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Article

INTERACTION OF A COPPER ATOM WITH RDX

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ABSTRACT

The effect of a copper atom on RDX molecule is considered within the constraints of density functional theory, at the level of UB3LYP/6-31++G(d,p), UB3LYP/LANL2DZ and UB3LYP/SBKJC. in all the cases, one of the nitro groups is distorted and nitrogen-oxygen bond is broken. the charge distribution indicates that Cu atom transfers some of its electron population to RDX, especially to atoms of the distorted NO_2 moiety. this partial redox process is supported by all the basis sets employed in the calculations. the structural and energetic properties of RDX in the presence of copper atom are discussed.

Keywords: Hexamine, RDX, 1,3,5-trinitrohexahydro-*sym*-triazine, Explosives, Copper, DFT calculations.

1. INTRODUCTION

Cyclotrimethylene trinitramine or 1,3,5-trinitrohexahydro-*sym*-triazine (RDX) [1] is an important explosive which has been in use for long. The most stable crystalline structure of RDX belongs to α–RDX. It is one of the most effective energetic materials with applications ranging from explosives and propellants [2]. RDX is mainly obtained in the industry by direct nitrolysis process (Woolwich) in which hexamethylene tetramine is directly treated with a large excess of strong HNO_3 [1,3-5] at a temperature of 20-25 °C. On the other hand, in the Bachman (Combination Process) process, which is also an industrial process for RDX, the reaction mixture contains HNO_3, NH_4NO_3, acetic anhydride and acetic acid in addition to hexamine [1,3,5].

Besides the experimental studies on RDX, there are some computational studies on its reaction mechanism [6], conformations and bond dissociation energies [7, 8] and gas-phase structure [9]. De Paz and Ciller [10] used Stewart's new semi–empirical method MNDO–PM3 (PM3) for the calculation of gas phase heat of formation of RDX. Catoire et al.,[11]

[♣] Correspondent author: Tel:+90 312 2103244, Fax:+90 312 2103200, E-mail: lturker@metu.edu.tr presented the thermochemical properties of RDX by means of the Density Functional Theory (DFT). In the study of Rice et al., [12], $\Delta H_f^o{}_{(RDX)}$ was calculated by using an isodesmic reaction and DFT method (B3LYP/6–31G(d) level). The value was obtained as 52.8 kcal/mol which was ~ 7 kcal/mol greater than the experimental value. Whereas, in the same study $\Delta H_f^o{}_{(RDX)}$ was calculated to be 45.3 kcal/mol by using atom–equivalent method (with a difference of –0.5 kcal/mol from the experimental value) and that of solid state has been found to be 20.8 kcal/mol (with a difference of +1.9 kcal/mol from the experimental value).

On the other hand, there exist some experimental and theoretical studies on RDX-metal interactions. Density functional theory study of interactions of cyclotrimethylene trinitramine (RDX) with metal-organic framework was reported [13]. Note that copper is one of the metals widely used (either alone or in the form of certain alloys) in ammunitions.

A mathematical flow model is described for one-dimensional detonations in mixtures of high explosives with small inert metal particles. The model and observed detonation velocities for mixtures of RDX and Cu are used to calibrate the assumed equation of state constant as a function of the particle mass fraction [14]. Methods to investigate the igniter /propellant interaction were reported. The tests were performed with black powder and some RDX/metal mixtures including copper [15]. Influence of metal substrates on the detection of explosive residues with laser-induced breakdown spectroscopy was studied [16]. It is demonstrated that despite the strong spectral variation in cyclotrimethylenetrinitramine (RDX) residues applied to various metal substrates, classification of the RDX residue independent of substrate type is feasible.

In the present study, effect of a copper atom on RDX molecule is considered within the constraints of DFT.

2. METHOD

The initial structure optimizations of all the structures leading to energy minima were achieved by using MM2 (molecular mechanics) method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [17,18] at the restricted level [19]. Then, structure optimizations were achieved by using various restricted Hartree-Fock (RHF) methods successively and finally optimizing within the framework of density functional theory (DFT, UB3LYP) [20,21] using basis sets 6-31++G(d,p), LANL2DZ and SBKJC. 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 [22,23]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [23] and Lee, Yang, Parr (LYP) correlation correction functional [24].

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding structure optimization). 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 one local minimum on the potential energy surface. All these computations were performed by using the Spartan 06 [25] package program.

