Desensitization of TNAZ via Molecular Structure Modification and Explosive Properties – A DFT Study

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Abstract

TNAZ (1,3,3-trinitroazetidine) is a highly nitrated four membered nitrogen heterocyclic ring with greater performance when compared to melt castable explosive, TNT (trinitrotoluene). Desensitization of explosives is a significant area in military use. One current method is to use additives and coatings for explosives, as in the case of RDX. Another tactic would be to attempt small molecular level chemical changes in the explosive that bring the expected decrease in sensitivity without noteworthy loss in performance. TNAZ has three nitro groups. We thought that conversion of the nitro groups to nitroso and amine groups may decrease the sensitivity. We have correlated the bond dissociation energies with sensitivity and h50 values obtained from Keshavarz relations. We have also investigated chemical hardness and Mulliken electronegativities employing the frontier molecular orbitals. Furthermore, the explosive properties, i.e. detonation velocity (*D*), and detonation pressure (*P*) have been questioned by using both Kamlet-Jacobs equations and Keshavarz relations. Detonation products and power index values have also been calculated. We have proved that molecular modification is an operative method in desensitization of TNAZ.

Keywords: TNAZ, Desensitization, Structural Molecular Modification, Kamlet-Jacobs equation

1. Introduction

Highly nitrated small ring heterocycles and carbocycles are interesting energetic materials due to their increased performance originating from the additional energy release (manifested as a higher heat of formation) upon opening of the strained ring system during decomposition. Nowadays, the most widely studied energetic small–ring compound is 1, 3, 3–trinitroazetidine, TNAZ.[1] It is a highly nitrated four membered nitrogen heterocyclic ring with improved performance in comparison to conventional melt castable explosive trinitrotoluene. The additional contribution of energy is expected from the strained ring system.[2–7] There are more than 16 methods reported for the synthesis of 1, 3, 3–trinitroazetidine.[8]

TNAZ, a high performance, melt castable explosive, has been proposed as potential replacement for TNT[9]. The low melting point of TNAZ (101 °C) enables processing of formulations on modified production lines. Its performance is approximately 30% greater than TNT. It shows excellent thermal stability (>180 °C).[10]

TNAZ has many added advantages over known explosives. It is a highly energetic material, more powerful than RDX, and is less vulnerable than most other nitramines.[11,12] Unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminum, steel, brass and glass.[13–15]

Desensitization of explosives is of great value in reducing their sensitivity in military use. One approach that is being tried toward these objectives is to use additives and coatings for explosives in which surfaces may play an important role. Many the examples exist in the literature, especially on RDX.[16]

Another approach would be to attempt some molecular level chemical changes in the explosive that bring the expected decrease in sensitivity without significant loss in power. TNAZ has three NO_2 groups. We thought that on converting the $-NO_2$ groups to $-NO$ or $-NH_2$ groups (Figure 1), one might decrease the sensitivity as well as brisance values. Furthermore, an understanding of the trend in energetic properties in going from TNAZ to azetidine derivatives might reveal factors which can be used in altering the sensitivity of explosives, in general,

via structural modification. Desensitization makes explosives much safer compared to their parents by preventing some accidental explosions triggered by various factors such as thermal and/or mechanical shock, static electric discharging, etc.

In the present study, some theoretical studies have been performed for TNAZ itself and eleven different azetidine derivatives.

2. Theoretical Methods

The preliminary geometry optimizations resulting in energy minima were completed employing MM2 followed by semi–empirical PM3 self–consistent fields molecular orbital (SCF–MO) methods[17] at the restricted level.[18,19] Afterwards, geometry optimizations were done within the framework of Density Functional Theory (DFT,

Figure 1. The Structures of TNAZ (1) and some azetidine derivatives

B3LYP)[20,21] at the restricted level[22] of 6–31G(d,p) basis set. The exchange term of B3LYP contains hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange.[21,22] The correlation term of B3LYP consists of Vosko, Wilk, Nusair (VWN3) local correlation functional[23] and Lee, Yang, Parr (LYP) correlation correction functional.[24]

