Design and Selection of Pyrazolo[3,4-d][1,2,3] Triazole-based High-energy Materials

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Abstract

In this study, we design a series of bridged energetic compounds based on pyrazolo[3,4-d][1, 2, 3]triazole to screen potential energetic materials with excellent detonation properties and acceptable sensitivities. The electronic structures, heats of formation, detonation velocity, detonation pressure, and impact sensitivity of the designed compounds were calculated using density functional theory. The results showed that the designed compounds have high positive heats of formation in the range of 1035.4 (A7) to 2851.4 kJ mol⁻¹ (D2). Moreover, the designed compounds have high crystal densities and heats of detonation, which significantly enhance detonation pressures and velocities. The detonation pressures and velocities are in the ranges of 6.23 (A1) to 9.65 km s⁻¹ (D3) and 15.7 to 43.9 GPa (E8), respectively. The impact sensitivity data also suggest that the designed compounds have impact sensitivities in an acceptable range. Considering detonation pressures, detonation velocities, and impact sensitivities, six compounds (C3, C5, D3, D5, E3, and F3) were screened as potential materials with high energy density, excellent detonation properties, and low impact sensitivities. Finally, the electronic structures of the screened compounds were simulated to provide further understanding on the physicochemical properties of these compounds.

1. Introduction

As a special important component of energy, energetic materials (such as propellant, explosive and initiator) have played an important role in the development of military and its equipments.¹⁻⁶ In the face of increasing armed conflicts around the world, the leaders of different countries pay significant attention to the development of national armaments and desire higher performance of energetic materials and frequency of replacement. At present, research on energetic materials is focussed on nitrogen-rich compounds with high energy density, excellent detonation performance, good thermal stability, and reduced amount of polluting gas in the process of explosion.⁷⁻¹¹ Scheme 1 shows the structures of some energetic compounds such as 1,3,5-trinitro-1,3,5-triazinane (RDX),¹² 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX),¹³ and cage structures 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20).¹⁴ Among these structures, the detonation performance of cage-like energetic compounds is stronger than that of chain-like energetic compounds. However, the synthetic steps for the cage-like energetic compounds are more complex than those for the chain-like energetic compounds. The annular nitrogen-rich energetic compounds combine the benefits of the chain-like and cage-like energetic compounds and lead the field of energetic materials.^{15, 16}

pyrazolo[3,4-d][1, 2, 3]triazole has good detonation performance and excellent impact sensitivity. Therefore, to obtain energetic compounds with better performance, several pyrazolo[3,4-d][1, 2, 3]triazole compounds were designed with the bridges of -C-C-, -C=C-, -N-N-, -N=N-, -C-N-, and -C=N-. Furthermore, the energetic groups such as -CN, -N₃, -NO₂, -NH₂, -NHNO₂, -NHNH₂, -CH(NO₂)₂, and -C(NO₂)₃ were connected to pyrazolo[3,4-d][1, 2, 3]triazole. Thereafter, the heat of formation, heat of detonation, velocity of detonation, pressure of detonation, and bond dissociation energy of these compounds were calculated using Gauss calculations. By comparing with the RDX and HMX, the energetic compounds with excellent

detonation performance and impact sensitivity were screened as reserve materials and for subsequent directional synthesis.

2. Results And Discussion

2.1 Frontier molecular orbital (FMO)

Highest occupied molecular orbitals (HOMO) and lowest non-occupied molecular orbitals (LUMO) are most frequently mentioned FMOs. They provide important information for predicting the chemical activity of compounds owing to their special status.¹⁷⁻²¹ The energy gap between the HOMO and the LUMO is an expression of this information. Therefore, the values of HOMO, LUMO, and the energy gap ($\Delta E_{\text{LUMO-HOMO}}$) were obtained from Gauss calculations and the results are summarized in Table 1. The maximum values of HOMO and LUMO were -4.89 eV (B6) and -0.56 eV (B6), respectively, while their minimum values were -8.89 eV (E8) and -4.61 eV (D8), respectively. Moreover, the maximum and minimum values of $\Delta E_{\text{LUMO-HOMO}}$ were 5.31 eV (A1) and 3.46 eV (B2), respectively. Therefore, we can make the conclusion that A1 was more stable than B2.