3. RESULTS AND DISCUSSIONS

Elemental copper is characterized with ....3d104s1 electronic configuration in the ground state [26]. The presence of an unpaired electron may cause Cu atom to interact with electron population of some nearby molecules.

3.1. Geometries

As seen in Figure 1 the structure optimizations all show that the presence of Cu atom in the vicinity of RDX molecule causes appreciable elongation of one of nitrogen-oxygen bonds of nitramine group. However, UB3LYP/6-32++G(d,p) type calculation yields a structure (1a, Conformer I) different from the structures obtained by using LANL2DZ (1c) and SBKJC (1d) basis sets. Structure 1b (conformer II) is obtained when structure 1c is reoptimized with UB3LYP/6-32++G(d,p) method. Structures 1a and 1b are two conformers in which nitramine groups occupy different equatorial and axial positions. Bond angles around amine nitrogen linked to NO_2 groups are in between 114°-123° in 1a and 117°-125° in 1b indicating nearly planar arrangement. In 1a one axial and one equatorial NO_2 groups exist whereas in 1b two axial NO_2 exist (see Figure 1). On the other hand, the reverse sequence of optimization process; namely UB3LYP/LANL2DZ optimization of UB3LYP/6-31++G(d,p) optimized structure yielded, the originally UB3LYP/LANL2DZ optimized structure in appearance.

In appearance, LANL2DZ and SBKJC basis sets yield similar structures, similar to conformer II (two nitro groups are axial). Bond angles about the amine nitrogen linked to distorted NO_2 group are in between 116°-125° in 1c and 117°-125° in 1d. Figure 2 depicts bond lengths of the structures obtained by using different basis sets.

Figure 1: RDX+Cu structure optimized by using different basis sets

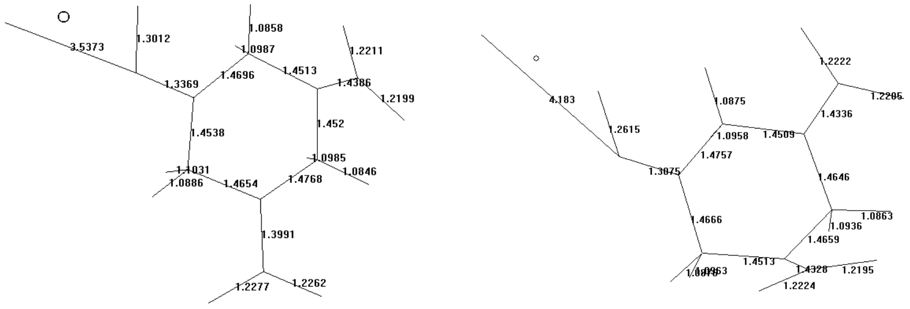
UB3LYP/6-31++G(d,p)
Conformer (I) **1a**

UB3LYP/6-31++G(d,p)
Conformer (II) **1b**

UB3LYP/SBKJC
1c

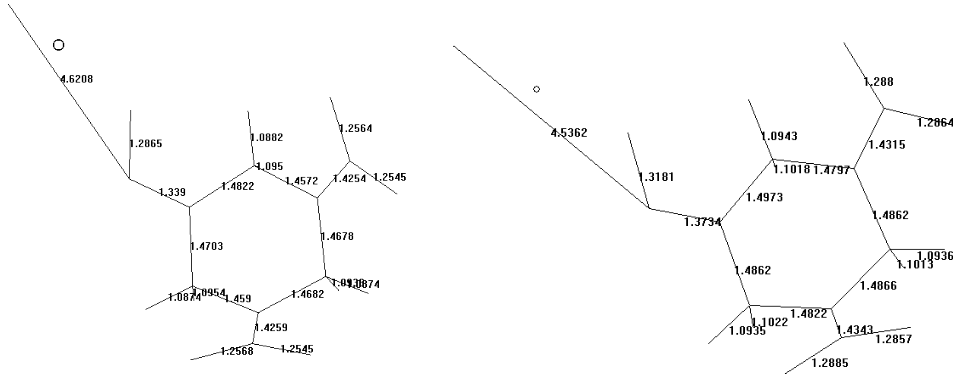
UB3LYP/LANL2DZ
1d

Figure 2: Bond lengths (10^{-10} m) in the optimized RDX+Cu system considered



UB3LYP/6-31++G(d,p)
Conformer (I)

