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A DFT treatment on nitro derivatives of pyrazine

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Abstract: In the present work, I carried out a theoretical investigation (density functional theory, DFT) on the structural and energetically properties of pyrazine and its nitro derivatives in the gas phase. All computations were done without any structural symmetry restrictions at 293.15 K and 1 atm. In first step of the calculations, all considered compounds were optimized at B3LYP/6-311G(d,p) level of theory. Then, the vibrational analysis of the molecules was done at the mentioned theoretical method. Also, the natural bond orbital (NBO) population analysis and assignment of the aromaticity properties of the compounds were studied. For good understanding of the structure of compounds, their NMR and IR spectra were considered. The heat of formation (HOF) of the molecules was computed by the isodesmic reaction method. From the bond dissociation energy (BDE) values of the studied materials, all of them are good candidates for high energy density materials (HEDMs).

Keywords: DFT study, Pyrazine, Energetic materials, Ballistic properties, Sensitivity.

Introduction

1,4-Diazabenzene or pyrazine is a symmetrical heterocyclic aromatic organic molecule with point group D_{2h}. In recent years, there has been a growing interest in the synthesis of molecules based on the pyrazine ring [1-8]. Preparation of pyrazine and its derivatives is done by many methods such as Staedel-Rugheimer and Gutknecht reactions [9]. The Staedel-Rugheimer pyrazine synthesis is performed by reaction of ammonia with 2-chloroacetophenone, following condensation and oxidation [10]. Also, the Gutknecht pyrazine synthesis is based on the self-condensation, but differing in the way the alpha-ketonamine is prepared [11]. Pyrazine derivatives have more usages such as antitumor, antibiotic and diuretic activities [12-18]. One important application of nitrogen-rich derivatives of this heterocyclic organic compound relates to the high energy density materials (HEDMs) [19-24]. Nowadays, many nitrogen-rich compounds based on nitro and amino derivatives of pyrazine were synthesized and characterized [25]. Nitro compounds are important in explosive chemistry [26]. In 2004, Jinshan Li and his co-workers studied the energetically properties of the nitro derivatives of pyrazine by B3LYP method and the 6-31++G(d,p) basis set with the Berny gradient approach without any symmetrically restriction, but they did not investigate the structurally properties of these materials [27]. In this work, the structural, spectroscopic, energytically, frontier molecular orbitals (FMOs) and acid-base properties, density of states (DOSs) and natural bond orbital (NBO) population analysis of nitropyrazines are investigated by density functional theory (DFT) method.

Computational methods

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All computational studies were performed with the Gaussian 03 package [28] using the B3LYP method with 6-311G(d,p) basis set in the gas phase. The designation B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [29] and the Lee, Yang, Parr (LYP) correlation correction function [30]. The geometry of compounds was optimized without any structural or symmetry restrictions.

Results and discussion

Structural properties study of the molecules:

In the present work, the nitro derivatives of pyrazine ring were investigated theoretically. The studied compounds are shown in Figure **1**. 2-Nitropyrazine, 2,3-nitropyrazine, 2,5-nitropyrazine, 2,6-nitropyrazine, 2,3,5-nitropyrazine and 2,3,5,6-nitropyrazine were named NP2, NP23, NP25, NP26, NP235 and NP2356, respectively. As mentioned above, the structural properties computation of the molecules were successful with DFT method at 293.15 K and 1 atmosphere; therefore, I used the DFT method for computing the properties of the structures. All calculations were carried out at B3LYP/6-311G(d,p) level of theory. The bond lengths, bond angles and dihedral angles of the molecules are listed in Table **1**. The geometry parameters of structures can explain the stability and reactivity of the molecules. It can be seen from the data of NP2 compound, the shortest bond in sextet ring is related to the N1-C2 bond (1.314 A^o). In contrast, the length of other C-N bonds of the ring is about 1.334 A^o. This shortening in N1-C2 bond corresponds to the electron-withdrawing influence of the nitro group that is attached to the C2 atom of pyrazine ring. The C-C bond length of hetero-aromatic ring is about 1.393 A^o. We can see the lengths of all six bonds in pyrazine framework of NP2 compound are not equal together. Then, it can be concluded that the reactivity of NP2 compound is more than the pyrazine molecule. Also, in other nitro compounds (NP23, NP25, NP26, NP235 and NP2356), the shortest bonds of pyrazine framework are related to the C-N bonds who attach to nitro substituents. The dihedral angles data of the compounds indicates that the pyrazine framework of the mono- and di-nitro derivatives is planar. In contrast, the pyrazine ring of the three- and four-substituted compounds has distortion angle in the range of 0.3-1.2 A^o.

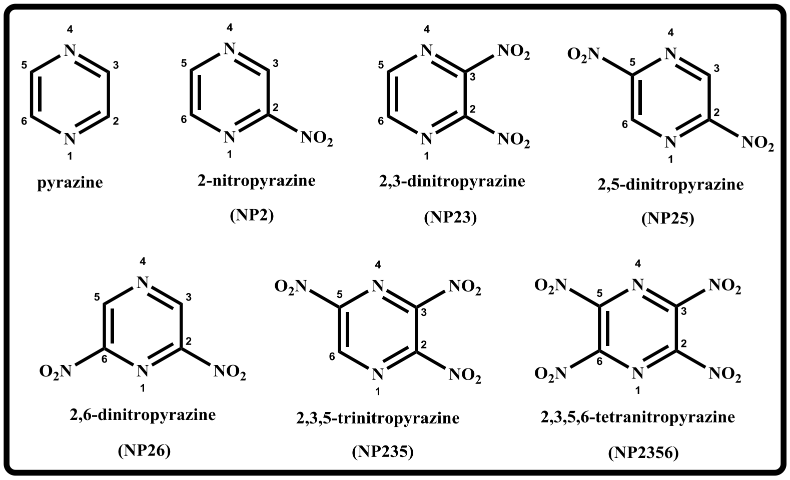


Figure 1: The structure of studied molecules.

Molecular electrostatic potential (MEP) is a technique for rapidly investigating the electrostatic properties of a compound. The MEP plots enable us to visualize the charge distributions of molecules and charge related properties of compounds. They also allow us to visualize the size and shape of structures [31-33]. Figure **2** indicates the 3D-MEP plots of studied molecules. Blue and red lopes of these plots are related to the positive and negative charge distributions on compounds, respectively. In pyrazine system, the negative charges distribute on nitrogen elements of ring due to the electron-withdrawing property of them. In contrast, the negative charge distribution in nitro derivatives of pyrazine is happened on nitro groups. We can see positive charge on pyrazine framework increases by increasing the number of nitro substituents on pyrazine ring. It can be concluded that the nucleophilic reaction tendency of molecules increases by high nitro- substitution of pyrazine system.

