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Theoretical studies on nitrogen rich energetic azoles

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Abstract Different nitro azole isomers based on five membered heterocyclics were designed and investigated using computational techniques in order to find out the comprehensive relationships between structure and performances of these high nitrogen compounds. Electronic structure of the molecules have been calculated using density functional theory (DFT) and the heat of formation has been calculated using the isodesmic reaction approach at B3LYP/6-31G* level. All designed compounds show high positive heat of formation due to the high nitrogen content and energetic nitro groups. The crystal densities of these energetic azoles have been predicted with different force fields. All the energetic azoles show densities higher than 1.87 g/cm^3. Detonation properties of energetic azoles are evaluated by using Kamlet-Jacobs equation based on the calculated densities and heat of formations. It is found that energetic azoles show detonation velocity about 9.0 km/s, and detonation pressure of 40GPa. Stability of the designed compounds has been predicted by evaluating the bond dissociation energy of the weakest C-NO$_2$ bond. The aromaticity using nucleus independent chemical shift (NICS) is also explored to predict the stability via delocalization of the π-electrons. Charge on the nitro group is used to assess the impact sensitivity in the present study. Overall, the study implies that all energetic azoles are found to be stable and expected to be the novel candidates of high energy density materials (HEDMs).

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Introduction

Heterocycles that contain a large amount of nitrogen are relatively dense, they possess higher heat of formation (HOF) due to higher percentage decomposition products usually dinitrogen. Additionally, smaller amounts of hydrogen and carbon contribute to a better oxygen balance; with enhanced good thermal stability more than normally is found with their carbocyclic analogues [1–5]. Five member nitrogen containing rings such as imidazole, pyrazole, and triazole are the natural framework for energetic materials as possesses high nitrogen content [6–8]. Their performance can be optimized and improved through substituting hydrogen atoms with explosophore like nitro, amino, azido etc. Among various explosophores, nitro group is a vital constituent of energetic materials. The performance of the polynitro compounds is enhanced by excellent oxygen balance; results in a higher exothermicity of the combustion and detonation process while ring strain improves HOF and density. Hence in the search of novel HEDMs, nitro azoles expected to be promising candidates.

The key properties of energetic materials in relation to its electronic structure are HOF, density (ρ$_o$), detonation velocity (D), detonation pressure (P) and sensitivity. The density functional theory methods can produce reliable geometries and energies with less time and computer resources [9–13]. Isodesmic approach has been employed

for computing heat of formation [14–17]. Density is a condensed phase property and its prediction involves challenges as it is associated with different intermolecular interactions, which affect the crystal pattern and cell volume. It is being widely predicted by crystal structure packing calculations as it is superior to the group additive approaches [18]. The general possible ways of improving the density are increasing the number of nitro groups which increases the opportunity for hydrogen bonding, introduction of smaller heterocyclic chains (such as imidazole, pyrazole, triazole, and tetrazole) and replacement of the single bonds with double bonds reduces the bond length, expected to decrease the molecular volume [19–21].

Recently, nucleus independent chemical shift (NICS) can be used as an indicator of aromaticity that usually correlates well with the energetic, structural and magnetic criteria. NICS was defined by Schleyer et al. as the negative value of the absolute magnetic shielding computed in centers of ring or 1 Å above the molecular plane [22–24]. NICS at an empty point in space equals zero and in principle does not require reference molecules and calibrating equations for evaluation of aromaticity [25]. Aromatic compounds are stable relative to some non-aromatic reference. In the present study, NICS of the azole isomers were predicted using density functional theory involving the gauge invariant atomic orbitals (GIAO) method for analyzing the relative stability of the designed molecules. Recently, Zhang et al. demonstrated the relationship between the impact sensitivities and electronic structures of some nitro compounds can be established by the charge analysis of the nitro group [26–28].