Vibrational analyses and the calculation of total electronic energies were performed using B3LYP/6–31G(d,p) type calculations for closed–shell systems. The frontier molecular orbital energies were obtained by HF/6–31G(d,p)//B3LYP/6–31G(d,p) method. The normal mode analysis for each compound yielded no imaginary frequencies which indicates each compound had at least a local minimum on the potential energy surface. The total electronic energies were corrected for zero point vibrational energies (ZPE). Gas phase heat of formations of all the molecules were calculated by a semi–empirical approach (PM3) over DFT (B3LYP/6–31G(d,p)) optimized geometries. Additionally the geometry optimizations and the single point calculations of all the structures were performed at UB3LYP/6–31G(d,p) theoretical level for bond dissociation energy (BDE) calculations. Note that in bond dissociation process open–shell systems are generated by the elimination of R radical via homolytic bond dissociation (radical dissociation process). The basis set superposition error (BSSE) analysis for bond dissociations were carried out with the counterpoise method, introduced by Boys and Bernardi[25], at the same level of theory. All the computations, except for BSSE, were performed using Spartan 06 software package.[26] BSSE analyses were performed at the same theoretical levels (UB3LYP/6–31G(d,p)) by Gaussian 03 software package. The normal mode analysis for each fragment resulted in no imaginary frequencies.
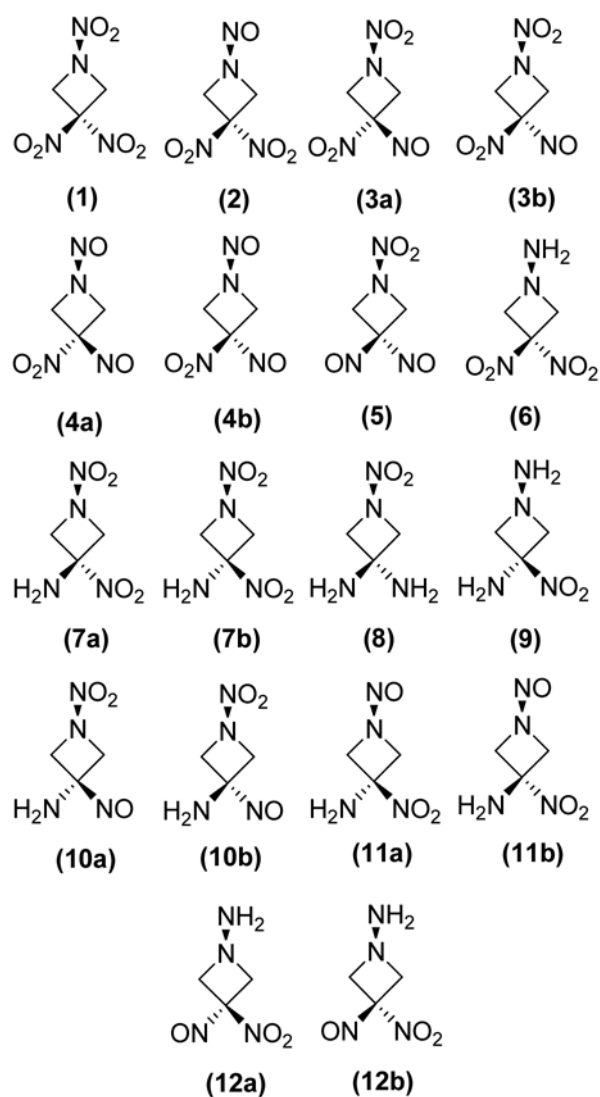
3. Results and Discussion

3. 1. The Geometries

All the structures presently considered have been thought to be the potential candidates of explosives (Figure 1). The geometry optimizations of the structures in Figure 1 were done at the B3LYP/6–31G(d,p) level. The bond lengths for the geometry optimized structures are presented in Table 1. The numbering in Table 1 is consistent with the numbering manner in Figure 2. The corresponding experimental X–ray diffraction values of TNAZ[27] are also shown in Table 1. The compatibility of the experimental and theoretical values of the bond lengths for TNAZ and the absence of imaginary frequencies in the potential energy diagrams are indications of the successful geometry optimization of the molecules. This compatibility also guarantees that bond lengths of other azetidine derivatives are close to the real values. Note that there are no experimental data for the azetidine derivatives to the best of our knowledge.
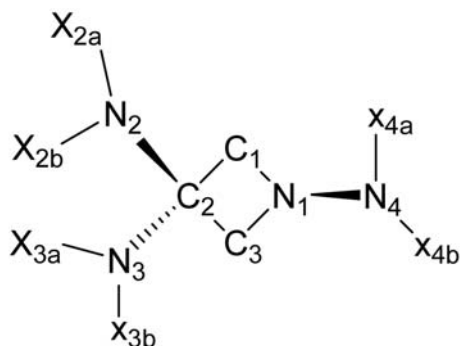
Figure 2. The numbering manner of TNAZ and azetidine derivatives

On the whole, a comparison between the experimental and theoretical bond lengths shows that the calculated results are slightly larger than the experimental values. For example, the observed crystal structure of TNAZ has shorter $N–NO_2$ bonds by approximately 0.04 Å than the calculated values, and the experimental $C–NO_2$ bonds are shorter than the calculated results by about 0.02 Å. These minor inconsistencies are mainly due to the solid–state effect, i.e., intermolecular interactions. Such interactions are not represented in the DFT calculations.[28]

3. 2. Relative Total Energies

In Table 2, the corrected absolute and relative total energies of the geometry optimized compounds calculated at the theoretical level of B3LYP/6–31G(d,p) are shown. When Table 2 is considered, it is obvious that compounds 3a, 4a, 7b, 11a and 12b are more stable than their stereoisomers 3b, 4b, 7a, 11b and 12a. The structures 10a and 10b are equal in energy. (See Figure–1 for structures).

It is essential to compare the energies of the isomeric structures in the evaluation of the stabilities. There are

5 different isomer groups on the basis of substituent groups. Note that 2, 3a, 3b (having 2 nitro and 1 nitroso groups); 4a, 4b, 5 (having 1 nitro and 2 nitroso groups); 6, 7a, 7b (2 nitro and 1 amino bearing isomeric group); 8, 9 (having 1 nitro and 2 amino groups); and 10a, 10b, 11a, 11b, 12a, 12b (possessing 1 nitro, 1 amino and 1 nitroso group) are isomers. It can be inferred from Table 2 that 2, 5, 7b, 8 and 11a seem to be the most stable in their corresponding isomer groups. Since total electronic energies of 3a, 4a, 10a, 11a, 7b and 12b are less than 3b, 4b, 10b, 11b, 7a and 12a (see Table 2). We continued the calculations with these less energetic molecules.

Table 2. The calculated (and corrected) absolute and relative total energies of TNAZ and azetidine derivatives at (DFT) B3LYP/6–31G(d,p) theoretical level.

