

Quantum chemical studies on the aminopolynitropyrazoles

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Received: 23 October 2010 / Accepted: 29 November 2010 / Published online: 31 December 2010
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Abstract We have explored the geometric and electronic structures, band gap, thermodynamic properties, density, detonation velocity and detonation pressure of aminopolynitropyrazoles using the density functional theory (DFT) at the B3LYP/aug-cc-pVDZ level. The calculated detonation velocity and detonation pressure, stability and sensitivity of model compounds appear to be promising compared to the known explosives 3,4-dinitro-1 H-pyrazole (3,4-DNP), 3,5-dinitro-1 H-pyrazole (3,5-DNP), hexahydro-1,3,5-trinitro-1,3,5-triazinane (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocane (HMX). The position of NH₂ group in the polynitropyrazoles presumably determines the structure, stability, sensitivity, density, detonation velocity and detonation pressure.

Keywords Density functional theory · Detonation velocity and pressure · Electron density · Heat of formation · Intramolecular interaction

Introduction

Polynitropyrazoles due to their high positive heats of formation and good thermal stability have recently drawn considerable attention by several explosives chemists [1–3]. Huttel and Buchele have synthesized N-nitropyrazole and its

substituted derivatives using acetyl nitrate [4]. Most of the dinitropyrazoles were synthesized by the thermal rearrangement of N-nitropyrazole derivatives in high boiling solvents benzonitrile and anisole [5–11]. However, in cold conc. sulfuric acid, the N-nitropyrazole was rearranged to 4-nitro-1 H-pyrazole [4]. Janssen et al. [6] synthesized 1,3-dinitro-1 H-pyrazole (1,3-DNP), 1,4-dinitro-1 H-pyrazole (1,4-DNP), 3,4-dinitro-1 H-pyrazole (3,4-DNP) and 3,5-dinitro-1 H-pyrazole (3,5-DNP) in higher yields. 4-Amino-3,5-dinitro-1 H-pyrazole (LLM-116 or ADNP) is known with the decomposition point 178 °C and exhibits the highest density 1.90 g/cm³ in the five-membered heterocyclic compounds [12]. 3,4,5-Trinitro-1 H-pyrazole, 1,3,4-trinitro-1 H-pyrazole and 5-amino-3,4-dinitro-1 H-pyrazole were synthesized in quantitative yields [13, 14]. 3,4,5-Trinitro-1 H-pyrazole (**R20** or TNP) was obtained in higher yield from 3,5-dinitro-1 H-pyrazole using 20 to 30% oleum mixed with nitric acid at 100 °C. TNP melts at 188 °C and decompose from 260 to 350 °C and its heat of decomposition is 255 Jg⁻¹, which is extremely low for an explosive. Li et al. [15] studied NO₂, NH₂, NF₂ and N₃ substituted pyrazoles and suggested for their synthesis as potential candidates for low vulnerable applications. The effect of CH₃, NH₂ and NO₂ groups on the structure and detonation properties of 3,4,5-trinitro-1 H-pyrazole have already been reported [16]. Substituting one of the hydrogen atoms of polynitropyrazoles by amino group increases the stability, heat of formation, density and performance. To our knowledge, there were no studies on the structure and explosive properties of these aminopolynitropyrazoles. Wherefore, it would be desirable before attempting synthesis of these compounds to be able to predict the heat of formation, density, detonation performance, stability and sensitivity.

The shock and thermal sensitivities of energetic compounds can be related to the electronic structure and the properties of trigger R-NO₂ (where, R=C, N and O) bonds such as electrostatic potentials, lengths, strength and so forth

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[17, 18]. The stronger these trigger bonds are, the more stable the energetic compound [19]. Kamlet and Adolph [20] gave the relation between the oxygen balance and impact sensitivity of energetic compounds. Mullay [21] correlated the impact sensitivity and molecular electronegativity of known polynitroarenes and polynitroaliphatic compounds. Politzer and coworkers [22, 23] related the bond dissociation energies (BDEs) of trigger bonds and molecular electrostatic potential maxima and the impact sensitivities. The level of impact sensitivity was related to the degree of positive charge buildup over the covalent bonds within the molecular frame work of the known explosives [24–27]. Highly sensitive explosives show large positive charge buildup localized over covalent bonds. Pospíšil [28] showed a relation between the crystal volume and the impact sensitivity. Zhang et al. [29, 30] correlated the molecular electronic structure to the impact sensitivities of known explosives by the nitro (NO₂) group charge analysis. Zeman [31] have related the impact and electric spark sensitivities, detonation and thermal decomposition and ¹³C and ¹⁵N NMR chemical shifts of polynitro compounds. The electric spark sensitivity was related to the squares of detonation velocities and reciprocal temperatures, the Piloyan activation energy and heats of fusion of the explosives [32]. Zhi and Cheng [33] gave the relationship between the electric spark sensitivity, the lowest unoccupied molecular orbital energy, Mulliken charge of the nitro group, number of aromatic rings and the number of substituents attached to the aromatic ring. The Mulliken charge of nitro group have also been used to evaluate the stability and are regarded as one of the structural parameters to asses impact sensitivity of energetic compounds [34, 35].

The present study aims to design the aminodinitropyrazoles, the possible isomers of LLM-116 or ADNP) and aminotrinitropyrazoles by structure-property relationship for the explosives applications. The density functional theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level have been carried to explore the geometry, band gap, heat of formation, crystal density, detonation velocity and pressure, impact sensitivity and spark sensitivity of model molecules. The stabilities of the compounds have been determined from total and frontier molecular orbital energies, trigger bond lengths and nitro group charge analysis. The impact sensitivities of the molecules have

been determined by nitro group charge analysis of the weakest bond. The spark sensitivities of the compounds were calculated from the nitro group charge of the weakest bond and the lowest unoccupied molecular orbital energies.