Table 1: Bond lengths (Aº), bond angles (degree) and dihedral angles (degree) of the compounds.

Bonds lengths (A) and angles (degree)	Pyrazine	NP2	NP23	NP25	NP26	NP235	NP2356
N1-C2	1.335	1.314	1.313	1.317	1.317	1.313	1.314
C2-C3	1.394	1.393	1.391	1.391	1.391	1.398	1.396
C3-N4	1.335	1.334	1.313	1.333	1.332	1.311	1.314
N4-C5	1.335	1.335	1.337	1.317	1.332	1.316	1.314
C5-C6	1.394	1.396	1.393	1.391	1.391	1.392	1.396
C6-N1	1.335	1.333	1.337	1.333	1.317	1.335	1.314
C2-H	1.086	-	-	-	-	-	-
C2-N	-	1.503	1.491	1.487	1.487	1.492	1.493
C3-H	1.086	1.082	-	1.084	1.084	-	-
C3-N	-	-	1.491	-	-	1.494	1.493
C5-H	1.086	1.085	1.084	-	1.084	-	-
C5-N	-	-	-	1.487	-	1.501	1.493
C6-H	1.086	1.085	1.084	1.084	-	1.081	-
C6-N	-	-	-	-	1.487	-	1.493
C6-N1-C2	115.97	115.68	116.57	116.10	114.55	117.45	117.59
N1-C2-C3	122.01	124.26	122.06	124.50	124.02	121.95	121.20
C2-C3-N4	122.01	119.90	122.06	119.39	119.90	121.27	121.21
C3-N4-C5	115.97	116.70	116.57	116.10	117.61	116.49	117.59
N4-C5-C6	122.01	122.13	121.37	124.50	119.90	123.46	121.20
C5-C6-N1	122.01	121.32	121.37	119.39	124.02	119.38	121.21
N1-C2-H	117.05	-	-	-	-	-	-
N1-C2-N	-	116.41	116.05	115.87	115.95	115.59	116.01
C3-C2-H	120.94	-	-	-	-	-	-
C3-C2-N	-	119.32	121.88	119.62	120.03	122.37	122.72
C2-C3-H	120.94	121.42	-	122.48	121.92	-	-
C2-C3-N	-	-	121.88	-	-	122.46	122.70
N4-C3-H	117.05	118.68	-	118.13	118.18	-	-
N4-C3-N	-	-	116.05	-	-	116.20	116.02
N4-C5-H	117.05	116.96	116.95	-	118.18	-	-
N4-C5-N	-	-	-	115.87	-	116.71	116.01
C6-C5-H	120.94	120.91	121.68	-	121.92	-	-
C6-C5-N	-	-	-	119.62	-	119.83	122.72
C5-C6-H	120.94	121.56	121.68	122.48	-	121.96	-
C5-C6-N	-	-	-	-	120.03	-	122.71
N1-C6-H	117.05	117.13	116.95	118.13	-	118.66	-
N1-C6-N	-	-	-	-	115.95	-	116.02
N1-C2-C3-N4	0.00	0.00	0.00	0.00	0.00	0.65	1.21
C2-C3-N4-C5	0.00	0.00	0.00	0.00	0.00	0.31	0.57
C3-N4-C5-C6	0.00	0.00	0.00	0.00	0.00	0.32	0.58
N4-C5-C6-N1	0.00	0.00	0.00	0.00	0.00	0.64	1.21
C5-C6-N1-C2	0.00	0.00	0.00	0.00	0.00	0.29	0.58
C6-N1-C2-C3	0.00	0.00	0.00	0.00	0.00	0.31	0.58

IR and NMR spectra analysis of molecules:

Vibrational spectroscopy or infrared (IR) spectroscopy relates to the infrared region of the electromagnetic spectrum (the light with a longer wavelength and lower frequency than visible light). The base of this method is on absorption spectroscopy. This technique can be used to characterize organic and inorganic molecules [34]. The study of IR spectra of polynitropyrazines gives us a good vision about them.

Harmonic frequencies (cm^{-1}), IR intensities (KM/Mole):

Pyrazine: 433.9544 (22.2593), 804.5291 (30.2090), 1035.9243 (38.7500), 1089.0507 (9.9562), 1163.7087 (6.7226), 1213.9615 (2.9347), 1441.8348 (32.8325), 1510.9470 (1.5988), 3149.1297 (6.2879) and 3163.5737 (73.3390).

NP2: 23.2684 (0.0018), 156.4465 (0.9828), 247.2513 (0.3446), 389.8690 (1.1463), 397.7828 (2.0553), 455.5956 (21.9535), 524.7299 (1.2113), 623.6347 (0.0177), 725.9643 (4.3405), 755.5272 (12.7813), 769.2267 (10.4993), 875.3909 (53.0324), 890.0037 (15.4928), 976.0236 (0.8932), 1006.0576 (0.1577), 1032.6218 (31.5808), 1069.1872 (8.5406), 1164.3464 (2.2725), 1196.5011 (12.7990), 1240.6415 (11.6941), 1322.7918 (0.8008), 1380.1452 (153.2187), 1424.6229 (59.2715), 1494.0561 (3.7441), 1577.8393 (2.2023), 1609.9130 (61.6639), 1658.5023 (184.5111), 3165.8448 (0.7833), 3182.6720 (20.7630) and 3216.3822 (0.9937).

