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Parimi Ashutosh, Satheesh Maroju and Rajasekhar Koorella

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Molecular design and theoretical properties of Nitramine based molecules as potential High Energy Materials

Parimi Ashutosh, Satheesh Maroju and Rajasekhar Koorella*

Advanced Centre of Research in High Energy Materials (ACRHEM), South Campus, University of Hyderabad, Gachibowli, Hyderabad 500046, Telangana, INDIA

*e-mail: krpsacrhem@uohyd.ac.in

Abstract: Six new molecules based on nitramine functionality were designed and predicted the theoretical properties using DFT calculations. All the Six molecules were found to exhibit better or comparable properties than the existing explosives RDX, HMX and useful for explosive applications.

Keywords: High Energy Materials, Design, Theoretical Properties, DFT Calculation, Explosive applications.

Introduction

High energy materials (HEMs) are the compounds which store chemical energy and mainly contains nitro ($-NO_2$) [1-5], azido ($-N_3$) [6-8], nitrate ester ($-ONO_2$) [9,10], nitramino ($-NNO_2$) [11-14] functional groups. Because of high energy materials release large amount of energy upon detonation, they are widely used in the military, industrial and mining applications [15]. Among the functional groups, compounds with nitramino ($-NNO_2$) functionality have been shown as stable and less sensitive explosives towards external stimuli. During the last decades, a large number of high energy materials were discovered with nitramine functionality [16]. Among them, RDX, HMX and CL-20 are well known nitramine class of explosives, widely used in explosive applications. The discovery of new high energy materials with improved performance than the existing is high demanding and challenging area for the chemists. Especially, the molecules with higher density exhibits higher detonation pressure. Hence, designing the molecules with higher density is a key factor before initiating the synthesis. It has been observed that the molecules of cyclic and caged structures possess higher density compared to acyclic molecules due to packed molecular arrangement. Furthermore, the increase in the number of C-N and N-N bonds in the structure increases the energy of molecule resulting in the higher detonation pressure. Density functional theory (DFT) is a widely used quantum mechanical modelling method to investigate the electronic structure of the molecule. In order to meet the requirements of high energy materials, six nitramine based molecules were designed and investigated the physical properties using DFT calculations. All the six molecules were shown better or comparable properties than the existing HEMs. Herein we describe the computational results of designed molecules and possible synthetic route of most promising molecules.

Computational Methods

Gaussian 09 software package was used to optimize the structures and post-optimization, the structures were found to be with no imaginary frequencies. B3LYP, with the basis set 6-311G++ (d, p) was used to compute the structures to an optimal minimum [17]. Material Studio (v.08) was used to perform polymorph calculations to obtain the theoretical maximum density of the structures [18]. DRIEDING was the force field which we have used during the polymorph calculations [19]. MOPAC 16 was used to compute heats of formation (HOF) of the molecules [20] and semi-empirical method PM7 was used to obtain the HOF data. EXPLO5 thermo-kinetic code was used to obtain detonation performance parameters [21]. BKW equation of state was used to calculate the detonation performance parameters with the values of constants $\alpha = 0.5$; $\beta = 0.38$; $\kappa = 9.32$; $\theta = 4120$; $\varepsilon = 1.00$, and the co-volumes set:1 was used to determine the detonation products [22].

Results and Discussion

The molecules were designed by considering bicyclic, caged and aromatic five or six membered ring systems with nitramine functionality and named as KR-1 to KR-6. The

Molecules KR-1, KR-2 and KR-3 shows ether linkage and KR-2 closely resembles the structure of TEX with additional bridged -NNO_2 functionality. By comparing the structure of KR-5 with rest of the molecules, it is observed that bridged and caged structures showed higher density with greater detonation properties compared to planar structures. It is also noted that by increasing the number of -NNO_2 groups in the molecules increases the density of molecule thereby increasing detonation properties.