Figure 1 shows the variation trend of the HOMO and LUMO values of the designed compounds with different substituent groups and bridging. As shown in the figure 1, the variations in the HOMO and LUMO values were consistent. For the designed compounds with substituents $-\text{N}_3$, $-\text{NH}_2$, and $-\text{NHNH}_2$, the HOMO and LUMO values increased. However, the HOMO and LUMO values decreased for the designed compounds with substituents $-\text{CN}$, $-\text{NO}_2$, $-\text{NHNO}_2$, $-\text{CH}(\text{NO}_2)_2$, and $-\text{C}(\text{NO}_2)_3$. In addition, Figure 1 shows the comparison between the HOMO values of the designed compounds with same substituents but different bridged connections. The compounds with $-\text{C}=\text{C}$ -bridged connections were larger than those with other bridged connections. For the substituents $-\text{CN}$, $-\text{NO}_2$, $-\text{NH}_2$, $-\text{NHNO}_2$, and $-\text{NHNH}_2$, the HOMO value of the $-\text{N}-\text{N}$ -bridged compounds was the lowest. Moreover, for the substituents $-\text{N}_3$, $-\text{CH}(\text{NO}_2)_2$, and $-\text{C}(\text{NO}_2)_3$, the HOMO value of the $-\text{C}-\text{N}$ -bridged compounds was the lowest. For same bridging connections, the HOMO values of the compounds with different substituents were compared. We found that for different bridging connections, the HOMO value of the compounds with the substituent $-\text{NHNH}_2$ was the highest. Furthermore, the HOMO value for the compounds with the substituent $-\text{C}(\text{NO}_2)_3$ was the lowest. Therefore, our results indicate that the $-\text{NHNH}_2$ energetic group and $-\text{C}=\text{C}$ - bridge was the most effective combination for increasing the HOMO value of the designed compounds. For a same bridging connection, the LUMO values of the compounds with different substituents were compared. It was found that the LUMO value of the compounds was the highest when the substituent was $-\text{NHNH}_2$ (except $-\text{C}-\text{C}$ -) lowest when the substituent was $-\text{C}(\text{NO}_2)_3$. Hence, we believe that for the designed compounds, the $-\text{NHNH}_2$ and $-\text{C}(\text{NO}_2)_3$ energetic groups could increase and decrease the LUMO values, respectively. The energy gap values of the compounds with a same substituent but different bridging connections, that is, the stability of the compounds, were compared. When the substituents were $-\text{N}_3$, $-\text{NO}_2$, $-\text{NHNO}_2$, $-\text{NHNH}_2$, and $-\text{C}(\text{NO}_2)_2$, the $\Delta E_{\text{LUMO-HOMO}}$ value of the designed compounds connected by $-\text{N}-\text{N}$ - bridging was the largest. When the

substituents were $-\text{CN}$, $-\text{NH}_2$, and $-\text{NHNH}_2$, the $\Delta E_{\text{LUMO-HOMO}}$ value of the compounds connected by $-\text{N}=\text{N}-$ bridging was the lowest. Moreover, when the substituents were $-\text{N}_3$, $-\text{NO}_2$, $-\text{NHNO}_2$, $-\text{CH}(\text{NO}_2)_2$, and $-\text{C}(\text{NO}_2)_3$, the $\Delta E_{\text{LUMO-HOMO}}$ value of the compounds connected by $-\text{C}=\text{C}-$ bridging was the lowest. We can conclude that the $-\text{N}-\text{N}-$ bridge could increase the stability of the compounds, while the $-\text{C}=\text{C}-$ and $-\text{N}=\text{N}-$ bridges could decrease the stability of the compounds. The $\Delta E_{\text{LUMO-HOMO}}$ values of the compounds with same bridging connections but different substituents were compared. The $\Delta E_{\text{LUMO-HOMO}}$ values of the compounds with $-\text{N}_3$ substituent were the lowest. In the cases of $-\text{C}-\text{C}-$, $-\text{N}-\text{N}-$, and $-\text{C}-\text{N}-$ bridging connections, the $\Delta E_{\text{LUMO-HOMO}}$ values of the compounds with the substituent $-\text{CN}$ were the largest, thereby indicating that the $-\text{CN}$ energetic group is the best, while the energetic group $-\text{N}_3$ is the worst among the eight substituents in enhancing the stability of the compounds.