UB3LYP/6-31++G(d,p)
Conformer (II)



UB3LYP/LANL2DZ

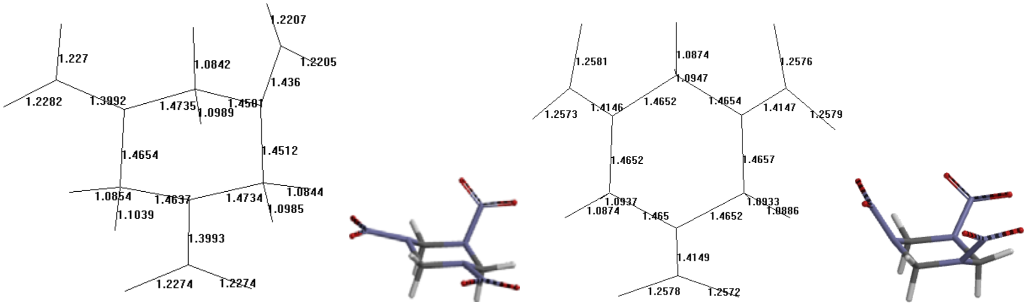
UB3LYP/SBKJC

Whereas, Figure 3 shows similar data for RDX. As seen there the optimization with LANL2DZ and SBKJC basis sets yield similar RDX structures, in which two of the nitro groups are on the same side (occupy axial positions), contrary to the case of 6-31++G(d,p) basis set. Note that 6-31G(d,p) basis sets and its diffuse form (eg; 6-31++G(d,p)) are available for elements H-Kr [27]. The LANL2DZ basis set is especially for the transition metal complexes (including Cu) [27-29]. The SBKJC is available for heavy atoms, Rb and heavier [27]. The bond lengths in conformers I and II are generally similar, except the N-O bond nearby the copper atom. In conformer II the elongated bond (actually nitrogen-oxygen distance) is 4.18 10^{-10} m whereas 3.53 10^{-10} m in conformer I. The LANL2DZ and SBKJC based optimizations yield the length of this bond as 4.62 10^{-10} m and 4.53 10^{-10} m, respectively. All these data indicate that copper atom causes cleavage of this particular bond. The distance between the Cu atom and other oxygen of the nitro group varies between 1.85-1.90 10^{-10} m depending on the type of basis set used. Nitramine bonds in RDX are in between 1.39-1.43 10^{-10} m (UB3LYP/6-31++G(d,p)); 1.41 10^{-10} m (UB3LYP/LANL2DZ); 1.39-1.43 10^{-10} m (UB3LYP/SBKJC). Whereas, in the presence of Cu atom, the nitramine bond incident to the distorted NO_2 group is 1.33 10^{-10} m, which means some electron population has been transferred from amine nitrogen to the nitro group perturbed by Cu. Table 1 shows the dipole moments and some distances to Cu atom in the structures considered.

Figure 3: Bond lengths (10^{-10} m) of RDX molecule in the optimized structure

UB3LYP/6-31++G(d,p)