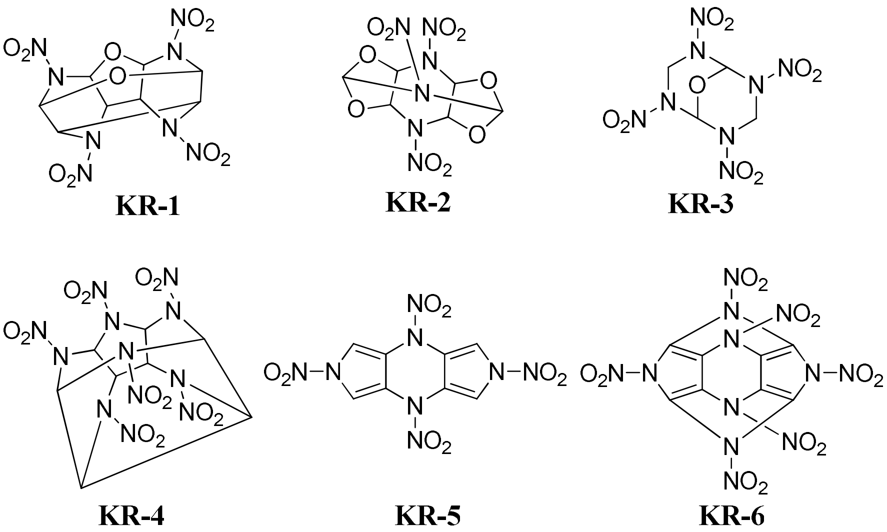


Figure 1. Structures of designed Molecules

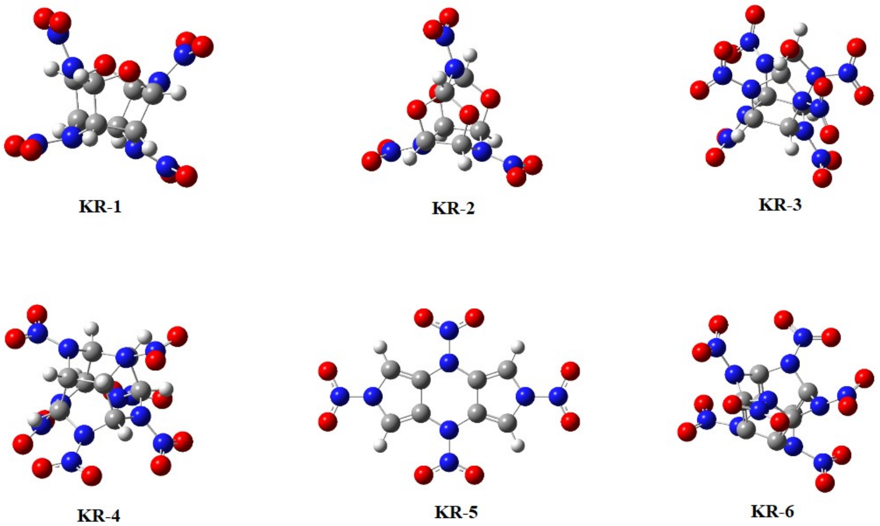


Figure 2. 3D Optimized Structures

The optimized minima structures suggest that there might be hydrogen bonding between the Oxygen-Hydrogen-Nitrogen atoms, which might add to the stability of the molecules (Figure 2). We have also studied the molecular electro static potential (MESP) maps of the molecules and suggest that, there is a decent amount of electronic distribution to maintain the structure stable and detonate only when ignited. However, this is just based on a single molecule, the real-time sensitivity is a subject to molecular dynamics study (Figure 3) [23].

