



# Destructive effect of magnesium and calcium atoms on TEX



Lemi Türker

Middle East Technical University, Department of Chemistry, 06800, Çankaya, Ankara, Turkey

## ARTICLE INFO

### Article history:

Received 3 October 2016  
 Received in revised form  
 9 February 2017  
 Accepted 20 February 2017  
 Available online 21 February 2017

### Keywords:

TEX  
 Magnesium  
 Calcium  
 Explosive  
 Structure  
 DFT calculations

## ABSTRACT

The interaction of TEX (an explosive recently attracts attention) with Mg and Ca atom(s) has been investigated within the limitations of density functional theory at the level of B3LYP/6-311++G(d,p). The effect of Mg in 1:1 mol ratio is very drastic on TEX and one of the NO<sub>2</sub> moieties is expelled as preform of nitrite ion. The second Mg atom in the composite (1:2 mol ratio of TEX:Mg) shows balancing effect of the first Mg atom, thus no bond cleavage occurs but some distortions happen. As for the effect of calcium, in 1:1 and 1:2 (TEX:Ca) ratios nitramine bond cleavage(s) occur(s) drastically. Some structural and quantum chemical data are presented.

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## 1. Introduction

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazawurtzitane, known as TEX (see Fig. 1) is an energetic material which has attracted attention in recent years [1]. The synthesis of TEX was achieved couple of decades ago by Boyer and coworkers starting with formamide and glyoxal [2]. Structurally TEX is a nitramine type explosive. Beside, two nitramine groups, it additionally contains two embedded five-membered cyclic dietheric (also can be considered as acetal) structures resembling 1,3-dioxalane structure.

TEX is much less sensitive to impact and friction stimuli as compared to the well known explosives, RDX and HMX. In addition to those properties, it possesses high density (1.99 g/cm<sup>3</sup>), excellent thermal stability (m.p > 240 °C) as well as high detonation velocity (8665 m/s) and pressure (370 kbar) [1–7].

The presence of two embedded 1,3-dioxalane structures in TEX molecule calls some well known reactions of ethers and acetals (acyclic or cyclic), such as the acid catalyzed ring opening reactions of cyclic ethers [8–10]. The embedded 1,3-dioxalane structure(s) in TEX can also be considered as full acetal of glyoxal (a dialdehyde (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>)). Note that acetal formation and destruction reactions are acid catalyzed [8–10]. Computations based on density functional

theory (DFT) have been highly employed on TEX molecule in order to predict the crystal densities [11], detonation velocity [12], bond dissociation energies and impact sensitivity [13], sensitivity and performance relation [14] etc. [15–17]. Zuo and coworkers considered the thermal stability of TEX in the presence of widely used RDX and HMX [18]. Various modeling work which involve TEX and other explosives within the realm of density functional theory (DFT) have been reported [19–21]. By employing the density functional theory at the B3LYP/6-31 + G(d,p) level of theory Schutt et al., calculated the heat of reactions of free dinitramidic acid (HN(NO<sub>2</sub>)<sub>2</sub>) with derivatives of 2,4-(R)-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>.0<sup>3,11</sup>]dodecane (R = H, CH<sub>3</sub>, F, NO<sub>2</sub>(TEX)) [22]. Zeng et al., calculated the heat of formation (HOF) for a caged wurtzitane analog compound (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX)) by using density functional theory (B3LYP method with 6-31 + G(d,p) basis set) [23].

On the other hand, certain metals usually are added into explosive compositions to improve their performances. Aluminum and magnesium are the most widely used materials for this purpose. Titanium, zirconium and tungsten are also used [24].

In the present study, interaction of magnesium and calcium atom(s) with TEX molecule (in 1:1 and 1:2 mol ratios) has been investigated within the limitations of density functional approach.

## 2. Methods of calculation

In the present study, all the theoretical methods have been

E-mail address: [lturker@metu.edu.tr](mailto:lturker@metu.edu.tr).

Peer review under responsibility of China Ordnance Society.

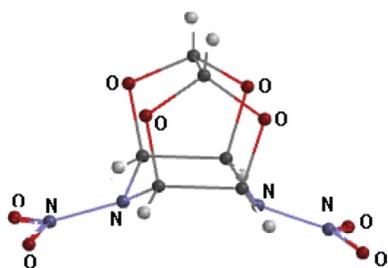


Fig. 1. Structure of TEX.

applied using the restricted level of theory, because all the structures considered are closed shell systems (no radicals) [25]. The initial optimizations of 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 [25,26]. Then, further structure optimizations were achieved using successively STO and RHF levels of theory (6-31G(d,p)) and then within the framework of Density Functional Theory (DFT, B3LYP/6-311++G(d,p)) [26–28]. All the structures are dealt in their singlet states (restricted type calculations have been done). 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 [29]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [30] and Lee, Yang, Parr (LYP) correlation correction functional [31].

Total electronic energy calculations of all the considered structures finally have been done at B3LYP/6-311++G(d,p) level. The normal mode analysis (at the same level of calculations) for each structure yielded no imaginary frequencies, which indicates that each compound has at least a local minimum on the potential energy surface. The total electronic energies were corrected for zero point vibrational energies (ZPVE or ZPE). All these computations were performed by using Spartan 06 package program at standard conditions of 298.15 K and 1.00 atm [32].