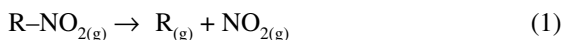| Compound	E_{total} kj/mol	E_{rel}
TNAZ (1)	−2065237	0
2	−1867847	197390
3a	−1867801	197436
3b	−1867799	197438
7b	−1673680	391557
7a	−1673669	391568
6	−1673570	391667
5	−1670411	394826
4a	−1670409	394828
4b	−1670351	394886
11a	−1476294	588943
11b	−1476257	588980
10a	−1476226	589011
10b	−1476226	589011
12b	−1476131	589106
12a	−1476128	589109
8	−1282065	783172
9	−1282003	783234

Table 1. The bond lengths (Å) of the geometry optimized TNAZ and azetidine derivatives calculated at the theoretical level of (DFT) B3LYP/6–31G(d.p)

						Bond Lengths in (Å)							
	TNAZ[a]	1	2	3a	4a	5	6	7b	8	9	10a	11a	12b
$C_2 – N_2$	1.501	1.523	1.524	1.538	1.523	1.507	1.519	1.547	1.447	1.573	1.529	1.568	1.508
$N_2 – X_{2a}$	1.210	1.224	1.224	1.198	1.197	1.205	1.224	1.227	1.019	1.226	1.207	1.226	1.201
$N_2 – X_{2b}$	1.212	1.219	1.219	–	–	–	1.221	1.227	1.019	1.228	–	1.225	–
$C_2 – N_3$	1.512	1.513	1.513	1.497	1.492	1.509	1.517	1.421	1.458	1.412	1.424	1.410	1.500
$N_3 – X_{3a}$	1.212	1.223	1.223	1.226	1.227	1.204	1.223	1.016	1.019	1.016	1.018	1.016	1.227
$N_3 – X_{3b}$	1.212	1.222	1.222	1.225	1.226	–	1.224	1.016	1.019	1.016	1.018	1.016	1.227
$N_1 – N_4$	1.356	1.397	1.347	1.396	1.343	1.394	1.464	1.389	1.381	1.468	1.385	1.337	1.464
$N_4 – X_{4a}$	1.221	1.225	1.221	1.225	1.223	1.228	1.023	1.227	1.229	1.024	1.228	1.226	1.023
$N_4 – X_{4b}$	1.224	1.225	–	1.226	–	1.225	1.023	1.227	1.230	1.023	1.228	–	1.023
$C_1 – C_2$	1.538	1.543	1.545	1.532	1.548	1.566	1.533	1.547	1.561	1.544	1.559	1.559	1.538
$C_3 – C_2$	1.534	1.542	1.545	1.551	1.547	1.534	1.533	1.545	1.572	1.544	1.561	1.556	1.539
$C_1 – N_1$	1.472	1.481	1.475	1.483	1.474	1.475	1.487	1.479	1.477	1.486	1.474	1.469	1.484
$C_3 – N_1$	1.473	1.481	1.477	1.478	1.477	1.482	1.487	1.480	1.475	1.487	1.474	1.472	1.486

[a] Experimental values at 298 K reported in ref.[27] All molecules possess C_1 point group. Only the most stable isomers are included.

3. 3. Bond Dissociation Energies (BDE)

In the present study, in order to compare the $C-NO_2$ and $N-NO_2$ bond strengths of the compounds, homolytic bond dissociation energy (BDE) calculations for the removal of nitrogen dioxide moiety from the structures were performed at UB3LYP/6-31G(d,p) level of theory. The expressions for the homolysis of $R-NO_2$ bond and for calculating its homolytic BDE are shown as follows:

$$R-NO_{2(g)} \rightarrow R_{(g)} + NO_{2(g)} \qquad (1)$$

$$BDE(R-NO_2) = [E_R + E_{NO2}] - E(R-NO_2) \qquad (2)$$

where $R-NO_2$ stands for the neutral molecule and $R^{.}$ and $NO_2^{.}$ for the corresponding product radicals after the bond dissociation; $BDE_{(R-NO2)}$ is the bond dissociation energy of the bond $R-NO_2$; $E(R-NO_2)$, E_R, and E_{NO2} are the zero-point energy corrected total energies of the parent compound and the corresponding radicals, respectively.[29–31] Furthermore, the basis set superposition error (BSSE) analyses were carried out.

The sensitivity behavior of an energetic material under different heat, impact, friction conditions may vary. In the present study, the "sensitivity" term denotes the "impact sensitivity" of a considered energetic material. Impact sensitivities of energetic compounds can be determined experimentally by physical tests, especially drop height test. Moreover, there are theoretical approaches for the computational determination of impact sensitivity. Murray et al.[32] have indicated that there is a relationship between the BDEs of the $N-NO_2$ and $C-NO_2$ trigger linkages and the electrostatic potentials on the molecular surfaces of some energetic molecules. There are various valuable studies in the literature[29,33–36] on the homolytic BDE of the nitro compounds such as nitroaromatic and nitramine molecules, which have revealed that there is a parallel correlation between the BDE for the weakest $R-NO_2$ bond scission in the molecule and its sensitivity. The usual trend is that the larger the homolytic BDE value for scission of $R-NO_2$ or $C-NO_2$ bonds are, the lower the sensitivity is.

Keshavarz et al has suggested valuable empirical methods for prediction of impact sensitivity of explosives.[37–41] Among these methods, we have chosen ref[42] for the impact sensitivity prediction of TNAZ and other molecules. h_{50} (impact drop height at which there is 50% probability (cm)) values have been associated with impact sensitivity. The higher the h_{50} value, the less sensitive the explosive. For a $C_aH_bN_cO_d$ type polynitro aliphatic explosive, h_{50} is given as

$$\log h_{50} = (81.40a + 16.11b - 19.08c + 1.089d)/\text{molecular weight} \qquad (3)$$

Desensitization of explosives is a hot topic in military use. Our approach in the current study is to attempt small structural changes in the explosive that bring the expected decrease in sensitivity without significant loss in power. TNAZ has three $-NO_2$ groups. We thought that on converting the NO_2 groups to $-NO$ or $-NH_2$ groups, one might decrease the sensitivity. To visualize the effect, we attributed the lowest sensitivity to the highest $N-NO_2$ and $C-NO_2$ BDEs. Furthermore, an understanding of the trend of energetic properties in going from TNAZ to azetidine derivatives might reveal the factors which can be used in altering the sensitivity of explosives, in general, via structural modification. Table 3 indicates BDE values. The consistency of our BDE values and the literature data