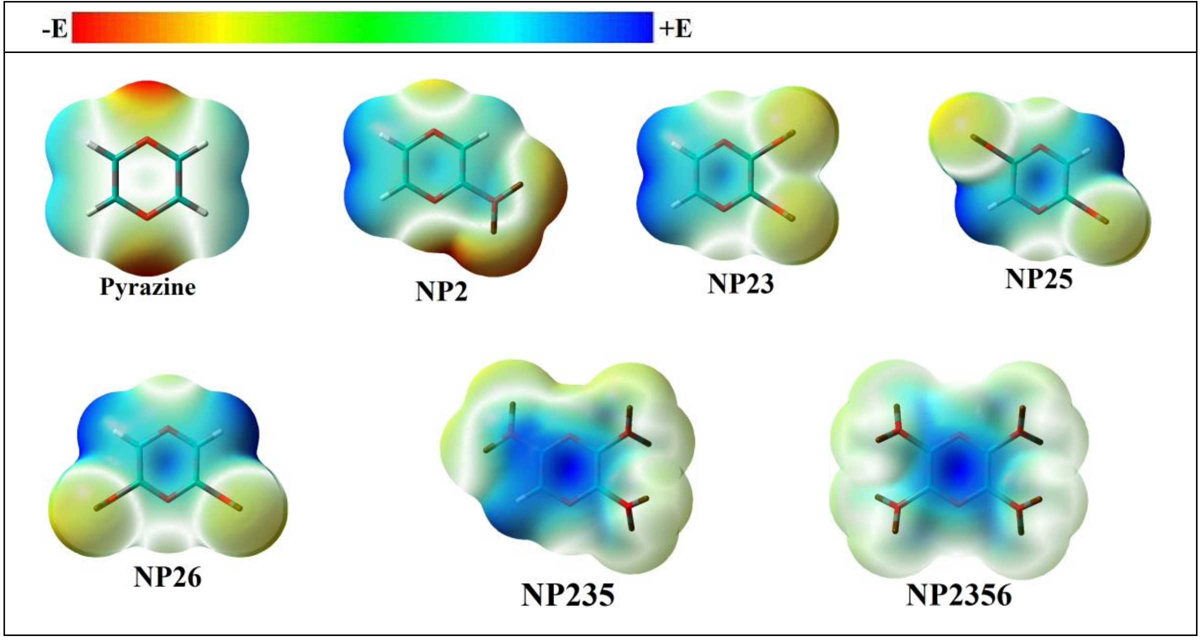


Figure 2: MEP plots of the pyrazine and its nitro derivatives.

NP23: 120.2266 (0.8960), 154.8081 (0.2099), 274.5837 (1.8180), 332.2963 (4.1421), 401.8203 (12.5473), 406.9819 (12.0357), 592.8058 (0.3328), 643.7889 (2.1463), 732.0669 (0.1469), 762.4375 (27.0195), 780.2663 (2.1590), 863.0426 (54.5215), 891.7892 (29.8599), 893.5464 (22.3232), 1087.2275 (3.8351), 1112.1533 (48.2280), 1216.2089 (26.9491), 1258.0440 (4.1290), 1265.1310 (0.1357), 1403.7580 (168.9108), 1410.4669 (77.7044), 1425.4601 (35.5775), 1479.0930 (0.0004), 1586.7527 (1.5278), 1606.9507 (1.0098), 1662.3435 (520.3935), 3183.2620 (0.0735) and 3198.5740 (10.2260).

NP25: 62.3003 (4.1222), 153.8700 (9.6070), 309.3196 (0.0004), 412.2930 (15.2480), 462.0016 (21.1368), 634.4930 (0.5823), 738.7509 (8.6042), 856.8775 (110.6160), 933.1075 (15.1186), 1041.2596 (39.4871), 1202.7175 (58.8720), 1242.1060 (0.0271), 1364.4442 (88.7318), 1423.3129 (223.6927), 1486.0342 (15.6590), 1647.2533 (587.2533) and 3191.8271 (3.3845).

NP26: 113.6236 (1.3089), 135.4036 (4.9266), 269.7861 (0.9977), 337.2386 (4.0884), 382.1114 (8.2535), 393.5507 (10.7911), 535.3668 (4.7234), 642.2068 (0.5844), 744.7023 (4.3046), 762.4151 (6.7794), 765.1546 (40.1375), 775.2315 (29.1010), 850.6590 (33.1789), 915.3103 (14.6596), 948.2454 (13.2289), 1032.7908 (29.4793), 1179.3858 (18.1261), 1222.8905 (62.4750), 1222.9602 (6.1128), 1243.6539 (1.6498), 1411.9714 (222.6607), 1426.8787 (56.2005), 1433.9648 (1.4397), 1481.0647 (0.9856), 1589.8880 (22.5870), 1605.7142 (6.0283), 1649.4096 (576.3980), 3187.6333 (1.7309) and 3191.2988 (1.1988).

NP235: 25.2742 (0.0182), 28.0566 (0.0234), 61.5747 (4.8833), 87.4746 (0.0425), 138.1103 (2.4005), 151.4572 (3.3662), 161.4101 (1.9830), 225.6380 (0.3385), 288.6048 (0.2443), 305.8857 (0.3014), 345.0299 (2.4032), 367.3166 (0.5559), 448.5268 (19.2063), 480.0770 (7.4272), 530.6177 (4.3075), 584.7458 (3.3370), 624.2418 (2.4954), 657.5699 (1.8497), 707.1339 (1.9783), 763.9413 (12.8085), 780.2632 (19.9405), 787.3045 (1.9155), 828.9765 (1.4168), 849.4816 (84.1616), 866.6812 (71.0855), 945.1413 (23.1481), 971.0265 (8.7613), 1097.9075 (27.5449), 1190.0714 (0.3352), 1226.5614 (7.9768), 1283.9942 (7.3587), 1364.9110 (2.1444), 1374.6000 (276.0788), 1384.0378 (116.1718), 1401.2066 (116.7446), 1452.0674 (12.2822), 1588.4108 (2.9287), 1604.3905 (16.9111), 1660.8872 (348.3009), 1664.0720 (239.8485), 1667.5536 (138.4657) and 3229.8403 (6.7126).

NP2356: 19.5497 (0.0078), 26.8553 (0.0217), 85.8721 (0.1437), 86.0671 (0.0021), 95.9255 (8.5237), 142.7023 (5.7795), 158.3669 (0.8438), 168.8098 (1.0115), 229.1394 (0.0033), 272.1152 (0.0092), 314.4856 (0.3886), 395.6399 (4.3806), 423.2092 (0.0276), 448.4193 (16.6789), 546.6076 (31.8616), 605.9267 (0.0251), 624.9830 (0.0448), 715.1186 (9.4113), 763.0746 (4.5803), 782.7848 (2.0377), 809.4316 (0.0001), 816.7294 (6.5480), 830.8723 (2.7888), 839.7348 (116.4756), 885.9535 (135.7945), 1004.1970 (0.4759), 1139.5384 (22.4888), 1241.5423 (0.0001), 1287.8226 (21.0895), 1360.6950 (53.1197), 1373.9298 (118.2113), 1375.9210 (11.4143), 1387.0713 (432.5681), 1399.2730 (0.0008), 1427.8460 (37.7891), 1585.7959 (0.0001), 1598.7309 (9.2063), 1664.0336 (560.4433), 1664.7354 (395.1590), 1669.1159 (47.2463) and 1670.2573 (0.0962).