The present study aims to design the novel nitrogen-rich azole isomers for the energetic material applications by systematic structure-property relationships. Molecules with bi & tri nitrogen heterocycles with varying nitro groups are designed and their structures are shown in Fig. 1. Density functional theory (DFT) is used for the prediction of HOF by employing isodesmic approach, while crystal density by force field based packing calculations. The stability of the designed molecules has been attempted by bond dissociation energy (BDE) and NICS, while the sensitivity correlations by atomic charge analysis on nitro groups.

Calculation methodology

All quantum mechanical calculations were performed with Gaussian 03 program suite [29]. The Becke three-parameter hybrid (B3) [30] functional was used along with Lee-Yang-Parr (LYP) [31, 32] correlation. For all optimization and harmonic vibrational frequency calculations, 6-31G* basis set has been employed. HOF has been predicted by

designing appropriate isodesmic reactions [33, 34]. In an isodesmic reaction, the number of each kind of formal bond is conserved according to bond separation reaction (BSR) rules. The target molecule is broken down into a set of heavy atom molecules containing same component bonds. BSR rules cannot be applied to the molecules with delocalized bonds and cage skeletons because of large calculated errors of HOFs. In view of the above, present study involves the design of isodesmic reactions in which the numbers of all kinds of bonds keep invariable to decrease the calculation errors of HOF. Imidazole, pyrazole, and triazole rings are kept intact while constructing isodesmic reactions and this approach proved to be reliable [35–37].

The density for crystal structure of all compounds was predicted by the rigorous molecular packing calculations using polymorph module of Material Studio Suite [38]. The calculation involves defining a molecule in an asymmetric cell unit, packing into a crystal under a given space group symmetry, geometry optimization to achieve energy minimized structure and removal of duplicate crystal structures by the clustering process as implemented in the polymorph module [39]. The approach was based on the generation of possible packing arrangements in all reasonable space groups ($P2_1/c$, $P\text{-}1$, $P2_12_12_1$, $P2_1$, $C2/c$, $Pbca$, $Pna2_1$, $Pbcn$, Cc, and $C2$) [40, 41] to search for the low-lying minima in lattice energy surface.

The empirical Kamlet-Jacobs [42–44] equations were employed to estimate the values of D and P for the high energy materials containing C, H, O and N as the following equations:

$$D = 1.01\left(NM^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.30\rho_o) \qquad (1)$$

$$P = 1.55\rho_o{}^2NM^{1/2}Q^{1/2} \qquad (2)$$

Where in above equations D is detonation velocity (km/s), P is detonation pressure (GPa), N is moles of gaseous detonation products per gram of explosives, M is average molecular weights of gaseous products, Q is chemical energy of detonation (kJ mol^{-1}) defined as the difference of the HOFs between products and reactants, and ρ_o is the density of explosive (g/cm^3).

Thermal and kinetic stability could be evaluated by the bond dissociation energy (BDE) and is defined as the difference between the zero point energy corrected total energies at 0K of the parent molecules and those of the corresponding radicals in the unimolecular bond dissociation [45–47]. In an energetic molecule, generally, C-NO$_2$ is the trigger bond which undergoes fission due to the applied heat or mechanical impact, so we have presented the BDE values of these bonds. In the present study, BDE of all out-of-rings

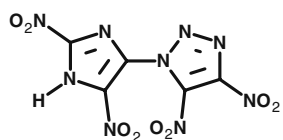**Fig. 1** Chemical structures of the azole isomers studied
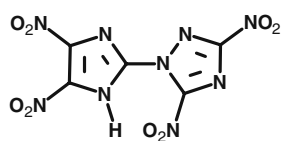
H1

1-(4,5-dinitro-1H-imidazol-2-yl)-3,5-dinitro-1H-1,2,4-triazole
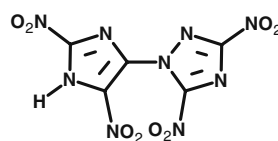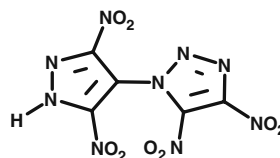
H2

