Dinitrohydrazines and Interaction of Them with Some Group-II Metals - DFT Treatment

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Abstract

Dinitrohydrazines and interaction of them with some group-II metals have been considered within the restrictions of density functional theory and the basis set applied (B3LYP/6-311++G(d,p)). Dinitrohydrazine has two isomers as *geminal* and *vicinal*. The calculations reveal that both of them are structurally stable. The *vicinal* form electronically is more stable and thermo chemically more favorable than the other isomer. The beryllium magnesium and calcium (1:1) composites of them are considered. The results indicate that only the beryllium composites (*geminal* and *vicinal*) are structurally intact while the others undergo decomposition due to reductive cleavage by the metals. The decompositions occurred exhibit variations from one composite to the other.

1. Introduction

N-nitrohydrazines have been somewhat neglected chemicals. However, Kalinin et al., managed to synthesize various N-nitrohydrazines and their salts starting from the silylhydrazines and nitrating with nitrogen pentoxide [1]. Picard and Boivin reported the nitration of N,N'-disubstituted hydrazines [2]. The nitration of N,N'-disubstituted hydrazines by means of nitric acid/acetic anhydride was found to yield in most of the cases the azo derivatives. An exception was N,N'-dibenzoylhydrazine which under the same conditions gave N,N'-dinitro- N,N'-dibenzoylhydrazine [2]. On the other hand, Ball interested on the nitrohydrazines as potential high energy materials and performed a series of calculations to determine the optimized structures, vibrational frequencies, and fundamental thermodynamic properties of nitrohydrazine and dinitrohydrazine

employing G2, G3 methods, and two complete basis set [3]. The results of enthalpies of formation calculations suggest that nitrohydrazines are indeed high energy materials, with decomposition energies per gram exceeding ammonium nitrate and TNT but less than RDX or HMX.

2. Method of Computation

The initial geometry optimizations of all the structures leading to energy minima have been achieved by using MM2 method followed by semi-empirical PM3 self consistent fields molecular orbital (SCF MO) method [4,5] at the restricted level [6,7]. Subsequent optimizations were achieved at Hartree-Fock level employing various basis sets. Then, geometry optimizations were managed within the framework of density functional theory [8,9] at the level of B3LYP/6-311++G(d,p) [6,10]. 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 [9,11]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [12] and Lee, Yang, Parr (LYP) correlation correction functional [13]. The vibrational analyses also have been 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 stands for the number of atoms in the system. This has indicated that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations have been done by using the Spartan 06 package program [14].

3. Results and Discussion

Dinitrohydrazines

Dinitrohydrazine (DNH) is a nitramine type explosive and has two configurational forms; *geminal* and *vicinal* namely 1,1-dinitrohydrazine and 1,2-dinitrohydrazine. Figure 1 shows the optimized structures and the direction of dipole moment vectors of those.
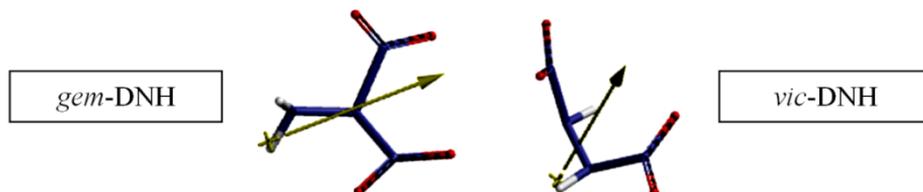

Figure 1. Optimized structures of *geminal* and *vicinal* dinitrohdrazines.

