

## Composites of zinc and *cis*-dinitroglycoluril isomers - A DFT treatment

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### ABSTRACT

An insensitive explosive, *cis*-1,4-Dinitroglycoluril also known as DINGU, is considered to investigate the compatibility of it and its nitramine isomers with zinc in 1:1 composites. The model composites of them have been subjected to density functional treatment at the level of B3LYP/6-31++G(d,p). Within the restrictions of the theory and the level of calculations performed, it has been found that two of the model composites considered are unstable and undergo N-NO<sub>2</sub> bond rupture. Only the third one, in which N-NO<sub>2</sub> bonds exist in different rings but nearby of each other is stable. Some physical and molecular orbital properties of the systems are obtained and discussed. © 2020 Knowledge Empowerment Foundation

### KEYWORDS

DINGU; Dinitroglycoluril; Explosives; Zinc; Density functional.

### INTRODUCTION

*cis*-1,4-Dinitroglycoluril which is also known as *cis*-DINGU or DINGU<sup>[1,2]</sup>, is an important explosive. Recently it has been of interest to the high energy materials community. *cis*-DINGU was first prepared by Franchimont and Klobbie as early as 1888<sup>[3,4]</sup>. Afterwards, various syntheses of *cis*-DINGU and its derivatives were described in the literature<sup>[5-9]</sup>. Till now *cis*-DINGU has been fully characterized<sup>[2,10,11]</sup>. In recent years *cis*-DINGU is incorporated as one of the potential ingredients for many low vulnerability ammunition applications<sup>[12]</sup>. It has been considered as an insensitive alternative to RDX (hexahydro-1,3,5-trinitro-*s*-triazine) and TNT (trinitrotoluene)<sup>[13]</sup>.

Many *cis*-DINGU based polymer bonded

explosives (PBXs) have been prepared<sup>[15,16]</sup>. They generally exhibit high explosion energy and low vulnerability, good physico-chemical stability, so that they are comparable to triaminotrinitrobenzene (TATB)-based PBXs. DINGU/Estane PBXs were investigated in detail<sup>[11]</sup>. Ternary compositions of *cis*-DINGU with TNT and RDX were patented<sup>[16]</sup>.

The preparation of *cis*-DINGU requires very simple and inexpensive starting materials as compared to TATB. Because of that, *cis*-DINGU based PBXs have much preference over TATB based PBXs<sup>[17]</sup>. Some toxicological publications on *cis*-DINGU are present in the literature<sup>[5-7,18]</sup> and the data have revealed that it would be only slightly toxic according to the classical guidelines. Also, in the literature, there are many studies on *cis*-DINGU including its synthesis<sup>[5-7]</sup>, structure

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determination (X-ray diffraction for *cis*-DINGU)<sup>[2]</sup>, evaluation of the solid-state formation enthalpy<sup>[19]</sup>, spectro-thermal decomposition<sup>[20]</sup>, mass-spectral fragmentation pathways<sup>[21]</sup>, modelization by molecular mechanics<sup>[22]</sup>, modelization by using AM1 and PM3 methods<sup>[23]</sup>. Some computational study exists in the literature where the performed DFT and *ab initio* calculations revealed some structural, quantum chemical and thermal properties of DINGU configurational isomers (*cis*- and *trans*- DINGU) in the gas phase<sup>[24,25]</sup>. Interaction of *cis*-1,4-Dinitroglycoluril and its isomers with magnesium was reported<sup>[26]</sup>. In the present study, interaction of *cis*-1,4-dinitroglycoluril (*cis*-DINGU) and two of its constitutional isomers with zinc are considered within the constraints of B3LYP/6-31++G(d,p) of DFT calculations.