### 3. Results and discussion

Metal additives are not uncommon in explosive composites. For condensed explosives, having metal particle additives, interaction of the detonation shock and reaction zone with solid inclusions yields high rates of momentum and heat transfer that consequently introduce non-ideal detonation phenomena [33,34].

Mg and Ca are just two of various elements used in fireworks (Mg is used as fuel and Ca salts for color agent) [35,36]. Mg can also be employed in thermobaric and enhanced blast explosives explosives as fuel [37]. Their wide application is due to their thermochemical properties that at the standard states Mg and Ca liberate considerable amount of heat energy (602 kJ/mol and 635 kJ/mol, respectively) as they form their oxides, MgO and CaO. Whereas Al, when oxides to  $Al_2O_3$ , produces 1669 kJ/mol of heat and 822 kJ/mol heat energy accompanies formation of  $Fe_2O_3$  at the standard states [38]. Mg and Ca are in the second group of the Periodic Table and are highly electro positive, namely easily

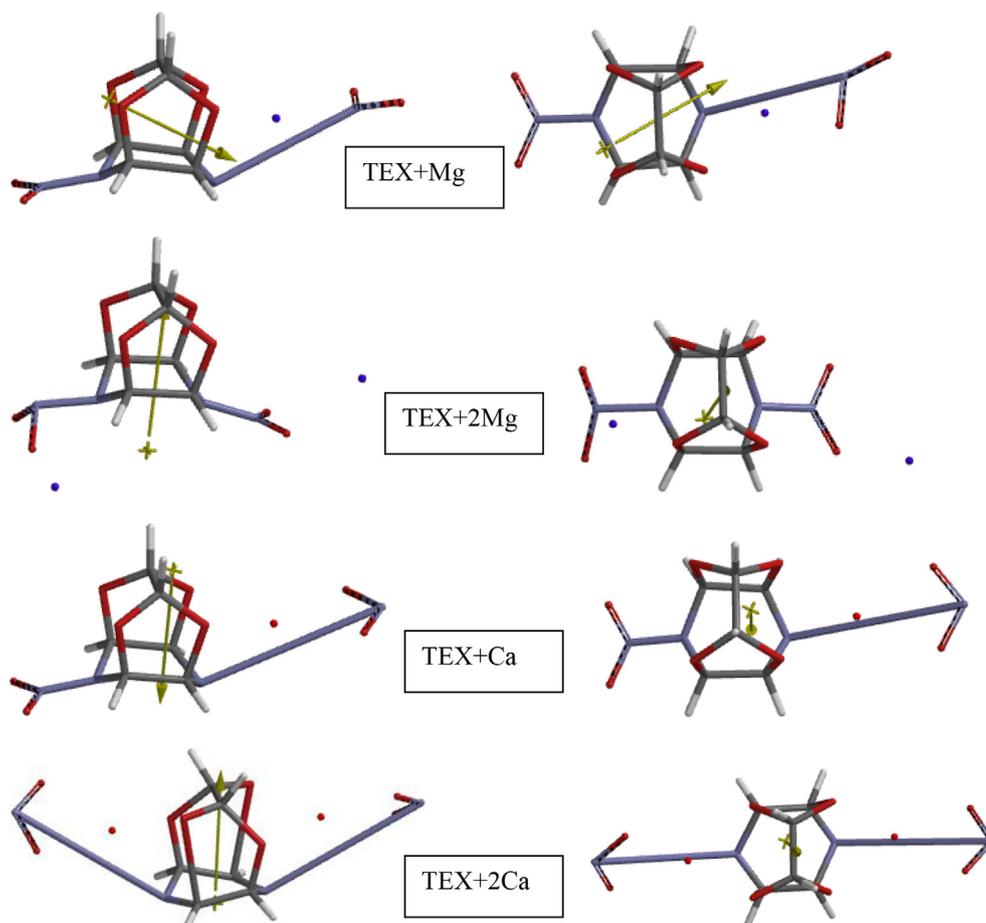


Fig. 2. Optimized structures of TEX composites considered (B3LYP/6-311++G(d,p)).

oxidized. Their oxidation potentials (2.87 V and 2.38 V for Ca and Mg, respectively) are much higher than for Al (1.66 V), Fe (0.44 V) and Zn (0.76 V) [38]. Therefore, Mg and Ca have more tendencies to reduce nitro groups than Al and Zn. Note that Zn in organic chemistry is employed to reduce nitro groups, like some other metals in various reactions.

Magnesium is a very reactive metal and makes an excellent fuel under the proper conditions in composition of explosives. Alkali (like Na,K) and alkali earth (like Mg,Ca,Ba) metals, in theory would make excellent high-energy fuels, but except for magnesium; they are too reactive and interact with moisture and atmospheric oxygen [24]. Therefore, their usage requires certain precautions. The most widely used metallic fuel is probably aluminum, followed by

magnesium. Calcium does not have any usage in that sense.

TEX contains etheric linkages (in the form of acetal). It is known that especially Mg forms complexes with ethers (such as in the Grignard reagents [39–41]) and thus it is expected to have some influence on the structure of TEX.

