Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Check for updates

Cite this: J. Mater. Chem. A, 2020, 8, 4193

Fused heterocycle-based energetic materials (2012–2019)

Haixiang Gao, *[a] Qinghua Zhang *[b] and Jean'ne M. Shreeve *[c]

Received 19th November 2019
Accepted 6th February 2020

DOI: 10.1039/c9ta12704f

rsc.li/materials-a

Fused cyclic energetic materials, a unique class of large conjugate structures which contain two or more rings that share two atoms and the bond between the rings, have been identified as promising contenders to traditional energetic materials. With a coplanar polycyclic structure, fused heterocyclic ring-based energetic materials feature considerably higher heats of formation (HOF) and ring-strain energy stored in the molecules. These result in attractive features of good energetic performance, enhanced thermal stability and low sensitivity toward destructive mechanical stimuli, which increases the safety of the synthesis, transfer, and storage of high-energy density compounds. This review addresses the chemistry of fused heterocyclic compounds, which provide valuable scaffolds for more powerful and less sensitive eco-friendly energetic materials. The reactions that are selected and discussed illustrate the versatility of 64 different fused heterocycles designed as building blocks for the synthesis of a wide range of high-performance energetic materials.

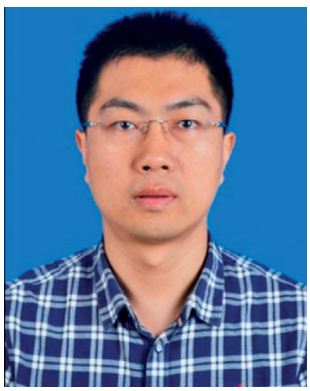
Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Introduction

Among energetic materials, traditional chemical explosives, such as black powder, potassium nitrate, ammonium perchlorate, nitroglycerine, and 2,4,6-trinitrotoluene (TNT), specifically represent the most influential materials in human history and have gained much attention in the chemical sciences. Trinitrotoluene (TNT) was first synthesized in 1863, which makes it one of the oldest and most commonly used explosives for industrial, mining and military applications. It is valued partly because of its insensitivity to mechanical stimuli; however, it is less powerful than the alternatives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX) (Table 1). TNT is considered the standard measure of strength for other explosives and RDX and HMX are

[a]Department of Applied Chemistry, China Agricultural University, Beijing 100193, China. E-mail: hxgao@cau.edu.cn
[b]Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China. E-mail: qinghuazhang@caep.cn
[c]Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, USA. E-mail: jshreeve@uidaho.edu

Haixiang Gao earned his PhD in 2002 from the Lanzhou Institute of Chemical Physics of the Chinese Academy of Sciences. He was a postdoctoral fellow at the Institute of Chemistry, CAS (2002–04) with Professor Buxing Han and at the University of Idaho (2004–07) with Professor Jean'ne M. Shreeve. Since 2007 he has been a faculty member at the China Agricultural University. His main scientific interests include the design and synthesis of ionic liquids (salts) and their application in the area of energetic materials or green chemistry.



Qinghua Zhang was born in Shandong (China) in 1979. He received his PhD in physical chemistry from the Chinese Academy of Sciences (China) in 2008. From 2010–2012, he worked as a CNRS associate researcher at the Poitiers University (France). From 2012–2013, he joined the group of Prof. Jean'ne M. Shreeve as a postdoctoral fellow at the University of Idaho, ID. Since 2014, he has served as a professor at the Institute of Chemical Materials, China Academy of Engineering Physics. His research interests include the synthesis of new high energy-density materials. He has published more than 100 papers in peer-reviewed journals.

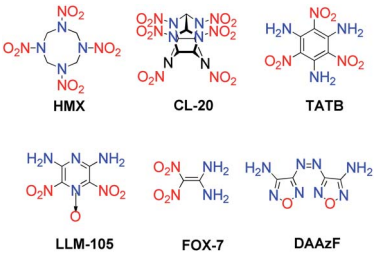
Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

considered as powerful chemical explosives and the benchmark for current HDEMs (High Density Energetic Materials) (Table 1). 2,4,6-Triamino-1,3,5-trinitrobenzene (TATB), a powerful explosive (somewhat more powerful than TNT but less than RDX), and one which is extremely insensitive to shock, vibration, fire, or impact. Hexanitrohexaazaisowurtzitane, also known as HNIW or CL-20, is more powerful than traditional HMX-based propellants, and is widely superior to conventional high-energy propellants and explosives.

The chemistry of energetic materials has been successfully explored. In the synthesis of energetic compounds, diverse backbones, such as aromatic, aliphatic, caged carbon and heterocyclic frameworks, have been selected. Usually, the backbone is used as fuel, and has no explosive properties. Explosophoric groups (*e.g.*, $-NO_2$, $-ONO_2$, N_3, $-N{=}N-$, N-oxide and NF_2, *etc.*) and moieties (*e.g.*, $NHNO_2$, $-C(NO_2)_3$, $-C(NO_2)_2H$, and $N(O){=}NNO_2$, among others) that can be covalently or ionically attached to the backbone of a molecule provide the energy.[2] With these groups, the oxidation of the C and H atoms by the O atoms in the molecules generates carbon mono- or dioxide and water to release the chemical energy that is stored in the core.[3]

Although many of the classical energetic materials are still effective, given the growing demand for high energy density materials (HEDMs) as propellants, explosives, and pyrotechnics with improved detonation performance for military and civilian applications, the design and synthesis of new HEDMs that contain a backbone with highly energetic functionalities are a key goal in their discovery and development.[4,5]

In general, the various strategies developed for introducing more of the highly energetic functional groups are capable of improving the detonation properties of the target molecules. However, in addition to detonation properties, molecular stability is also a primary criterion for evaluating the overall performance of energetic materials. Energetic properties (detonation velocity and pressure), stability and sensitivity of HEDMs are often observed to be inversely related. Modern HEDMs still have several drawbacks, including low stability and high sensitivity because of their high energy content. For example, HMX and CL-20 are high-performance explosives, but they are more sensitive than and lack the stability of well-known insensitive explosives such as TATB, 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 1,1-diamino-2,2-dinitroethene (FOX-7) and 3,3′-diamino-4,4′-azofurazan (DAAzF) (Scheme 1). Therefore, an accurate understanding of the relationship between molecular structure and energetic and physical properties and of the trade-off between the high energetic performance of an explosive and its good stability is essential for designing and developing effective methods to synthesize the next generation of HEDMs.