### METHOD OF CALCULATION

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method<sup>[27,28]</sup> at the restricted level<sup>[29,30]</sup>. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory (DFT, B3LYP)<sup>[31,32]</sup> finally at the levels of 6-31++G(d,p) (restricted closed-shell). 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<sup>[32,33]</sup>. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional<sup>[35]</sup> and Lee, Yang, Parr (LYP) correlation correction functional<sup>[36]</sup>. The vibrational analyses were also done. The total electronic energies

are corrected for the zero point vibrational energy (ZPE). 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. All these calculations were done by using the Spartan 06 package program<sup>[37]</sup>.

### RESULTS AND DISCUSSION

The isomers of *cis*-dinitroglycoluril of the present concern are shown in Figure 1. Note that *cis*ness of them is based on the position of the hydrogens at the fusion points of the rings. The dinitro case engenders three constitutional isomers of the nitroglycolurils, whereas less or more nitro having ones results only a single structure.

Figure 2 shows the optimized structures as well as the direction of the dipole moment vectors. The optimized structures all have C1 point group.

Presently zinc composites of these isomers are considered. Figure 3 shows the optimized structures of the composites and the direction of the dipole moments. TABLE 1 includes the N-NO<sub>2</sub> bond lengths in the composites.

Zinc atom has  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$  ground state electronic configuration. It is widely used in various inorganic and organic reactions, especially as reducing agent or forming some organozinc compounds<sup>[38]</sup>.

As seen in Figure 3 and TABLE 1 in all the composites considered the zinc atom causes elongation of one of the N-NO<sub>2</sub> bonds compared to the other N-NO<sub>2</sub> bond in the same structure. However, the elongation in B+Zn composite is not as drastic as the others.

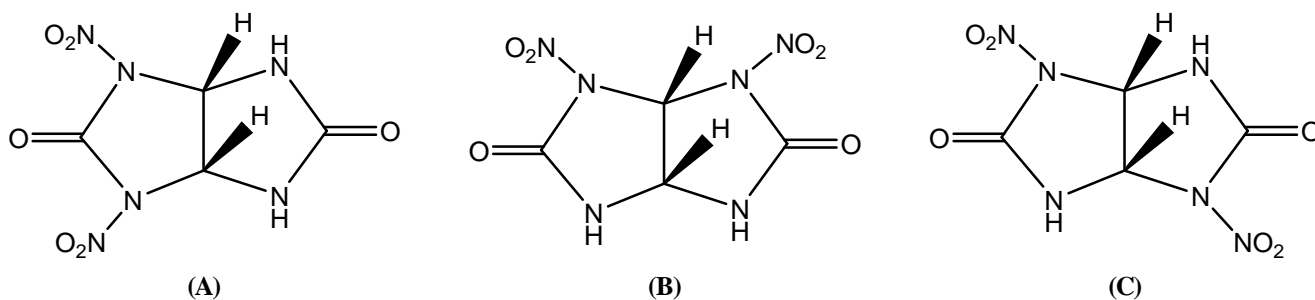


Figure 1: Structures of *cis*-DINGU isomers.

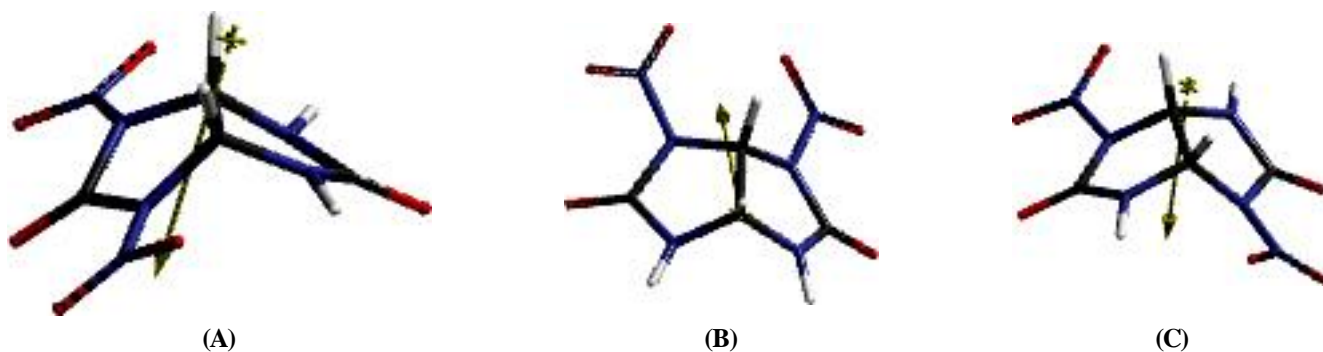


Figure 2: Optimized structures of the parents considered.