Methods and computational details

The density functional theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level have been performed to optimize the geometry of the model compounds using Gaussian 03 package [36]. The method and the basis set has already yielded satisfactory results with B3LYP/aug-cc-pVDZ level [15, 16]. All the geometries of the compounds have been optimized without applying symmetry or structural constraints. Vibrational frequencies have also been calculated for the optimized structures to characterize the nature of the stationary points, zero-point energy and thermal correction. The stationary points for each molecule have positively been identified as true local minima on the potential energy surfaces with no imaginary frequencies. All the correction terms were estimated by using the following set of equations [37]:

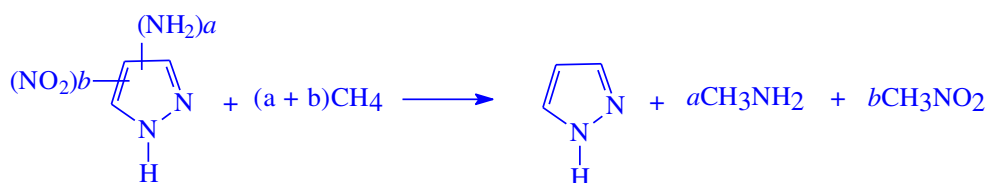
$$[H(T) - H(0)]_{\text{trans}} = \frac{5}{2} RT \quad (1)$$

$$[H(T) - H(0)]_{\text{rot}} = \frac{3}{2} RT \quad (2)$$

$$[H(T) - H(0)]_{\text{vib}} = RT \sum_{i=1}^f \left(\frac{h\nu_i}{kT} \right) \frac{\exp \frac{-h\nu_i}{kT}}{(1 - \exp \frac{-h\nu_i}{kT})}, \quad (3)$$

where k is the Boltzmann's constant, h is the Planck's constant, f is the number of vibrational degrees of freedom ($3N-5$ for linear and $3N-6$ for nonlinear molecules with N being number of atoms in the molecule), ν_i is i th vibrational frequency, R is the gas constant, H is the enthalpy and T is the temperature.

The isodesmic reactions have been employed to calculate the heat of formation ($\Delta_f H$) of the model compounds. This approach has been proved to be simple and reliable [38, 39]. The heats of formation of the compounds at 298.15 K were calculated using the following isodesmic reaction.



The number of all kinds of bonds keeps invariable to decrease the calculation errors of the heat of formation. The basic structural unit pyrazole ring keeps invariable and the molecules are changed into methane, nitromethane and aminomethane. The $\Delta_f H$ of the designed molecules can be obtained when the heats of reaction ($\Delta_r H$ or Q) are known.

$$\Delta_r H = \Delta E_0 + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta_T H + \Delta nRT, \quad (4)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero point energies (ZPE) of the products and reactants; $\Delta_T H$ is the difference between the thermal correction from 0 to 298.15 K of the products and reactants. The $\Delta(PV)$ value in Eq. 4 is the PV work term. It equals to ΔnRT for the reaction of ideal gases. For isodesmic reactions, $\Delta n=0$.

The optimized structures were taken as input geometry to determine the crystal densities (ρ) with the consistent-valence force field (cvff) and Ewald summation method using Accelrys's Materials Studio 4.1 package [41]. The calculation involves defining a molecule in an asymmetric cell unit, packing into crystal under a given space group symmetry, structure optimization to achieve an energy-minimized structure and removal of duplicate crystal structures by clustering process as implemented in the Polymorph module [42]. Kamlet and Jacob semi-empirical equations were used to determine detonation pressure and detonation velocity [43].

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2 \quad (5)$$

$$D = 1.01 \left(NM^{1/2}Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (6)$$

where P is the detonation pressure in GPa, D is the detonation velocity in km/s, N is the number moles of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, Q is the energy of explosion in kcal/g of explosive and ρ is the crystal density in g/cm^3 . Depending upon the composition of the explosive, the possible detonation products of the compounds were written based on the modified Kistiakowsky-Wilson rules [44]. The oxygen balance (Ω) is related to Q , D and P , detonation products and sensitivity or stability of the compounds [20, 43, 44]. It also represents the lack or excess of O_2 needed to produce the most stable products N_2 , H_2O , CO and CO_2 in the explosive compounds. D is a linear function of Ω and it is improved by taking into the consideration of the number of NO_2 groups. The Q value reaches maximum for the model compounds containing four NO_2 groups corresponds to the oxidation of carbon to CO_2 and nitrogen to N_2 .

The relationship between the impact sensitivity and electronic structure of designed compounds has been determined by the charge analysis of nitro (NO_2) group. Charge on the nitro group ($-Q_{NO_2}$) has been calculated by the sum of the net Mulliken atomic charges on the nitrogen (Q_N) and oxygen atoms (Q_{O1} and Q_{O2}) in the nitro group [29, 30, 34, 35]. Mulliken charges have been chosen to evaluate the stability and sensitivity of the molecules because the Mulliken charges are qualitatively correct and reproducible. We also have predicted the electric spark sensitivity from the nitro group charge ($-Q_{NO_2}$) and the lowest unoccupied molecular orbital (LUMO) of the molecule [33]. The stability was determined from the total energy as well as from the frontier molecular orbital energy gaps of the molecule.

Results and discussion

This section presents and discusses the results including the heat of formation, chemical energy of detonation, density, detonation velocity, detonation pressure, stability, impact sensitivity and electric spark sensitivity for the model compounds computed from the B3LYP/aug-cc-pVDZ level.