Because of all the above said points it would be interesting to consider the interaction of Mg and Ca atoms with TEX molecule within the realm of DFT.

### 3.1. Compositions and structures

Complexation of Mg with ethers has been studied extensively since the discovery of Grignard reaction [8,9,39–41]. TEX being a

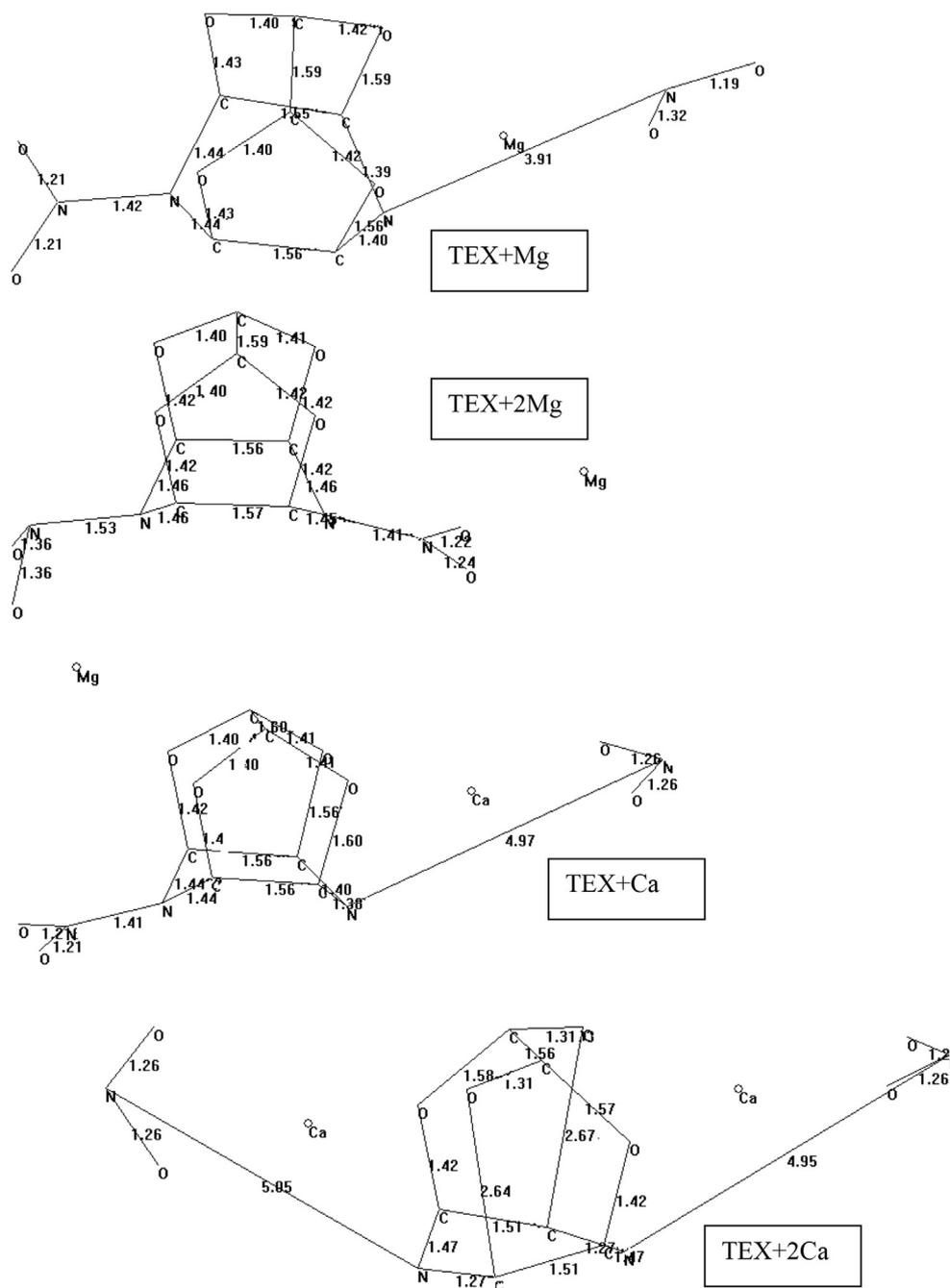


Fig. 3. Bond lengths of the optimized structures of TEX composite systems presently considered (B3LYP/6-311++G(d,p)).