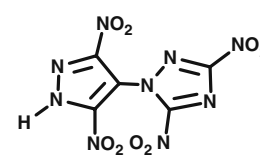1-(2,5-dinitro-1H-imidazol-4-yl)-3,5-dinitro-1H-1,2,4-triazole
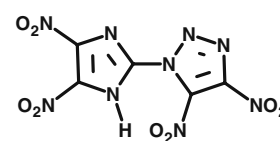
H3

1-(4,5-dinitro-1H-imidazol-2-yl)-4,5-dinitro-1H-1,2,3-triazole
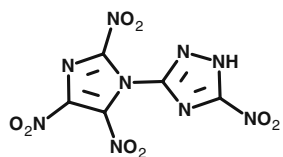
H4

1-(2,5-dinitro-1H-imidazol-4-yl)-4,5-dinitro-1H-1,2,3-triazole
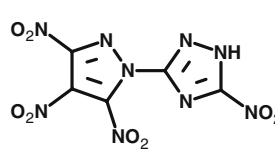
H5

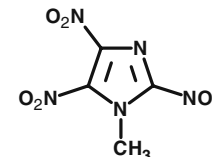1-(3,5-dinitro-1H-pyrazol-4-yl)-4,5-dinitro-1H-1,2,3-triazole

H6

1-(3,5-dinitro-1H-pyrazol-4-yl)-3,5-dinitro-1H-1,2,4-triazole

H7

5-nitro-3-(2,4,5-trinitro-1H-imidazol-1-yl)-1H-1,2,4-triazole

H8

5-nitro-3-(3,4,5-trinitro-1H-pyrazol-1-yl)-1H-1,2,4-triazole

MTNI

1-methyl-2,4,5-trinitroimidazole

C-NO$_2$ bonds have been calculated at B3LYP/6-31G* level using this equation:

$$BDE_{298}(R_1 - R_2) = [\Delta_f H_{298}(R_1) + \Delta_f H_{298}(R_2)]$$
$$- \Delta_f H_{298}(R_1 - R_2). \quad (3)$$

Where, $R_1 - R_2$ is the neutral molecule, and R_1 and R_2 are the corresponding radicals [48]. Nucleus independent chemical shifts (NICS) at the ring center of the different rings of the designed compounds in the gas phase were predicted using the gauge invariant atomic orbitals (GIAO) method. B3LYP hybrid functional with 6-31G* basis set was employed for the prediction at centers of ring. NICS values of the individual rings has been represented NICS (1) for the rings having two nitrogens in the ring (imidazole and pyrazole), while NICS (2) for the rings having three nitrogens in the ring (triazoles). The NICS (1) and NICS (2) values have been listed in the Table 1.

Atomic charges have been computed for the optimized geometries of designed molecules by natural bond orbital (NBO) analysis [25] at B3LYP/6-31G* level. In the present study, charge on the nitro group ($-Q_{NO_2}$) has been considered for its correlation to impact sensitivity.

$$Q_{NO_2} = Q_N + Q_{O_1} + Q_{O_2} \quad (4)$$

Charge on the nitro group ($-Q_{NO_2}$) is calculated by the sum of net Mulliken charges on the nitrogen (Q_N) and oxygen atoms (Q_{O_1} and Q_{O_2}) in the nitro group.