UB3LYP/LANL2DZ



UB3LYP/SBKJC

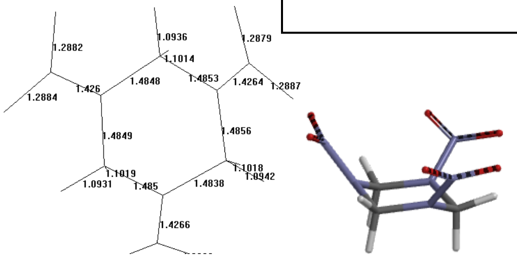


Table 1: Dipole moments and Cu-O and Cu-N distances of the optimized structure

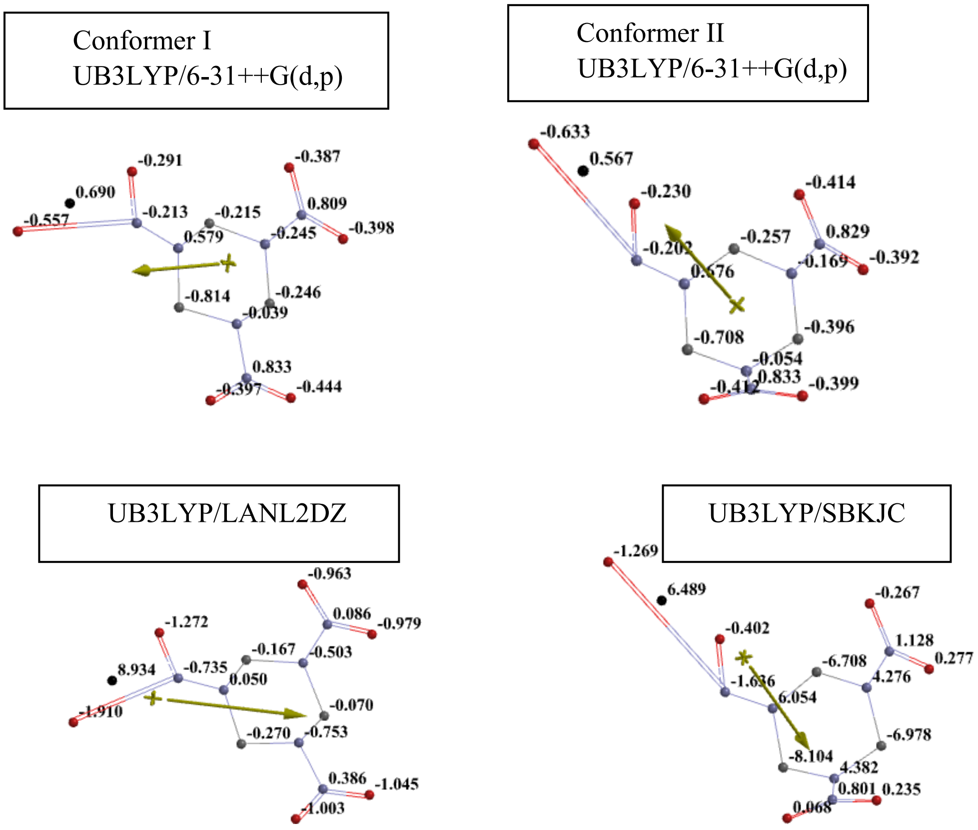
Method	**Dipole moment**	**Cu-O***	**Cu-N**	**Cu-O**
UB3LYP/6-31++G(d,p) Conformer **I** (**1a**)	2.93	1.71	2.02	1.87
UB3LYP/6-31++G(d,p) Conformer **II** (**1b**)	13.54	1.70	2.61	1.85
UB3LYP/LANL2DZ	162.36	1.78	2.89	1.90
UB3LYP/SBKJC	94.44	1.75	2.84	1.86

Dipole moments in Debye, distances in 10^{-10} m. * Oxygen of the broken bond.

3.2. Charges

Figure 4 shows the electrostatic charge distribution on the optimized structures containing Cu atom. Two of the nitramine groups have amine nitrogen atoms possessing negative charge development. Whereas, the amine nitrogen linked to the distorted NO_2 group has positive charge accumulation. In each case, the copper atom acquires certain positive charge. Therefore, some electron population from the amine nitrogen and the copper atom should have been delivered to the nitrogen of the distorted NO_2 group. Indeed, negative charge develops on all the atoms of the distorted NO_2 group. So, the copper atom is oxidized whereas the distorted nitro group is reduced (partial oxidation and reduction). The distorted NO_2 group should have some partial resemblance to NO_2- group. Adjacent negative charges on the atoms of the distorted NO_2 group causes the N-O bond elongation and thus its cleavage. However, the charge distribution over the RDX moiety varies depending on the basis set employed (see Figure 4). So, conformers I and II have dipole moments possessing similar directional orientation whereas LANL2DZ and SBKJC based-optimized structures have oppositely oriented dipole moments to the previous two cases (see Figure 1). Also note that SBKJC based-optimized structure has some unusually high (in absolute values) charges on certain sites.

Figure 4: The electrostatic charges on the optimized RDX+Cu system



3.3. Energies

Table 2 shows the zero point energies (ZPE) and the corrected total energies (Ecorr) of the structures shown in Figure 1. As seen in Table 2 conformer I is more stable than conformer II. Note that both of them are the yield of UB3LYP/6-31++G(d,p) optimization. The single point calculation on the structure obtained by UB3LYP/LANL2DZ optimized structure, namely UB3LYP/6-31++G(d,p)//UB3LYP/LANL2DZ yields corrected total energy value less negative (Table 2, 5th energy value) than the respective energies of conformers I and II. Therefore, 6-31++G(d,p) basis set results in more stable optimized structure for conformer I. On the other hand, UB3LYP/LANL2DZ// UB3LYP/6-31++G(d,p) calculation (on conformer I yields less negative corrected total energy than UB3LYP/LANL2DZ (6th and 3rd energy values, respectively). Similar calculation on conformer II also yields less negative energy (7th and 3rd energy values, respectively). When the energies 6th and 7th are considered, LANL2DZ basis set results yields more stable conformer II than conformer I.