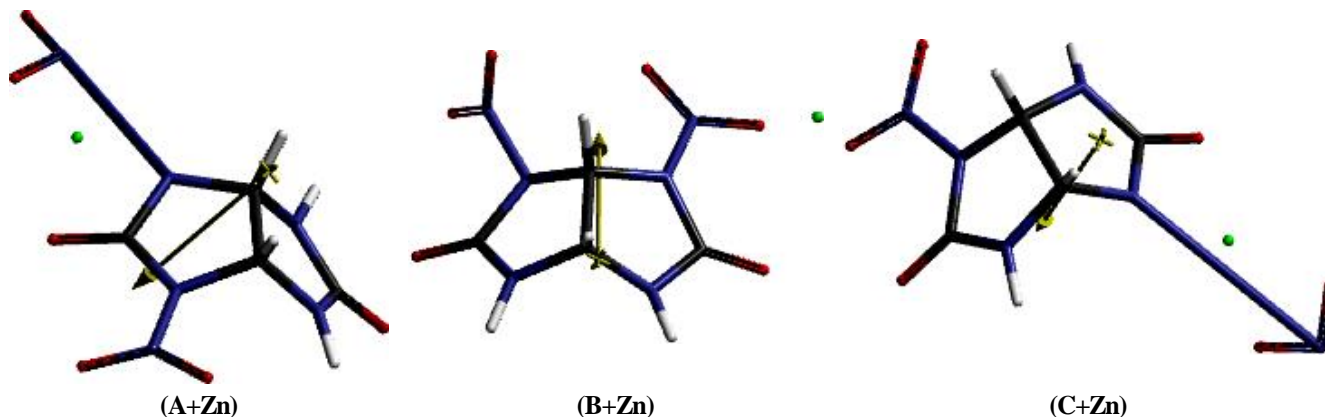


Figure 3: Optimized structures of the composites considered.

TABLE 1: The N-NO<sub>2</sub> bond/distance (Å) in the composites considered.

A	B	C
4.153, 1.399	1.464, 1.394	4.291, 1.395

Figure 4 shows the electrostatic potential (ESP) charges on the atoms of the composites. As seen in the figure in all the cases the zinc atom acquires some positive partial charge such that the order is C+Zn>A+Zn > B+ Zn. Note 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<sup>[37]</sup>.

The zinc atom transfers some electron population to the organic partner. The location of Zn in the optimized composites and the eagerness of the organic partner for electrons are some of the main factors affecting the transfer of electron population in these composites.

Figure 5 displays the electrostatic potential maps of the composites where the blue/bluish and red/reddish regions stand for positive and negative potential regions respectively.

TABLE 2 shows some energies of the parent isomers where E, ZPE and E<sub>c</sub> stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The corrected total electronic energy values indicate that the electronic stability order is C>A>B. The same order is obtained for the E<sub>c</sub> values of the respective composite systems (TABLE 3). Although, composite systems A+Zn and C+Zn are actually decomposed by the action of Zn, in each case the assembly of the system consisting of NO<sub>2</sub> moiety and the remnant structure constitutes the above mentioned stability order.

TABLE 4 displays the HOMO, LUMO energies and the interfrontier molecular orbital (FMO) energy gaps ( $\Delta\epsilon$ ) of the present isomers (parents). The HOMO energies follow the order of C<B<A whereas for the LUMO energies the order of A<C<B holds. The FMO energy gap ( $\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$ ) values result the order of C>B>A.