Table 1

Calculated E_{HOMO} and E_{LUMO} (eV) and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) of the designed compounds

Compd.	A1	A2	A3	A4	A5	A6	A7	A8
HOMO	-8.43	-6.65	-8.75	-5.70	-7.50	-5.42	-8.33	-8.85
LUMO	-3.12	-2.61	-3.96	-0.63	-2.88	-0.68	-4.06	-4.65
$\Delta E_{\text{LUMO-HOMO}}$	5.31	4.04	4.79	5.07	4.62	4.74	4.27	4.20
Compd.	B1	B2	B3	B4	B5	B6	B7	B8
HOMO	-7.77	-6.11	-7.80	-5.10	-6.79	-4.89	-7.51	-8.04
LUMO	-3.49	-2.65	-3.96	-0.73	-2.91	-0.56	-3.98	-4.50
$\Delta E_{\text{LUMO-HOMO}}$	4.28	3.46	3.84	4.37	3.88	4.33	3.53	3.54
Compd.	C1	C2	C3	C4	C5	C6	C7	C8
HOMO	-8.51	-6.69	-8.79	-5.91	-7.65	-5.68	-8.31	-8.84
LUMO	-3.24	-2.56	-3.87	-0.82	-2.74	-0.61	-3.94	-4.60
$\Delta E_{\text{LUMO-HOMO}}$	5.27	4.13	4.92	5.09	4.91	5.07	4.37	4.24
Compd.	D1	D2	D3	D4	D5	D6	D7	D8
HOMO	-8.46	-6.61	-8.64	-5.58	-7.27	-5.31	-8.35	-8.86
LUMO	-4.38	-2.84	-4.42	-1.60	-3.26	-1.40	-4.13	-4.61
$\Delta E_{\text{LUMO-HOMO}}$	4.08	3.77	4.22	3.98	4.01	3.91	4.22	4.25
Compd.	E1	E2	E3	E4	E5	E6	E7	E8
HOMO	-8.39	-6.74	-8.77	-5.80	-7.55	-5.48	-8.44	-8.89
LUMO	-3.17	-2.73	-3.93	-0.69	-3.07	-0.69	-4.28	-4.88
$\Delta E_{\text{LUMO-HOMO}}$	5.22	4.01	4.84	5.11	4.48	4.79	4.16	4.01
Compd.	F1	F2	F3	F4	F5	F6	F7	F8
HOMO	-8.19	-6.42	-8.41	-5.40	-7.13	-5.16	-7.99	-8.52
LUMO	-3.80	-2.81	-4.03	-0.98	-3.07	-0.81	-4.28	-4.88
$\Delta E_{\text{LUMO-HOMO}}$	4.39	3.61	4.38	4.42	4.06	4.35	3.71	3.64

2.2 Heats of formation

Heats of formation (HOF) is an indicator of energy content, which plays an important role in predicting the detonation characteristics of high-energy materials.²²⁻²⁵ Table 2 shows necessary data for the calculation of the HOF values, including total energies (E_0), thermal corrections (H_T), zero-point energies (ZPEs), molecular

properties, and HOF (ΔH_f) of the designed compounds. The gas-phase and solid-phase HOFs are expressed as $\Delta H_{f,gas}$ and $\Delta H_{f,solid}$, respectively. Figure 2 shows that the trends of $\Delta H_{f,gas}$ and $\Delta H_{f,solid}$ variations are coincident. According to calculations, the $\Delta H_{f,solid}$ values of the designed compounds were positive, and the $\Delta H_{f,solid}$ values ranged from 1035.4 (A7) to 2851.4 kJ mol⁻¹ (D2). The range of the $\Delta H_{f,solid}$ values fulfils our aim for designing the energetic materials.