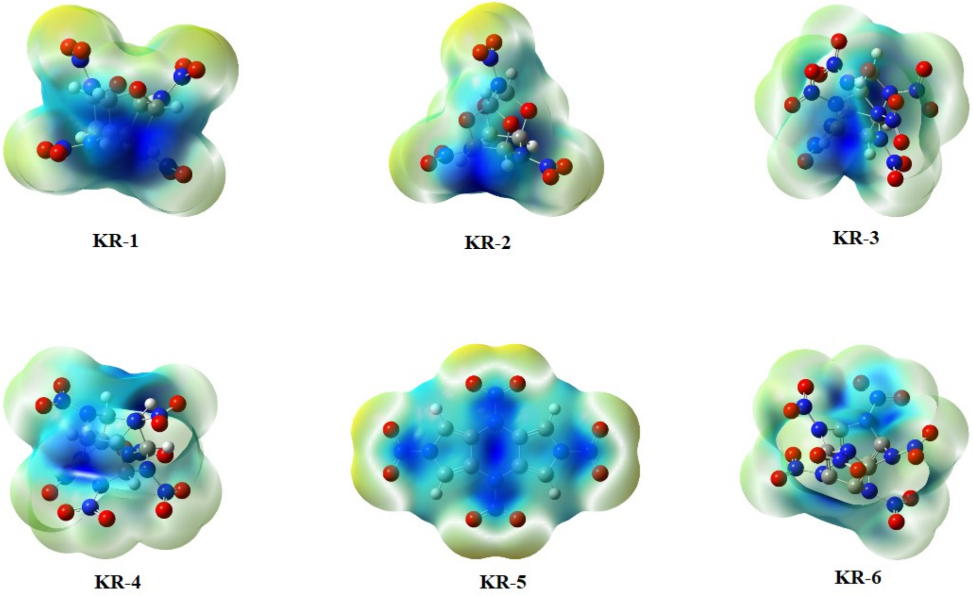

KR-1 **KR-2** **KR-3**
KR-4 **KR-5** **KR-6**

Figure 3. Molecular Electro Static Potential maps of the Designed Molecules

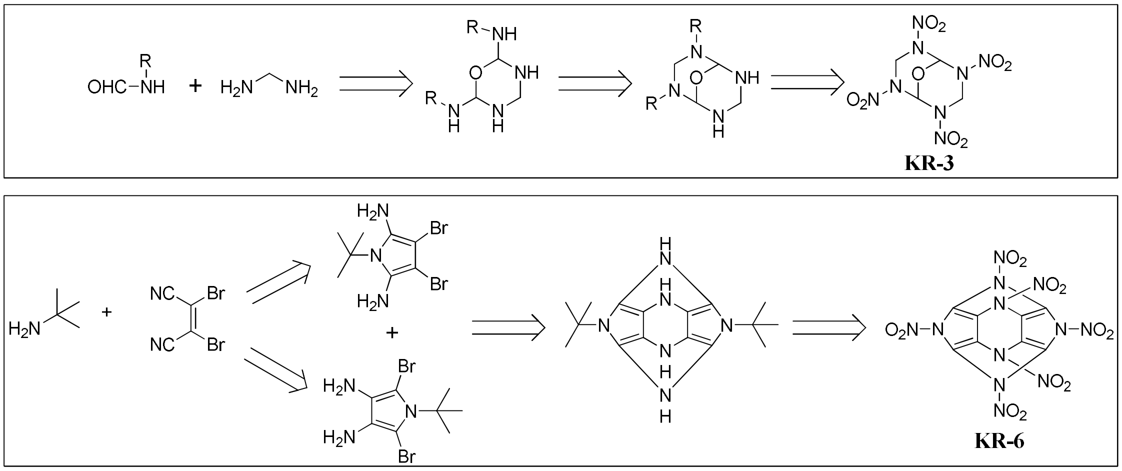
The detonation calculations were evaluated, and the results are listed in the Table 1. The potential energetic characteristics of designed molecules have been assessed by comparing with those of known contemporary explosives. All these molecules have found to exhibit density value ranging from 1.85 to 2.10 and detonation velocity from 8.35 to 10.71 Km/s. Among them, KR-6 has found to exhibit highest density of 2.1 g/cc along with the maximum detonation velocity of 10.712 Km/s which is higher than most of the existing high energy materials. In order to compare the accuracy of computational results, benchmark calculations have been performed with experimental properties of known explosive molecules and observed that calculated values seem in agreement with the experimental data [24].

Molecule	Density (g/cc)		HOF (KJ/mol)	Oxygen Balance (%)	Detonation Pressure (GPa)	Detonation Velocity (Km/s)
KR-1	1.94		-110.69	-42.53	31.86	8.506
KR-2	2.04		-527.14	-24.83	35.14	8.784
KR-3	2.03		-169.4	-7.04	43.29	9.683
KR-4	2.05		364.55	-27.57	41.71	9.489
KR-5	1.85		-47.03	-47.03	30.56	8.353
KR-6	2.10		-14.03	-14.03	58.52	10.712
RDX	1.818a	1.82b	91.21	-21.6	36.28	9.041
HMX	1.92a	1.91b	153.32	-21.6	39.41	9.309
FOX-7	1.89a	1.885b	-42.07	-21.6	35.56	8.969
CL-20	2.00a	2.04b	393.33	-10.95	43.28	9.604
TNAA	1.87a	1.88b	-134.0	30.11	24.31	7.783
a: Theoretical values; b: Experimental values						

Table 1. Detonation Performance Parameters of the Designed and known molecules

It is noteworthy that the amount of carbon in the molecules played a key role in determining the detonation performance. Molecules KR-1 and KR-2, despite having decent density values, fall short to the expected detonation performance due to the amount of carbon atoms they have. Of the designed six molecules, KR-3 and KR-6, as they have reduced carbon content, exhibit brilliant detonation pressure and detonation velocity values. Especially molecule KR-6, has been found the best explosive molecule with its density 2.10 g/cc, detonation velocity 10.712 Km/s and detonation pressure close to 60 GPa.