Results and discussion

Energetic azoles are rich in nitrogen and the designed molecules having nitrogen content of about 40% and oxygen balance is -12.7%. The present study brings out

Table 1 Predicted NICS (ppm) values for designed compounds

Compd.	H1	H2	H3	H4	H5	H6	H7	H8
NICS (1)	-14.4	-14.2	-14.9	-14.3	-15.7	-15.7	-15.9	-16.9
NICS (2)	-12.7	-12.7	-13.7	-12.9	-13.1	-12.8	-12.8	-12.9

the structure-property relationships of energetic azole isomers possessing molecular formula $C_5HN_9O_8$ by comparing their characteristics like gas phase HOFs, density (ρ_o), detonation performance (D and P), stability and the insensitivity. The predicted energetic properties of the designed molecules have been compared with 1-methyl-2,4,5-trinitroimidazole (MTNI) to evaluate the performance. MTNI is an insensitive melt-cast high explosive, whose explosive performance is comparable to RDX and its sensitivity is intermediate between RDX and TNT [49, 50].

Heat of formation

The HOF is the indicative of the energy content of the high energy materials and hence, important to predict accurately. The energy of high nitrogen compounds is derived from their high positive HOFs rather than from the combustion of the carbon backbone or ring strain as traditional and modern energetic polynitro compounds. The zero point energies and thermal correction at the B3LYP/6-31G* level have been calculated for designed azole isomers. The calculated total energies at 298K upon inclusion of zero-point energy and thermal corrections and experimental gas phase HOFs [34, 51–54] of the reference compounds imidazole, pyrazole, triazoles, CH_4, NH_3, CH_3NO_2, CH_3NH_2 are listed in Table 2. Previous studies [55] show that the theoretically predicted values are in good agreement with experiments by choosing the appropriate reference compounds in the isodesmic reaction. The numbers of electron pairs and chemical bond types are conserved in the isodesmic reaction [56–58]. Fig. 2 represents the constructed isodesmic reaction scheme for the designed molecules. The calculated gas phase HOFs at 298.15K using isodesmic approach have been shown in Table 3.

The calculated HOFs of the designed molecules have been compared with MTNI to evaluate the performance. The predicted gas phase HOF of MTNI using isodesmic reaction approach is 170.41 kJ mol^{-1} which is comparable with earlier reported values by Su et al. (173.4 and 176.15 kJ mol^{-1}) [3, 8]. The high positive HOFs for the reference azole skeletons confirm that these will contribute for the positive HOFs of the designed isomers. The HOFs for predicted compounds show high positive values in the range of 420 to 660 kJ mol^{-1}. The high HOFs can be attributed to the presence of a large number of N-N and C-N bonds and energetic nitro groups. The molecules H1 and H2 differ only by the position of 1,2,4-triazole ring on the imidazole. H1 shows higher HOF than H2, this may be due to the repulsion associated with the adjacent nitro groups in the imidazole ring. Similar is observed in the case of H3 and H4 too. In general, it is observed that energy contribution by pyrazole and 1,2,3-triazole rings are higher than the imidazole and 1,2,4-triazole rings, respectively. Among the designed molecules, the molecules H5 and H6 show higher HOFs viz., 586.5 and 663.8 kJ mol^{-1}, respectively. This may be attributed to the presence of adjacent bulky nitro groups and energetic pyrazole/ triazole rings. Comparison of H7 and H8 reveals that, H8 has higher HOFs due to the higher repulsive energy between three adjacent nitro groups on the pyrazole ring. The adjacent nitro groups can affect the free orientation and arrangement on the ring and causes the repulsion. Overall study shows that all designed compounds possess higher positive HOFs than the MTNI due to the presence of four nitro groups and nitrogen-rich heterocyclic framework.

Density

Density has been referred to as the primary physical parameter in detonation performance because detonation velocity and pressure of the explosives increase proportionally with the packing density and square of it, respectively. Fig. 3 shows the relation between density

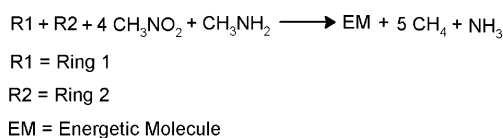**Table 2** Total energy (E_0) at 298K and gas phase HOF for the reference compounds at the B3LYP/6-31G* level

