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# Nitrogen analogs of TEX − A computational study

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**Abstract**

TEX, a well-known nitramine type explosive, has been subjected to centric perturbations by replacing its etheric (acetal) oxygens with nitrogen atoms one by one. The structural features, stabilities and IR and UV-VIS spectra of new structures formed are investigated. For this purpose, density functional theory has been employed at the B3LYP/6-31G (d,p) and B3LYP/6-311G(d) levels. In general the calculations revealed that the oxygen−nitrogen replacement resulted in more energetic but less sensitive structures than TEX.


*Keywords:* TEX; Explosives; Nitramines; Cyclic amines; Aminals; DFT calculations

## 1. Introduction

TEX (4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazawurtzitane) (see Fig. 1) has attracted attention in recent years as one of the novel energetic materials [1]. It was first synthesized by Boyer and coworkers [2]. Their synthesis started with form amide and glyoxal and in a two-step synthesis involving a piperazine derivative as an intermediary product, TEX is obtained. It is a nitramine and additionally contains two embedded five-membered cyclic dietheric (also can be considered as acetal) structures resembling to 1,3-dioxalane.

TEX is much less sensitive to impact and friction stimuli as compared to the well known explosives, RDX and HMX. Moreover, it has high density (1.99 g/cm$^3$), excellent thermal stability (m.$p$ > 240 °C) as well as its high detonation velocity (VOD: 8665 m/s) and pressure (370 kbar) [1−7].

In the literature, based on density functional theory (DFT), various computational works have piled up on TEX molecule in order to predict some of its properties, such as the crystal density [8], bond dissociation energies and impact sensitivity [9], detonation velocity [10], sensitivity and performance relation [11]. One of the studies was about the influence of RDX and HMX on the thermal stability of TEX [12]. DFT calculations were employed in various modeling work which involve TEX and other explosives [13−15]. The density functional theory at the B3LYP/6-31 + G(d,p) level of theory was employed to calculate the heat of reactions of free dinitramidic acid ($HN(NO_2)_2$) with derivatives of 2,4-(R)-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0$^{5,9}$0$^{3,11}$] dodecane (R = H, F, $CH_3$, $NO_2$(TEX)) [16]. Also, the heat of formation (HOF) for a caged wurtzitane analog compound, 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX) was obtained by density functional theory (B3LYP method with 6-31 + G(d,p) basis set) [17].

In the present work, centric perturbations [18] have been performed on the etheric (acetal) oxygen atoms present in the structure of TEX by replacing them with nitrogen atoms (considering isomeric structures) in order to get more nitrogenous materials which are thought to be candidates for explosives.

## 2. Methods of calculation

All the theoretical methods were applied using the restricted level of theory because all the structures are closed shell systems (no radicals) [19]. The initial optimizations of

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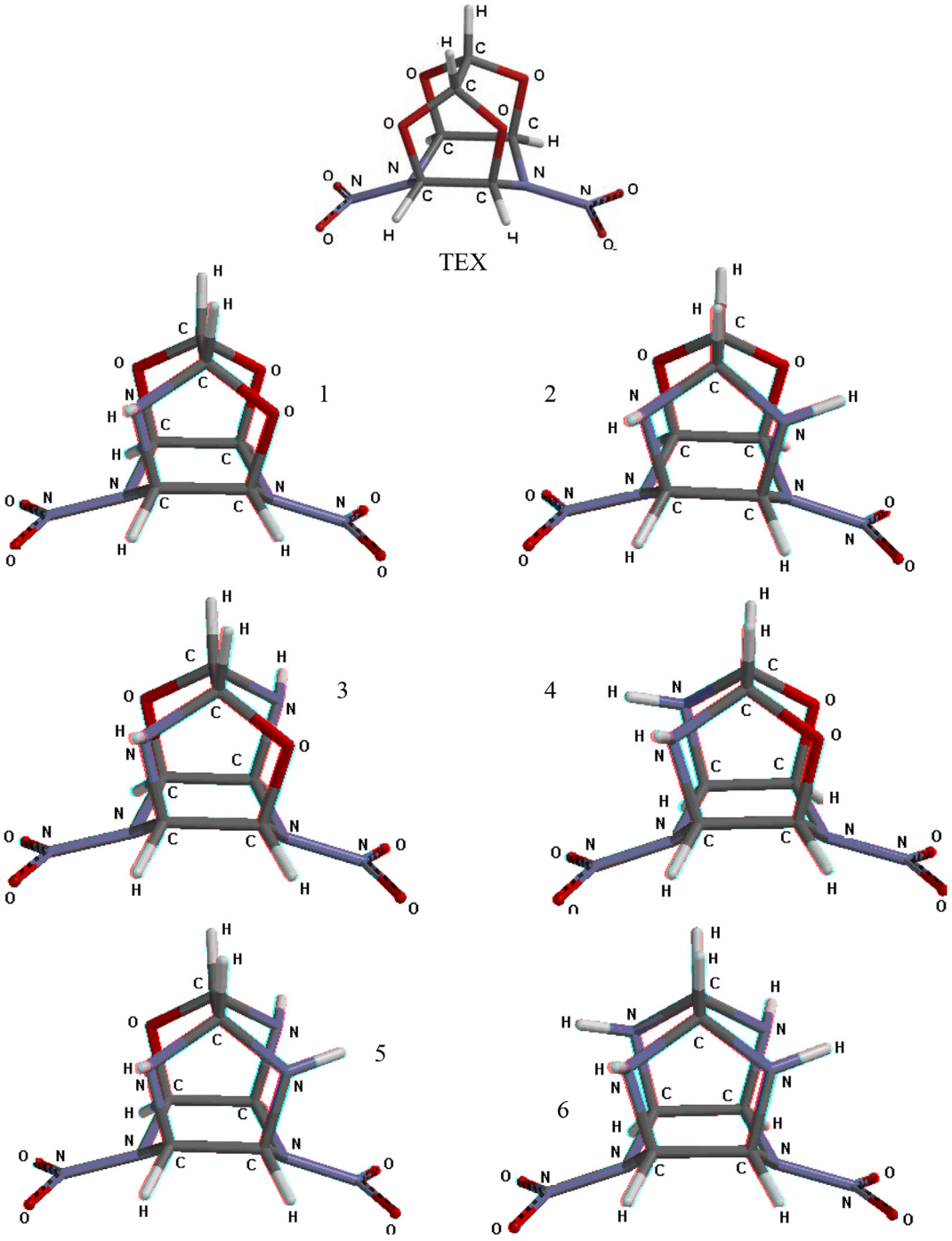


Fig. 1. Structures of the present concern.

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 [19,20]. Then, further structure optimizations were achieved by using STO and RHF levels of theory (6-31G (d,p)) and then within the framework of Density Functional Theory (DFT, B3LYP) [20–22] at the levels of 6-31G(d,p) and 6-311G(d). All the presently considered structures are dealt in their singlet states (restricted type calculations have been done). 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 [23]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [24] and Lee, Yang, Parr (LYP) correlation correction functional [25].

The normal mode analysis (at the same theoretical levels as the optimizations) 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