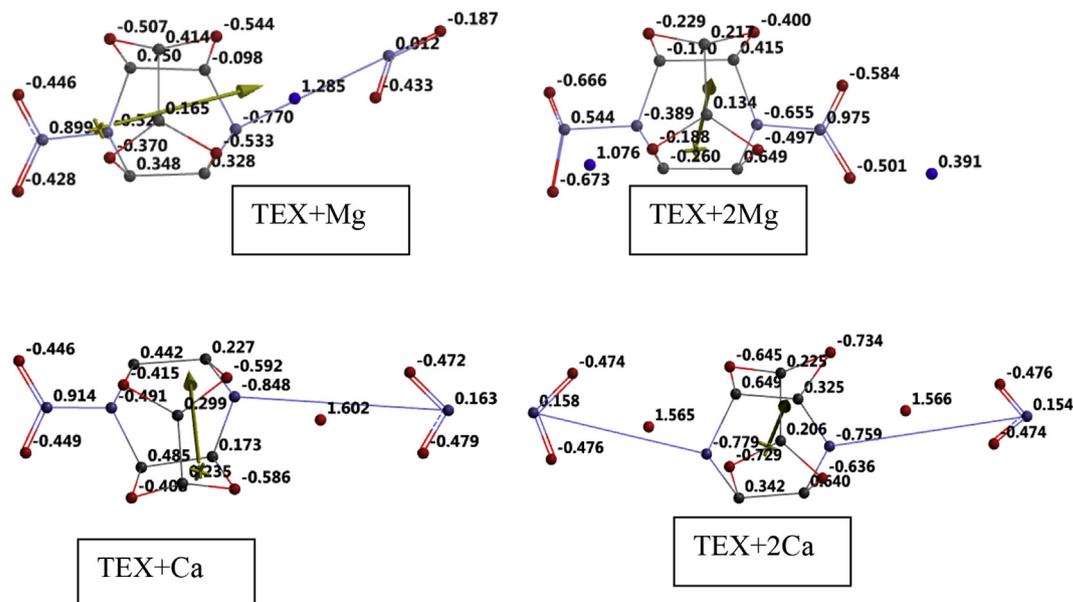


Fig. 4. Electrostatic charges in the composite systems considered (B3LYP/6-311++G(d,p)).

cyclic ether (it has four etheric linkages) should form complexes with Mg. Starting from this idea, quantum chemical investigation has been achieved presently. For that purpose 1-2 atoms of Mg and Ca is/are introduced in the vicinity of TEX molecule. The composite systems (TEX + nMe; n: 1,2,; 8.48, 15.64% Mg, and 14.13, 26.06% Ca, respectively) is/are optimized structurally as described in the method part. Fig. 2 shows the optimized structures (B3LYP/6-311++G(d,p)).

As seen in the figure, Mg atom causes the cleavage of one of the nitramine bonds in TEX + Mg composition (see Fig. 3). However, the presence of second Mg atom shows some counter effect and in TEX+2 Mg composite, TEX molecule preserves its bond integrity, albeit the fact that some bond elongations and distortions. It is to be noted that although Mg atom exhibits some tendency to complex with oxygen of ordinary ethers, such as diethyl ether or tetrahydrofuran, in the case of TEX + Mg, the etheric oxygen bonds on the Mg side are only slightly affected. This is also true for TEX + Ca composition. Whereas, the presence of second Ca atom, highly perturbs not only the nitramine bonds, but also affects the etheric

bonds unequally (see Fig. 3).

Fig. 3 shows the bond lengths of the optimized structures of TEX composites considered. Fig. 4 shows the electrostatic charge distribution in the composites of the present concern. Note that the metal atoms are all positively charged. The Ca atom(s) is/are more positive than Mg atoms in their counterpart compositions. While those destructive interactions happen, the nature of the leaving group (NO<sub>2</sub>) seems to be resembling the nitrite ion. Fig. 5 displays the local ionization maps of the TEX composites in which leaving group NO<sub>2</sub> moiety(s) is/are relatively electron rich with respect to the remnant of TEX structure.

The dipole moments (in Debye unit) of the composites are 1.86 and 4.38, for Mg and 1.63 and 4.80, for Ca in 1:1 and 1:2 TEX: Metal compositions, respectively (see Fig. 2 for their directions).

### 3.2. Energies

Table 1 shows the total electronic energies ( $E$ ), the zero point vibrational energies (ZPE) and the corrected total electronic energies ( $E_c$ ). Note that the energies in the table hold for the composite systems in the perturbed forms shown in Fig. 2. Initially constructed composite systems having TEX molecule in the intact form undergo some sorts of perturbations and lower the energy, mostly by expelling one or two NO<sub>2</sub> group(s).

### 3.3. IR spectra

Fig. 6 shows the calculated IR spectra of the composites. As seen there the spectra for TEX + Mg and TEX+2 Mg are very similar in appearance. Only some band shifts occur. The bands at 1647 cm<sup>-1</sup>

Table 1  
Various energies of the composites.

Composition	$E$	ZPE	$E_{corr}$
TEX + Mg	-3290513.89	417.72	-3290096.17
TEX+2 Mg	-3815578.39	423.64	-3815154.75
TEX + Ca	-4544317.54	413.66	-4543903.88
TEX+2Ca	-6323894.38	393.15	-6323501.23

Energies in kJ/mol. B3LYP/6-311++G(d,p).

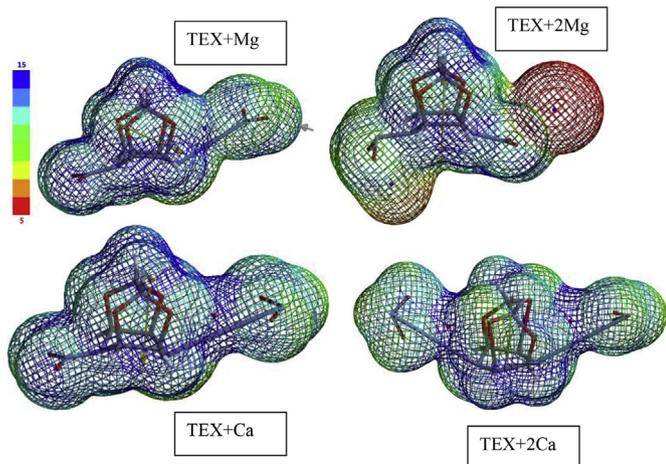


Fig. 5. Local ionization maps of the TEX composites (B3LYP/6-311++G(d,p)).