Nuclear magnetic resonance (NMR) spectroscopy is a technique that measures the magnetic properties of certain atomic nuclei. It determines the physical and chemical properties of atoms or the molecules in which they are contained. It relies on the nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state and chemical environment of molecules. The chemical shift data of the nucleus of the studied molecules can give us good information about their structures [35]. Here, nucleus shielding (ppm) for structures were calculated by using B3LYP/6-311G(d,p) level.

Pyrazine: C (33.224), N (-118.451) and H (23.258).

NP2: N1 (-92.820), N4 (-130.726), C2 (25.263), C3 (37.618), C5 (29.264), C6 (36.880), H3 (22.138), H5 (22.942) and H6 (23.316). NO_2 group: N (-133.582) and O (-308.975 and -342.043).

NP23: N1 and N4 (-97.271), C2 and C3 (32.428), C5 and C6 (34.104), H5 and H6 (23.240). NO_2 groups: N (-140.302) and O (-403.378).

NP25: N1 and N4 (-95.880), C2 and C5 (21.367), C3 and C6 (43.437), H3 and H6 (23.451). NO_2 groups: N (-147.391) and O (-402.722).

NP26: N1 (-52.266), N4 (-147.175), C2 and C6 (24.410), C3 and C5 (41.360), H3 and H5 (23.044). NO_2 groups: N (-145.444) and O (-402.093).

NP235: N1 (-111.739), N4 (-78.689), C2 (27.459), C3 (33.146), C5 (29.631), C6 (36.748) and H6 (22.284). NO_2 groups: N [N_{C2} (-132.455), N_{C3} (-128.786) and N_{C5} (-123.652)] and O [O_{C2} (-375.011 and -374.869), O_{C3} (-361.903 and -367.967) and O_{C5} (-350.488 and -316.380)].

NP2356: N1 (-85.902), N4 (-85.925), C2 (32.134), C3 (32.098), C5 (32.112) and C6 (32.115). NO_2 groups: N [N_{C2} (-125.542), N_{C3} (-125.573), N_{C5} (-125.515) and N_{C6} (-125.586)] and O [O_{C2} (-371.625 and -368.830), O_{C3} (-368.962 and -371.690), O_{C5} (-368.718 and -371.560) and O_{C6} (-369.035 and -371.716)].

Aromaticity of Compounds:

An aromatic ring current is an effect observed in aromatic molecules such as benzene and naphthalene. If a magnetic field is directed perpendicular to the plane of the aromatic system, a ring current is induced in the delocalized π electrons of the aromatic ring. The aromatic ring currents are relevant to NMR spectroscopy, as they dramatically influence the chemical shifts of ^1H nuclei in aromatic molecules [36]. The nucleus-independent chemical shift (NICS) is a computational method that calculates the absolute magnetic shielding at the center of a ring. The values are reported with a reversed sign to make them compatible with the chemical shift conventions of NMR spectroscopy. In this method, negative NICS values indicate aromaticity and positive values antiaromaticity [37]. As can be seen from the data of Table **2**, the aromaticity order of studied molecules is: NP2356 > NP235 > NP25 > NP23 > NP26 > NP2 > Pyrazine. This order shows the nitro groups increase the aromaticity of pyrazine ring. Because of two reasons, this factor can't be correct to describe the aromaticity property of these moleccules. Firstly; dihedral angles data (Table **1**) show us trinitropyrazine and tetranitropyrazine compounds are not planar. So, these compounds can't have more aromaticity than other molecules. Secondly; the Wiberg bond order data of compounds (Table **2**) indicate that the bond orders in nitro derivatives are not equal together. It can be seen from the data, the C-N bonds of nitro compounds are longer than the C-C bonds of pyrazine framework of molecules. So, we have to study another factor to describe the aromaticity of these molecules. In 1991, Clive Bird reported new index for aromaticity property of five-membered, six-membered, and fused five and six-membered heterocycles [38, 39]. The variation coefficient for the bond orders of a heterocycle compound is given by the expression:

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\Sigma(N-\bar{N})^2}{n}}$$

Where $\overline{\mathrm{N}}$ is the arithmetic mean of the various bond orders (N), and n is the number of bonds. The Bird aromaticity index is expressed by following formulas:

$$BIRD\ Index = 100(1 - \frac{V}{V_K})$$

The non-delocalized Kekule variation coefficient (V_K) of bond orders is 35, 33.3 and 35 for a five-membered ring heterocycle, a six-membered ring heterocycle and a five-membered ring fused to the six-membered ring heterocycle, respectively. From the data of Table **2**, the BIRD index order of compounds is: Pyrazine > NP2 > NP26 > NP25 > NP23 > NP2356 > NP235. We can see the aromaticity of pyrazine molecule is more than the nitro derivatives. Also, this order indicates the aromaticity property of pyrazine system decreases by increasing the number of nitro groups on the system. The mentioned order is consistent with the dihedral angles and bond orders of molecules. So, the BIRD index can describe the correct aromaticity property of these molecules.

Table 2: NICS and BIRD indices and Wiberg bonds orders of the molecules.

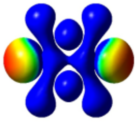
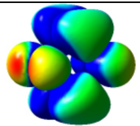
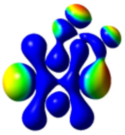
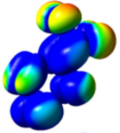
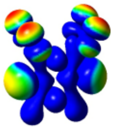
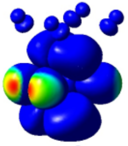
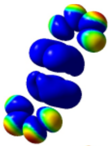
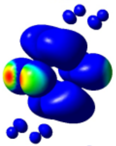
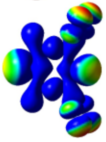
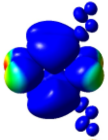
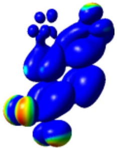
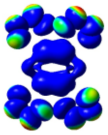
Compound	NICS(0)	BIRD Index	$n_{(N1-C2)}$	$n_{(C2-C3)}$	$n_{(C3-N4)}$	$n_{(N4-C5)}$	$n_{(C5-C6)}$	$n_{(C6-N1)}$
Pyrazine	-5.992	98.311	1.432	1.415	1.432	1.432	1.415	1.432
NP2	-7.611	95.093	1.438	1.370	1.432	1.431	1.406	1.422
NP23	-9.089	90.996	1.455	1.330	1.455	1.400	1.425	1.400
NP25	-9.099	94.763	1.436	1.377	1.417	1.436	1.377	1.417
NP26	-8.866	95.055	1.418	1.378	1.433	1.433	1.378	1.418
NP235	-10.178	90.335	1.455	1.319	1.447	1.409	1.381	1.400
NP2356	-11.566	90.754	1.425	1.332	1.425	1.425	1.332	1.425

* n: Wiberg bond index matrix

Frontier molecular orbitals (FMOs):

In organic chemistry, frontier molecular orbital (FMO) theory is an application of molecular orbital (MO) theory describing HOMO and LUMO interactions [40]. The frontier molecular orbitals (FMOs) of the studied molecules and their energies are listed and shown in Table **3**.