It can be seen from Figure 2 that the compounds with same substituents but different bridging connections exhibit consistent changes in the HOF values. The HOF values for different bridging connections are in the following order: $-C-C- < -C=C- < -C-N- < -C=N- < -N-N- < -N=N-$. This proves that the HOF values of the compounds connected by the bridges containing N atoms were higher than those containing C atoms. The HOF values of the designed compounds were different when different substituents of the same bridge were attached. For the compounds linked by $-C=C-$, $-N=N-$, and $-C=N-$ bridges, the HOF values were in the following order: $-NH_2 < -CH(NO_2)_2 < -NO_2 < -C(NO_2)_3 < -NHNO_2 < -NHNH_2 < -CN < -N_3$. For the compounds linked by $-C-C-$ and $-C-N-$ bridges, the order of the HOF values was $-CH(NO_2)_2 < -NH_2 < -NO_2 < -C(NO_2)_3 < -NHNO_2 < -NHNH_2 < -CN < -N_3$. This shows that the $-N_3$ group was an excellent substituent for increasing the HOF of the designed compounds. In summary, for enhancing the HOF of a designed compound, the $-N=N-$ bridge and $-N_3$ substituent was the most effective combination, while the $-C-C-$ bridge and $-NH_2/-CH(NO_2)_2$ substituent was the most unfavourable combination.

Table 2

Calculated total energies (E_0), thermal corrections (H_T), zero-point energies (ZPE), molecular properties and heats of formation (ΔH_f) of the designed compounds

Compd.	$E_0(\text{a.u.})$	ZPE (kJ mol ⁻¹)	H_T (kJ mol ⁻¹)	$\Delta H_{f,gas}$ (kJ mol ⁻¹)	A (Å ²)	ν		ΔH_{sub} (kJ mol ⁻¹)	$\Delta H_{f,solid}$ (kJ mol ⁻¹)
							(kcal mol ⁻¹) ²		
A1	-1226.187475	475.4	58.2	1825.8	356.3	0.169	256.5	199.8	1626.0
A2	-1511.613309	520.7	69.0	2656.2	395.5	0.246	115.9	224.1	2432.1
A3	-1675.311254	515.1	66.8	1263.1	361.6	0.166	225.9	200.9	1062.2
A4	-1078.641448	673.9	54.2	1224.7	319.1	0.249	226.5	178.1	1046.6
A5	-1896.750323	695.4	78.8	1487.4	428.4	0.180	232.1	262.2	1225.2
A6	-1299.964997	853.1	66.4	1721.3	366.0	0.248	261.7	217.8	1503.5
A7	-2650.840866	838.7	108.9	1391.4	523.6	0.140	206.7	356.0	1035.4
A8	-3468.903380	843.9	137.9	1641.6	590.5	0.067	154.5	424.4	1217.2
B1	-1224.955055	411.6	57.0	1962.5	349.3	0.188	206.0	191.8	1770.7
B2	-1510.385246	457.5	67.6	2781.9	388.1	0.248	100.3	215.2	2566.7
B3	-1674.078428	451.0	65.7	1400.7	356.6	0.177	190.5	194.6	1206.1
B4	-1077.416035	610.9	52.8	1343.7	311.6	0.238	237.0	172.8	1170.9
B5	-1895.519808	631.5	77.8	1619.2	425.8	0.165	222.8	256.9	1362.3
B6	-1298.734184	788.4	66.4	1854.1	375.5	0.247	225.6	221.6	1632.5
B7	-2649.605741	774.2	108.2	1535.1	527.4	0.132	196.1	358.4	1176.7
B8	-3467.664624	778.8	135.3	1792.3	605.1	0.061	137.1	441.6	1350.7
C1	-1258.185010	412.9	57.0	2163.7	342.3	0.157	252.4	186.9	1976.8
C2	-1543.611802	458.8	67.4	2991.8	379.4	0.235	132.3	211.8	2780.0
C3	-1707.303688	451.3	65.8	1613.3	346.4	0.147	246.6	188.1	1425.2
C4	-1110.644111	613.9	51.3	1550.0	291.2	0.248	223.8	158.6	1391.4
C5	-1928.747634	633.0	77.5	1825.9	417.4	0.141	243.2	247.6	1578.3
C6	-1331.958767	790.3	65.2	2068.7	358.8	0.243	244.9	209.6	1859.1
C7	-2682.832056	775.9	107.6	1745.6	515.3	0.124	228.7	346.0	1399.6
C8	-3500.893770	780.7	137.2	1998.1	583.1	0.061	160.5	414.0	1584.1
D1	-1256.961111	346.5	55.9	2259.0	344.9	0.183	203.7	187.5	2071.5
D2	-1542.396997	392.4	66.4	3063.4	383.1	0.250	106.0	212.0	2851.4
D3	-1706.076650	383.5	65.6	1716.4	353.1	0.154	199.2	190.0	1526.4