TABLE 5 stands for the similar energy values of the composite systems. Their HOMO energies exhibit the order of C+Zn >A+ Zn >B+ Zn. Whereas their LUMO energies fall in to the order of A+ Zn< B+ Zn<

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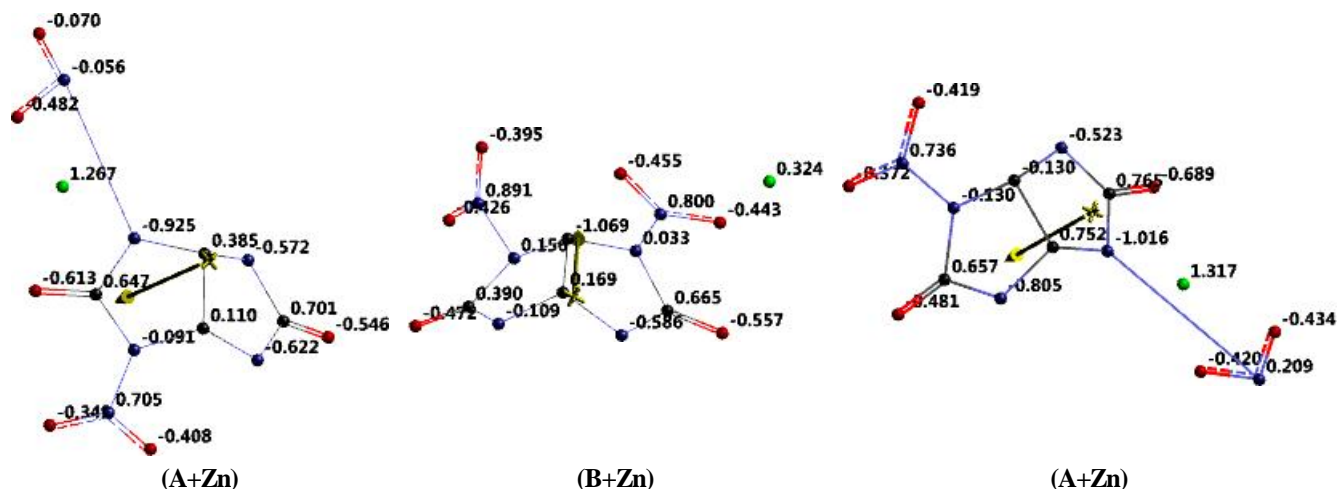


Figure 4: The ESP charges on the atoms of the composites considered.

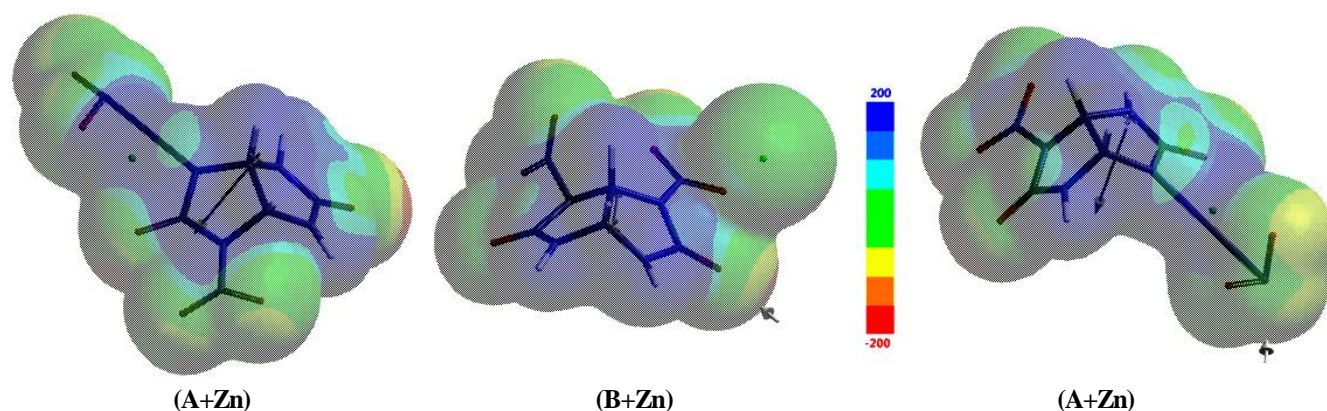


Figure 5: Electrostatic potential maps of the composites.