Heat of formation

We have performed at the outset, structure optimization of the molecules at the B3LYP/aug-cc-pVDZ level and their optimized structures are shown in Fig. 1. All the model compounds belong to C_1 point group. The geometry, trigger bond lengths and total energies have been found to be varied with the position of NH_2 group. The isodesmic reactions have been used for the calculation of the heat of formation ($\Delta_f H$) of the model compounds. It has been shown in several studies that the calculated $\Delta_f H$ values were in good agreement with the experimental values by choosing appropriate reference compounds in the isodesmic reaction [38]. In isodesmic reaction the number of electron pairs and the bonds are conserved in order to compensate the systematic errors by following bond separation reaction rules. The molecular total energies, the zero point energies, the values of thermal correction to enthalpy and the heats of formation of the title compounds with the reference compounds pyrazole, methane, nitromethane and aminomethane computed from the B3LYP/aug-cc-pVDZ level are summarized in Table 1. The experimental $\Delta_f H$ of the reference compounds were taken from Ref. [40]. To the best of our knowledge, no experimental $\Delta_f H$ values of the designed compounds are available. It is seen from Table 1 that the $\Delta_f H$ values are related to the positions of NH_2 and NO_2 groups in the given series. The calculated $\Delta_f H$ values

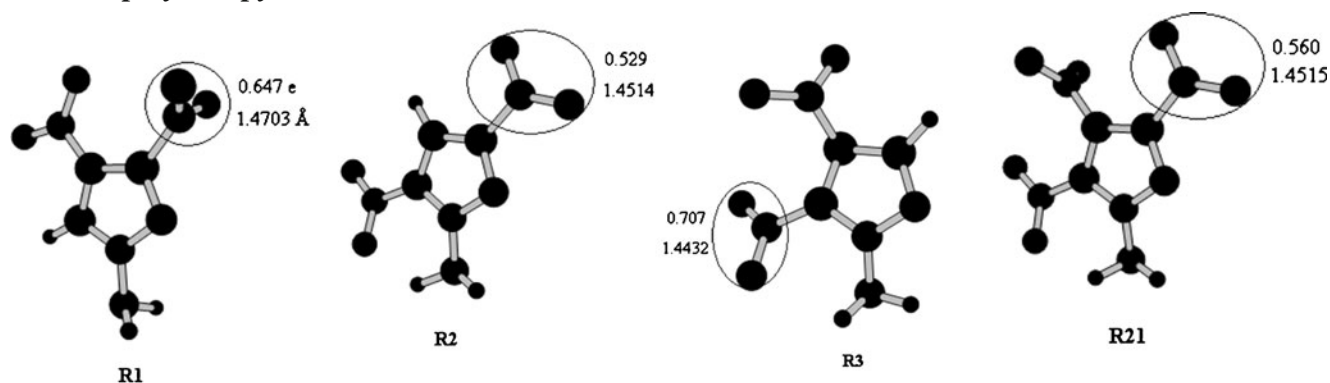
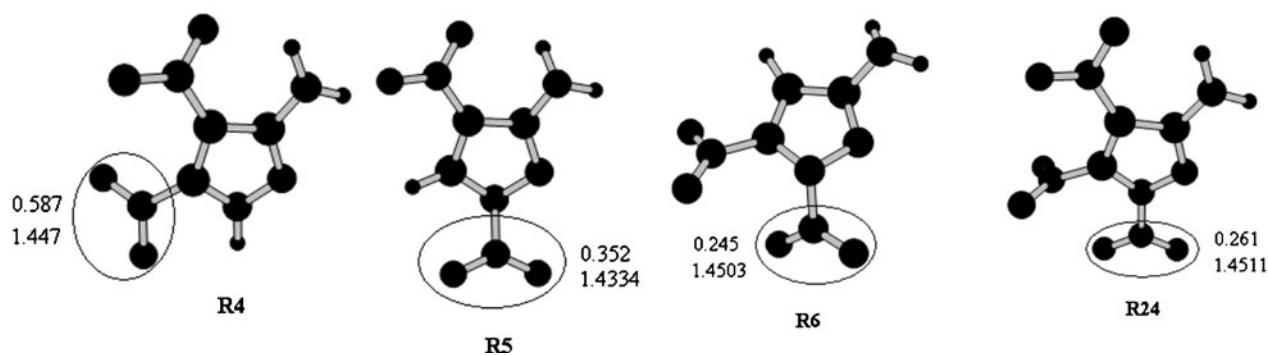
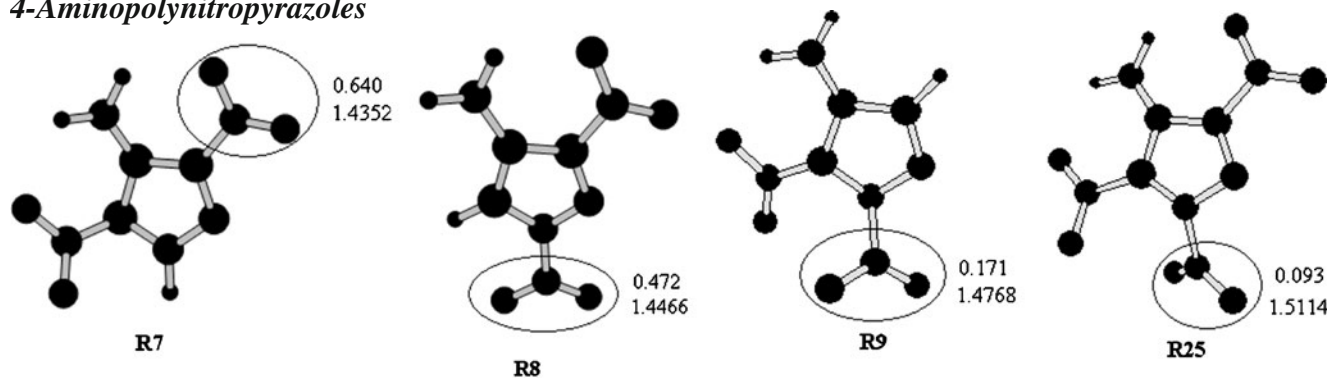
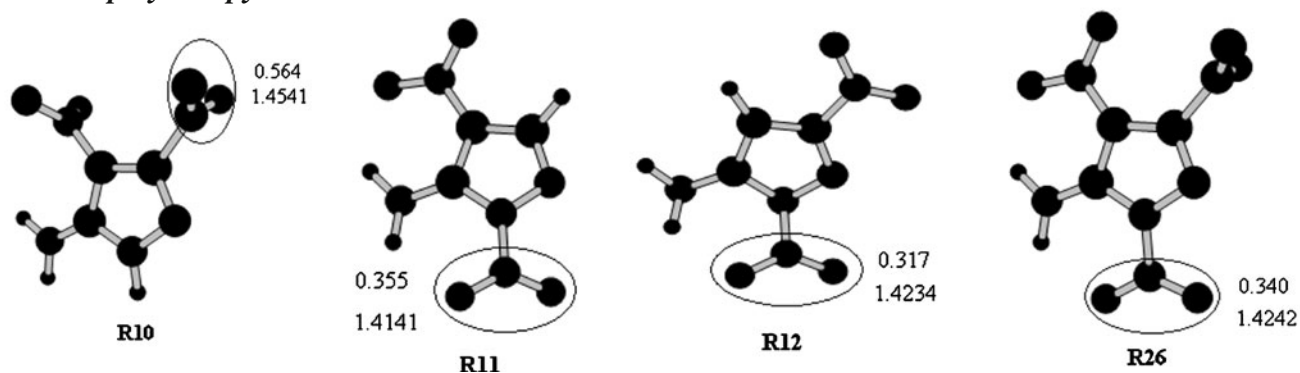
1-Aminopolynitropyrazoles*3-Aminopolynitropyrazoles**4-Aminopolynitropyrazoles**5-Aminopolynitropyrazoles*