In the case of *geminal* form the dipole moment (3.50 D) vector originates from somewhere around NH_2 moiety of the hydrazine backbone towards the nitro groups. Note that the *geminal* dinitrohydrazine molecule is not a true push-pull type system because of the valency of the nitrogen atom bearing the two nitro groups. However, the lone pair of that nitrogen atom may delocalize over the nitro groups (acquiring itself some positive charge) even may be assisted by the lone pair of NH_2 moiety (α-effect [15]). Consequently some of the σ-electron population of the N-N bond should shift to $N(NO_2)_2$ moiety, thus the NH_2 group gets some positive charge as a whole (see Figure 2) (note that one of the nitro groups has more over all positive charge than the other one). Whereas the dipole moment of the *vicinal* isomer is 2.90 D, it is less than the *geminal* one due to opposing effects of NNO_2 groups. Figure 2 shows the electrostatic potential (ESP) charges on the atoms of the dinitrohydrazines. 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 [14].
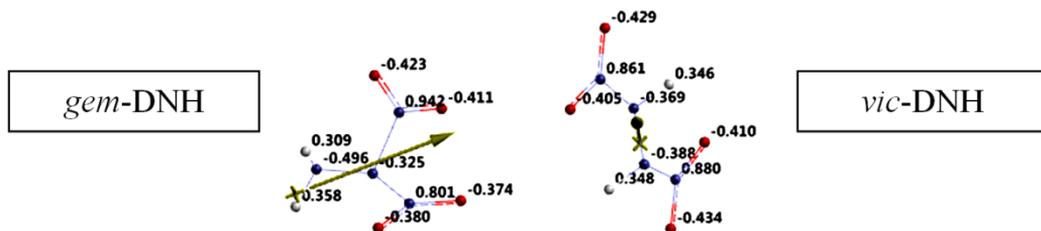

Figure 2. The ESP charges on atoms of the dinitrohydrazines.

Figure 3 shows the electrostatic potential maps of the dinitrohydrazines where the blue regions relatively stand for the most positive potential field and red ones, if exists any, the most negative ones.
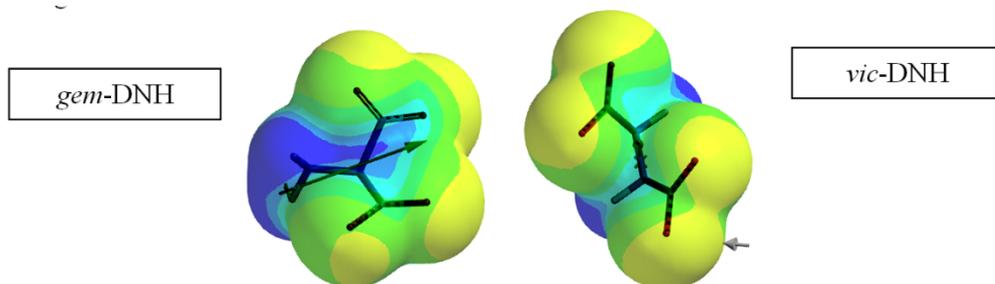

Figure 3. Electrostatic potential maps of the dinitrohydrazines.

Table 1 shows some energies of the dinitrohydrazines where E, ZPE and E_C stand for total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. As seen in the table, of the two forms of dinitrohydrazine the *vicinal* isomer electronically is more stable than the *geminal* one.

Table 1. Some energies of the dinitrohydrazines.

Structures	E	ZPE	E_C
gem-DNH	-1367840.61	145.83	-1367694.78
vic-DNH	-1367903.46	152.35	-1367751.11

Energies in kJ/mol.

Table 2 contains some standard state thermodynamic properties of the dinitrohydrazines. As seen in the table, the *vicinal* isomer is more exothermic and more favorable to form compared to the *geminal* one.

Table 2. Some thermodynamic properties of the dinitrohydrazines.

Structures	H^o (kJ/mol.)	S^o (J/mol^o)	G^o (kJ/mol.)
gem-DNH	-1367686.759	346.76	-1367790.147
vic-DNH	-1367744.746	336.02	-1367844.933

Figure 4 (see also Table 3) displays some of the molecular orbital energy levels of the dinitrohydrazines. The *geminal* isomer is characterized with higher HOMO but lower LUMO energies compared to the *vicinal* form. Consequently, the *geminal* one has much narrower frontier molecular orbital energy gap ($\Delta\varepsilon$), thus should be more susceptible to impact stimulus because there exists an adverse correlation between the impact sensitivity and $\Delta\varepsilon$ value [16,17].