Table 3. The homolytic bond dissociation energies (BDE) of $C-NO_2$ and $N-NO_2$ bonds of TNAZ and azetidine derivatives calculated at (DFT) UB3LYP/6–31G(d.p) theoretical level and h_{50} values calculated according to Keshavarz relations[42]

| | BDE (kJ/mol) | | | Keshavarz |
	$C_{(2)}-N_{(2)}O_2$	$C_{(2)}-N_{(3)}O_2$	$N_{(1)}-N_{(4)}O_2$	h_{50} (cm)
TNAZ (1)	165.23 (167)*	165.23	160.22 (162.8)*	18
2	163.85	163.81	–	22
3a	–	62.29	163.1	
4a	62.85	–	–	30
5	–	–	167.02	
6	166.48	166.48	–	46
7b	186.1	–	155.82	
8	–	–	181.36	184
9	211.82	–	–	
10a	–	–	173.14	68
11a	198.31	–	–	
12b		231.65		

* Data in parenthesis are the literature values taken from ref.[43] for BDE of $C-NO_2$ bond of TNAZ and ref.[44] for BDE of $N-NO_2$ bond of TNAZ. Numbers in parenthesis below the element symbols indicate the positions. Only the most stable isomers are considered.

(available for some of the compounds)[43,44] increases the reliability of the method employed in the present article.

We have designated the smallest BDE of the molecules and compared them with those of other molecules and considered the h_{50} values obtained by Keshavarz relations. When the nitro (NO_2) group on N_1 atom of TNAZ is replaced with nitroso (NO) group (compound 2), the difference between the smallest BDEs becomes 3.59 kJ/mol. This extra energy resulted in desensitization of TNAZ. This desensitization is obvious from the h_{50} values. The value increases from 18 cm to 22 cm. However, the conversion of nitro (NO_2) group on C_2 atom of TNAZ in the same manner (compound 3a), drops the BDE dramatically to 62.29 kJ/mol. The molecule becomes more sensitive. We thought that this drop is due to the instability of isomer (compound 3a) when compared with the isomers in its group (2 nitro and 1 nitroso groups having isomer group).

When both nitro groups on C_2 of TNAZ are replaced with nitroso groups (compound 5), the difference between the smallest BDEs becomes 6.80 kJ/mol. Also, the increase of h_{50} value from 18 to 30 cm supports the idea of desensitization. However, conversion of TNAZ into compound 4a results in sensitization of TNAZ. This is again due to the instability of compound 4a in its isomer group (1 nitro and 2 nitroso groups bearing isomer group).

Conversion of the nitro group on the N_1 of TNAZ into amino group (NH_2) group (compound 6) results in a difference of 6.26 kJ/mol between the smallest BDEs. Also, this desensitization is clear from the increase of h50 values from 18 cm to 46 cm. Conversion of nitro group on C_4 atom into amino group (compound 7b) does not decrease the BDE dramatically. This conversion is not useful for desensitization.

Alteration of both nitro groups on C_2 with amino groups (compound 8) and conversion of one of the nitro group on C_2 and other nitro group on N_1 with amino groups increases BDE tremendously. Thus, this type molecular structural modification seems to be beneficial for desensitization purpose. Similarly, the increase of h_{50} value from 18 to 184 supports desensitization phenomena.

Stereochemically variable introduction of one nitroso and one amino groups into TNAZ accomplishes compounds 10a, 11a and 12b (each one having one nitro, one nitroso and one amino groups). All the conversions lead to a remarkable rise in BDEs, accordingly an effective decrease in sensitivity is expected theoretically. Such type of variation of functional groups of TNAZ is very advantageous for depressing sensitivity as seen from the increase of h_{50} values from 18 cm to 68.

In conclusion, introduction of an amino group into TNAZ desensitizes more as compared to the introduction of nitroso group. Additionally, replacement of two of the nitro groups with nitroso groups produces the same effect with the replacement of one nitro group with an amino group.

3. 4. The Frontier Molecular Orbitals

Mulliken electro negativities (χ_M) and chemical hardness (η) are significant assets in mirroring chemical reactivity of compounds. The χ_M and η values are calculated according to formulas given:

$$\chi_M = (I + A)/2 \qquad (4)$$

$$\eta = (I - A)/2 \qquad (5)$$

where I and A are the ionization potential and electron affinity, respectively.[45] Note that $I = -\varepsilon_{HOMO}$ and $A = -\varepsilon_{LUMO}$ within the rationality of the Koopmans' theorem.[46] The HOMO, LUMO, $\Delta\varepsilon$ energies ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$), Mulliken electro negativities (χ_M) and chemical hardnesses (η) of TNAZ and other azetidine derivatives calculated at HF/6–31G(d,p)//B3LYP/6–31G(d,p) theoretical level are shown in Table 4. Hartree–Fock is preferred over DFT in the frontier molecular orbital calculations due to the absence of Hartree–Fock type orbital concept in DFT.[47]

TNAZ (1) is the most electronegative of all; therefore it is less susceptible to oxidation when compared to others. The χ_M trend of the compounds shows partial parallelism with the total electronic energies. Generally, the most stable isomers in the corresponding isomer groups are more electronegative than the other group members, except for 3 and 10a.

The chemical hardness (η) value of a compound expresses the kinetic stability of the corresponding compound[48–58] and it is acknowledged that the harder compounds show higher kinetic stability.[48] The chemical hardness values of the questioned compounds are between 6 and 7b. TNAZ, the thermodynamically most stable of all, shows also good kinetic stability.

The highest value belongs to compound 8. It is the kinetically most stable one; whereas it shows very poor thermodynamic stability.