Table 3: Frontier molecular orbitals of the molecules and their energies.

Compound	HOMO orbital	HOMO (a.u.)	LUMO orbital	LUMO (a.u.)	Δε (eV)
Pyrazine		-0.25700		-0.06058	5.345
NP2		-0.28996		-0.11492	4.763
NP23		-0.31239		-0.11448	5.385
NP25		-0.31344		-0.11745	5.333
NP26		-0.31361		-0.11653	5.363
NP235		-0.33590		-0.16189	4.735
NP2356		-0.34334		-0.17701	4.526

The high occupied molecular orbital (HOMO) figures of the compounds show the electron transition from pyrazine framework to nitro substituents by adding more nitro groups to pyrazine system. It can be seen from the data of the FMOs energies, the HOMO and LUMO energies of compounds decreases by increasing the number of nitro substituents on pyrazine system. So, the reactivity of molecules increases when the number of nitro groups increases on pyrazine system. The HOMO/LUMO energies gaps order of molecules is: NP23 > NP26 > pyrazine > NP25 > NP2 > NP235 > NP2356. The HOMO/LUMO energies gap of a molecule expresses the kinetic stability of the corresponding compound and it is acknowledged that the compounds with high HOMO/LUMO energies gap show higher kinetic stability [40]. It can be deduced that trinitro and tetranitro derivatives of pyrazine system have low kinetic stability between all nitro derivatives of pyrazine system.

The global reactivity descriptors (Mulliken electronegativity χ_M, electronic chemical potential μ, chemical hardness η, and electrophilicity index ω) of a molecule can be obtained by following formulas [41]:

$$\chi_M = \frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2}$$

$$\mu = -\chi_M$$

$$\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2}$$

$$\omega = \frac{\mu^2}{2\eta}$$

The global reactivity indices and dipole moments of the studied compounds are collected in Table 4. The more electronegative molecule (the higher Mulliken electronegativity value) is the less susceptible to oxidations than other molecules [42]. The χ_M order of compounds is: pyrazine > NP2 > NP23 > NP26 > NP25 > NP235 > NP2356. We can see the electronegativity of compounds increases by increasing the number of nitro groups on pyrazine system. NP2356 is the most electronegative of all studied molecules; therefore it is less susceptible to oxidation when compared to others. The chemical hardness value of a molecule similar to the frontier orbitals energies gap expresses the kinetic stability of the corresponding system [43]. Also, the electrophilicity index order of the molecules is: NP2356 > NP235 > NP25 > NP26 > NP2 > NP23 > pyrazine. It is concluded that the nitro groups increase the electrophilicity property of the pyrazine system.

Table 4: The dipole moment and global reactivity indices of the studied molecules.

Compound	Dipole moment (Debye)	χ (eV)	μ (eV)	η (eV)	ω (eV)
Pyrazine	0.0000	-4.321	4.321	2.673	3.492
NP2	4.1631	-5.509	5.509	2.382	6.370
NP23	5.8664	-5.808	5.808	2.693	6.263
NP25	0.0000	-5.863	5.863	2.667	6.444
NP26	3.5971	-5.852	5.852	2.682	6.385
NP235	3.0059	-6.773	6.773	2.368	9.686
NP2356	0.0006	-7.078	7.078	2.263	11.075

Density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level. In general a DOS is an average over the space and time domains occupied by the system [44]. The DOS of studied molecules (Figure **3**) were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV using GaussSum 3 [45]. The LUMO and HOMO indicates the ability to obtain and denote an electron, respectively. We can see, the LUMO number of systems increase when the number of nitro substituents increases. So, the nitro groups increase the tendency of pyrazine system to obtain an electron. Then, it can be deduced that NP2356 is more susceptible to reduction when compared to others.

Natural bond orbital (NBO) study of compounds:

Natural bond orbital (NBO) analysis stresses the role of intermolecular orbital interaction in the compound. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs. This analysis can use to investigate the acid-base properties of hydrogen and nitrogen atoms of molecules [46]. The hydrogen atoms attached to carbon atoms with less p orbital are acidic. In contrast, the nitrogen atoms with more p orbitals have base property. The NBO analysis data of compounds are listed in Table **5**.

According to the calculation, σ(C-H) bonds in the pyrazine system are formed from an $sp^{2.35}$ hybrid on carbon atoms with s orbital on hydrogen atoms. Also, the lone pair of nitrogen atoms of pyrazine system is formed from an $sp^{2.43}$ hybrid. In NP2, the N1 and N4 atoms have $sp^{2.50}$ and $sp^{2.38}$ hybrids, respectively. So, only the N1 atom is basic. On the other hand, the σ(C3-H), σ(C5-H) and σ(C6-H) bonds of NP2 are formed from $sp^{2.20}$, $sp^{2.32}$ and $sp^{2.30}$ hybrids on carbon atoms. These hybrids indicate that all three hydrogen atoms of NP2 are acidic.