Scheme 1 Structures of some known energetic materials.

To achieve an ideal combination of high detonation pressure and velocity, good stability (high thermal stability and low sensitivity) and environmentally friendly decomposition gases, chemists around the world have made significant efforts that have resulted in the generation of superior HEDMs *via* the construction of strained ring or cage systems, nitrogen-rich compounds, energetic salts, cocrystals, metal–organic frameworks and molecular perovskite high-energetic materials, among others.[3,5–7]

Recently, fused cyclic energetic materials, a unique class of large conjugate structures containing two or more rings that share two atoms and the bond between the rings, have been identified as promising contenders to traditional energetic materials. Fused heterocyclic ring-based energetic materials with a coplanar polycyclic structure exhibit considerably higher heats of formation (HOF) and ring-strain energy stored in the molecules and show obvious characteristics of good energetic performance, enhanced thermal stability and low sensitivities toward destructive mechanical stimuli which increases the safety of the synthesis, transfer, and storage of HEDMs.[8,9] Thus far, the limited number of fused cyclic backbones available for the preparation of different molecules has hindered their expansion in the field of HEDMs. Therefore, this research area is attracting attention, since it is particularly interesting to study these systems in order to develop various types of new HEDMs with satisfactory detonation properties and sensitivity properties.

This review covers the most recent progress in the field of fused cyclic energetic materials since 2012. The fused ring systems are divided into four parts based on the number and type of rings found in the backbone. Five reference compounds are used for comparison purposes (TNT, TATB, RDX, HMX, CL-20), all the data (density, heat of formation, detonation pressure

Jean'ne M. Shreeve is a Montana native. She received a BA in chemistry at the University of Montana, an MS in analytical chemistry at the University of Minnesota, and a PhD in inorganic chemistry at the University of Washington, Seattle. She has been at the University of Idaho since 1961 where she has served as chemistry department head and vice president for research and graduate studies. In 2011, Shreeve was named a University Distinguished Professor. Her research interests include the design, syntheses, characterization, and reactions of energetic materials, fluorine-containing compounds, and energetic ionic liquids.

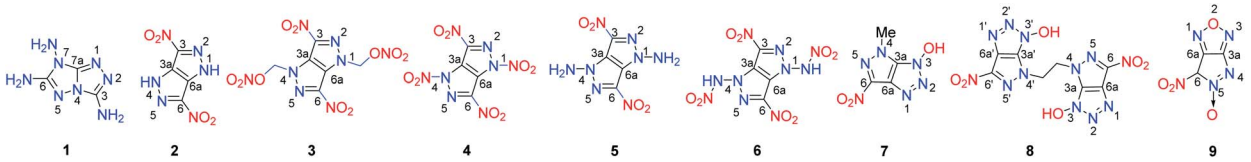
This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

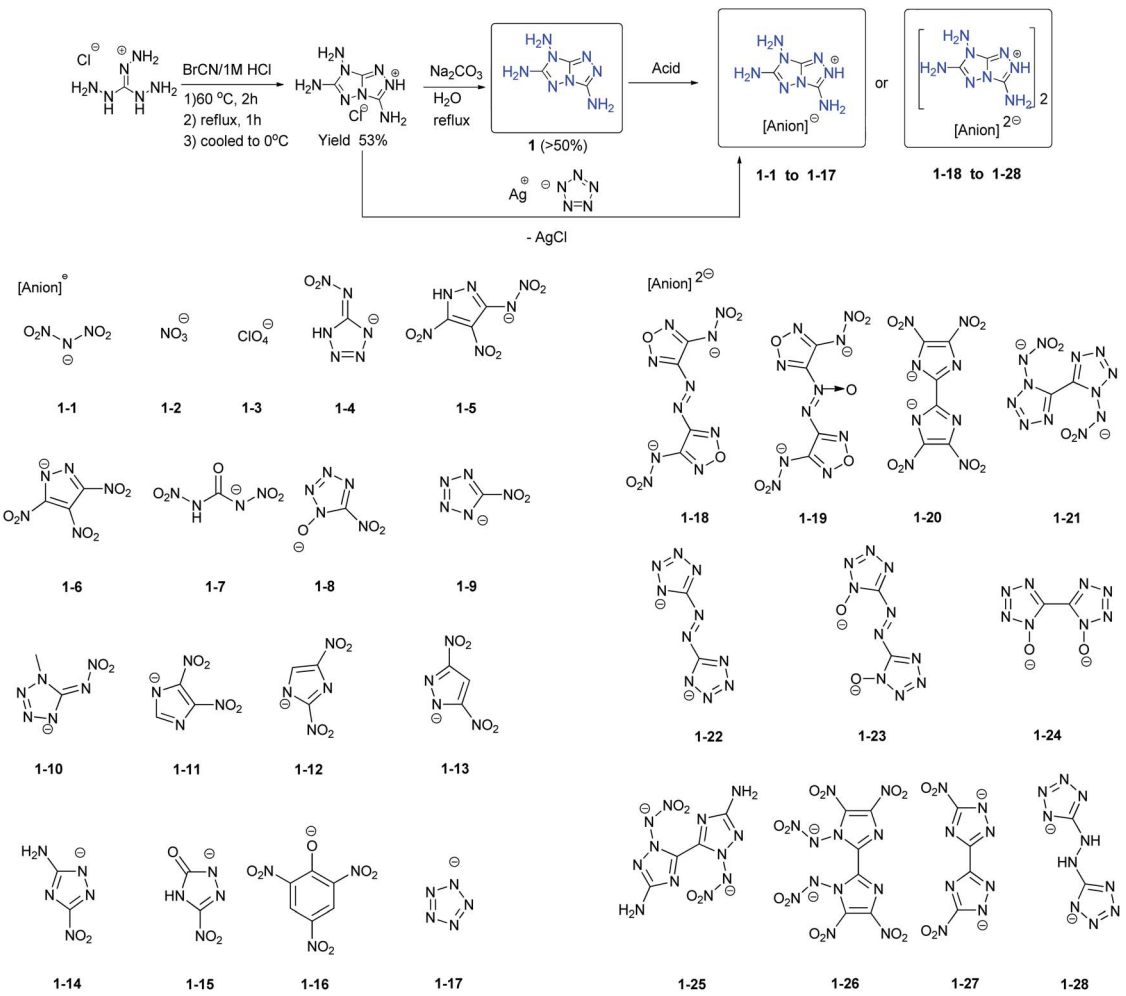
Table 1 Physicochemical and energetic properties of 5 known energetic compounds