TABLE 2: Some energies of the isomers (parents) considered.

Structure	E	ZPE	$E_c$
A	-2453561.34	329.87	-2453231.47
B	-2453540.11	328.99	-2453211.12
C	-2453573.80	330.45	-2453243.35

Energies in kJ/mol.

TABLE 3: Some energies of the composites considered.

Structure	E	ZPE	$E_c$
A+Zn	-7124916.73	322.65	-7124594.08
B+Zn	-7124616.68	330.57	-7124286.11
C+Zn	-7124973.60	325.88	-7124647.72

Energies in kJ/mol.

TABLE 4: The HOMO, LUMO energies and  $\Delta\epsilon$  values of the isomers (parents) considered.

Structure	HOMO	LUMO	$\Delta\epsilon$
A	-817.69	-331.42	486.27
B	-827.22	-275.31	551.91
C	-848.40	-289.74	558.66

Energies in kJ/mol.

TABLE 5: The HOMO, LUMO energies and the interfrontier molecular orbital energy gaps ( $\Delta\epsilon$ ) of the composites considered.

Structure	HOMO	LUMO	$\Delta\epsilon$
A+Zn	-726.58	-296.32	430.26
B+Zn	-594.77	-281.71	313.06
C+Zn	-759.45	-273.62	485.83

Energies in kJ/mol.

C+ Zn. Consequently, their  $\Delta\epsilon$  values follow the order of B+ Zn > A+ Zn > C+ Zn.

Figure 6 displays some of the molecular orbital energy levels of the composite systems. As seen in the figure, the structurally stable system, B+Zn, is characterized with higher HOMO energy level as compared to the others. Note that its next highest occupied molecular orbital (NHOMO) is much lower than the HOMO level as compared to the other cases.

Which factors dictate the relative stabilities of the composites is/are the matter of question. Relatively speaking why structure-B is almost inert against Zn