Compd.	E_0 (au)	HOF (kJ/mol)
CH_4	-40.46935	-74.6
NH_3	-56.50961	-45.9
CH_3-NH_2	-95.78444	-22.5
CH_3-NO_2	-244.95385	-74.7
Imidazole	-226.13859	129.5
Pyrazole	-226.12249	179.4
1,2,4-triazole	-242.18479	192.7
1,2,3-triazole	-242.15867	271.7

$$R1 + R2 + 4\ CH_3NO_2 + CH_3NH_2 \longrightarrow EM + 5\ CH_4 + NH_3$$

R1 = Ring 1
R2 = Ring 2
EM = Energetic Molecule

Fig. 2 Isodesmic reactions scheme for designed molecules

Table 3 Predicted explosive characteristics for designed compounds

| Compd.	HOF (kJ/mol)	D (km/s)	P (GPa)	BDE (kJ/mol)	-Q$_{NO2}$ (e)
H1	445.01	8.92	36.13	262.16	0.137
H2	420.02	9.03	37.44	261.33	0.179
H3	535.15	9.41	41.50	251.92	0.158
H4	510.24	9.11	37.96	253.58	0.162
H5	586.47	9.26	39.54	267.27	0.167
H6	663.87	9.39	40.73	260.29	0.186
H7	444.92	8.95	36.52	249.55	0.165
H8	506.21	9.07	37.51	250.98	0.103
MTNI	170.41	8.82	34.75	250.34	0.170

and detonation velocity. The densities of designed compounds have been predicted using five different force fields such as Dreiding, Cvff, Pcff, Compass, and Universal presented in Table 4 to assess the reliability of the classical force fields for predicting the densities of energetic azoles. Density predicted from Cvff force field is used for the calculation of detonation characteristics as it provides marginally better results for nitro compounds [59]. Predicted density of MTNI molecule (1.82 g/cm^3) using Cvff force field is found close to experimental value (1.79 g/cm^3) [60]. The density for designed molecules has been found to be remarkably high and varies from 1.86 to 1.98 g/cm^3. The molecule H3 shows the highest density (1.98 g/cm^3) while, H1, H7, and H8 shows lowest density of about 1.88 g/cm^3. Analysis of molecular framework of H3 reveals that the two azole rings attached via C-N linkage are perpendicular to each other, minimizes the torsional strain and avoids the steric hindrance between nitro groups. This molecular arrangement minimizes the total molar volume and further, improves the density via intra and intermolecular hydrogen bonding. The repulsion associated with the adjacent nitro

groups affects the molecular orientation in space and hence, molecules H1, H7, and H8 exhibits lower densities. The predicted minimum energy crystal structures for the H1, H3, and H7 are shown in Fig. 4. H2 shows density higher than H1. This may be due to adjacent nitro groups on the imidazole of H1 which causes the repulsion while; H2 shows less repulsion due to the better arrangement of nitro groups on the rings. Similar trend is found in the case of H5 and H6 and their predicted densities are 1.92 and 1.93 g/cm^3, respectively. Replacement of 1,2,4-triazole in H1 with 1,2,3-triazole in H3 increases the density. In general, pyrazole derivatives show higher densities than imidazole and this is clearly seen in pyrazole ring based molecules viz, H5, H6 and H8 in comparison to imidazole based molecules H4, H2, and H7.

Detonation performance

The detonation velocity (D) and detonation pressure (P) of the molecules have been computed by Kamlet-Jacobs empirical equations and summarized in Table 3. The