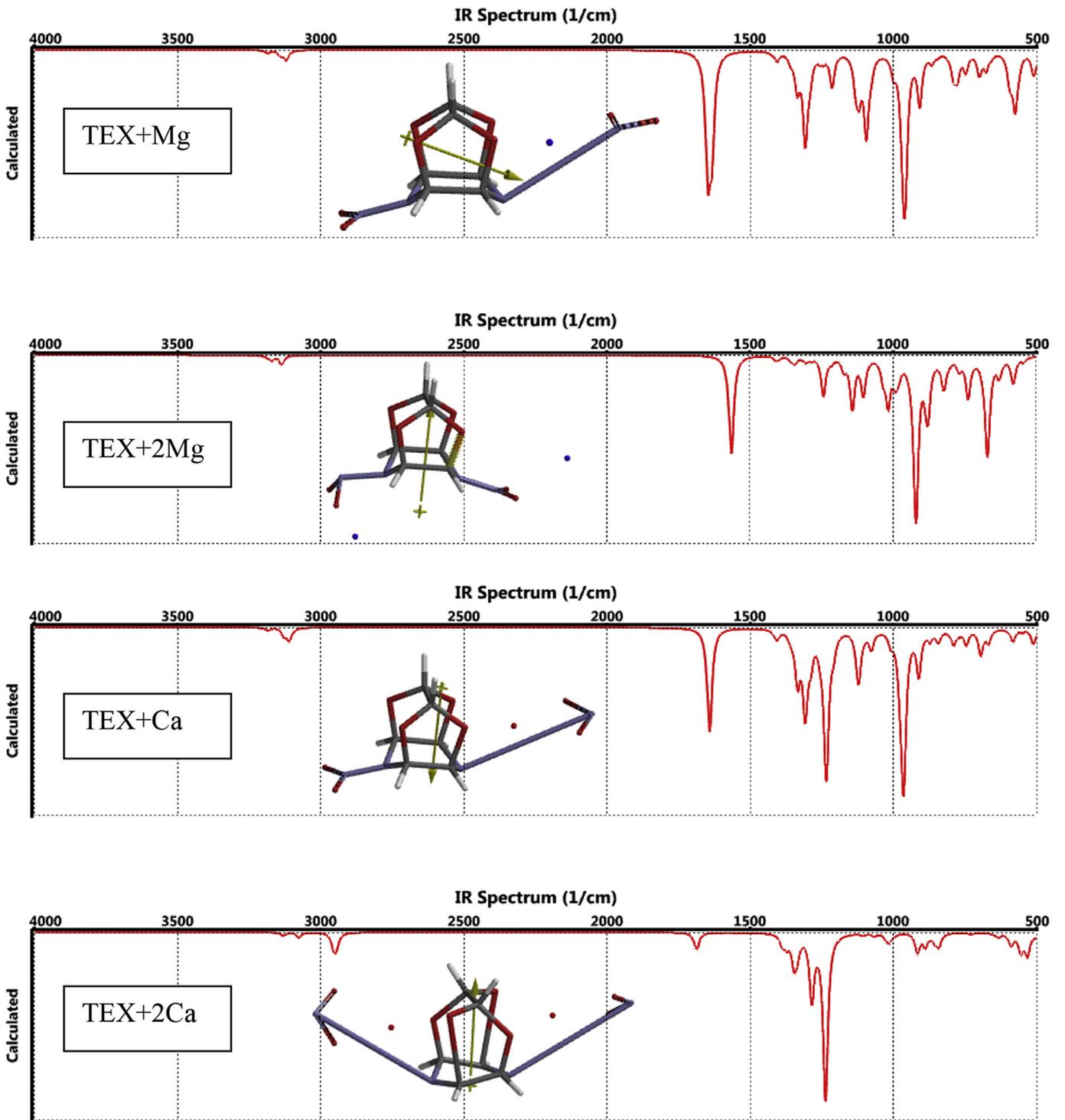


Fig. 6. IR spectra of the TEX composites considered (B3LYP/6-311++G(d,p)).

and  $1565\text{ cm}^{-1}$  stand for stretching of  $\text{NO}_2$  group still attached to main body of TEX.

The IR spectra for calcium composites are quite different from each other. The band at  $1641\text{ cm}^{-1}$  (stretching of  $\text{NO}_2$  group still linked to the remnant of TEX) in the TEX + Ca composite is mostly lost in TEX+2Ca case. Also, the one at  $957\text{ cm}^{-1}$  (bending of rings) does not appear in the presence of second Ca atom.

#### 3.4. Molecular orbital energies and frontier molecular orbitals

Fig. 7 shows some of the molecular orbital energy levels of the composite Mg and Ca systems presently the focus of concern. As seen in the figure, by the presence of second Mg atom the highest occupied molecular orbital (HOMO) energy level raises up, whereas the lowest unoccupied molecular orbital (LUMO) energy level decreases in unequal extents. The presence of second Ca atom in the optimized composite structure lowers the LUMO but raises the HOMO energy levels (note that in the figure for the Ca case, the energy scales are different. The figure should not mislead).