Table 3 includes the HOMO, LUMO energies and the interfrontier molecular orbital energy gap ($\Delta\varepsilon$) values ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) of the dinitrohydrazines. The *vicinal* isomer has lower HOMO but higher LUMO energy level. Note that in general electron donating substituents raise up both of the frontier molecular orbital energies whereas electron attracting ones lower the both energy levels. Conjugation on the other hand, raises up the HOMO, but lowers the LUMO energy levels [15]. In the dinitrohydrazines, these effects should be operating at different extends depending on the location of NO_2 and NH_2 groups.
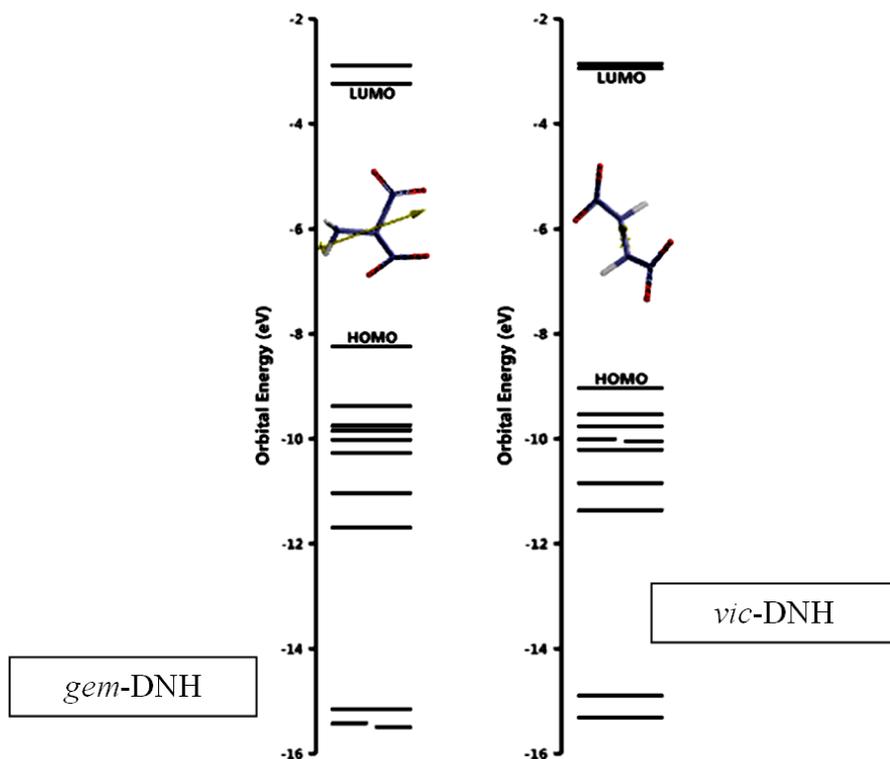
Figure 4. Some of the molecular orbital energy levels of the dinitrohydrazines.

Table 3. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the dinitrohydrazines.

Structures	HOMO	LUMO	$\Delta\varepsilon$
gem-DNH	-795.12	-312.68	482.44
vic-DNH	-871.07	-283.56	587.51

Energies in kJ/mol.

Figure 5 displays the HOMO and LUMO patterns of the dinitrohydrazines.