Table 2: ZPE and corrected total energies of the structures considered

Optimization method	ZPE	E_{corr}
UB3LYP/6-31++G(d,p) Conformer **I**	367.79	-6662465.16
UB3LYP/6-31++G(d,p) Conformer **II**	368.51	-6662439.55
UB3LYP/LANL2DZ	364.13	-2869899.11
UB3LYP/SBKJC	358.9	-975390.06
UB3LYP/6-31++G(d,p) //UB3LYP/LANL2DZ	362.58	-6662407.62
UB3LYP/LANL2DZ// UB3LYP/ 6-31++G(d,p) Conformer **I**	367.66	-2869811.37
UB3LYP/LANL2DZ// UB3LYP/ 6-31++G(d,p) Conformer **II**	369.2	-2869846.97

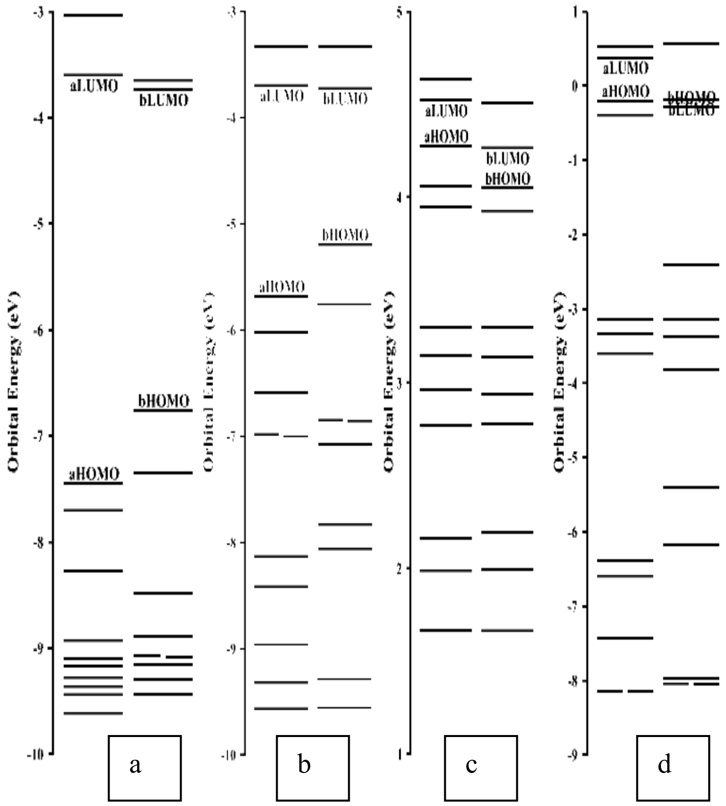
Energies in kJ/mol.

3.4. Molecular orbital energies

Figure 5 shows the molecular orbital energy spectra of the system. Conformer I possesses more condensed spacing of the lower lying occupied molecular orbital energy levels compared to conformer II. Consequently, it is more stable than the later one. Stereochemically, conformer I has one equatorial and one axial nitramine groups which should be more stable than conformer II with two axial groups. Note that one amine nitrogen has a nearly planar form in all the structures. Conformer I and II are characterized with large HOMO-LUMO energy separation (UB3LYP/6-31++G(d,p)). So they should be rather insensitive systems, because sensitivity (impact) is claimed to be associated with existence of closely spaced frontier molecular orbitals (FMO) namely the HOMO and LUMO [30]. On the contrary, UB3LYP/LANL2DZ and UB3LYP/SBKJC based calculations result relatively much closely spaced FMOs. Table 3 shows the FMO energies and interfrontier energy gaps ($\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$) of the systems considered.

Note that some of them are α- and some β-type orbitals because the composite system is an open shell due to unpaired electron of Cu atom. Table 4 contains similar data for RDX molecule. Comparison of the data in Tables 3 and 4 shows that Cu atom raises up the FMOs of RDX in the cases of UB3LYP/6-31++G(d,p) and UB3LYP/LANL2DZ but lowers when UB3LYP/SBKJC type calculations considered.