This situation usually arises whenever some sorts of increased delocalization occurs (extended conjugation) [42]. Most probably the Mg atom nearby the distorted  $\text{NO}_2$  group interacts strongly with it. A similar argument should hold for the Ca atom. However, in this case the narrowing of interfrontier molecular orbital (FMO) energy gap is less pronounced as compared to the respective Mg case.

Table 2 displays the HOMO, LUMO energies and the HOMO-LUMO energy gap ( $\Delta\epsilon$ ). As seen there, the presence of second metallic atom in both the Mg and Ca cases causes the narrowing of the interfrontier energy gap [42]. So in the respective electronic

**Table 2**  
Various energies of the composites.

Composition	HOMO	LUMO	$\Delta\epsilon$
TEX + Mg	-701.71	-254.21	447.50
TEX+2 Mg	-450.81	-346.64	104.17
TEX + Ca	-705.96	-234.25	471.71
TEX+2Ca	-677.76	-301.48	376.28

Energies in kJ/mol. B3LYP/6-311++G(d,p)

spectra, a bathochromic effect is expected and the calculated UV-VIS spectra exhibit this fact for TEX+2 Mg and TEX+2Ca cases as compared to their respective mono metallic compositions (see Fig. 8).

Fig. 8 shows the UV-VIS spectra for the TEX composites considered. As seen in Fig. 7 and Table 2, the presence of second Mg atom causes an appreciable narrowing of the interfrontier molecular orbital energy gap. Thus it is accompanied by a bathochromic shift to visible region of the spectrum. The bathochromic effect caused by the presence of second Ca atom is less pronounced as compared to the Mg case. Note that the direction of the dipole moments strikingly change by the insertion of second Mg atom in to the system. This type of change does not occur in the case of Ca insertion. All these data imply that the second Mg atom is more influential on some sort of conjugative effects than the second Ca atom is.

Fig. 9 shows the HOMO and LUMO pattern of the composites. In the case of TEX + Mg, the HOMO is constituted by the expelled  $\text{NO}_2$  moiety around the Mg atom. Whereas, the LUMO gets contribution from the remnant of TEX molecule, especially from the remaining nitramine moiety.

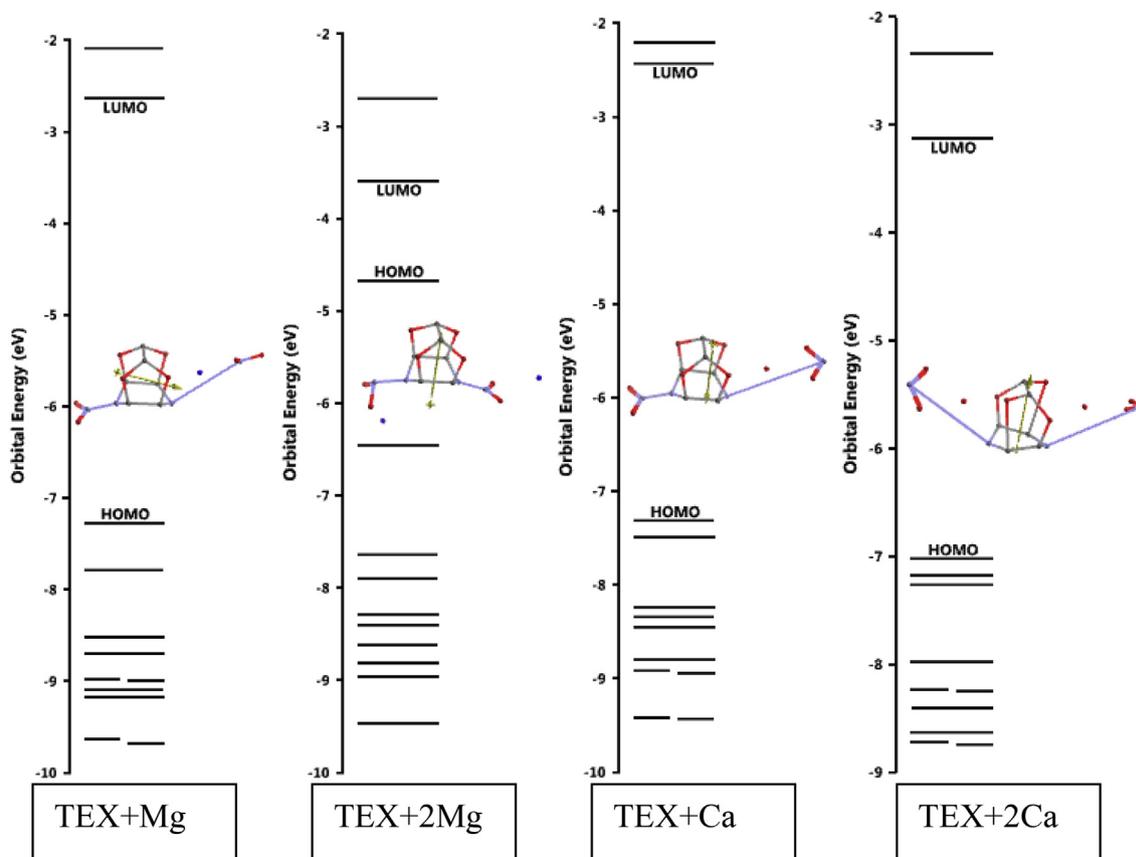


Fig. 7. Molecular orbital energy spectra of the composite systems (B3LYP/6-311++G(d,p)).