Fig. 3 Plot of density (g/cm3) versus velocity of detonation (km/s)
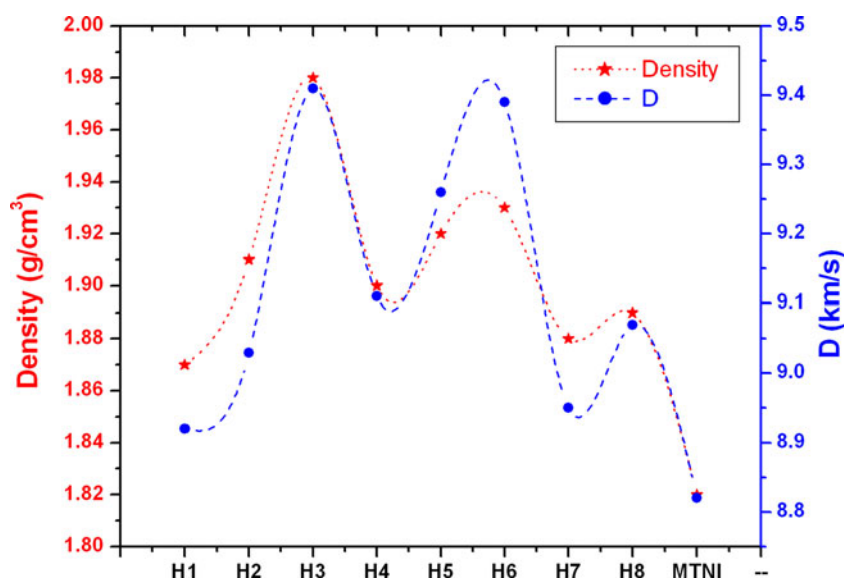
Table 4 Densities (g/cm³) of the most stable polymorphs obtained from different force fields

| Compd.	Force field				
	Dreiding	Cvff	Pcff	Compass	Universal
H1	1.97	1.87	1.87	2.12	1.82
H2	2.03	1.91	1.93	2.17	1.88
H3	2.06	1.98	1.88	2.22	1.92
H4	2.01	1.90	1.92	2.22	1.85
H5	2.01	1.92	1.92	2.25	1.90
H6	2.01	1.93	1.99	2.16	1.87
H7	1.96	1.88	1.92	2.14	1.77
H8	2.05	1.89	1.87	2.15	1.94
MTNI	1.85	1.82	1.79	2.10	1.80

calculated D and P values differ for energetic isomers as they posses different density and HOF. Detonation performance is mainly dependent on crystal density (Fig. 3) and less on HOF of the compound. Molecules H3, H5, and H6 show higher performance in comparison to others due to their higher densities and HOFs. The calculated D and P for these compounds are higher than 9.25 km/s and 39.5 GPa, respectively. The substitution of 1,2,4-triazole with the 1,2,3-triazole enhances the performance in H3 and H4 as compared to H1 and H2, respectively. Introduction of pyrazole in H5 improves the performance of the compound than its imidazole isomer H4 due to its higher density and HOFs. This shows that nitro groups and the five membered heterocycles that contain large amount of nitrogen could be responsible for the high performance of these compounds. All designed molecules show higher detonation performance than MTNI which may be due to the better oxygen balance, higher densities and HOFs.

Thermal stability

Stability of the energetic compounds is the prime importance for the practical interest of the explosive material. The present study explores the stability of the designed compounds by analyzing bond dissociation energy (BDE) and nucleus independent chemical shift (NICS).
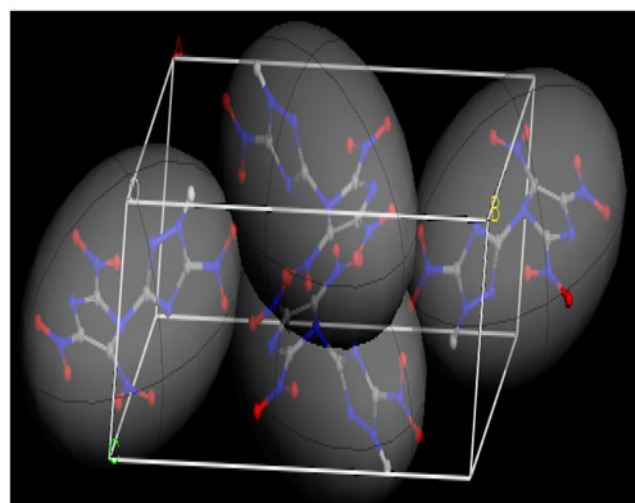
Bond dissociation energy