Fig. 1 Optimized structures of aminopolynitropyrazoles with the trigger linkage encircled computed at the B3LYP/aug-cc-pVDZ level. The nitro group charge ($-Q_{\text{NO}_2}$) in e and the trigger length in Å

Table 1 Calculated electronic energies (E_0), zero-point energies (ZPE), thermal correction to enthalpy (H_T) and gas phase heats of formation (HOF) at the B3LYP/aug-cc-pVDZ level and experimental gas phase heats of formation of aminopolynitropyrazoles and their reference compounds

HEM	E_0 a.u.	ZPE a.u.	H_T a.u.	$\Delta_f H$ kJ mol ⁻¹
R1	-690.6183985	0.092317	0.103572	136.93
R2	-690.6218158	0.092331	0.103218	136.83
R3	-690.6217358	0.092332	0.103368	122.60
R4	-690.6617320	0.092601	0.103633	187.66
R5	-690.6431944	0.091327	0.102608	204.96
R6	-690.6186803	0.090978	0.102178	141.33
R7 (LLM-116)	-690.6747163	0.093195	0.103955	154.42
R8	-690.6297066	0.091433	0.102416	169.65
R9	-690.6225297	0.091234	0.102252	151.24
R10	-690.6286803	0.091222	0.102383	183.14
R11	-690.6463260	0.092189	0.102867	212.10
R12	-690.6306958	0.091123	0.102293	172.57
R21	-895.1282330	0.094385	0.108100	243.75
R24	-895.1445915	0.093181	0.107231	289.20
R25	-895.1507101	0.093757	0.107266	305.08
R26	-895.1587202	0.094100	0.107659	325.10
Pyrazole	-226.233670	0.070971	0.075657	179.4 ^a
CH ₄	-40.520622	0.044261	0.048080	-74.6 ^a
CH ₃ NO ₂	-245.054716	0.049551	0.054835	-80.8 ^a
CH ₃ NH ₂	-95.873895	0.063532	0.067919	-22.5 ^a

^a Experimental values from Ref.
40

of model compounds are superior (≈ 140 to 325 kJ mol⁻¹) and appear to be promising compared to the experimental $\Delta_f H$ values of 3,4-DNP (120.1 kJ mol⁻¹), 3,5-DNP (93.73 kJ mol⁻¹), RDX (70.63 kJ mol⁻¹) and HMX (74.88 kJ mol⁻¹). The highest and lowest $\Delta_f H$ of the aminodinitropyrazoles **R3** and **R11** are 122.6 and 212 kJ mol⁻¹ respectively. The **R1** and **R2**, **R7** and **R9**, **R5** and **R11** compounds show nearly equal $\Delta_f H$ values (136 , 150 , 205 kJ mol⁻¹ respectively). The substituting hydrogen at the N1 position increased the heat of formation compared to 3,4-DNP and 3,5-DNP however, the calculated values are markedly lower compared to 3-, 4-, and 5-aminodinitropyrazoles (**R4** to **R12**). The $\Delta_f H$ values of 5-aminodinitropyrazoles (**R10**, **R11** and **R12**) are close to 3-aminodinitropyrazoles (**R4**, **R5** and **R6**). Furthermore, the model molecules **R24**, **R25** and **R26** have shown higher $\Delta_f H$ values 289.2 , 305.1 and 325.1 kJ mol⁻¹ respectively) compared to the most stable compound **R20** (244.6 kJ mol⁻¹). The values of $\Delta_f H$ obtained are for the gas phase compounds and in reality they should be for the solid phase, which would diminish the magnitude of $\Delta_f H$ values. The discrepancies in the $\Delta_f H$ or Q values among the isomers are caused by the relative positions of NH₂ and NO₂ groups in the molecule. Overall, the heats of formation of the compounds appear to be quite large positive values, which is one of the characteristics of energetic materials, i.e., they can be regarded as endothermic materials.