No.	T_m[a], °C	T_d[b], °C	d[c], g cm^{-3}	D[d], m s^{-1}	P[e], GPa	HOF[f], kJ mol^{-1}/kJ g^{-1}	OB[g], %	IS[h], J	FS[i], N	Ref.[j]
TNT	81	295	1.65	7303	21.3	−59.3/−0.26	−73.97	15	353	1
TATB	350	~360	1.94	8544	32.1	−154.2/−0.60	−55.78	50	360	1
RDX	205	210	1.80	8795	34.9	70.7/0.32	−21.61	7.5	120	1
HMX	—	280	1.91	9144	39.2	74.8/0.25	−21.61	7	120	1
CL-20	—	210	2.04	9706	45.2	397.8/0.91	−10.95	4	94	1

[a] Melting point. [b] Decomposition temperature (onset). [c] Density. [d] Detonation velocity (calculated). [e] Detonation pressure (calculated). [f] Heat of formation (calculated). [g] Oxygen balance (based on CO_2) for $C_aH_bO_cN_d$, 1600 $(c–a–b)$/MW; MW = molecular weight. [h] Impact sensitivity. [i] Friction sensitivity. [j] Reference. All the quantity symbols are used in all the tables in this review.



Scheme 2 [5,5]-Bicyclic heterocyclic energetic materials.



Scheme 3 Synthesis of 1 and its salts.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

and detonation velocity) (Table 1) are from the EXPLO 5 (Version 6.01).[1] It is hoped that the review will provide an overview of the fundamental methodology of building fused heterocyclic rings and introducing "explosophoric" groups into them to design and synthesize new HEDMs while concomitantly addressing aspects such as stability, detonation performance and providing a comprehensive comparison and discussion that will certainly stimulate further studies.

[5,5]-Bicyclic heterocyclic energetic materials

[5,5]-Bicyclic heterocycles are the simplest fused rings for building molecules of energetic materials. In recent years, several [5,5]-bicyclic heterocycle-fused energetic materials were synthesized (Scheme 2). As is the case for other fused ring compounds, the construction of the backbone is the first step in obtaining new energetic materials. 3,6,7-Triamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole (**1**) is a bis-triazole fused heterocyclic ring with three amino groups on its backbone which is synthesized readily through the cascade cyclization of cyanogen bromide with triaminoguanidinium chloride followed by alkalization with Na_2CO_3 (Scheme 3). Recently, by reaction with selected energetic acids, a series of energetic salts containing the 3,5,7-triamino-7*H*-*s*-triazolo[5,1-*c*]-*s*-triazolium cation were prepared.[8–10] The calculated detonation velocities and pressures of **1** and its salts fall in the range of 8052–9477 m s^{-1} and 24.1–33.9 GPa, respectively (Table 2). Most of their performance levels are comparable to those of RDX with respect to thermal stability, detonation properties and sensitivity. Their performance arises mainly because the three amino groups on the rings facilitate the formation of extensive intermolecular hydrogen bonds between the cation and anion in its salts.

Among these molecules, compounds **1-21**, **1-22** and **1-27** are the most promising candidates for potential applications as HEDMs. These salts combine good stability with excellent explosive properties (D > 9200 m s^{-1} and P > 30 GPa), all of which meet the required criteria for mechanical (IS = 7.5 J, FS > 120 N) or thermal (T_d > 200 °C) stimuli. These studies demonstrate that **1** and its energetic salts involve a ready synthetic route, good stability toward thermal and mechanical stimuli, and high energetic performance making them promising energetic building blocks for designing new HEDMs.