Figure 6 shows the local ionization potential maps of the dinitrohydrazines. In the local ionization potential map conventionally red regions on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. On the other hand, regions having blue color represent areas where ionization is relatively difficult.
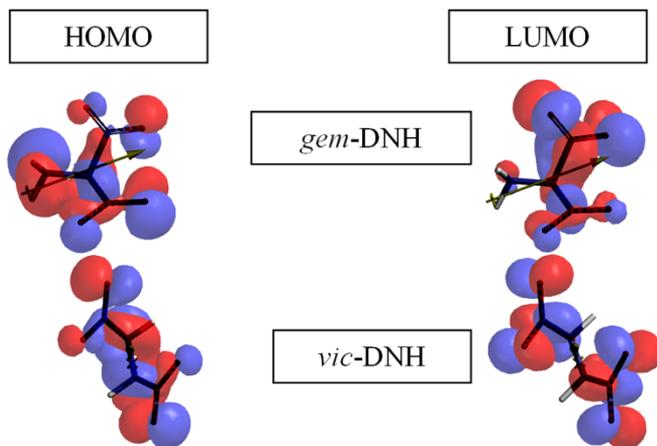
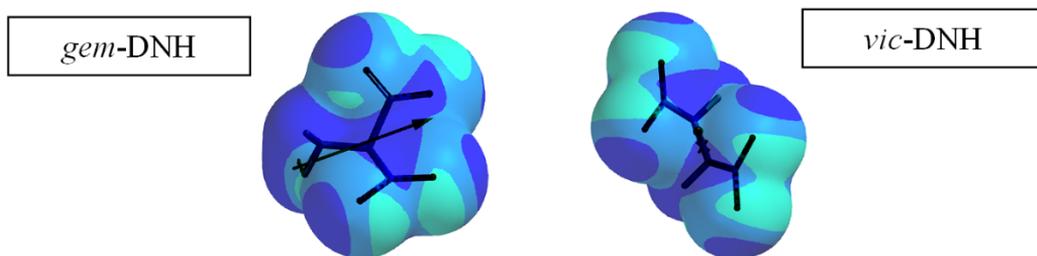**Figure 5.** The HOMO and LUMO patterns of the dinitrohydrazines.

Figure 6. Local ionization potential maps of the dinitrohydrazines.

Figure 7 shows the LUMO maps of the dinitrohydrazines. A LUMO map displays the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value.
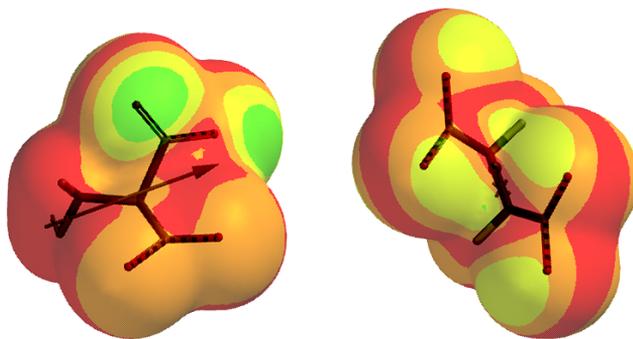

Figure 7. The LUMO maps of the dinitrohydrazines.

The metal composites of dinitrohydrazines

Only, group-II metals of either Be, Mg or Ca has been considered as the metallic component of the composite system. These alkaline-earth metals have different degrees of reducing power. As the counter part of the possible redox reactions, the dinitrohydrazines (DNH) stand for good candidates.

Figure 8 shows the optimized structures as well as the direction of the dipole moment vector of the DNH composite systems considered. However, note that most of the composites considered undergo decomposition. In the case of beryllium both of the *geminal* and *vicinal* isomers remain intact, contrary to magnesium and calcium cases.