The BDE could evaluate the strength of bonding that is fundamental to understand chemical process and provide useful information for understanding the stability of designed compounds. Recent reports revealed the relationship between BDE and stability; a higher value of the BDE brings stability in the respective compounds [33, 61]. The
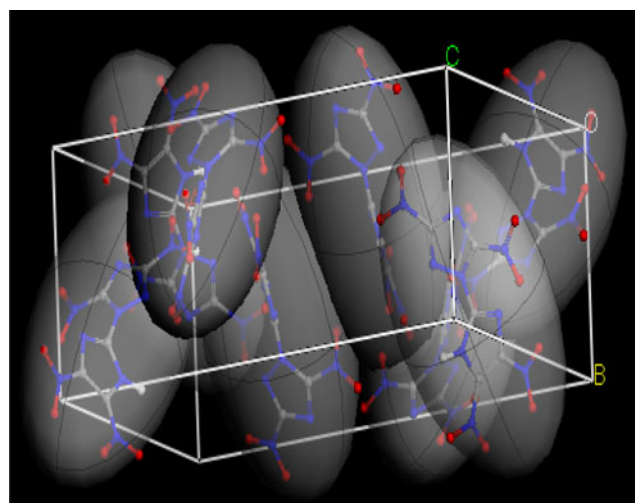
(a)
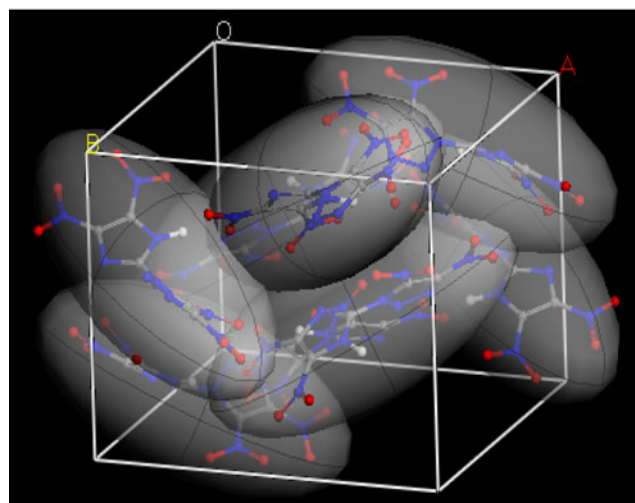
(b)

(c)

Fig. 4 Predicted crystal structures for the (**a**) H1, (**b**) H3, and (**c**) H7

calculated bond dissociation energies (kJ mol^{-1}) of designed molecules are listed in Table 3. According to the criteria of HEDMs, BDE should be higher than 80-120 kJ mol^{-1} [62, 63]. Predicted BDE of MTNI molecule (250.34 kJ mol^{-1}) is found very close to earlier reported values [8]. BDE is dependent on the electronic structure of the molecules and among the energetic azole isomers studied H1, H2, H5, and H6 show BDE higher than 260 kJ mol^{-1}. In these compounds, nitro groups are far from each other due to the perpendicular arrangement of the azole rings which cause less repulsion between nitro groups. The nitro groups are attached to hetero aromatic ring and hence bond strength of C-NO$_2$ increases via π-electron delocalization. In case of H3 and H4 where the attachement of 1,2,3-triazole on imidazole ring differs, exhibits BDE of about 252 kJ mol^{-1}. The repulsion between adjacent nitro groups is very high in these molecules. Similarly, H7 and H8 possess three nitro groups on imidazole and pyrazole rings, respectively and hence these compounds show lower BDE in the series. Overall study showed that designed molecules are having high BDE of about 250 kJ mol^{-1} and hence these molecules are expected to be stable. All designed molecules possess BDE higher than MTNI may be due to the extended conjugation in molecular skeleton.

