption and fluorescence spectra of uracil in the gas phase and in aqueous solution: A TD-DFT quantum mechanical study. *Journal of the American Chemical Society, 126*(44), 14320-14321.

Jeffrey, G. A., and Jeffrey, G. A., (1997). *An introduction to hydrogen bonding: Oxford university press New York.* 12

Jeong, K., Jeon, Y., and Kwon, S., (2017). Assessment of various DFT, DFT-D, and MP2 methods for studying FOX-7 detonation properties. *Journal of Molecular Modeling, 23*, 1-6.

Karelson, M., Lobanov, V. S., and Katritzky, A. R., (1996). Quantum-chemical descriptors in QSAR/QSPR studies. *Chemical reviews, 96*(3), 1027-1044.

Klapötke, T. M., (2022). *Chemistry of high-energy materials*: Walter de Gruyter GmbH & Co KG.

Koch, E. C., (2019). Insensitive high explosives: III. Nitroguanidine–synthesis–structure–spectroscopy–sensitiveness. *Propellants, Explosives, Pyrotechnics, 44*(3), 267-292.

Koopmans, T., (1934). About the assignment of wave functions and eigenvalues to the individual electrons of an atom. *Physica, 1*(1-6), 104-113.

Kuklja, M., Rashkeev, S., and Zerilli, F., (2004). Ab initio Calculations of the Electronic Structure of 1, 1-Diamino-2, 2-Dinitroethylene. *Paper presented at the AIP Conference Proceedings.*

Manna, M. S., Das, C. K., and Ghanta, S., (2021). Design of CHNO based new hetero-cyclic high energy density molecules: a theoretical survey. *Structural Chemistry, 32*, 1095-1104.

Mondal, T., Saritha, B., Ghanta, S., Roy, T., Mahapatra, S., and Prasad, M. D., (2009). On some strategies to design new high energy density molecules. *Journal of Molecular Structure: THEOCHEM*, *897*(1-3), 42-47.

O'boyle, N. M., Tenderholt, A. L., and Langner, K. M., (2008). Cclib: a library for package-independent computational chemistry algorithms. *Journal of computational chemistry,* 29(5), 839-845.

Östmark, H., Langlet, A., Bergman, H., Wingborg, N., Wellmar, U., and Bemm, U., (1998). *FOX-7–A new explosive with low sensitivity and high performance.* Paper presented at the The 11th International Detonation Symposium, Colorado, USA.

Prasad, P. N. and Williams, D. J., (1991). Introduction to nonlinear optical effects in molecules and polymers: Wiley New York. 1.

Pravica, M., Liu, Y., Robinson, J., Velisavljevic, N., Liu, Z., and Galley, M., (2012). A high-pressure far-and mid-infrared study of 1, 1-diamino-2, 2-dinitroethylene. *Journal of Applied Physics*, 111(10).

Prendergast, R., (2018). A Solid-State Theoretical and Experimental Analysis of Nitroguanidine and Gunshot Residues. *Syracuse University,*

Shao, Y., Molnar, L., Jung, Y., Kussmann, J., Ochsenfeld, C., Brown, S., and O’Neill, D., (2006). Spartan’08, Wavefunction, Inc. Irvine, CA. *Phys. Chem. Chem. Phys, 8,* 3172-3191.

Sorescu, D. C., Boatz, J. A., and Thompson, D. L., (2001). Classical and quantum-mechanical studies of crystalline FOX-7 (1, 1-diamino-2, 2-dinitroethylene). *The Journal of Physical Chemistry A, 105*(20), 5010-5021.

Sorescu, D. C., Boatz, J. A., and Thompson, D. L., (2003). First-principles calculations of the adsorption of nitromethane and 1, 1-diamino-2, 2-dinitroethylene (FOX-7) molecules on the Al (111) surface. *The Journal of Physical Chemistry B,* 107(34), 8953-8964.

Sun, Q., Zhang, Y., Xu, K., Ren, Z., Song, J., and Zhao, F., (2015). Studies on thermodynamic properties of FOX-7 and its five closed-loop derivatives. *Journal of Chemical & Engineering Data, 60*(7), 2057-2061.

Taylor, D. E., Rob, F., Rice, B. M., Podeszwa, R., and Szalewicz, K., (2011). A molecular dynamics study of 1, 1-diamino-2, 2-dinitroethylene (FOX-7) crystal using a symmetry adapted perturbation theory-based intermolecular force field. *Physical Chemistry Chemical Physics, 13*(37), 16629-16636.

Vijayaraj, R., Subramanian, V., and Chattaraj, P. (2009). Comparison of global reactivity descriptors calculated using various density functionals: a QSAR perspective. *Journal of chemical theory and computation,* 5(10), 2744-2753.