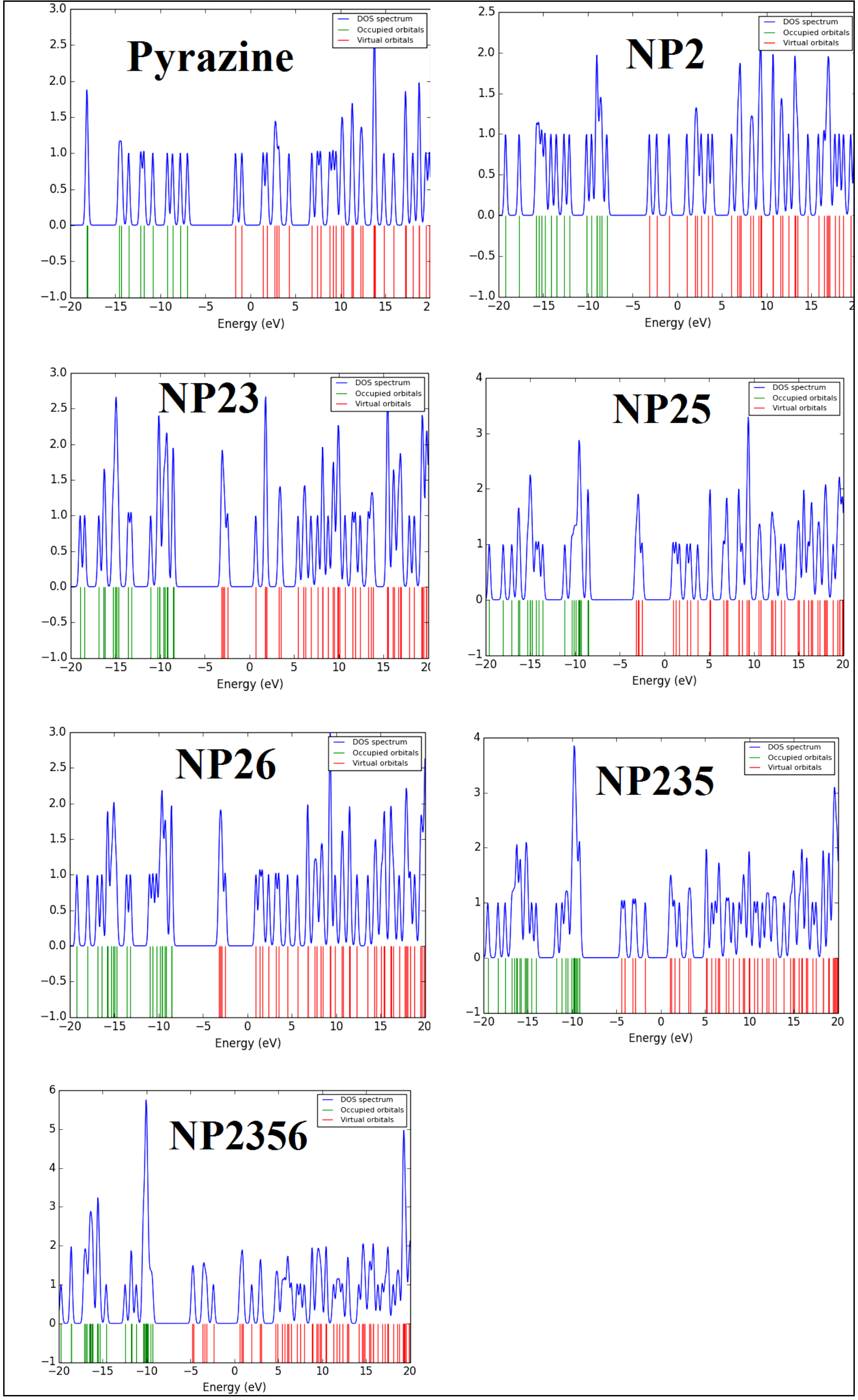


Figure 3: Density of states (DOS) plots of the pyrazine and its nitro derivatives.

The acidic power order of them is: C3-H > C6-H > C5-H. The hybrid of N1 and N4 atoms of NP23 is $sp^{2.49}$. This hybrid gives the basic property to the nitrogen atoms of pyrazine ring in this molecule. The hydrogen atoms of σ(C5-H) and σ(C6-H) bonds are acidic. These bonds are formed from $sp^{2.28}$ hybrid on carbon atoms and s orbital on hydrogen atoms. For NP25, the C-H bonds and lone pair of nitrogen atoms are formed from $sp^{2.22}$ and $sp^{2.47}$ hybrids, respectively. So, the hydrogen atoms of NP25 are more acidic than the pyrazine. Because of the more p orbital on nitrogen atoms of pyrazine framework, this molecule's nitrogen atoms have basic property. In NP26, lone pair of nitrogen atoms is formed from $sp^{2.55}$ (N1) and $sp^{2.40}$ (N4) hybrids. So, only the N1 atom of NP26 has more basic property than the pyrazine. On other hand, the σ(C3-H) and σ(C5-H) are formed from $sp^{2.22}$ hybrid on carbon atoms. This hybrid causes that the hydrogen atoms of NP26 have acidic property. Also, the hydrogen atom of NP235 is more acidic than the pyrazine. The hybrid of σ(C6-H) is $sp^{2.16}$. The lone pair of N1 and N4 atoms of NP235 is formed from $sp^{2.46}$ and $sp^{2.60}$ hybrids, respectively. It can be seen that both nitrogen atoms are basic, but the basic property of N4 atom is more than the N1 atom. Also, the nitrogen atoms of NP2356 are formed from $sp^{2.60}$ hybrid on lone pair of them. This hybrid causes the nitrogen atoms of NP2356 molecule be more acidic than the pyrazine.

Table 5: The dipole moment and global reactivity indices of the studied molecules.

Compounds	Bonds	Occupancy	Population/Bond orbital/Hybrids
Pyrazine	σ(C2-H), σ(C3-H), σ(C5-H) and σ(C6-H)	1.98181	59.84% C ($sp^{2.35}$), 40.16% H (s)
	LP(N1) and LP(N4)	1.92174	N ($sp^{2.43}$)
NP2	σ(C3-H)	1.97964	61.63% C3 ($sp^{2.20}$), 38.37% H (s)
	σ(C5-H)	1.98097	60.28% C5 ($sp^{2.32}$), 39.72% H (s)
	σ(C6-H)	1.98191	60.41% C5 ($sp^{2.30}$), 39.59% H (s)
	LP(N1)	1.90012	N1 ($sp^{2.50}$)
	LP(N4)	1.91990	N4 ($sp^{2.38}$)
NP23	σ(C5-H) and σ(C6-H)	1.98063	60.72% C ($sp^{2.28}$), 39.28% H (s)
	LP(N1) and LP(N4)	1.89893	N ($sp^{2.49}$)
NP25	σ(C3-H) and σ(C6-H)	1.98010	61.25% C ($sp^{2.22}$), 38.75% H (s)
	LP(N1) and LP(N4)	1.90145	N ($sp^{2.47}$)
NP26	σ(C3-H) and σ(C5-H)	1.97953	61.15% C ($sp^{2.22}$), 38.85% H (s)
	LP(N1)	1.89259	N1 ($sp^{2.55}$)
	LP(N4)	1.91043	N4 ($sp^{2.40}$)
NP235	σ(C6-H)	1.97953	62.37% C6 ($sp^{2.16}$), 37.63% H (s)
	LP(N1)	1.89733	N1 ($sp^{2.46}$)
	LP(N4)	1.87751	N4 ($sp^{2.60}$)
NP2356	LP(N1)	1.87653	N1 ($sp^{2.60}$)

Detonation properties of molecules:

One of the main properties of the nitro aromatic compounds is the detonation properties of them. The important parameters of an energetic material are oxygen balance (OB_{100}), heat of formation (ΔH), density (ρ), heat of explosion (Q) and ballistic properties namely detonation velocity (D) and detonation pressure (P). Oxygen balance (OB_{100}) is an expression that is used to indicate the degree to which an explosive can be oxidized. OB_{100} was calculated as follows [47]:

$$OB\% = \frac{-1600}{\text{Mol. wt}} \times \left(2a + \frac{b}{2} - c\right)$$

Where:

a = number of atoms of carbon, b = number of atoms of hydrogen, c = number of atoms of oxygen.