Crystal density

Crystal density (ρ) is the essential parameter in determining the performance properties of energetic compounds. The accurate prediction of crystal density is difficult. Group or volume additivity method although is simple and rapid, it cannot give reliable results [45, 46]. The crystal packing method is more reliable however it requires extensive computational resources. In this study, the B3LYP/aug-cc-pVDZ level optimized structures of the designed molecules have been taken to determine the crystal densities using Materials Studio 4.1 package with the consistent-valence force field (cvff) and Ewald summation method. This approach used in polymorph is based on the generation of possible packing arrangements in all reasonable space groups and searches for the low lying minima in the lattice energy surface. The number of space groups of the compounds is limited although there are 230 crystal space groups in nature. Most of the organic crystals crystallizes in only a few of the common space groups such as C2/c, P2₁, P2₁/c, P2₁2₁2₁, P-1, Pbc_a, Pbc_n, Pna2₁, CC and C2 space groups. The high density polymorph was sorted out from the large number of potential crystal structures and the lattice parameters. The calculated and the experimental densities of pyrazole are 1.24 and 1.25 g/cm³ respectively [47]. It is known that the density of the pyrazole increases with an increase in the number of NO₂ groups. The higher densities of the compounds can be achieved if the molecule

has NH₂ group that brings intra- or inter-molecular hydrogen bonding with NO₂ groups or pyridine like nitrogen atom of the same or adjacent molecule. The calculated lowest energy crystal characteristics of the possible aminopolynitropyrazoles are presented in Table 2. From the results it is clear that all the molecules fall under the following five space groups, viz., P2₁, P2₁/c, P2₁2₁2₁, Pbc_a and Pna2₁. The experimental densities of 3,4-DNP, 3,5-DNP and **R20** are 1.81, 1.80 and 1.867 g cm⁻³ respectively. The compound **R11** has the lowest density of 1.75 g cm⁻³. The experimental and theoretically predicted density values of **R7** are 1.90 and 1.84 g cm⁻³ respectively and thus the error is 3.16%. The amino group has increased the densities from 1.86 to 1.93 g cm⁻³ for trinitropyrazoles. The compounds **R20**, **R24**, **R25** and **R26** have higher densities 1.93, 1.92, 1.90 and 1.90 g/cm³ respectively compared to the densities of HMX (1.92 g/cm³) and TATB

(1.93 g/cm³). The errors in the calculated densities of the compounds are expected to be less than five percent [16, 48–50] and the increase of densities is as per the group additivity method.

Detonation performance

Detonation velocity (D) and detonation pressure (P) are important parameters for evaluating the performance and applicability of the energetic materials. Kamlet-Jacob semi-empirical equations were used to calculate the detonation velocity and detonation pressure. With the increasing number of NO₂ groups of pyrazole, density, detonation velocity and detonation pressure increases so do oxygen balance and heat of formation. If the number of NO₂ groups of the molecule is equal to three, D and P reach the largest value for the polynitropyrazoles. However, the pyrazole

Table 2 Crystal characteristics of aminopolynitropyrazoles computed from the B3LYP/aug-cc-pVDZ level

HEM	Cell volume Å ³	Total energy kJ mol ⁻¹	Space group	Crystal system	a, b, c (Å) α, β, γ	Density g cm ⁻³
R1	635.9353	-57.8541	P2 ₁ 2 ₁ 2 ₁	rhombic	10.99, 11.60, 4.96 α=β=γ=90°	1.81
R2	646.7447	-9.3724	P2 ₁ /C	monoclinic	7.84, 8.42, 9.87 α=β=90°, γ=97°.29°	1.80
R3	1262.5260	-47.3859	Pbc _a	rhombic	17.28, 9.16, 7.97 α=β=γ=90°	1.82
R4	317.5006	-40.9177	P2 ₁	monoclinic	7.37, 7.85, 6.91 α=β=90°, γ=52°.74°	1.81
R5	669.9322	-37.1408	P2 ₁ /C	monoclinic	13.58, 6.42, 9.76 α=β=90°, γ=128°.15°	1.77
R6	646.0911	-35.9428	P2 ₁ 2 ₁ 2 ₁	rhombic	11.69, 10.86, 5.12 α=β=γ=90°	1.80
R7 (LLM-116)	644.4541	-16.9371	P2 ₁ 2 ₁ 2 ₁	rhombic	9.20, 9.63, 6.53 α=γ=β=90°	1.84 (1.90) ^b
R8	647.1526	-2.29083	P2 ₁ 2 ₁ 2 ₁	rhombic	7.01, 9.42, 9.82 α=β=γ=90°	1.77
R9	648.0433	-14.11675	P2 ₁ /C	monoclinic	6.85, 8.43, 7.51 α=β=90°, γ=131°.59°	1.77
R10	646.0844	-35.8432	P2 ₁ 2 ₁ 2 ₁	rhombic	11.96, 10.68, 6.22 α=β=γ=90°	1.80
R11	656.7571	-37.2213	P2 ₁ /C	monoclinic	15.19, 9.57, 11.81 α=β=90°, γ=157°.51°	1.75
R12	644.3211	-23.4754	P2 ₁ 2 ₁ 2 ₁	rhombic	9.44, 9.75, 6.99 α=β=γ=90°	1.80
R21	748.9260	-89.9462	Pna2 ₁	rhombic	8.93, 12.75, 6.57 α=β=γ=90°	1.93
R24	755.2976	-92.1173	Pna2 ₁	rhombic	9.19, 12.80, 6.49 α=β=γ=90°	1.92
R25	764.3019	-82.3239	P2 ₁ /C	monoclinic	8.49, 9.19, 9.84 α=β=90°, γ=95°.95°	1.90
R26	760.2333	-36.2589	P2 ₁ /C	monoclinic	12.13, 9.20, 9.75 α=γ=90°, β=135°.72°	1.90