Figure 9 shows the ESP charges on atoms of the DNH composites considered. The order of positive charges developed on the metal components are Be(*vic*)<Be(*gem*)< Mg(*vic*)<Mg(*gem*)<Ca(*gem*)<Ca(*vic*). The electron population transferred from metal to the most electrophilic site of the dinitrohydrazine moiety should shuffle electron distribution of the whole molecule and during the optimization process some bonds are ruptured to minimize the energy of the system.
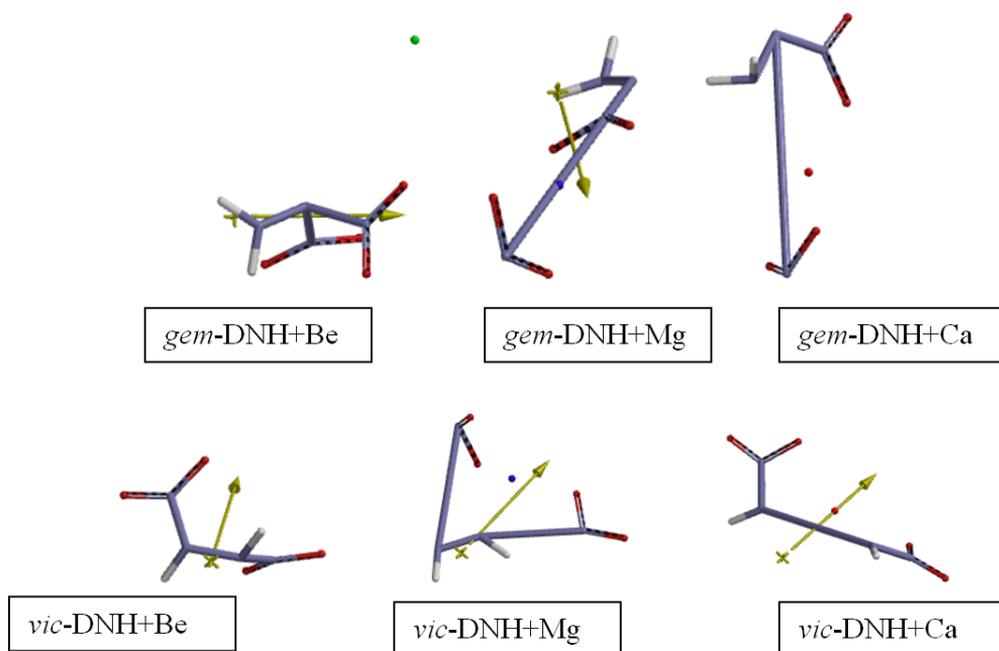

gem-DNH+Be   *gem*-DNH+Mg   *gem*-DNH+Ca

vic-DNH+Be   *vic*-DNH+Mg   *vic*-DNH+Ca

Figure 8. Optimized structures of the DNH composite systems considered.
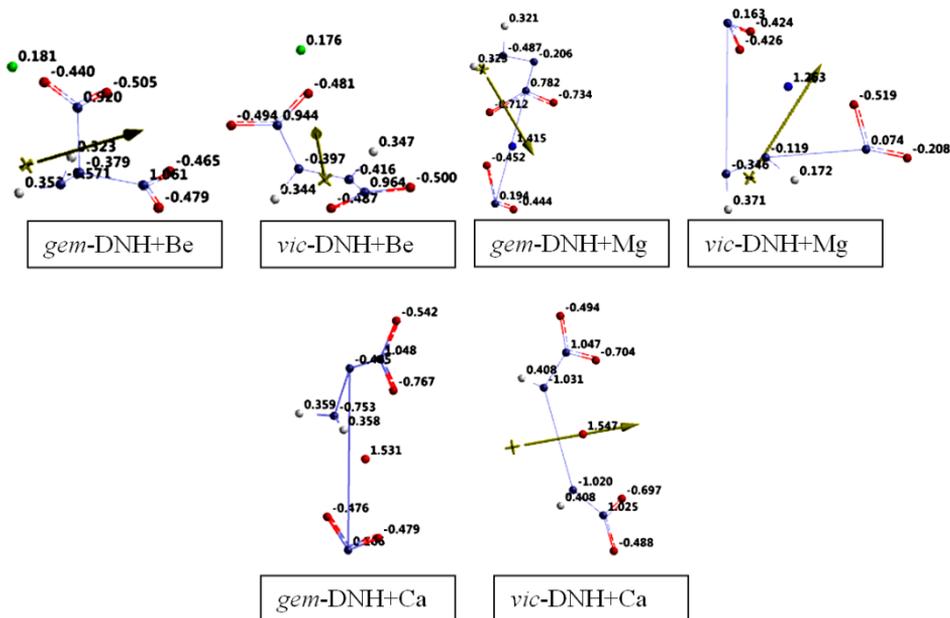
Figure 9. The ESP charges on atoms of the DNH composites considered.