In this study, isodesmic reaction method was employed for HOF calculations. In isodesmic reaction, the numbers of bonds and bond types are preserved on both sides of the reaction. The accuracy of HOF obtained computationally is conditioned by the reliability of HOF of the reference compounds. The isodesmic reaction for HOF calculation is shown in Scheme **1**.

$$\mathbf{Ar\text{-}NO_2 + CH_4 \longrightarrow Ar\text{-}H + CH_3NO_2}$$

Scheme 1: The isodesmic reaction for HOF calculations.

For an isodesmic reaction, heat of reaction ΔH at 293.15 K can be calculated from the following equations:

$$\Delta H_{293} = \Sigma\Delta H_{f,P} - \Sigma\Delta H_{f,R}$$

$$\Delta H_{293.15K} = \Delta E_{293.15K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT = \Sigma\Delta H^{\circ}_{f,P} - \Sigma\Delta H^{\circ}_{f,R}$$

Where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the heats of formation of products and reactants at 293.15 K, respectively. ΔE_0 and ΔZPE correspond to the total energy difference and the zero point energy difference between products and reactants at 0 K, respectively. ΔH_T is the changes in thermal correction to enthalpies between products and reactants. Δ(PV) equals ΔnRT for reaction in gas phase. For isodesmic reactions, Δn=0 [48].

The ballistic properties can be predicted by the following empirical Kamlet-Jacob equations [49]:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.3\rho)$$

$$P=1.558\rho^2NM^{1/2}Q^{1/2}$$

Stoichiometric ratio ($C_aH_bO_cN_d$)			
parameters	$c\geq 2a+b/2$	$2a+b/2>c\geq b/2$	$b/2>c$
N	$(b+2c+2d)/4M_W$	$(b+2c+2d)/4M_W$	$(b+d)/2M_W$
M	$4M_W/(b+2c+2d)$	$(56d+88c-8b)/(b+2c+2d)$	$(2b+28d+32c)/(b+d)$
Q	$(28.9b+94.05a+0.239\Delta H_f^{\circ})/M_W$	$[28.9b+94.05(c/2-b/4)+0.239\Delta H_f^{\circ}]/M_W$	$(57.8c+0.239\Delta H_f^{\circ})/M_W$

Where D: detonation velocity in km/s, P: detonation pressure in GPa, ρ: density of a compound in g/cm^3, N: moles of gaseous detonation products per gram of explosive (in mol/g), M: average molecular weight of gaseous products (in g/mol), Q: chemical energy of detonation in kJ/g.

The oxygen balance, density, volume, heat of formation, energy, heat of explosion and ballistic properties of the studied compounds are listed in Table **6**. It also includes experimental and theoretical performance values of TNT, RDX and HMX taken from the literature. From the data of the Table **6**, the detonation velocity of pyrazine and its nitro derivatives is in the following manner: HMX > RDX > NP235 > NP2356 > NP23 > NP26 > NP25 > TNT > NP2 > pyrazine. Also, the detonation pressure order of the studied compounds is: HMX > RDX > NP23 > NP235 > NP2356 > NP26 > NP25 > TNT > NP2 > pyrazine. The results indicate that the more nitro groups the compounds have, the better the ballistic properties are. From the detonation velocity and pressure orders of compounds, it is obvious that the performance of di-, tri- and tetra- nitro derivatives of pyrazine is better in usage than TNT.

Table 6: Predicted oxygen balances, densities and detonation properties of the studied molecules.

Compound	OB_{100}	Energy (kcal/mol)	HOF (kJ/mol)	Q (kJ/g)	V* (cm^3/mol)	ρ (g/cm^3)	D (km/s)	P (GPa)
Pyrazine	-199.906	-165853.940	197.500	589.755	64.841	1.234	4.873	8.144
NP2	-95.983	-294208.940	169.144	1204.886	80.863	1.546	6.169	15.335
NP23	-47.057	-422551.095	187.047	1432.755	89.447	1.901	8.288	31.464
NP25	-47.057	-422554.226	174.270	1414.793	98.061	1.734	7.745	26.014
NP26	-47.057	-422553.702	176.380	1417.759	97.360	1.746	7.787	26.403
NP235	-18.605	-550903.806	172.966	1529.710	120.319	1.787	8.336	30.693
NP2356	0.000	-679245.102	199.680	1630.615	153.935	1.689	8.308	29.450
TNT**	-74.003	-553910.940	52.470	1361.620	124.920	1.640	7.110	19.000
RDX**	-21.618	-562334.120	168.900	1597.390	124.920	1.780	8.880	34.750
HMX**	-21.618	-794768.020	270.410	1633.880	157.530	1.880	9.280	39.210

* Average molar volumes from 100 singlepoint calculations at the B3LYP/6-311G(d,p) level of theory.

** Ref. [50]

The detonation of a $C_aH_bO_cN_d$ type explosive will result in the formation of smaller molecules. In order to clarify the decomposition products, a set of rules was developed by Kistiakowsky and Wilson [51]. The number of moles of detonation products of the studied molecules is shown in Table **7**. We can see that all compounds release seven moles of gaseous products by detonation. The most hazardous detonation product is carbon monoxide (CO). It is a colorless and odorless poisonous gas that is extremely harmful to human health. The NP2356 is the only nitro derivative of pyrazine that does not produce carbon monoxide. So, this compound seems to be the most environment friendly explosive in terms of detonation products.

The energetic materials release heat and gases by an explosive reaction. The amount of work done by the explosive is computed by the volume of gaseous products. The standard conditions (273.15 K, 1 atm) also enable one to make comparisons between different energetic materials. 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 energetic compound. The heat of explosion and the volume of gaseous products can be associated to obtain the value for the explosive power as shown in the following formula [52]:

Explosive Power = Q.V

The value for the explosive power is then compared with the explosive power of a stansard explosive, namely picric acid, to obtain power index, as shown in the following formula [52]:

$$\%Power\ Index = \frac{Q.V}{Q_{PA}.V_{PA}} \times 100$$

Table 7: Gaseous decomposition products of the molecules using the Kistiakowsky and Wilson rules.