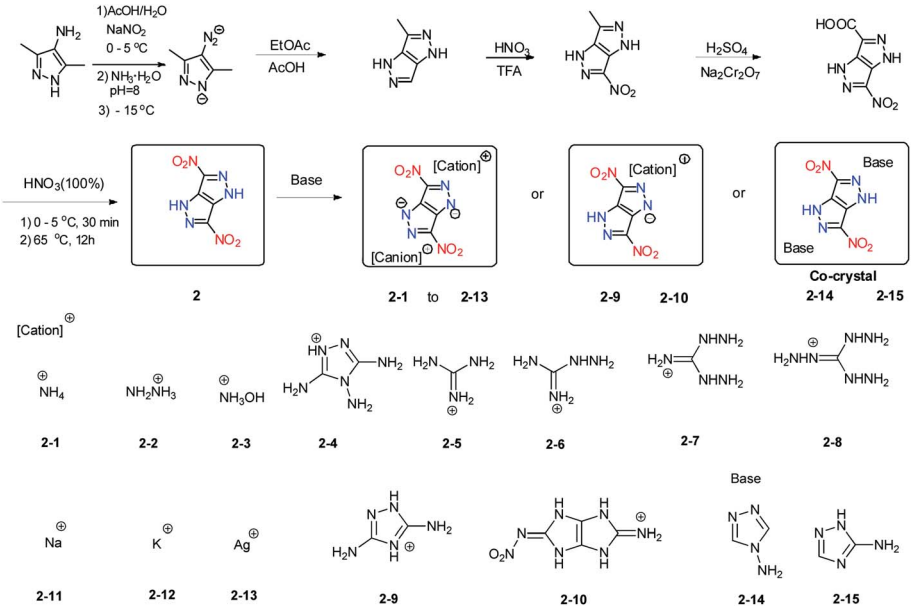
3,6-Dinitropyrazolo[4,3-*c*]pyrazole (**2**) is an attractive energetic material with low sensitivity to external mechanical stimuli and favourable thermal stability because it has a stable fused ring backbone. It was synthesized through a modified synthesis process with enhanced efficiency and reproducibility (Scheme 4).[11] Due to the acidity of **2**, it is straightforward to synthesize a series of its energetic salts (**2-1** to **2-13**) through either neutralization or metathesis reactions (Scheme 4).[11,12] Compound **2** and its salts exhibit outstanding thermal stabilities (209–395 °C). The densities of the salts of **2** fall in the range between 1.66 and 2.20 g cm^{-3}, which places

Table 2 Physicochemical and energetic properties of **1** and its salts

No.	T_m, °C	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
1	—	251	1.73	8580	25.9	470.5/3.06	−93.43	40	360	13
	—	245	1.73	9385	29.7	446.7/2.90		40	360	8
1-1	—	199	1.82	9090	33.9	463.3/1.78	−33.7	6	160	13
1-2	—	279	1.78	8765	29.7	274.5/1.26	−47.89	40	360	13
	—	280	1.78	9005	30.2	261.5/1.20		40	360	8
1-3	—	257	1.77	8216	28.1	325.9/1.28	−31.42	15	240	13
	—	264	1.78	8312	28.1	314.6/1.24		9	216	8 and 13
1-4	—	226	1.73	8618	27.9	763.7/2.69	−56.30	10	240	13
1-5	—	211	1.80	8704	31.3	666.0/1.79	−42.99	25	240	13
1-6	—	208	1.74	8365	28.3	582.9/1.63	−42.55	40	360	13
1-7	—	167	1.81	8881	32.3	424.4/1.39	−36.82	6	120	13
1-8	—	222	1.73	8814	29.0	691.7/2.43	−47.69	25	360	8
1-10	—	237	1.65	8760	26.9	783.9/2.63	−69.74	8	360	8
1-11	—	207	1.71	8189	24.7	446.8/1.43	−61.49	22	—	14
1-12	152	226	1.70	8113	24.1	422.4/1.35	−61.49	>40	—	14
1-13	120	246	1.72	8286	25.4	490.0/1.57	−61.49	35	—	14
1-14	218	232	1.68	8549	25.6	561.9/1.98	−70.62	>40	—	14
1-15	—	256	1.70	8232	24.2	353.0/1.24	−61.93	>40	—	14
1-16	—	278	1.79	8162	25.9	191.6/0.50	−64.71	15	—	14
1-17	—	121	1.62	7791	24.6	853.8/3.79	−71.1	>40	>360	15
1-18	—	243	1.73	8052	24.0	867.7/1.46	−56.53	10	120	13
1-19	—	246	1.80	8457	27.6	918.8/1.51	−52.42	8	120	13
1-21	—	224	1.76	9242	32.0	1845.5/3.26	−53.67	7.5	108	8
1-22	—	200	1.72	9360	30.7	1811.8/3.82	−77.57	20	360	8
1-23	—	210	1.73	9289	31.5	1834.1/3.62	−66.35	30	360	8
1-25	185	200	1.71	8977	29.0	1674.0/2.82	−67.29	30	360	10
1-26	—	203	1.85	8899	33.8	1455.2/1.96	−40.95	10	120	16
1-27	—	311	1.75	8718	27.7	1208.2/2.26	−68.86	30	—	14
1-28	—	219	1.74	9477	31.4	1138.0/3.53	−80.60	>40	—	14

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 4 Synthesis of **2** and its energetic salts.