^b Experimental value taken from Ref. 12

with four NO₂ groups, Q, D and P were found to be decreased probably due to the unduly positive oxygen balance that deviate largely from the perfect oxygen balance [16]. Therefore, it is clear that the Q, D and P increases to the largest value as the number of NO₂ groups is equal to three in pyrazole. The experimental detonation velocity and detonation pressure of 3,4-DNP and 3,5-DNP are 8.24 km/s, 28.80 GPa and 8.15 km/s, 28.52 GPa respectively. The calculated performance properties of 4-amino-3,5-dinitro-1 H-pyrazole (**R7**) are 8.0 km/s, 28.60 Gpa respectively. As for the isomeric compounds, the calculated densities are close to each other with the largest deviation of 0.05 to 0.15 g/cm³ so, D and P are also close since they are mainly determined by ρ and ρ_2 respectively [43]. The calculated detonation characteristics of the title compounds are presented in Table 3. The detonation characteristics of aminotrinitropyrazoles were found to be superior compared to the explosives **R20** (D 9.25 km/s, P 38.60) RDX (D 8.75 km/s, 34.7 Gpa) and HMX (D 8.96 km/s, P 35.96 Gpa). The model molecules **R21**, **R24**, **R25** and **R26** ($\rho \approx 1.9$ g/cm³, D ≈ 9.0 km/s and P ≈ 40.0 GPa) appear to be potential candidates for high explosives. Overall, the explosive properties of aminodinitropyrazoles are expected to show 80 to 85% performance of HMX while the aminotrinitropyrazoles exceed the performance of HMX.

Impact sensitivity correlations

The impact sensitivity is measured by the height, from where a given weight falling upon compound gives a 50% probability of initiating an explosion. The impact sensitivity ($h_{50\%}$) of the model compounds has been predicted from the electronic structures by the Mulliken atomic charge analysis of nitro (NO₂) group. As for NO₂ group in nitro compounds, they are very strong electrophiles, i.e., they have a strong ability to withdraw electrons. This ability can also be represented by the net atomic charges of the nitro group. The higher negative charge the nitro group possesses, the lower the electron withdrawing ability and therefore the more stable the nitro compound. In nitro-containing compounds, C-NO₂, N-NO₂ and O-NO₂ bonds denoted by X-NO₂ bond are usually the weakest in the molecule and their breaking is often the initial step in the decomposition or detonation. Normally, the charge on nitro group ($-Q_{NO_2}$) is calculated by the sum of the net Mulliken atomic charges on the nitrogen (Q_N) and oxygen atoms (Q_{O1} and Q_{O2}) in the nitro group. V_{mid} is an approximation of the electrostatic potential at the midpoint C-N or N-N bond (Q_C , Q_N charges of carbon and nitrogen respectively and R being the bond length). The computed $-Q_{NO_2}$, midpoint electrostatic potential, trigger bond lengths of the molecules are presented in Table 4. The

Table 3 The density (ρ), chemical energy of detonation (Q), detonation velocity (D) and detonation pressure (P) of the model compounds, RDX and HMX

HEM	ρ g cm ⁻³	Q kcal g ⁻¹	D km s ⁻¹	P GPa
R1	1.81	0.78	7.82	27.23
R2	1.80	0.80	7.82	27.17
R3	1.82	0.85	8.02	28.74
R4	1.81	0.85	8.00	28.42
R5	1.77	0.88	7.92	27.56
R6	1.80	0.80	7.81	27.04
R7 (LLM-116)	1.84 (1.90) ^b	0.81	8.00	28.57
R8	1.77	0.83	7.81	26.78
R9	1.77	0.80	7.75	26.37
R10	1.80	0.80	7.80	27.02
R11	1.75	0.88	7.90	27.10
R12	1.80	0.83	7.91	27.76
R21	1.93	1.47	9.31	40.13
R24	1.92	1.43	9.20	38.80
R25	1.90	1.38	9.02	37.15
R26	1.90	1.38	9.02	34.15
3,4-DNP	1.77 (1.81)	1.07(1.25)	8.25 (8.24)	29.92 (28.80)
3,5-DNP	1.82 (1.80)	1.05 (1.21)	8.33 (8.15)	30.10 (28.52)
R20	2.00 (1.867)	1.51	9.40 (9.25)	41.60 (38.60)
RDX	1.78 (1.82)	1.25 (1.27)	8.86 (8.75)	34.23 (34.70)
HMX	1.90 (1.92)	1.25 (1.27)	9.10 (8.96)	39.40 (35.96)