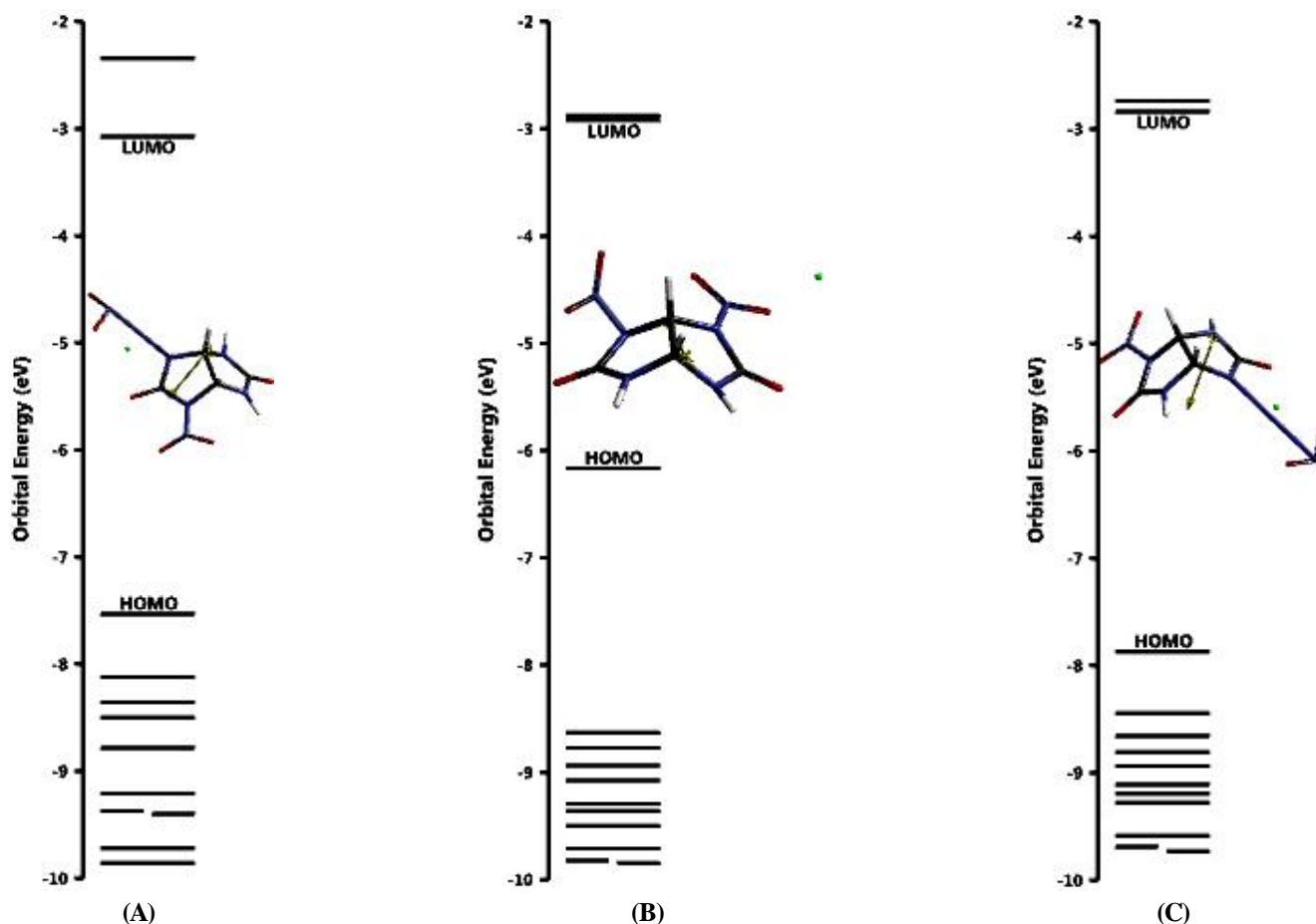


Figure 6: Some of the orbital energies of the composites.

TABLE 6: Chemical hardness ( $\eta$ ), absolute electronegativity ( $\chi$ ) and dipole moments of the isomers (parents) considered.

Structure	$\eta$ (kJ/mol.)	$\chi$ (kJ/mol.)	DM (Debye)
A	243.135	574.555	4.63
B	275.955	551.265	8.10
C	279.33	569.07	4.40

whereas structures A and C undergo cleavage of an N-NO<sub>2</sub> bond. TABLE 6 lists the chemical hardness ( $\eta$ ), absolute electronegativity ( $\chi$ )<sup>[39,40]</sup> and the dipole moment (DM) values of the parent isomers.

B has the lowest electronegativity  $\chi$ . The order of electronegativities is A>C>B. Whereas, the charge on the Zn atom in the composites follow the order of C>A>B. Thus B is not as eager to take electrons from Zn as the others. Note that  $\eta$  and  $\chi$  are formulated as<sup>[39,40]</sup>,

$$\eta = -(\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})/2$$

$$\chi = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$$

The hardness values of the parents cannot explain

the observed structural stability of composite B+Zn whereas the lowest  $\chi$  value of B among the others can. The dipole moment of B is distinguishably higher than the others. Interaction of atoms/molecules is a complicated phenomenon and function of various attractive and repulsive forces in action<sup>[41]</sup>. Some interactions could be mainly charge-controlled whereas some are orbital-controlled. In most of the cases both factors contribute at different extents in to the interaction energy. In the preset case the Zn atom donates some electron population to the organic partner in the composites. In the case of B+Zn the accepted electron population is stabilized within the organic partner whereas in the case of others, an NO<sub>2</sub> moiety is expelled from the structure.