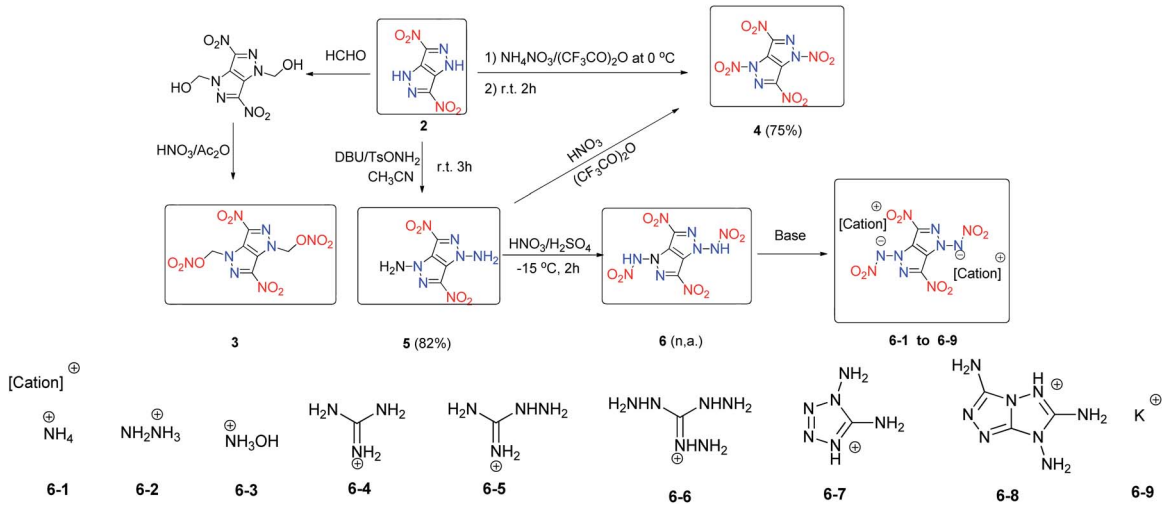
them in a class of relatively dense HEDMs. Their detonation velocities (7948–9005 m s^{-1}) and detonation pressures (22.5–35.4 GPa) are comparable to those of TNT and RDX. Most of the salts have acceptable friction sensitivities (80 to 360 N) and impact sensitivities (12 to >40 J) (Table 3). In studying the reactions of **2** with 3-amino-1,2,4-triazole and 4-amino-1,2,4-triazole, two energetic cocrystals composed of **2** and 3-amino-1,2,4-triazole (**2-14**) or 4-amino-1,2,4-triazole (**2-15**), respectively, with a molar ratio of 1 : 2 were obtained.[11] The amino groups in 3-amino-1,2,4-triazole and 4-amino-1,2,4-triazole are able to provide sufficient hydrogen bond donor character driving them to cocrystallization with **2**. Compared to **2**, cocrystals **2-14** and **2-15** have comparable explosive power and low sensitivities to impact and friction. These features make the salts and cocrystals of **2** potentially useful candidates for further investigation as thermally stable and insensitive HEDMs.

In addition to the production of energetic salts from **2**, modification of the compounds is also a facile way to generate new energetic materials. A series of derivatives of **2** were synthesized by using versatile *N*-functionalization strategies (Scheme 4).[17] In that study, treating **2** with formaldehyde under acidic conditions gave the *N*,*N*′-dihydroxymethyl intermediate, and after nitration by using fuming HNO_3 and acetic anhydride 3,6-dinitropyrazolo[4,3-*c*]pyrazole-1,4-dinitrate (**3**) was obtained. *N*-nitration of **2** by NH_4NO_3 in trifluoroacetic anhydride gave 1,3,4,6-tetranitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole and Table 2 (**4**) was obtained in good yield by the amination of **2** with

Table 3 Physicochemical and energetic properties of **2** and its salts

No.	T_m, °C	T_d, °C	*d*, g·cm^{-3}	*D*, m·s^{-1}	*P*, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
2	—	336	1.85	8250	27.4	322.6/1.94	−40.38	15	160	12
2-1	160	328	1.69	8212	25.4	133.7/0.38	−55.13	> 40	360	12
2-2	174	327	1.82	9005	35.4	550.9/1.92	−54.92	29	360	12
2-3	—	247	1.72	8860	30.3	467.0/2.04	−36.34	16	160	12
2-4	—	287	1.71	8036	24.5	595.2/1.87	−71.31	> 40	360	12
2-5	—	289	1.67	8230	24.6	423.1/1.20	−70.83	> 40	360	12
2-6	318	324	1.68	7948	22.5	738.9/1.93	−69.31	> 40	360	12
2-7	213	222	1.69	8400	25.6	531.2/1.38	−68.03	> 40	360	12
2-8	—	209	1.71	8732	28.0	454.7/1.04	−66.94	> 40	360	12
2-9	208	215	1.76	8814	29.9	692.9/1.49	−51.14	12	80	12
2-10	—	238	1.79	8355	27.9	1144.8/2.17	−56.66	23	160	12
2-11	—	395	2.14	—	—	1683.3/3.25	−26.44	14	160	12
2-12	—	365	2.20	—	—	1599.5/2.56	−23.33	> 40	160	12
2-13	—	327	3.27	—	—	152.9/0.43	−15.54	29	160	12
2-14	252	282	1.70	8024	23.9	322.6/1.94	−74.26	>40	>360	11
2-15	231	284	1.68	8234	25.6	133.7/0.38	−74.26	>40	>360	11

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 5 Synthesis of **2** to **6** and energetic salts of **6**.

O-tosylhydroxylamine ($TsONH_2$). Nitration of **5** gave 1,3-dinitramino-4,6-dinitro-1,4-dihydropyrazolo-[4,3-*c*]pyrazole (**6**) (Scheme 5).[17] In addition, a series of energetic salts (**6-1–6-9**) was prepared by treating **6** with a variety of bases. Compounds **4**, **6**, and **6-3** exhibit high densities and excellent detonation properties (Table 4), which surpass those of HMX. Compared with **2**, compounds **4** and **6** also have higher oxygen balances and densities, highlighting their application potential as energetic oxidizers. The potassium salt **6-9** is a competitive compound as a green primary explosive since it is very sensitive but has good density and thermal stability (Table 4). All of these compounds exhibit good physical and detonation properties and can be variously classified as green primary explosives, fuel-rich propellants, secondary explosives, or propellant oxidizers.