Nucleus independent chemical shift (NICS)

Negative values of NICS indicate shielding presence of induced diatropic ring currents understood as aromaticity at specific point [64]. Table 1 represents the predicted NICS values for azole isomers at the ring center. The more negative NICS represents the more aromaticity through π-electron delocalization, results in enhanced stability, bond length and equalization. The NICS at the ring center for the imidazole, pyrazole, 1,2,4-triazole, and 1,2,3-triazole are -14.4, -15.02, -13.8, and -14.6 ppm, respectively. The presence of electron withdrawing nitro groups on the azoles enhances the diatropic ring current of the corresponding ring and NICS value become more negative. The imidazole, pyrazole rings of MTNI, H7 and H8 shows more negative NICS -16.55, -15.9 and -16.7 ppm, respectively. The presence of three nitro groups in heterocyclic ring of MTNI, H7 and H8 increases the electron density at the ring centers. In general, diatropic ring current increases due to the substitutions and the electrons are expected mainly to be located on the nitrogen atoms because of its comparably higher electronegativity than carbon atom. In H5 and H6, two nitro groups on the pyrazole ring in the molecular framework shows NICS values higher than -15 ppm. In all designed molecules NICS of the triazole rings found to be lower than the imidazole and pyrazole rings of the corresponding molecules. The replacement of

the 1,2,4-triazole with 1,2,3-triazole increases the ring current on its attached ring like imidazole or pyrazole and this can be clearly seen by comparing H1-H3, H2-H4, and H5-H6.

Impact sensitivity correlations

According to the criteria of high energy materials, compounds should be stable and insensitive enough for the practical use and safe handling. The relationship between the impact sensitivity and electronic structures of some nitro compounds can be established by the charge analysis of nitro group [26]. The higher negative charge the nitro group possesses, the lower the electron attraction ability and therefore the more stable the nitro compound. Computed $-Q_{NO_2}$ values of molecules are presented in Table 4. The higher $-Q_{NO_2}$, the larger is the impact insensitivity and hence $-Q_{NO_2}$ can be regarded as the criteria for estimating the impact sensitivities. Among the designed compounds H2 and H6 show $-Q_{NO_2}$ values higher than MTNI (0.170e). The nitro groups in these compounds are away from each other and minimize the repulsion and steric hindrance. H8 shows lower value of the $-Q_{NO_2}$ due to the presence of three adjacent nitro groups on the pyrazole ring. $-Q_{NO_2}$ of the H3 and H4 are 0.158 and 0.162e, respectively. The adjacent nitro groups in H3 increases the sensitivity of the molecule more than H4. The compounds H1, H5 and H7 show $-Q_{NO_2}$ values higher than 0.130e.

Conclusions

Electronic structures of the designed energetic azoles have been studied using the density functional theory at the B3LYP/6-31G* level. The HOF of azole isomers has been computed by designing appropriate isodesmic reactions and the detonation characteristics using Kamlet-Jacobs method. Results revealed that the azole isomers possess very high positive HOFs due to the presence of high nitrogen content five membered azoles. Crystal density has been predicted using molecular packing calculations using the Cvff force field and the predicted density is above 1.90 g/cm^3. Designed molecules have detonation velocity higher than 9.1 km/s and pressure above 37GPa. Analysis of BDE and NICS reveals that energetic azoles are expected to be stable. Charge on the nitro group has been analyzed to correlate the impact sensitivity and it has been found that designed molecules are having better impact insensitivity. Energetic properties of the designed molecules are compared with 1-methyl-2,4,5-trinitroimidazole and found that these molecules have higher energetic performance with better insensitivity. A structure-property

relationship on these energetic azole isomers demonstrates that these molecules will be promising candidates for future HEMs.

References

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