On the other hand, anionic forms of the parent isomers (see Figure 7) exhibit different structural stability compared to their neutral forms and the zinc composites. The anion of B undergoes cleavage of N-NO<sub>2</sub> bond whereas the other anions keep their integrity.

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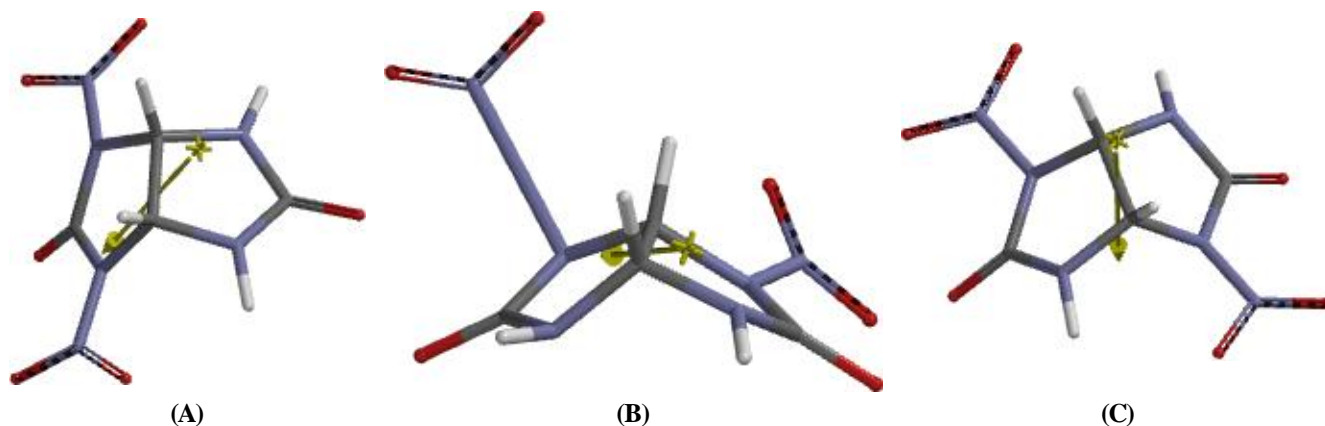


Figure 7: Optimized structures of the anionic forms of the parents (UB3LYP/6-31++G(d,p)).

Electronic stability/instability exhibited by the anions of the parent isomers has revealed that the relevant property in the composites is not dictated only by the electron population loaded on to the parents but also the location of the zinc atom which perturbs the molecular orbitals and the electron distribution of the parents. The perturbed systems then acquire new electronegativities, thus determines the electron population to be transferred from the zinc atom. Consequently, the electronegativity of B+Zn composite is the least among the other composites as parent B among the set of parents considered. TABLE 7 shows some energies of the parent anions. The electronic stability of the anions is B>A>C however B has a broken N-NO<sub>2</sub> bond (the length/distance is 2.53 Å).

TABLE 7: Some energies of the parent anions.

Isomer	E	ZPE	Ec
A	-2453747.22	319.04	-2453428.18
B	-2453779.04	315.21	-2453463.83
C	-2453724.61	318.46	-2453406.15

Energies in kJ/mol.

## CONCLUSION

Modeling study presently considered within the constraints of DFT and the level of calculations performed reveals that *cis*-DINGU and its constitutional nitramine isomers in 1:1 composites are incompatible with zinc except the case in which N-NO<sub>2</sub> bonds exist in different rings but nearby of each other. The metal transfers some electron population to the organic component causing the cleavage of N-NO<sub>2</sub> bond. The expelled NO<sub>2</sub> moiety and the remnant of the organic

component possess some partial negative while the magnesium acquires the opposite charge. The stable composite should be investigated in future in terms of its ballistic characteristics.

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