A novel fused backbone, pyrazolo[3,4-*d*][1,2,3]triazole, was synthesized by treating a chloro-substituted nitropyrazole with hydrazine hydrate in a one-pot procedure and then 3-hydroxy-4-methyl-6-nitro-pyrazolo[3,4-*d*][1,2,3]triazole (**7**) (Scheme 6) can be obtained accordingly.[18] Although dinitropyrazole derivatives are considered attractive energetic materials due to their good physical and detonation properties, molecules comprised of a triazole ring fused with a pyrazole ring are relatively rare. In a further study of this reaction, 1,2-bis(4-chloro-3,5-dinitro-1*H*-pyrazol-1-yl)ethane was chosen as the precursor, and 4,4′-(ethane-1,2-diyl)bis(6-nitropyrazolo[3,4-*d*][1,2,3]triazole) (**8**) was synthesized *via* a similar cyclization reaction as **7**. In addition, the energetic salts **7-1** to **7-6** and **8-1** to **8-7** were prepared through metathesis reactions. These salts exhibit good detonation properties with relatively low sensitivities. The overall energetic evaluation highlights the fused pyrazolo[3,4-*d*][1,2,3]triazole ring as a useful framework for building advanced HEDMs (Table 5).

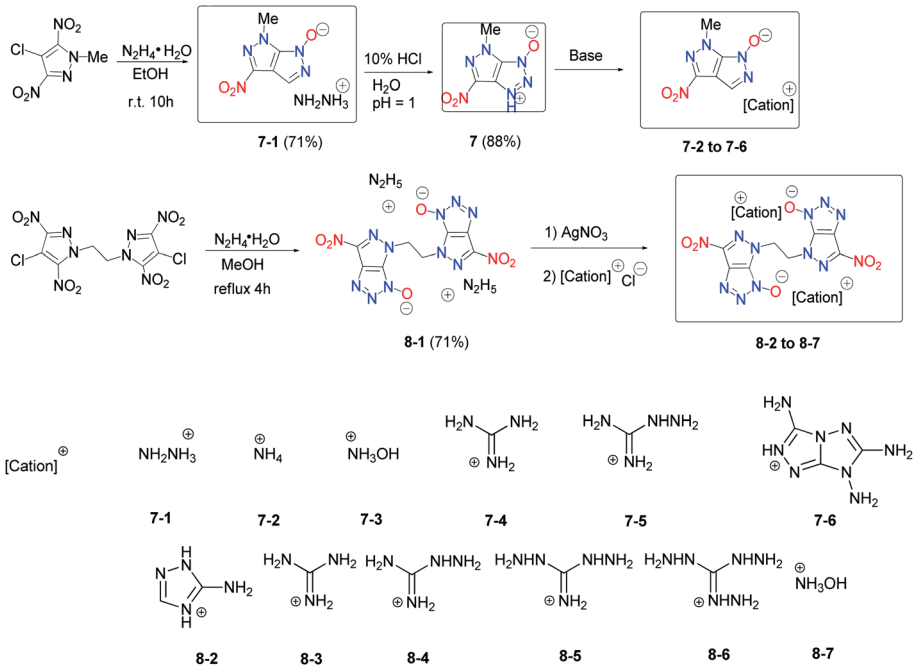
Compounds **1** to **8** are all azole-based [5,5]-bicyclic heterocycles. The addition of a furazan group to the fused ring should improve the oxygen balance and increase the heat of formation of the energetic materials. To date, limited furazan-containing [5,5]-bicyclic heterocyclic energetic materials were reported. By nitration of adjacent chlorohydroximoyl and amino groups followed by KI reduction, the potassium salt of 6-nitro-6*H*-pyrazolo[3,4-*c*]furazan-5-oxide (**9-1**) was synthesized (Scheme 7).[19] Neutral

Table 4 Physicochemical and energetic properties of compounds **3** to **6** and energetic salts of **6**

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
2	336	1.85	8250	27.4	322.6/1.94	−16.2	15	160	17
3	206	1.82	8674	33.1	133.7/0.38	−18.38	10	120	17
4	145	1.95	9460	40.9	550.9/1.92	0.00	3	20	17
5	230	1.84	8864	33.9	467.0/2.04	−42.08	7	120	17
6	128	1.93	9507	41.8	595.2/1.87	−5.03	2	20	17
6-1	181	1.81	8977	35.9	423.1/1.20	−18.17	10	120	17
6-2	174	1.85	9399	39.5	738.9/1.93	−20.93	5	60	17
6-3	170	1.88	9495	41.3	531.2/1.38	−8.33	7	120	17
6-4	190	1.68	8295	26.9	454.7/1.04	−36.67	35	360	17
6-5	153	1.71	8612	29.3	692.9/1.49	−37.74	30	360	17
6-6	141	1.70	8884	30.8	1144.8/2.17	−39.52	10	80	17
6-7	163	1.78	9166	36.0	1683.3/3.25	−27.78	5	60	17
6-8	203	1.83	8993	33.1	1599.5/2.56	−48.53	10	120	17
6-9	208	2.11	8306	31.2	152.9/0.43	0.00	2	20	17

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 6 Synthesis of 7 and energetic salts 7-1 to 7-6 and 8-1 to 8-7.

compound **9** containing the fused pyrazolo[3,4-*c*]furazan N-oxide was obtained *in situ* (not isolated) by acidifying **9-1**. Subsequently, the energetic salts **9-2** to **9-9** were obtained with excellent detonation properties (D = 9174 m s^{-1} and P = 39.1 GPa) but are highly sensitive to impact and friction. Therefore, **9-3** is a potential candidate for use as a primary explosive. Additionally, **9-6** and **9-9** are promising with respect to their detonation properties, thermal stability and sensitivity to impact (Table 6).