D4	-1109.430268	544.7	52.4	1618.3	306.6	0.250	268.4	174.1	1444.2
D5	-1927.530190	565.9	77.0	1904.2	419.9	0.163	227.8	251.6	1652.6
D6	-1330.749987	722.9	65.7	2125.0	370.2	0.237	237.4	217.4	1907.6
D7	-2681.615258	709.2	106.9	1822.4	524.4	0.108	210.5	352.7	1469.7
D8	-3499.674889	713.9	136.6	2080.3	598.1	0.060	131.9	431.7	1648.6
E1	-1242.197528	444.4	57.5	1969.3	339.7	0.150	290.9	187.0	1782.3
E2	-1527.618116	489.4	68.5	2813.4	393.4	0.232	137.4	224.4	2589.0
E3	-1691.319732	484.0	65.9	1410.4	347.7	0.154	252.7	190.6	1219.8
E4	-1094.645999	642.1	54.2	1382.6	316.8	0.250	233.7	177.4	1205.2
E5	-1912.757343	664.8	78.2	1639.3	423.6	0.171	228.6	256.1	1383.2
E6	-1315.971047	821.2	66.4	1875.1	362.5	0.245	260.2	214.4	1660.7
E7	-2666.850234	808.2	107.9	1536.9	506.4	0.135	218.8	336.6	1200.3
E8	-3484.911244	813.0	137.5	1791.2	589.6	0.064	168.8	423.6	1367.6
F1	-1240.972421	379.8	56.4	2073.4	346.7	0.176	226.7	190.4	1883.0
F2	-1526.405296	425.7	66.9	2885.6	385.3	0.250	117.3	215.7	2669.9
F3	-1690.094136	418.6	65.0	1515.2	345.1	0.163	184.1	183.4	1331.8
F4	-1093.437138	578.7	52.5	1444.6	308.7	0.249	270.4	175.6	1269.0
F5	-1911.537762	599.4	77.3	1728.3	422.8	0.169	252.6	257.3	1471.0
F6	-1314.755070	756.2	66.0	1955.5	372.6	0.239	275.7	223.6	1731.9
F7	-2665.625925	742.6	107.4	1638.5	522.9	0.121	209.5	352.8	1285.7
F8	-3483.684797	747.2	137.1	1898.3	598.8	0.066	152.1	435.0	1463.3

2.3 Detonation properties

Table 3 shows the values of oxygen balance (OB), density (ρ), heat (Q), detonation velocity (D), detonation pressure (P), and impact sensitivity (h_{50}).^{26, 27} When the OB value is positive, oxygen is in surplus during the detonation process and consume a significant amount of energy. When the OB value is negative, oxygen cannot completely oxidize the energetic materials, which results in lower detonation performance. To highlight the properties of our synthetic materials, the data of RDX and HMX, which are the most classical explosives at present, were also listed in Table 3.

It can be seen in Table 3 that all the OB values of A8 (3.81%), B8 (1.91%), C3 (18.78%), C7 (16.92%), C8 (5.70%), D3 (15.09%), D5 (19.83%), D7 (14.55%), D8 (7.62%), E8 (0.95%), F7 (-20.64%), and F8 (2.86%) were

better than those of RDX and HMX (-21.6%). Among them, the OB values of A8, B8, C8, D8, E8, and F8 are closest to zero, which indicate that a compound burns fully when it contains $-\text{C}(\text{NO}_2)_3$. The values of ρ , Q , D , and P were in the ranges of 1.52 (A6) to 7.62 g cm⁻³ (D8), 822.82 (A4) to 1747.66 cal g⁻¹ (B8), 6.23 (A1) to 9.65 km s⁻¹ (D3), and 15.7 to 43.9 GPa (E8), respectively.