In order to understand the feasibility of synthesis, we have evaluated the possible synthetic route of two promising molecules KR-3 and KR-6. The retrosynthetic analysis of KR-3 and KR-6 indicates that, these molecules can be synthesized from commercially available starting materials methane diamine and (Z)-2,3-Dibromo-2-butene-1,4-dinitrile respectively as shown in Scheme 1.



Scheme 1. Retrosynthetic analysis of KR-3 and KR-6

The expected detonation products of designed molecules were calculated and shown in Figure 5. It is observed that in all the cases the major detonated product is Nitrogen and in majority cases, the least detonated product is Carbon monoxide. The other detonated products include water, carbon and carbon dioxide, representing the environmental compatibility of explosives after detonation.

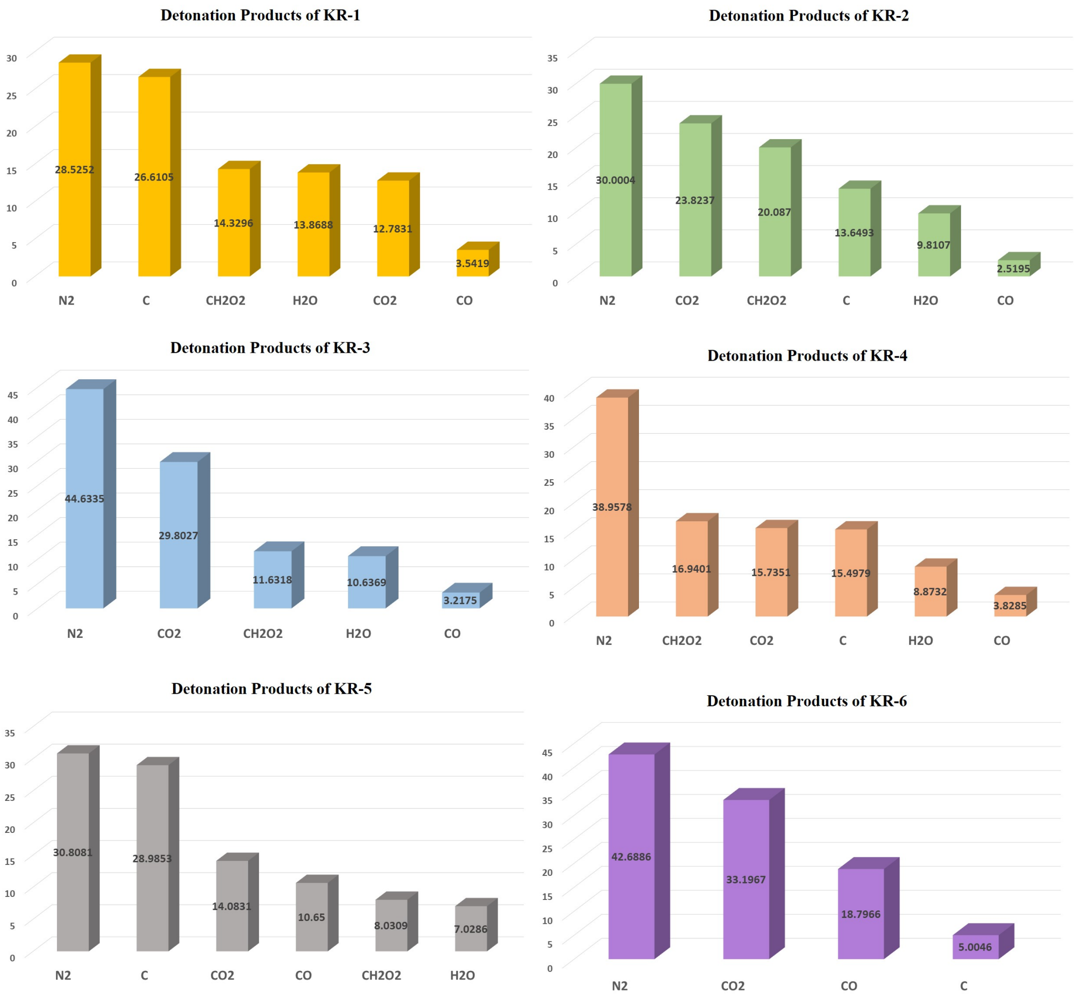


Figure 4. Calculated detonation products of Nitramine based compounds