Figure 5: Molecular orbital energies of the system. a) UB3LYP/6-31++G(d,p) Conformer I; b) UB3LYP/6-31++G(d,p) ConformerII; c) UB3LYP/SBKJC; d) UB3LYP/LANL2DZ



As seen in Figure 6 the HOMO and LUMO of conformer I and II (UB3LYP/6-31++G(d,p)) spread not only the nitramine group but over Cu atom as well. The d-atomic orbitals of Cu atom also contribute the LUMO. Cu atom denotes some electron population to the nitrogen atom and maybe accepting some from oxygen atoms into its empty d-orbitals.

Whereas, contribution to HOMO is little or nil in the cases of LANL2DZ and SBKJC basis sets, respectively. So UB3LYP/6-31++G(d,p) calculations represents a different picture from the others.

Table 3: The frontier molecular orbitals and interfrontier energy gaps of the structures considered

Optimization method	HOMO	LUMO	Δε
UB3LYP/6-31++G(d,p) Conformer **I**	-6.8 β	3.7 β	10.5
UB3LYP/6-31++G(d,p) Conformer **II**	-5.2 β	-3.7 β	1.5
UB3LYP/LANL2DZ	-0.2 α	-0.2 β	0
UB3LYP/SBKJC	4.3 α	4.3 α	0

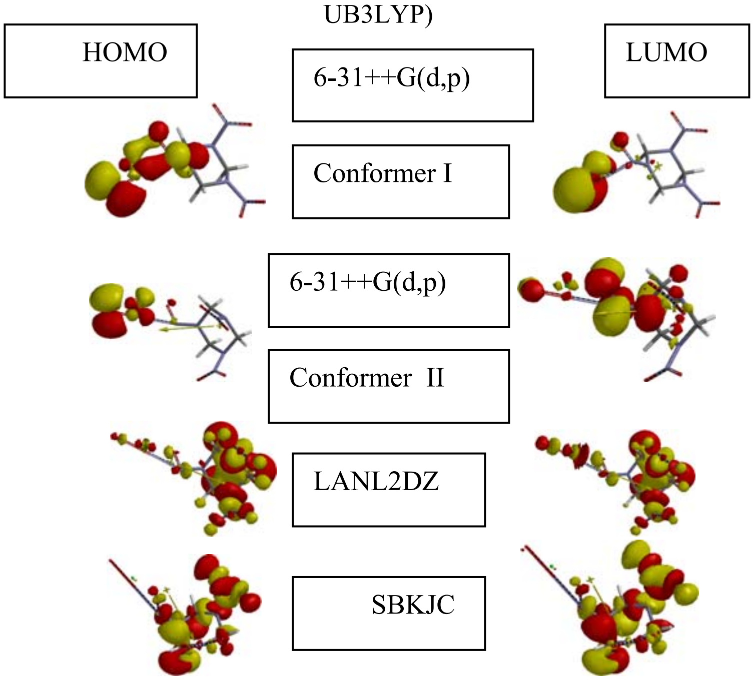
Energies in eV. α and β stand for alpha and beta type orbitals. $\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$.

Table 4: The frontier molecular orbital energies and interfrontier energy gap of RDX

Optimization Method	HOMO	LUMO	Δε
UB3LYP/631++G(d,p)	-8.87	-2.89	5.98
UB3LYP/LANL2DZ	-8.65	-3.02	5.63
UB3LYP/SBKJC	4.57	4.57	0

Energies in eV. $\Delta\varepsilon=\varepsilon_{LUMO}-\varepsilon_{HOMO}$

Figure 6: The HOMO and LUMO patterns of the optimized system (the functional is UB3LYP)



4. CONCLUSION

The present DFT study indicates that copper atom interacts with RDX molecule (in vacuum conditions), causing elongation of the nitrogen-oxygen bond of one of NO_2 groups. The elongation occurs whatever the basis set used (6-31++G(d,p), LANL2DZ or SBKJC) and it is so much that the bond cleaves. Moreover, the charge development indicates that Cu atom transfers some of electron population to RDX moiety. As a conjecture, in the solid phase this effect of Cu should be enhanced and change some ballistic properties of RDX and may cause some drastic results, at least, the shelf-life of RDX should be affected.

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