^b The values in parenthesis are from the experiments

Table 4 Trigger lengths, nitro group charge ($-Q_{\text{NO}_2}$), midpoint electrostatic potential (V_{mid}), electric spark sensitivity (E_{ES}) frontier orbital energies and their gaps of the model compounds

HEM	Bond	Length Å	$-Q_{\text{NO}_2}$ e	V_{mid}	E_{ES} J	LUMO a.u	HOMO a.u	$\Delta E_{(\text{LUMO-HOMO})}$ a.u
R1	C3-NO ₂	1.47027	0.647	1.4762	9.705	-0.11659	-0.31099	0.19440
	C4-NO ₂	1.43470	0.563	2.1425	8.852			
R2	C3-NO ₂	1.45143	0.529	0.6931	9.165	-0.13931	-0.29331	0.15400
	C5-NO ₂	1.43194	0.523	0.7067	9.095			
R3	C4-NO ₂	1.44139	0.666	2.3421	10.957	-0.13887	-0.29324	0.15437
	C5-NO ₂	1.44325	0.707	1.0560	10.953			
R4	C4-NO ₂	1.42740	0.810	2.9746	12.050	-0.14071	-0.26737	0.12666
	C5-NO ₂	1.44705	0.587	1.3628	9.784			
R5	C4-NO ₂	1.42537	0.721	2.7052	10.990	-0.13546	-0.26810	0.13264
	N1-NO ₂	1.43388	0.352	1.5231	7.247			
R6	C5-NO ₂	1.36852	0.557	0.8213	9.142	-0.13258	-0.27021	0.13763
	N1-NO ₂	1.45026	0.245	1.5032	5.972			
R7 (LLM-116)	C3-NO ₂	1.43518	0.639	1.4256	10.031	-0.13049	-0.27220	0.14171
	C5-NO ₂	1.34134	0.683	1.7907	10.468			
R8	C3-NO ₂	1.44383	0.631	1.3201	10.125	-0.13699	-0.26108	0.12409
	N1-NO ₂	1.44662	0.472	1.4310	8.510			
R9	C5-NO ₂	1.41383	0.673	1.6750	10.726	-0.12472	-0.27149	0.14677
	N1-NO ₂	1.47679	0.171	1.2622	5.626			
R10	C3-NO ₂	1.45415	0.564	0.5020	9.157	-0.12650	-0.27768	0.15118
	C4-NO ₂	1.43021	0.642	1.8230	6.680			
R11	C4-NO ₂	1.41160	0.782	2.7713	11.330	-0.12547	-0.27587	0.15040
	N1-NO ₂	1.41413	0.355	1.6930	6.992			
R12	C3-NO ₂	1.46429	0.551	0.6040	9.157	-0.13158	-0.26576	0.13418
	N1-NO ₂	1.42326	0.317	1.8530	6.780			
R21	C3-NO ₂	1.45150	0.560	1.6025	9.906	-0.15460	-0.30701	0.15241
	C4-NO ₂	1.46652	0.702	1.9420	11.350			
	C5-NO ₂	1.43311	0.585	1.7947	10.161			
R24	C4-NO ₂	1.42686	0.702	3.0627	11.187	-0.14892	-0.28276	0.13384
	C5-NO ₂	1.47155	0.609	1.1240	10.252			
	N1-NO ₂	1.45115	0.261	1.7050	6.706			
R25	C3-NO ₂	1.44456	0.630	1.4398	10.604	-0.15412	-0.29010	0.13598
	C5-NO ₂	1.41505	0.673	1.6466	11.042			
	N1-NO ₂	1.51136	0.093	1.4574	5.150			
R26	C3-NO ₂	1.47278	0.645	1.3353	10.380	-0.14093	-0.29595	0.15502
	C4-NO ₂	1.41451	0.717	3.0767	11.111			
	N1-NO ₂	1.42422	0.340	1.7260	7.281			

higher $-Q_{\text{NO}_2}$, the larger the impact insensitivity and hence $-Q_{\text{NO}_2}$ can be regarded as the criteria for estimating the impact sensitivities.

$$-Q_{\text{NO}_2} = Q_{\text{N}} + Q_{\text{O1}} + Q_{\text{O2}} \quad (7)$$

$$V_{\text{mid}} = \frac{Q_{\text{C}}}{0.5R} + \frac{Q_{\text{N}}}{0.5R} \quad (8)$$

Calculated $-Q_{\text{NO}_2}$ for all the model compounds except **R6** (0.245 e) and **R9** (0.171 e) varying from 0.352 to 0.810 e. As per predicted by Zhang et al. [34, 35] these values are higher

with respect to TNT (0.249 e), FOX-7 (0.365 e), RDX (0.134 e), HMX (0.112 e), TNAZ (0.114 e), LLM-105 (0.292 e), NTO (0.264 e), DNPP (0.305 e), CL-20 (0.081 e), ONC (0.146 e) and are found to be more insensitive. The presence of NO₂ group at N1 position of 3,4-dinitro-1 H-pyrazole (3,4-DNP), 3,5-dinitropyrazole (3,5-DNP), 3,4,5-trinitropyrazole (**R20**) increases the impact sensitivity. Moreover, the impact sensitivity can also be used to show the stability of designed compounds and the stability here may be attributed to the presence of π -excessive aromatic heterocyclic ring, delocalization of π -electrons and presence of a new type of intramolecular N-H \cdots O and N \cdots O interactions.