Compounds	Formula	Number of moles of detonation products						
		N_2	H_2O	CO	CO_2	H_2	C	Total
Pyrazine	$C_4H_4N_2$	1	-	-	-	2	4	7
NP2	$C_4H_3N_3O_2$	1.5	1.5	0.5	-	-	3.5	7
NP23	$C_4H_2N_4O_4$	2	1	3	-	-	1	7
NP25	$C_4H_2N_4O_4$	2	1	3	-	-	1	7
NP26	$C_4H_2N_4O_4$	2	1	3	-	-	1	7
NP235	$C_4HN_5O_6$	2.5	0.5	2.5	1.5	-	-	7
NP2356	$C_4N_6O_8$	3	-	-	4	-	-	7
Picric acid*	$C_6H_3N_3O_7$	1.5	1.5	5.5	-	-	0.5	9
TNT*	$C_7H_5N_3O_6$	1.5	2.5	3.5	-	-	3.5	11
RDX*	$C_3H_6N_6O_6$	3	3	3	-	-	-	9
HMX*	$C_4H_8N_8O_8$	4	4	4	-	-	-	12

* Ref. [50]

The power index values of pyrazine, its nitro derivatives, picric acid, TNT, RDX and HMX are listed in Table **8**. The power index values of considered compounds reside in the following order: TNT > NP2 > HMX > RDX > NP23 > NP26 > NP25 > Picric Acid > Pyrazine > NP235 > NP2356. We can see, the compound NP2 indicates better performance than HMX, RDX and picric acid. It can be deduced that the performance of compounds decreases when the number of nitro substituents increase on pyrazine system.

Table 8: The power index values of the studied molecules, picric acid, TNT, RDX and HMX.

Compound	Q (kJ/g)	V (dm3/g)	Q×V	Power Index %
Pyrazine	589.755	1.960	1156.101	95.698
NP2	1204.886	1.255	1512.081	125.165
NP23	1432.755	0.923	1322.273	109.453
NP25	1414.793	0.923	1305.854	108.094
NP26	1417.759	0.923	1308.592	108.321
NP235	1529.710	0.730	1116.356	92.408
NP2356	1630.615	0.604	984.085	81.459
Picric acid*	1372.860	0.880	1208.070	100.000
TNT*	1417.540	1.085	1538.690	127.368
RDX*	1598.390	0.908	1450.860	120.097
HMX*	1634.890	0.908	1484.660	122.895

* Ref. [50]

The field of explosives sensitivity includes all effects of externally imposed physical conditions on the behavior of energetic compounds. There are principally five types of sensitivity: friction, shock, spark, and heat and impact sensitivity. In this study, the impact sensitivity of the considered energetic materials is investigated. Impact sensitivity measurements of energetic compounds can be done experimentally or theoretically. There are several valuable studies in the literature on the hemolytic bond dissociation energy (BDE) of the nitro compounds, which have proved that there is a parallel correlation between the BDE for the weakest Ar-NO_2 bond in the molecule and its sensitivity. The ordinary trend is that the greater the hemolytic BDE value for scission of -O-NO_2, -N-NO_2 and -C-NO_2 bonds are, the lower the sensitivity is [50]. The energy required for bond hemolysis at 293.15 K temperature and 1 atmosphere pressure corresponds to the energy of reaction A-B → A^{o} + B^{o}, which is the bond dissociation energy of the compound A-B by definition. Therefore, the bond dissociation energy can be given in terms of follow equation:

$$BDE_{(A-B)} = E_{(A^{\circ})} + E_{(B^{\circ})} - E_{(A-B)}$$

Where A-B corresponds for the structures, A^{o} and B^{o} stand for the corresponding product radicals after the bond dissociation, $BDE_{(A-B)}$ is the bond dissociation energy of bond A-B [47]. Table **9** indicates the hemolytic BDE values. The BDE values of RDX and HMX are 175.26 kJ/mol and 180.02 kJ/mol, respectively [50]. From the data of the Table **9**, all compounds are more insensitive than both RDX and HMX. According to suggestion of Chung, the bond dissociation energy more than 20 kcal/mol corresponds for a compound to be considered as a viable candidate of high energy density material (HEDM) [53]. Therefore, we can conclude that the all considered compounds are viable candidate of HEDMs.

Table 9: The hemolytic bond dissociation energies (BDE) of the nitro derivatives of pyrazine.

Compounds	Parent energy (hartrees)	Fragment energy (hartrees)	NO_2 energy (hartrees)	BDE (kcal/mol)
NP2	-468.851396	-263.637990	-205.123898	56.167
NP23 (2)	-673.377468	-468.181512	-205.123898	45.217
NP23 (3)	-673.377468	-468.181512	-205.123898	45.217
NP25 (2)	-673.382457	-468.181988	-205.123898	48.049
NP25 (5)	-673.382457	-468.181988	-205.123898	48.049
NP26 (2)	-673.381623	-468.181535	-205.123898	47.810
NP26 (6)	-673.381623	-468.181535	-205.123898	47.810
NP235 (2)	-877.920361	-672.720148	-205.123898	47.888
NP235 (3)	-877.920361	-672.719871	-205.123898	48.062
NP235 (5)	-877.920361	-672.710318	-205.123898	54.057
NP2356 (2)	-1082.445064	-877.244905	-205.123898	47.855
NP2356 (3)	-1082.445064	-877.244905	-205.123898	47.855
NP2356 (5)	-1082.445064	-877.244905	-205.123898	47.855
NP2356 (6)	-1082.445064	-877.244905	-205.123898	47.855

Key to the notation: B(L) stands for the radical obtained from B structure by removing the functional group at position L.

Conclusion

In the present study, the structural and energetically properties of nitro derivatives of pyrazine were investigated by density functional theory (DFT) method. All molecules were optimized at B3LYP/6-311G(d,p) level of theory. All calculations were done in gas phase without any structural restrictions at standard conditions (293.15 K and 1 atmosphere). In vibrational computations, no imaginary frequencies were shown for all considered molecules. So, it proves the accuracy of my calculations. The dihedral angles data of compounds showed that 2,3,5-trinitropyrazine and 2,3,5,6-tetranitropyrazine are not planar. From the BIRD indices, the aromaticity of pyrazine molecule is more than the nitro derivatives. The energies gaps of the frontier molecular orbitals of compounds indicated that trinitro and tetranitro derivatives of pyrazine system have low kinetic stability between all nitro derivatives of pyrazine system. It was deduced from the data of the ballistic properties of the considered compounds that the performance of di-, tri- and tetra-nitro derivatives of pyrazine is better in usage than TNT. Also, the all considered compounds were viable candidate of HEDMs according to the Chung suggestion.

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