Table 4 includes some energies of the composite systems considered. In the beryllium and calcium cases *vic*-DNH+Be and *vic*-DNH+Ca systems are electronically more stable than their corresponding *geminal* counterpart but this is not valid for the magnesium case. Of course, one must keep in mind that except the *geminal* and *vicinal* beryllium composites the rest are decomposed systems. The decomposition patterns are interesting. In the presence of magnesium N-NO$_2$ bond of the *geminal* isomer is broken only, but in the case of *vicinal* isomer both of the NO$_2$ bonds undergo bond cleavage. Whereas in the calcium case, rupture of N-NO$_2$ bond of the *geminal* isomer but (NO$_2$)HN-NH(NO$_2$) bond of the *vicinal* isomer is affected.

Table 4 . Some energies of the composites considered.

	E	ZPE	E_C
gem-DNH+Be	-1406360.32	146.86	-1406213.46
vic-DNH+Be	-1406423.05	152.39	-1406270.66
gem-DNH+Mg	-1893718.32	146.82	-1893571.5
vic-DNH+Mg	-1893677.31	135.73	-1893541.58
gem-DNH+Ca	-3147421.24	142.60	-3147278.64
vic-DNH+Ca	-3147479.49	148.80	-3147330.69

Energies in kJ/mol.

Table 5 contains the HOMO, LUMO energies and $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) values of the composite systems considered. The HOMO energy of *gem*-DNH+Be is lower than *vic*-DNH+Be. A similar behavior happens for the magnesium case. Whereas, in the calcium case the HOMO of *vic*-DNH+Ca is lower than *gem*-DNH+Ca. As for the LUMO energy order, *vic*-DNH+Mg < *gem*-DNH+Be < *vic*-DNH+Be < *gem*-DNH+Mg < *gem*-DNH+Ca < *vic*-DNH+Ca. Consequently, $\Delta\varepsilon$ order becomes *vic*-DNH+Mg < *gem*-DNH+Be < *vic*-DNH+Be < *gem*-DNH+Mg < *gem*-DNH+Ca < *vic*-DNH+Ca.

Table 5. The HOMO, LUMO energies and $\Delta\varepsilon$ values of the composites considered.

Structure	HOMO	LUMO	$\Delta\varepsilon$
gem-DNH+Be	-602.70	-306.96	295.74
vic-DNH+Be	-600.68	-283.72	316.96
gem-DNH+Mg	-686.45	-263.81	422.64
vic-DNH+Mg	-671.28	-404.02	267.26
gem-DNH+Ca	-713.22	-245.48	467.74
vic-DNH+Ca	-784.90	-195.21	589.69

Energies in kJ/mol.