[5,6]-Bicyclic and [6,6]-bicyclic heterocyclic energetic materials

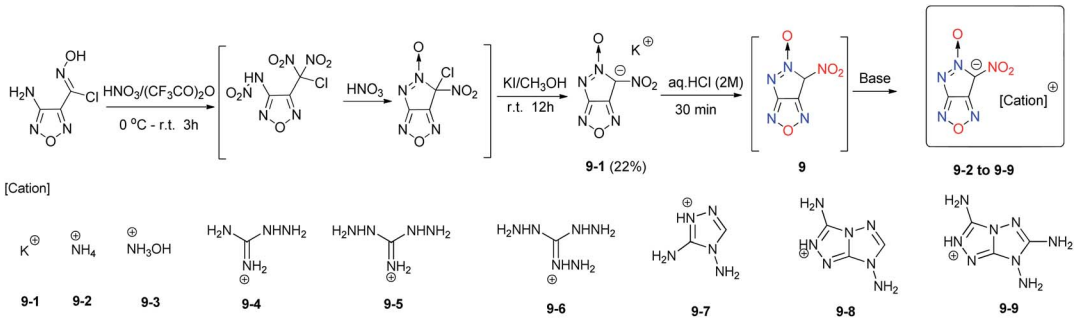
In contrast to [5,5]-bicyclic heterocyclic energetic materials, energetic materials with [5,6]-bicyclic and [6,6]-bicyclic heterocyclic backbones feature a 6-membered ring that can either increase the nitrogen content or provide positions where additional energetic functional groups can be introduced. Approximately 30 [5,6]-bicyclic and [6,6]-bicyclic heterocyclic energetic materials were found (Scheme 8).

A promising approach for the synthesis of 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazine 2-oxide (**10**) was suggested.[20] The proposed pathway for the formation of the fused ring of [1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazine involves the cleavage of a tetrazole ring and the cyclization of a C–N bond with a nitro group (Scheme 9). Compound **10** is highly hygroscopic, but this limitation was overcome by transforming it into its energetic salts **10-1** to **10-6** through neutralization reactions. The densities of these salts fall between 1.77 to 1.97 g cm^{-3}.

Table 5 Physicochemical and energetic properties of compounds 7 and energetic salts 7-1 to 7-6 and 8-1 to 8-7

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
7	101	1.70	8183	27.6	414.4/2.25	−60.83	6	—	18
7-1	146	1.71	8724	30.9	549.6/2.54	−85.51	8	—	18
7-2	144	1.67	8341	26.3	393.1/1.96	−87.93	15	120	9
7-3	112	1.76	8859	31.9	439.4/2.02	−74.02	8	120	9
7-4	192	1.62	7911	22.5	371.0/1.53	−92.49	40	360	9
7-5	181	1.64	8196	24.3	485.3/1.88	−90.20	25	240	9
7-6	188	1.74	8519	27.5	916.4/2.71	−87.77	15	160	9
8-1	122	1.69	8570	28.2	1096.3/2.55	−63.24	6	80	9
8-2	85	1.70	8115	24.9	1254.9/2.35	−74.85	20	160	9
8-3	155	1.63	7865	22.4	774.4/1.27	−72.67	40	360	9
8-4	162	1.61	7979	23.0	1021.4/1.99	−71.54	15	240	9
8-5	143	1.65	8344	25.6	1257.7/2.31	−70.53	25	360	9
8-6	168	1.66	8526	26.7	1452.0/2.53	−69.63	30	360	9
8-7	101	1.75	8698	31.3	881.9/2.04	−51.82	10	160	9

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

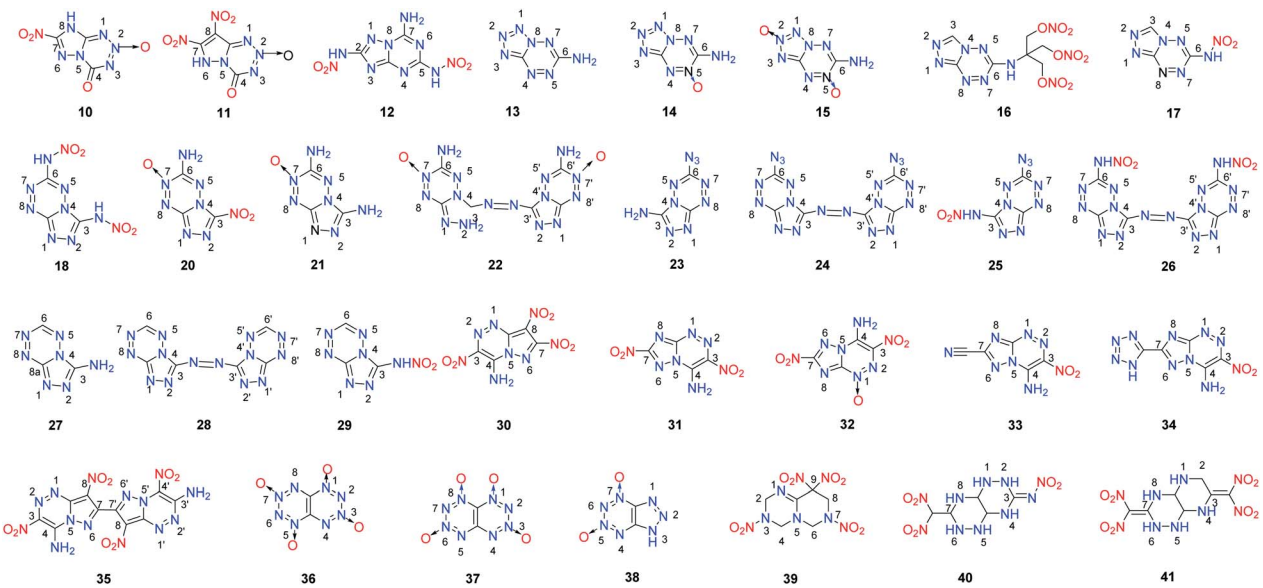


Scheme 7 Synthesis of **9** and its energetic salts.