Stability correlations

The stability of a molecule is usually measured by the total energy (for isomers), bond length, bond dissociation energy, frontier molecular orbital energies and their gaps, nitro group charge and so on. We have evaluated the stabilities of the title compounds from the total and frontier orbital energies and bond lengths of trigger linkages. Fukui et al. [51] have noticed the prominent role played by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in governing the chemical reactions of the compounds. It has been revealed in several investigations that the band gap $\Delta E_{(LUMO-HOMO)}$ between the LUMO and HOMO is an important stability index of the molecules [52, 53]. A large band gap implies high stability and small band gap implies low stability. In turn high stability indicates low chemical reactivity and low stability indicates high reactivity. In other words, the smaller the band gap between HOMO and LUMO, the easier the electron transition and lower the stability of the explosive will be. From Table 4, it is clear that the energies of LUMO varies from -0.11659 to -0.13931 a.u and HOMO from -0.3109 to -0.27587 a.u for aminodinitropyrazoles while the energies of LUMO varies from -0.14892 to -0.15460 a.u and HOMO from -0.30701 to -0.28276 a.u for aminotrinitropyrazoles. The frontier orbital energy gap varies from 0.1944 to 0.1241 a.u for aminodinitropyrazoles and 0.13384 to 0.15241 a.u for aminotrinitropyrazoles, which indicates all the model compounds are stable. As for the aminodinitropyrazoles, the band gap of **R1** is the largest (0.19440 a.u) and **R8** is the smallest (0.12409 a.u) indicating the former is more stable than the later. However, the molecule **R4** (0.12666 a.u) shows slightly higher band gap value compared to **R8**. The compounds **R1**, **R2**, **R3**, **R11** and **R26** appear to be more stable and the stability here refers to the chemical or photochemical processes with electron transfer or electron leap. Therefore, the decreasing order of stability aminodinitropyrazoles is as follows: **R1**>**R3**~**R2**~**R10**>**R11**>**R9**>**R7**>**R6**>**R5**>**R12**>**R4**>**R8** and the decreasing order of aminotrinitropyrazoles is as follows: **R26**>**R21**>**R25**>**R24**. The C-NO₂ and N-NO₂ are trigger bonds in these compounds and the resonance in pyrazole ring strengthens these bonds thereby the molecules gets stabilized. Also, the larger the length of trigger bonds of the molecule, the easier the dissociation or breakdown is, thus the molecule becomes lesser stable. As per the total energies of the compounds concerned, the most stable and least stable compounds are **R1** (-690.618385 a.u) and **R7** (-690.6747163 a.u) respectively. The higher the total energy of the molecule, the lower the stability of the molecule. The discrepancies in the above orders is due to the slight variations in total energies, trigger bond lengths and the band gap values among the isomers are caused by the relative position of nitro and amino groups.

Electric spark sensitivity correlations

The electric spark sensitivity of explosives is usually determined by subjecting the explosive compound to a high-voltage discharge from the capacitor. It is the degree of sensitivity of the energetic compound to the electric discharge. Skinner et al. [54] gave the relationship between the electric spark sensitivity and the reciprocal temperature. Zeman [31, 32] gave the relationship between the electric spark sensitivity (E_{ES}), the squares of detonation velocity (D), reciprocal temperatures, the Piloyan activation energy and the heats of fusion of the energetic compounds. Wang et al. [55, 56] have shown suitable correlations between the electric spark sensitivity, detonation velocity and detonation pressure of the nitramines and nitroarenes. We have calculated the electric spark sensitivity of the model compounds using the following equation [33]:

$$E_{ES}(J) = (-1)^{n1} 10.16Q_{NO2} - 1.05_{n1} n2 E_{LUMO} - 0.20, \quad (9)$$

where $n1$ is the number of aromatic rings, $n2$ is the number of substituted groups attached to the aromatic ring like alkyl (-R) or amino (-NH₂) groups, $-Q_{NO2}$ is the minimum Milliken charges of the NO₂ group and E_{LUMO} (in eV) is the lowest unoccupied molecular orbital energy. We have taken $n2$ as one as the number of substituent groups of the model compounds as zero. As per calculated by Zhi et al. [33], the calculated electric spark sensitivity values of the title compounds **R11** (7.0 J) and **R12** (6.78 J) are nearly equal to TNT (6.94 J). All the aminidinitropyrazoles have shown higher E_{ES} values and however, the compound **R6** has shown lowest E_{ES} value (5.92 J). The aminotrinitropyrazoles have higher E_{ES} values compared to TNT, the highest and lowest electric insensitive compounds are **R21** (9.91 J) and **R25** (5.15 J).

Conclusions

The energy of detonation (Q), density (ρ), detonation velocity (D) and detonation pressure (P), stability, impact insensitivity and electric spark insensitivity were increased markedly by substituting the hydrogen(s) of the polynitropyrazoles. The detonation properties ($D \approx 9.50$ km/s, and $\approx P$ 43 Gpa) of designed molecules appear to be promising compared to RDX and HMX. The discrepancies in the explosive properties among aminodinitropyrazoles are caused by the relative position of NH₂ and NO₂ groups. The model compounds satisfy the criteria as the high energy density materials. The nitro group charge analyses of the compounds suggest that the energetic C3-NO₂, C5-NO₂ or N-NO₂ bond is often the trigger site during

the initiation of explosion or detonation. On the whole, the performance, stabilities or sensitivities of title compounds vary with the relative positions of NH₂ and NO₂ groups and the compounds **R1**, **R2**, **R3**, **R21** and **R26** have shown exceptionally higher performance and better stability or insensitivity.

Acknowledgments The first author acknowledges the sustaining financial support from Defence Research Development Organisation (DRDO), India through Advanced Centre of Research in High Energy Materials (ACRHEM). Department of Science and Technology (DST), India is thanked for the computational facility at the University of Hyderabad through Centre for Modeling Simulation and Design (CMSD).

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