As shown in Figure 3, the substituent groups such as $-\text{N}_3$, $-\text{NO}_2$, $-\text{NHNO}_2$, $-\text{CH}(\text{NO}_2)_2$, and $-\text{C}(\text{NO}_2)_3$ can increase the density, detonation heat, detonation velocity, and detonation pressure of the designed compounds. In contrast, the substituent groups such as $-\text{CN}$, $-\text{NH}_2$, and $-\text{NHNH}_2$ can decrease these quantities. In Figure 3(a), it can be seen that for a compound with same substituent group but different bridging groups, the rule is $-\text{C}-\text{C}- < -\text{C}=\text{C}- < -\text{C}-\text{N}- < -\text{N}-\text{N}- < -\text{C}=\text{N}- < -\text{N}=\text{N}-$. This indicates that the bridging group $-\text{N}=\text{N}-$ can enhance the density of the designed compounds. Moreover, when the compounds are connected by the same bridge but have different substituents, the rule is $-\text{NHNH}_2 < -\text{NH}_2 < -\text{CN} < -\text{N}_3 < -\text{NHNO}_2 < -\text{NO}_2 < -\text{CH}(\text{NO}_2)_2 < -\text{C}(\text{NO}_2)_3$, which indicates that the $-\text{C}(\text{NO}_2)_3$ substituent can increase the density of the designed compounds. From Table 3, the change trend of Q is basically the same as ρ , and the combination $-\text{N}=\text{N}-/-\text{C}(\text{NO}_2)_3$ plays an essential role in enhancing the explosion heat. We can conclude from Figure 3(b) and (c) that different bridges have the same influence on D and P , that is, in the following order: $-\text{C}-\text{C}- \boxtimes -\text{C}=\text{C}- \boxtimes -\text{C}-\text{N}- \boxtimes -\text{C}=\text{N}- \boxtimes -\text{N}-\text{N}- \boxtimes -\text{N}=\text{N}-$ (except for the $-\text{C}(\text{NO}_2)_3$ energetic group). When the bridging connections are $-\text{C}-\text{C}-$, $-\text{C}=\text{C}-$, $-\text{N}-\text{N}-$, $-\text{C}-\text{N}-$, and $-\text{C}=\text{N}-$, the effect of different substituents on the designed compounds was in the following order: $-\text{CN} < -\text{NH}_2 < -\text{NHNH}_2 < -\text{N}_3 < -\text{NHNO}_2 < -\text{NO}_2 < -\text{CH}(\text{NO}_2)_2 < -\text{C}(\text{NO}_2)_3$. When the bridge was $-\text{N}=\text{N}-$, the effect of different substituents on the compounds was in the following order: $-\text{CN} < -\text{NH}_2 < -\text{NHNH}_2 < -\text{N}_3 < -\text{NHNO}_2 < -\text{CH}(\text{NO}_2)_2 < -\text{NO}_2 < -\text{C}(\text{NO}_2)_3$. The combination of $-\text{N}=\text{N}-$ and $-\text{C}(\text{NO}_2)_3$ can significantly affect the energy performance of the designed compounds and enhance their energy.

Figure 3(d) shows the comparison between the h_{50} values of the compounds with different substituents but same bridge. For the bridges $-\text{C}-\text{C}-$, $-\text{N}-\text{N}-$, and $-\text{C}-\text{N}-$, the h_{50} value of the compounds with the $-\text{NH}_2$ substituent was the highest. Furthermore, for the bridges $-\text{C}=\text{C}-$, $-\text{N}=\text{N}-$, and $-\text{C}=\text{N}-$, the h_{50} value of the compound with the $-\text{N}_3$ substituent was the highest. Besides, we found that the $-\text{C}(\text{NO}_2)_3$ substituent would decrease the h_{50} values of the designed compounds, while the $-\text{N}_3$ and $-\text{NH}_2$ substituents would increase the h_{50} values. The h_{50} values of the compounds with the $-\text{C}(\text{NO}_2)_3$ were the lowest. When the compounds were connected with same bridge but different substituents, the h_{50} values of the compounds bridged by $-\text{C}-\text{C}-$ were the highest, while those of the compounds bridged by $-\text{N}=\text{N}-$ were the lowest when the substituents were $-\text{NHNO}_2$, $-\text{NHNH}_2$, $-\text{CH}(\text{NO}_2)_2$, and $-\text{C}(\text{NO}_2)_3$.