3. 5. Explosive Properties

Explosive outcomes of energetic materials can be evaluated by the determination of the explosive properties, namely detonation velocity (D) and detonation pressure (P). The empirical Kamlet-Jacobs[59–64] equations are employed for the calculations of these properties as follows:

$$D = 1.01 (N M_{ave}^{1/2} Q^{1/2})^{1/2} (1 + 130 \rho) \qquad (6)$$

$$P = 1.558 \rho^2 N M_{ave}^{1/2} Q^{1/2} \qquad (7)$$

where each term in equations 6 and 7 is defined as follows: D, detonation velocity (km/s); P, detonation pressure (GPa); ρ, density of a compound (g/cm^3); N,

Table 4. The HOMO, LUMO, $\Delta\varepsilon$ energies ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$), Mulliken electronegativities (χ_M) and chemical hardnesses (η) values of TNAZ and azetidine derivatives calculated at HF/6-31G(d.p)//B3LYP/6-31G(d.p) theoretical level.

	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta\varepsilon$	χ_m	η
TNAZ(1)	–13.03	0.99	14.02	6.02	7.01
2	–11.95	1.13	13.08	5.41	6.54
3a	–12.35	0.81	13.16	5.77	6.58
4a	–11.65	1.68	13.33	4.99	6.67
5	–11.98	1.06	13.04	5.46	6.52
6	–10.54	1.67	12.21	4.44	6.11
7b	–12.15	2.00	14.15	5.08	7.08
8	–11.22	3.17	14.39	4.03	7.20
9	–9.78	2.70	12.48	3.54	6.24
10a	–11.11	2.10	13.21	4.51	6.61
11a	–11.16	2.20	13.36	4.48	6.68
12b	–10.29	1.84	12.18	4.23	6.07

moles of gaseous detonation products per gram of explosive; M_{ave}, average molecular weight of gaseous products; Q, chemical energy of detonation (kJ/g). The parameters N, M_{ave}, and Q are calculated according to the chemical composition of each explosive as listed in Table 5.[28] Here, the parameters N, M_{ave}, and Q were calculated according to the chemical composition of each explosive as listed in the second column of Table 5.

($\Delta H^{\circ}_f(c)$) of compounds (Table 6). Keshavarz has related condensed phase heat of formation of an energetic compound[73] to its molecular structure. For a $C_aH_bN_cO_d$ type nitramine, $\Delta H_f(c)$ (kJ/mol) is given as,

$$\Delta H^{o}_{f}(c) = 29.68a - 31.85b + 144.2c - 88.84d - \\ 88.84n_{OH} - 39.14n_{N-NO2} - 45.62n_{C=O} + \quad (8) \\ 256.3n_{l}^{o} - 380.5n_{=CNN} + 30.20\, n_{O-NO2}$$

Table 5. Stoichiometric relations for the calculations of the N, M_{ave} and Q parameters of $C_aH_bO_cN_d$ type explosives.[28]

	Stoichiometric Relations		
Parameter	$c \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$b/2 > c$
N	(b + 2c + 2d)/4M	(b + 2c + 2d)/4M	(b + d)/2M
M_{ave}	4M/(b + 2c + 2d)	(56d + 88c – 8b)/(b + 2c + 2d)	(2b + 28d + 32c)/(b + d)
$Q \times 10^{-3}$	$(28.9b + 94.05a + 0.239\Delta H^{o}_{f})/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H^{o}_{f}]/M$	$(57.8c + 0.239\Delta H^{o}_{f})/M$

In Table 5, M is the molecular weight of the compound (in g/mol); ΔH^{o}_f is the gas phase standard heat of formation of the compound (in kJ/mol). Earlier studies[65–77] have reported that the gas phase standard heat of formation ($\Delta H^{o}_f(g)$ / 6–31G(d,p)) geometry optimized TNAZ and other azetidine derivatives to calculate the gas phase heat of formations in gas phase. The density of each compound is defined as the molecular weight divided by the molar volume. The molar volume was calculated using a Monte Carlo integration technique implemented in the Gaussian 03 software package.[68] Ω values show % oxygen balance of the compounds in the study. Molecular volume and density results are given with standard deviation in order to show the accuracy of the method. The predicted densities and detonation properties of TNAZ and other azetidine derivatives are listed in Table 6. It also includes experimental and theoretical performance values of TNT[69], RDX[28,67,70–72] and HMX[28,71,72] taken from the literature.

We have also calculated detonation velocity and pressure employing condensed phase heat of formation

where n_{OH}, $n_{N–NO2}$, $n_{C=O}$ and $n_{O–NO2}$ are the number of specified functional groups, n_l^o is equal to 0 and 1 for existence of hydrogen in molecule and hydrogen free compound, respectively. $n_{=CNN}$ is the number of structural moiety =C–NN in the energetic compound.

Keshavarz has also suggested very simple methods for the investigation of detonation velocity(D)[74], detonation pressure (P)[75] and detonation temperature (T_{det}).[76] The detonation velocity for both $C_aH_bN_cO_d$ type and $C_aH_bN_cO_dAl_e$ type explosive is given as,

$$D = 1.64 + 3.65\rho_o - 0.135a + 0.117c + \\ 0.0391d - 0.295n_{-NRR'} - 0.620n_{Al} - 1.41n_{NO3\,salt} \quad (9)$$

where D is expressed in km/s; ρ_o is the density in (g/cm³), n_{NRR}' is the number of specific group –NH$_2$, NH$_4^+$ and five member ring with three (or four) nitrogens in any explosive as well as five (or six) member ring in cage nitramines. n_{Al} is equal to the number of moles of aluminum except that its value can be changed according to some conditions.[74]

Table 6. Predicted densities and detonation properties of TNAZ and azetidine derivatives at the theoretical level of B3LYP/6–31G(d,p).