The Infrared spectrum of all the six designed molecules has been predicted by DFT calculations. The IR spectrum of KR-1 to KR-3 shows the N-O symmetric stretching vibration at 1660 cm^{-1} whereas asymmetric stretch shows at 1310 cm^{-1} and stretching frequency of C-N is at 1290 cm^{-1}. Since these molecules possess ether linkage, C-O-C stretch observed in the region 950-1150 cm^{-1}. On the other hand KR-5 and KR-6 contains Pyrrole ring system along with nitramine functionality. The IR indicates N-O symmetric stretching vibration at 1670 cm^{-1} and asymmetric stretch at 1350 cm^{-1} along with the C-N stretching at 1120 cm^{-1} (Figure 5).

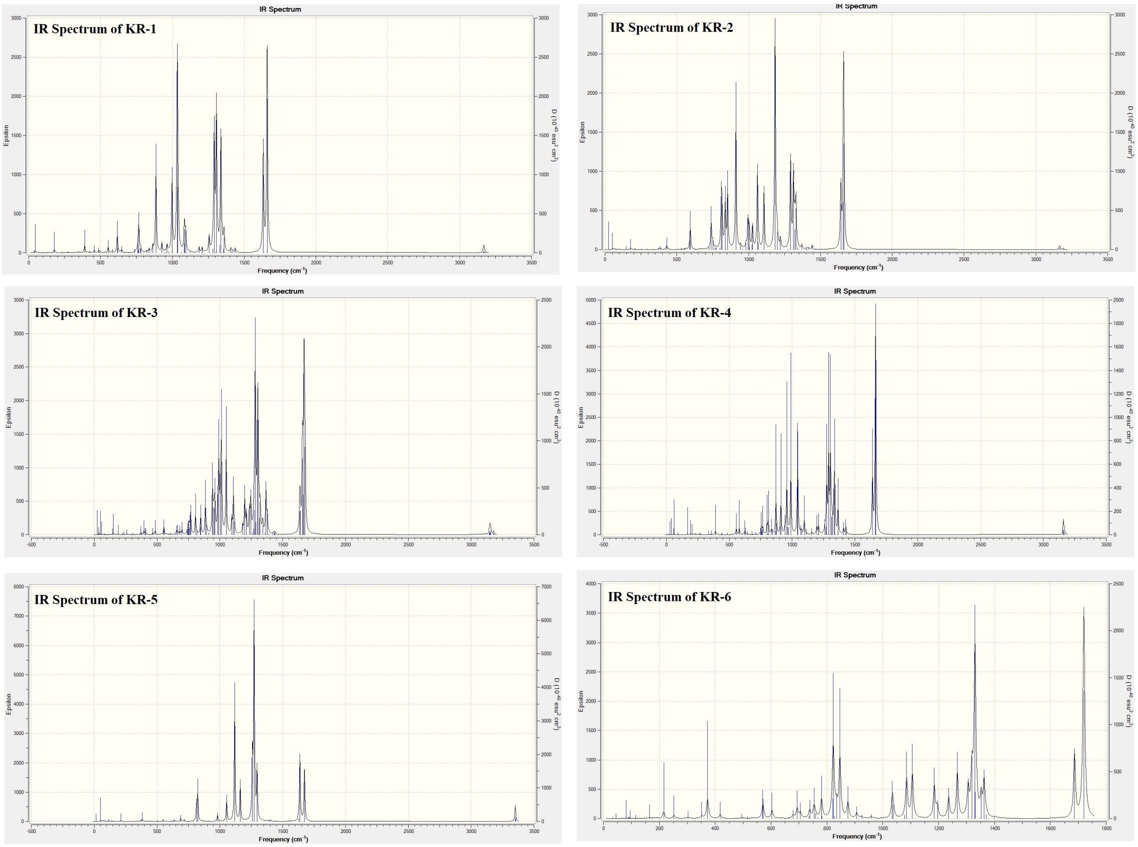


Figure 5. Calculated infrared spectra of Nitramine based compounds

Conclusions

In conclusion, we have designed six molecules based on nitramine functionality and evaluated the properties for explosive applications. All the designed molecules were found better or comparable explosive properties than the known explosives RDX and HMX. Furthermore, the molecules can easily be synthesized from commercially available starting materials.

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