In summary, six compounds (C3, C5, D3, D5, E3, and F3) were selected as candidates for energetic materials considering the detonation performance and impact sensitivity. For further analysis, their electronic structures, such as the FMO distribution and the electrostatic potential surface were simulated.

Table 3

Calculated oxygen balance (OB), densities (ρ), heats of detonation (Q), detonation velocities (D), detonation pressures (P) and impact sensitivity (h_{50}) of the designed compounds

Compound	OB ^a	ρ (g cm ⁻³)	Q (cal g ⁻¹)	D (km s ⁻¹)	P (GPa)	h_{50} /cm
A1	-120.93	1.56	1129.69	6.23	15.7	36.2
A2	-70.59	1.66	1424.69	7.74	25.3	55.5
A3	-37.74	1.83	1536.83	8.44	31.9	35.5
A4	-115.79	1.52	822.82	6.66	17.7	55.8
A5	-39.67	1.77	1471.33	8.32	30.4	38.8
A6	-105.49	1.52	987.19	7.26	21.0	55.7
A7	-29.09	1.85	1580.24	8.68	34.0	29.2
A8	-3.81	1.98	1715.55	9.52	42.5	11.8
B1	-116.96	1.59	1237.42	6.27	16.1	41.1
B2	-67.00	1.69	1510.94	7.80	26.0	56.0
B3	-34.12	1.86	1600.08	8.57	33.2	38.4
B4	-111.26	1.55	926.64	6.82	18.8	53.2
B5	-36.51	1.80	1532.06	8.46	31.7	35.3
B6	-101.66	1.53	1077.81	7.34	21.6	55.5
B7	-26.75	1.87	1619.99	8.77	34.9	27.4
B8	-1.91	1.99	1744.86	9.57	43.0	10.5
C1	-97.11	1.62	1365.48	6.89	19.7	33.2
C2	-50.73	1.72	1620.54	8.34	30.0	52.7
C3	-18.78	1.89	1709.98	9.12	38.0	30.8
C4	-88.89	1.60	1086.75	7.58	23.7	55.7
C5	-23.05	1.82	1616.75	8.91	35.4	29.2
C6	-83.06	1.57	1214.00	7.97	25.9	54.9
C7	-16.92	1.89	1690.68	9.13	38.0	25.3
C8	5.70	2.02	1635.27	9.62	43.9	10.3
D1	-93.02	1.65	1439.21	6.86	19.8	39.8
D2	-47.06	1.75	1670.31	8.34	30.4	56.5
D3	-15.09	1.92	1747.66	9.23	39.2	32.7
D4	-84.21	1.62	1135.41	7.59	23.9	55.9
D5	-19.83	1.85	1637.85	9.00	36.6	34.9

D6	-79.12	1.59	1252.52	7.99	26.2	53.1
D7	-14.55	1.90	1704.86	9.15	38.3	21.5
D8	7.62	2.03	1588.71	9.54	43.3	10.2
E1	-108.99	1.59	1234.70	6.54	17.6	31.2
E2	-60.64	1.69	1512.89	8.03	27.5	51.9
E3	-28.24	1.87	1609.16	8.79	35.1	32.5
E4	-102.30	1.55	944.40	7.08	20.2	56.1
E5	-31.34	1.80	1535.05	8.62	33.0	36.7
E6	-94.25	1.54	1087.42	7.58	23.1	55.1
E7	-23.00	1.87	1629.33	8.89	35.9	27.9
E8	0.95	2.00	1721.89	9.65	43.9	11.1
F1	-104.96	1.62	1312.06	6.53	17.7	38.0
F2	-57.00	1.72	1567.83	8.04	27.9	56.5
F3	-24.59	1.90	1654.58	8.91	36.3	35.0
F4	-97.69	1.59	1000.96	7.17	21.1	55.8
F5	-28.16	1.82	1562.54	8.69	33.7	36.1
F6	-90.36	1.56	1140.29	7.63	23.6	53.5
F7	-20.64	1.89	1648.89	8.96	36.6	24.5
F8	2.86	2.01	1684.36	9.59	43.5	11.6
RDX	-21.6	1.82	1590.7	8.75	34.0	28.0
HMX	-21.6	1.91	1633.9	9.10	39.0	32.0
^a For the explosive C _a H _b O _c N _d : OB = (c-2a-0.5b)/M _w , where M _w is the molecular weight.						