Compound	Ω %	ΔH°f(g)[a] (kJ/mol)	ΔH°f(c)[b] (kJ/mol)	Q (kJ/g)	V[c] (cm3/mol)	ρ (g/cm3)	GAS PHASE D[d] (km/s)	GAS PHASE P[d] (GPa)	CONDENSED PHASE D[e] (km/s)	CONDENSED PHASE P[e] (GPa)	D[f] (km/s)	Keshavarz P[f] (GPa)	T_det[f] K
TNAZ(1)	−16.67	127.46 (125.05)	−33.74	1740.43	109.28	1.77	8.92	34.97	8.65	32.89	8.41	32.33	4890
2	−27.27	189.02	94.24	1715.06	101.65	1.75	8.73	33.25	8.56	31.98	8.30	31.08	5120
3a	−27.27	202.39	55.10	1733.22	103.96	1.71	8.60	31.80	8.34	29.91	8.14	29.51	5121
4a	−40.00	266.20	183.08	1707.95	98.49	1.65	8.23	28.40	8.07	27.35	7.86	26.62	5397
5	−40.00	293.05	143.94	1748.05	96.26	1.69	8.42	30.25	8.14	28.26	8.02	28.14	5398
6	−49.38	171.56	119.38	1613.76	99.08	1.65	8.22	28.44	8.12	27.76	7.60	24.06	4743
7b	−49.38	123.82	80.24	1543.32	97.33	1.69	8.25	29.01	8.16	28.40	7.73	25.30	4743
8	−96.97	115.44	194.22	1084.77	92.11	1.45	7.13	19.62	7.35	20.87	6.48	13.48	4528
9	−96.97	175.71	233.36	1193.90	91.64	1.46	7.33	20.84	7.49	21.73	6.52	13.76	4529
10a	−65.75	209.41	169.08	1530.48	92.07	1.61	7.82	25.25	7.73	24.70	7.39	21.90	5005
11a	−65.75	183.76	208.22	1488.49	92.61	1.59	7.72	24.47	7.77	24.80	7.34	21.43	5005
12b	−65.75	252.54	208.22	1601.07	93.13	1.59	7.85	25.28	7.76	24.70	7.33	21.33	5005
TNT	−73.98	52.47		1361.62	124.92	1.64	7.11	19.00					
RDX	−21.61	168.90		1597.39	124.92	1.78 (1.81)	8.88 (8.75)	34.75 (34.70)					
HMX	−21.61	270.41		1633.88	157.53	1.88 (1.90)	9.28 (9.10)	39.21 (39.30)					

Similarly, Keshavarz has proposed detonation pressure[75] for both $C_aH_bN_cO_d$ type and $C_aH_bN_cO_dAl_e$ type explosive,

$$P = -2.335 + 10.586\rho_o^{\,2} - 1.239a - 0.183b + 0.650c + 0.540d - 2.471\,n_{-NHx} - 6.308\,n'_{Al} \quad (10)$$

where P is expressed in GPa, ρ_o is the density in (g/cm³), n_{-NHx} is the number of –NH₂, NH₄⁺ or five (or six) member ring in cage nitramines; n_{Al} is a function of the number of moles of Al which can be determined according to equations in ref[75].

Detonation temperature (T_{det}) is another important parameter in the investigation of explosives. Keshavarz et. al. has projected a simple method[76] to assess the detonation temperature using molecular structure and gas phase heat of formation $\Delta H_f(g)$. For a $C_aH_bN_cO_d$ type non–aromatic explosive, detonation temperature is given,

$$T_{det}/1000 = 149.0 - 1513.9\,a' - 196.5b' - 2066.1c' - 2346.2\,d' + 1.2\,\Delta H'_f(g) \quad (11)$$

where T_{det} is expressed in Kelvin, a', b', c', d' and $\Delta H'_f(g)$ are a, b, c, d and gas phase heat of formation of explosive divided by molecular weight of explosive,[7] respectively.

The detonation velocity and pressure values (calculated using $\Delta H^o_f(g)$ and Kamlet–Jacobs) for TNAZ are in accordance with the literature data.[72,77] When Table 6 is considered, it is obvious that the performance of TNAZ lies between well–known explosives HMX and RDX and is better in usage than its alternate, TNT.

The performances of TNAZ and other azetidine derivatives are in the following manner (See Figure 3): TNAZ (1) >2> 3a> 5> 7b> 4a> 6> 12b> 10a> 11a> 9> 8> TNT. The results show that the more nitro groups the compounds have, the better the explosive properties are. TNAZ has the highest detonation properties as we expected.

Replacement of nitro groups with nitroso groups (on going from TNAZ to compounds 2, 3, 4a and 5) slightly

[a] Gas phase standard heat of formation values obtained from the PM3 single point calculations[65–67] over B3LYP/6–31G(d,p) geometry optimized structures.

[b] Condensed phase heat of formation values obtained from Keshavarz relation[73]

[c] Average molar volumes from 100–single point calculations at the B3LYP/6–31G(d,p) level.[28]

[d] Detonation velocity and pressure results obtained from Kamlet–Jacobs equations using gas phase heat of formation data.

[e] Detonation velocity and pressure results obtained from Kamlet–Jacobs equations using condensed phase heat of formation data.