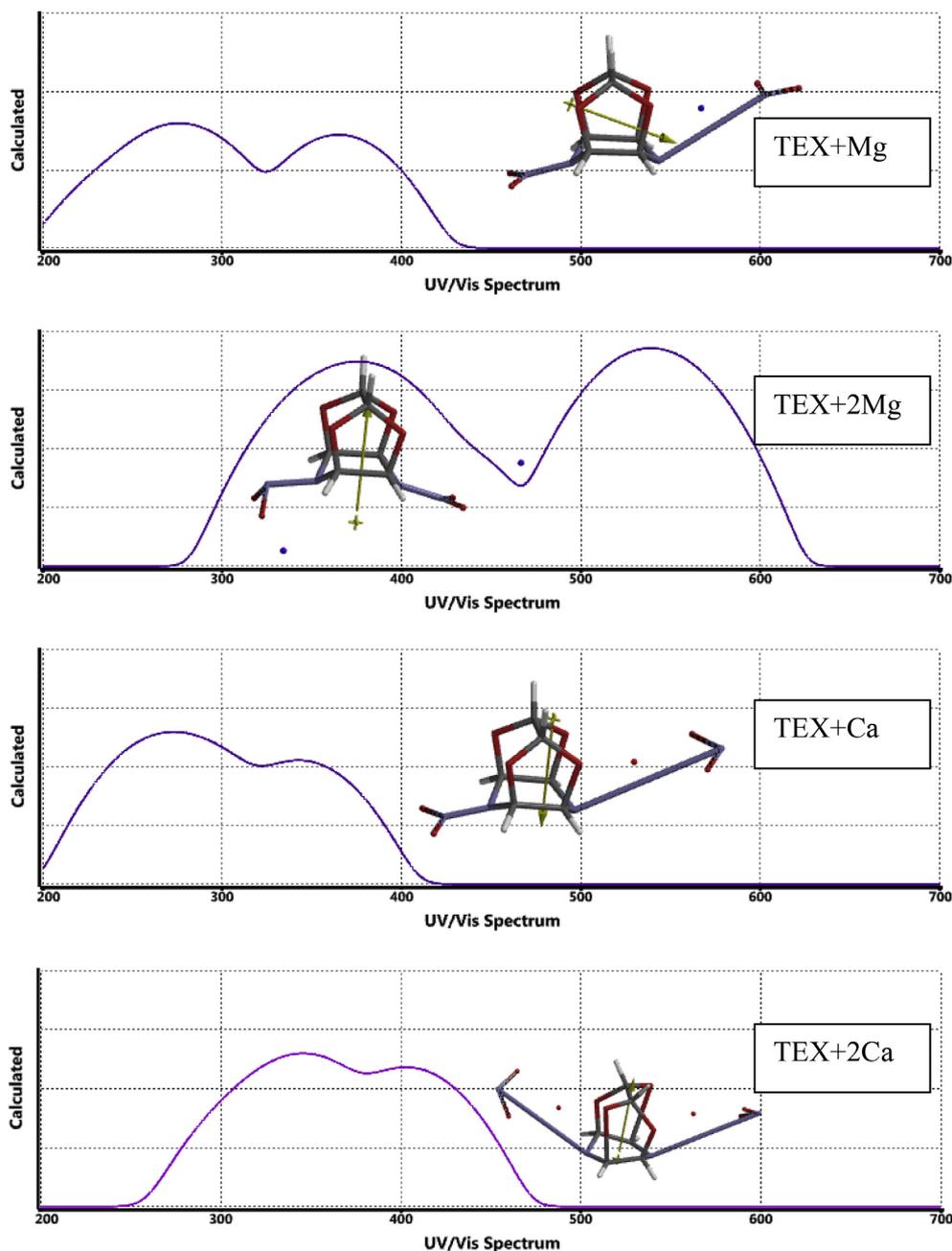


Fig. 8. UV-VIS spectra of the TEX composites considered (B3LYP/6-311++G(d,p)).

In the TEX+2 Mg composite, the HOMO gets contribution from the nitramine bond atoms nearby the less positive Mg atom (see Fig. 4) whereas the LUMO is constituted by the distorted nitramine bond atoms and the Mg atom nearby which is more positive than the other Mg atom.

On the other hand, TEX + Ca systems are characterized by effective contributions of etheric oxygen atoms into the HOMO. In the case of TEX + Ca composite, the LUMO is mainly on the intact nitramine bond atoms. As for the TEX+2Ca case, the contributions to LUMO are only from the remnant of TEX molecule and the expelled NO<sub>2</sub> moieties contribute nil. The properties mentioned above for the HOMO and LUMO have been implicitly reflected into the electrostatic maps for the TEX composites where around the expelled/distorted NO<sub>2</sub> group(s) nearby the metal atom, more

negative potential develops (Fig. 10). Those site atoms contribute the HOMO. The cage of TEX remnant is generally possesses positive potential.