Some of the molecular orbital energy levels of DNH composite systems considered are depicted in Figure 10. Structurally intact composites (only DNH+Be isomers) exhibit quite similar molecular orbital energy spectra. The magnesium and calcium composites in which dinitrohydrazine molecule decomposed possess rather different molecular orbital energy spectra of the respective *geminal* and *vicinal* isomers, because of the different decomposition patterns thus the products.
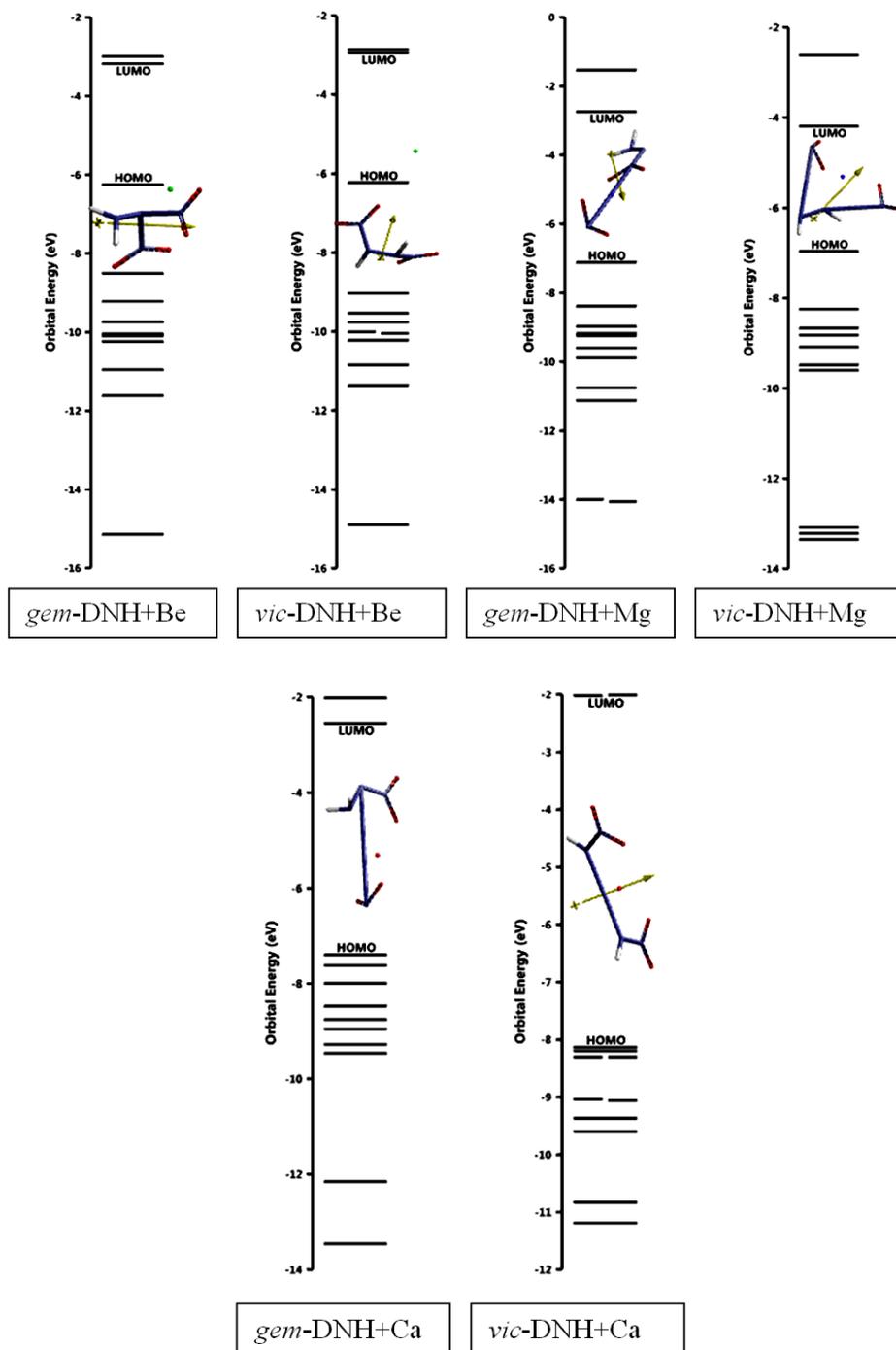
Figure 10. Some of the molecular orbital energy levels of DNH composites considered.

4. Conclusion

In the present DFT treatise, within the constraints of the theory and the basis set employed, reveals that dinitrohydrazines are electronically stable and thermodynamically favorable. Of the two forms, the *vicinal* isomer is more stable and favorable than the *geminal* one. The beryllium composite is stable electronically and structurally intact but the magnesium and calcium composites are not so and dinitrohydrazine component undergoes decomposition either in the *geminal* or *vicinal* form. The magnesium composites exhibit N-NO$_2$ bond rupture. Although, only one of the N-NO$_2$ bond is affected in the *geminal* form, both of them are ruptured in the case of *vic*-DNH+Mg. In the calcium case, only one of the NO$_2$ bond of the *geminal* isomer cleaves. Whereas, in the vicinal form (NO$_2$)HN-NH(NO$_2$) bond undergoes bond rupture. All these reductive decompositions of dinitrohydrazines may open new horizons for the syntheses or conversions by extending the search to other group metals.

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