[f] Detonation velocity and pressure results obtained from Keshavarz empirical relations.[74–76] Data in parenthesis are the experimental values taken from ref.[77] for $\Delta H^o_f(g)$ of TNAZ, ref.[78] for density of TNAZ, ref.[79] for detonation velocity of TNAZ, ref.[80] for detonation pressure of TNAZ, ref.[69] for TNT, refs.[67,70–72] for RDX and refs.[71,72] for HMX.
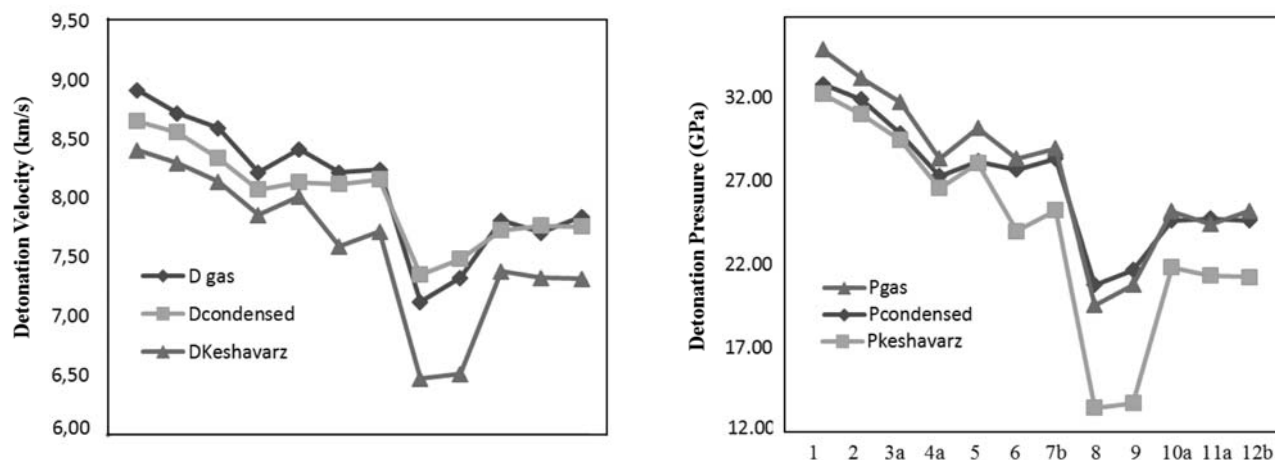
Figure 3. Detonation velocity and pressure calculated according to Kamlet-Jacobs equations using gas phase and condensed phase heat of formation and according to Keshavarz relations.

decreases explosive properties. Whereas, amino group replacements (from TNAZ to compounds 6, 7b, 8 and 9) decreases detonation velocity and pressure more. The compounds 10a, 11a and 12b have one nitro, one nitroso and one amino group. These isomers (10a, 11a and 12b) are better in performance and the most insensitive isomer groups in the present study.

As seen from Figure 3, detonation velocity and pressure values calculated employing $\Delta H^o_f(g)$ and $\Delta H^o_f(c)$ are quite analogous. Whereas detonation values calculated using Keshavarz relations are somehow lower, however they follow the same trend with the results of Kamlet–Jacobs. The Keshavarz detonation relations provide timesaving calculations with quite satisfactory results.

The detonation temperature is another substantial parameter in the examination of explosives. Detonation reaction of an explosive is enormously fast and the heat produced by detonation increases the temperature of gases, which lead them to expand and work on surroundings.[76] The detonation temperature of TNAZ and other azetidine derivatives are in the following manner 4a = 5 $(C_3H_4N_4O_4) > 2 = 3$ $(C_3H_4N_4O_5) > 10a = 11a = 12b$ $(C_3H_6N_4O_3) >$ TNAZ $(C_3H_4N_4O_6) > 6 = 7b$ $(C_3H_6N_4O_4) > 8 = 9(C_3H_8N_4O_2)$. As seen from the sequence, as the number of oxygen and hydrogen atoms increases, detonation temperature decreases.

3. 5. 1. Detonation Products

The detonation of a $C_aH_bO_cN_d$ type explosive will result in the formation of smaller molecules, i.e., CO_2, CO, H_2O, etc. In order to clarify the decomposition products, a set of rules was developed by Kistiakowsky and Wilson.[81] Table 7 shows the number of moles of detona-

Table 7. Gaseous decomposition products of TNAZ and other azetidine derivatives using the Kistiakowsky and Wilson Rules

| | Formula | Number of moles of detonation products | | | | | | Total |
		N_2	H_2O	CO	CO_2	H_2	C_{solid}	
TNAZ(1)	$C_3H_4N_4O_6$	2	2	2	1	–	–	7
2	$C_3H_4N_4O_5$	2	2	3	–	–	–	7
3a	$C_3H_4N_4O_5$							
4a	$C_3H_4N_4O_4$	2	2	2	–	–	1	7
5	$C_3H_4N_4O_4$							
6	$C_3H_6N_4O_6$	2	3	1	–	–	2	8
7b	$C_3H_6N_4O_4$							
8	$C_3H_8N_4O_2$	2	2	–	–	2	3	9
9	$C_3H_8N_4O_2$							
10a	$C_3H_6N_4O_3$							
11a	$C_3H_6N_4O_3$	2	3	–	–	–	3	8
12b	$C_3H_6N_4O_3$							
Picric Acid	$C_6H_3N_3O_7$	3/2	3/2	11/2	–	–	1/2	9
TNT	$C_7H_5N_3O_6$	3/2	5/2	7/2	–	–	7/2	11
RDX	$C_3H_6N_6O_6$	3	3	3	–	–	–	9
HMX	$C_4H_8N_8O_8$	4	4	4	–	–	–	12

tion products of the compounds questioned in the present study.

When total amount of gas produced upon detonation is considered, the compounds 8 and 9 seem to be the most gas releasing ones. These compounds produce as much gas as well known explosives Picric Acid and RDX. The next group of compounds producing less gas upon detonation contain 5, 6, 10a, 11a and 12b. Since TNAZ, 2 and 3a do not produce solid carbon, they produce the most amount of gas upon detonation.

The most hazardous detonation product is carbon monoxide (CO). It is a colorless, odorless poisonous gas that is extremely harmful to human health. Compounds 2 and 3 produce 3 moles of carbon monoxide upon detonation. TNAZ, compounds 4 and 5 produce 2 moles when compounds 6 and 7 only produce 1 mole of carbon monoxide. TNAZ is the only compound that produces CO_2 upon detonation.