2.4 Electronic structures

To investigate the electronic structure and properties of these compounds, the LUMO–HOMO and electrostatic potential (ESP) orbitals were studied. Figure 4 shows the LUMO and HOMO distributions of the selected compounds (C3, C5, D3, D5, E3, and F3). It can be clearly seen that the LOMO and HOMO distributions of each compound are different. The LUMOs of C3, C5, and E3 were mainly distributed on the energetic groups and rings on one side, while those of D3, D5, and F3 were mainly distributed on the energetic groups and bridging structures. The HOMOs of C3, C5, D3, D5, and F3 were mainly distributed on the parent structure, while that of E3 was mainly distributed on the energetic group and ring on one side. The

$\Delta E_{\text{LUMO-HOMO}}$ values of the six screened compounds (C3, C5, D3, D5, E3, and F3) were in the range of 4.01 eV (D5) to 4.92 eV (C3), which were relatively stable. Therefore, we conclude that the compound C3 has the most stable structure.

The molecular surfaces of the six screened compounds were quantitatively analysed using the Multiwfn software, and then the distribution of the ESP was obtained using the VMD software. The molecular interactions and chemical reaction sites could be visualized on the ESP surface.²⁸⁻³⁰ Figure 5 shows the ESP analysis of the selected compounds (C3, C5, D3, D5, E3, and F3). In Figure 5, the positive and negative potentials are represented by red and blue colours, respectively. In addition, the area ratio of the positive and negative potentials is also provided. The positive potential was mainly distributed on the ring and the hydrogen atoms, while the negative potential was mainly distributed on the outer ring and the energetic groups. Global maximal ESPs of C3, C5, D3, D5, E3, and F3 were calculated as 62.05, 57.86, 44.86, 60.49, 62.69, and 45.12 kcal mol⁻¹, respectively. Moreover, all the global maximal ESPs of these compounds were distributed around the substituent group. The global minimal ESPs of the compounds C3, C5, D3, D5, E3, and F3 were calculated as -25.32, -30.40, -23.42, -31.16, -25.65, and -23.13 kcal mol⁻¹, and these ESPs were distributed around nitrogen of the heterocycle. Besides, there were more positive ESP regions than the negative ones, which suggests that it is a nucleophilic reaction.

Conclusion

In this study, the HOF, ρ , Q, D, P, and h_{50} of the designed compounds were calculated using density functional theory. The calculated results show that all the designed compounds have high positive values of HOF owing to their coplanar structures, which resulted in higher values of HOF of the designed compounds compared to RDX and HMX. Besides, we found that the combination of the $-\text{N}=\text{N}-$ bridge and $-\text{N}_3$ substituent was most effective in enhancing the HOF of the designed compounds. Our findings suggested that the combination of the $-\text{N}=\text{N}-$ bridge and $-\text{C}(\text{NO}_2)_3$ substituent was most effective in increasing the D and P values of the designed compounds. The $-\text{C}-\text{C}-$ bridge and $-\text{N}_3/-\text{NHNH}_2$ substituents were most effective increasing the impact sensitivity of the designed compounds. By comparing the detonation performance (D and P) and impact sensitivity, six compounds (C3, C5, D3, D5, E3, and F3) with excellent overall performance and great potential for military applications were screened.

Declarations

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Conflicts of interest/Competing interests

The authors declare that they have no conflict of interest.

Ethical approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Availability of data and materials

The data sets supporting the results of this article are included within the article and its additional files.

Code availability

Not applicable.

Authors Contribution

The authors: X. H. Jin, L. H. Liu, J. H. Zhou, B. C. Hu, contribute equally to this paper.

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Figures

Figure 1

E_{HOMO} , E_{LUMO} and $\Delta E_{LUMO-HOMO}$ of the designed compounds.

Figure 2

$\Delta H_{f,solid}$ of the designed compounds.

Figure 3

ρ , D , P and h_{50} of the designed compounds.

Figure 4

Distribution of FMOs of the selected compounds.

Figure 5

ESP and ratios of positive and negative potentials.

Figure 6

Scheme 1. RDX, HMX and cl-20 structures

Figure 7

Scheme 2. The designed high energy materials based on pyrazolo[3,4-d][1,2,3] triazole

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