#### 4. Conclusion

The present study, within the limitations of the DFT level of calculations, indicates that Mg and Ca can deteriorate the chemical structure of TEX molecule. Hence, it is not a suitable additive material to increase/improve certain thermal behavior of TEX. Topologically symmetrical chemical structure of TEX is perturbed at different extent and pattern depending on the Mg and Ca atom contents of the composite. In contrast to usual interaction of Mg with ethers, (etheric oxygen coordinates with Mg) in the case of

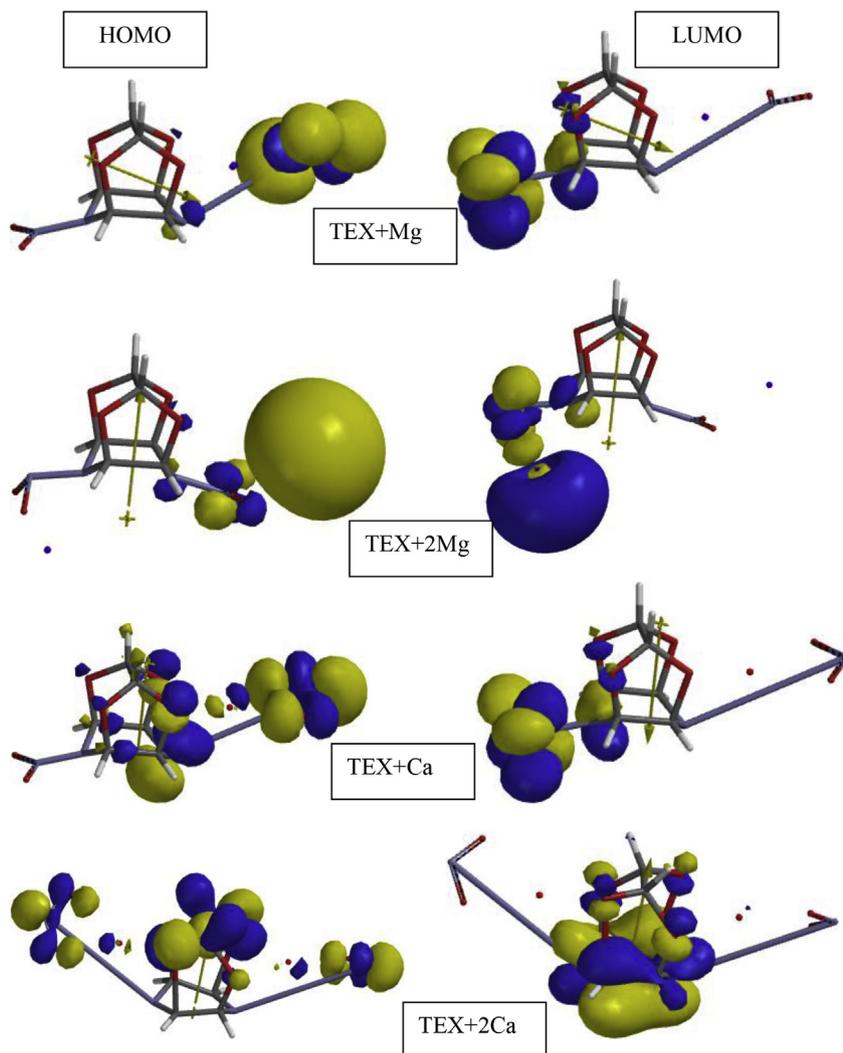


Fig. 9. Frontier molecular orbitals of the TEX composites (B3LYP/6-311++G(d,p)).

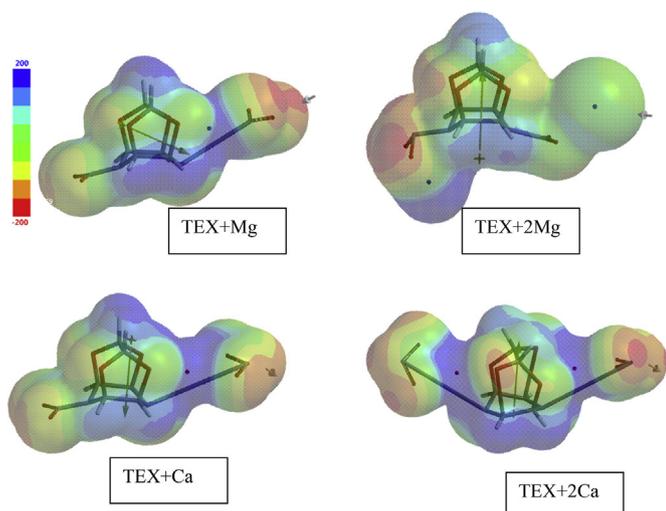


Fig. 10. Electrostatic potential maps of the TEX composites (B3LYP/6-311++G(d,p)).

TEX, Mg (also Ca) denotes electron(s) to nitramine  $\text{NO}_2$  moiety. Hence, any contact of TEX with those alkaline earth metals should

be avoided in the preparation or manufacture of ammunitions.

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