Compounds 8, 9, 10, 11 and 12 seem to be the most environment friendly when detonation products of other azetidine derivatives are considered. TNAZ and other derivatives produce less CO when compared to those of Picric Acid, TNT, RDX and HMX. It is appropriate to consider TNAZ as an environment friendly explosive in terms of detonation products.

3. 5. 2. Explosive Power and Power Index

Heat and gases are released in an explosive reaction. The volume of gas produced will provide information on the amount of work done by the explosive. Standard conditions must be established in order to measure the volume of generated gas, since the volume of gas varies according to the temperature. The standard conditions (273 K, 1atm) also enable one to make comparisons between different explosives. Division of the value of total volume of gas produced upon detonation by the molecular weight gives an idea of how much gas is released per gram of explosive.

The heat of explosion Q can be calculated as expressed in section 3.5. The volume and Q values can be combined to give the value for the explosive power[82] as shown in the following equation:

$$\text{Explosive power} = QV \tag{8}$$

The value for the explosive power is then compared with the explosive power of a standard explosive (picric acid) to obtain power index, as shown in the following equation:

$$\text{Power index} = [QV / Q(\text{picric acid})V \\ (\text{picric acid})] \times 100 \tag{9}$$

Table 8 shows the power index values of TNAZ, azetidine derivatives, Picric Acid, TNT, RDX and HMX and the deviation of values relative to TNAZ (ΔPI). The power index values of TNAZ and other azetidine derivatives are between 118 – 163% and in the following manner: 12b> 10a> 11a> 9> 6> 5> 7b> 4a> 8> 3a> TNT> 2> HMX> RDX> TNAZ (1)> Picric Acid. The results show that TNAZ is as favorable as RDX and HMX in terms of power index. The compounds 10a, 11a and 12b having one nitro, one nitroso and one amino group have the highest power index value of all.

4. Conclusion

Presently, theoretical studies have been performed on TNAZ itself and eleven different azetidine derivatives. The corrected absolute and relative total energies of the geometry optimized structures have been calculated at the theoretical level of B3LYP/6–31G(d,p). We have

Table 8. The power index values of TNAZ, azetidine derivatives, Picric Acid, TNT, RDX and HMX

Compound	Q (kJ/g)	V(dm³/g)	QxV	Power Index %	ΔPI
TNAZ (1)	1740.43	0.82	1421.35	118	0
2	1715.06	0.89	1527.96	126	8
3a	1733.22	0.89	1544.14	128	10
4a	1707.95	0.98	1673.80	139	21
5	1748.05	0.98	1713.09	142	24
6	1613.76	1.11	1785.09	148	30
7b	1543.32	1.11	1707.18	141	23
8	1084.77	1.53	1656.75	137	19
9	1193.90	1.53	1823.42	151	33
10a	1530.48	1.23	1878.50	155	37
11a	1488.49	1.23	1826.97	151	33
12b	1601.07	1.23	1965.15	163	45
Picric Acid	1372.86	0.88	1208.07	100	–18
TNT	1417.54	1.09	1538.69	127	9
RDX	1598.39	0.91	1450.86	120	2
HMX	1634.89	0.91	1484.66	123	5

correlated the bond dissociation energies with sensitivity. TNAZ has three NO_2 groups. We have proved that on converting the nitro groups to nitroso and amino groups, it is possible to decrease the sensitivity without significant loss in power. The introduction of an amino group into TNAZ desensitizes the molecule more when compared to the introduction of nitroso group. Besides, replacement of two of the nitro groups with nitroso groups makes the same effect with the replacement of one nitro group with an amino group. It is obvious that as the number of amino group increases, BDE values also increases, consequently sensitivity decreases, however explosive property might be lost. As for explosive effects, replacement of nitro groups with nitroso groups (on going from TNAZ to compounds 2–5) slightly decreases explosive properties. Whereas, amino group replacements (from TNAZ to compounds 6, 7b, 8 and 9) decrease detonation velocity and pressure more. Compounds 8–12 seem to be the most environment friendly when detonation products of all azetidine derivatives are considered. Note that the compounds 10a, 11a and 12b have one nitro, one nitroso and one amino group. These isomers not only have the highest power index values but also are optimum structures in performance and the most insensitive isomer group in the present study. TNAZ is as favorable as RDX and HMX in terms of power index. All the compounds investigated showed better explosive properties than TNT. They are all potential candidates for insensitive high explosives. They are all alternative to TNT whenever lower sensitivity is required. We have proved that molecular modification is a functioning method in both desensitization of TNAZ and reduction of its explosive effects.

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Povzetek

TNAZ (1,3,3-trinitroazetidin) je spojina, ki jo sestavlja štiričlenski dušikov heterociklični obroč ter tri nitro skupine. V primerjavi z npr. z TNT (trinitrotoluen) ima boljše eksplozivne lastnosti. V tem delu smo proučevali vpliv molekulske strukture spojine na te lastnosti. Glede na zgradbo TNAZ lahko pričakujemo, da s pretvorbo nitro skupin v nitrozo ali amino skupine lahko reguliramo eksplozivno občutljivost, kar smo kolerirali s energijo razcepa kemijskih vezi. Proučevali smo tudi vpliv kemijske trdote in Mullikenove elektronegativnosti na eksplozivne lastnosti. Z uporabo Kamlet-Jacobsove enačbe smo reziskovali tudi balističen lastnosti, kot so hitrost detonacije (*D*) in detanacoisjki tlak (*P*). Napovedali smo produkte detonacije in indeks moči. Dokazali smo, da z modifikacijo molekule lahko bistveno vplivamo na eksplozivno občutljivost TNAZ.