Table 6 Physicochemical and energetic properties of compounds **9** and its energetic salts

No.	T_m, °C	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
9-1	—	175	2.04	7973	28.6	159.0/0.76	−15.30	2	40	19
9-2	—	179	1.80	8777	33.6	285.9/1.52	−34.02	3	60	19
9-3	—	152	1.87	9174	39.1	336.8/1.65	−23.52	2	40	19
9-4	—	163	1.69	8343	27.2	375.1/1.53	−48.95	12	120	19
9-5	106	131	1.75	8741	30.0	478.7/1.84	−49.20	10	120	19
9-6	119	141	1.76	8957	31.6	591.7/2.15	−49.42	15	240	19
9-7	151	153	1.77	8545	29.2	351.6/1.22	−53.30	18	240	19
9-8	105	164	1.76	8540	29.1	630.2/1.92	−56.74	15	240	19
9-9	—	186	1.81	8741	30.8	809.7/2.49	−56.58	20	360	19

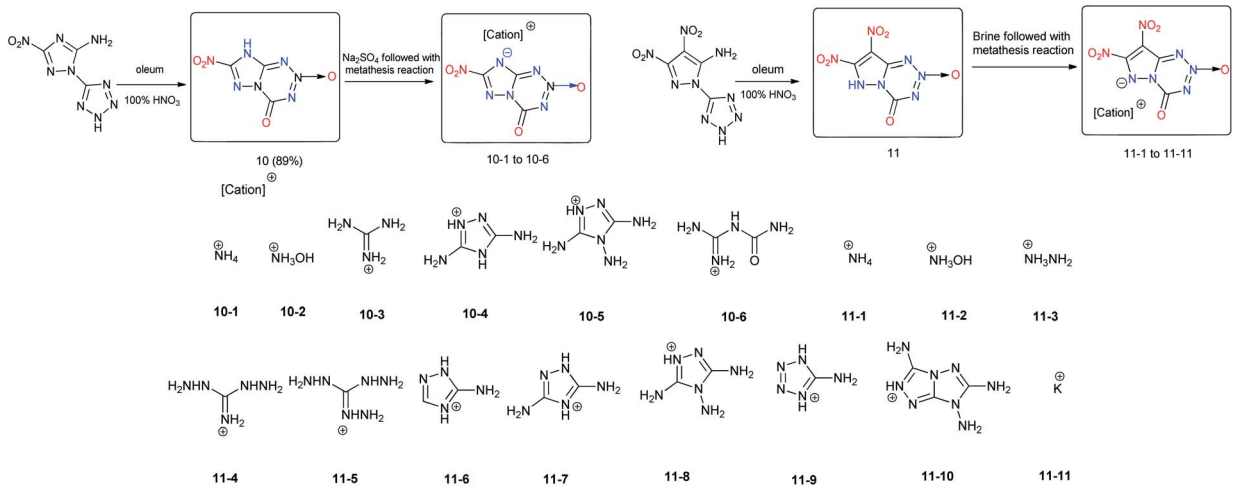
These energetic salts are thermally stable, most of them with decomposition temperatures above 230 °C, which tend to be insensitive to external stimuli. Their detonation pressures and velocities are within the ranges 25.2 to 39.5 GPa and 7856 to 9069 m s^{-1}, respectively. The hydroxylammonium salt **10-2** exhibits satisfactory density (1.97 g cm^{-3}), high thermal stability (T_d = 197 °C), low sensitivities (IS > 40 J, FS = 324 N), and excellent detonation velocity (9069 m s^{-1}) and pressure (39.5 GPa), making it superior to RDX (Table 7). The combination of high performance and low sensitivity of **10-2** highlights its potential to be used as an HEDM. This strategy of building fused [1,2,4]triazolo[5,1-*d*][1,2,3,5]tetrazine rings provides an efficient approach for designing stable HEDMs with low sensitivities. 7,8-Dinitro-4-oxo-4,6-dihydropyrazolo[5,1-*d*][1,2,3,5]



Scheme 8 [5,6]-Bicyclic and [6,6]-bicyclic heterocyclic energetic materials.

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



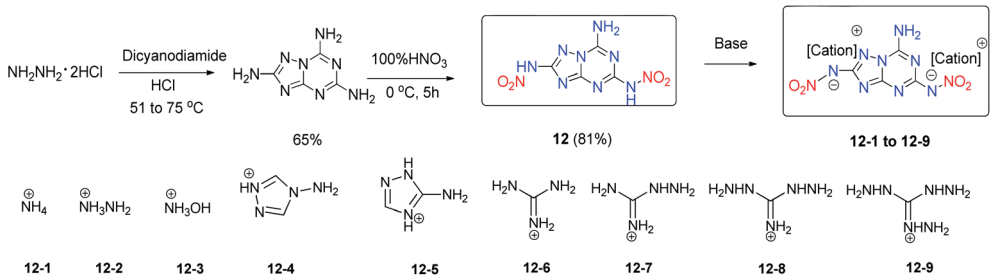
Scheme 9 Synthesis of **10**, **11** and their energetic salts.

tetrazine 2-oxide (**11**) was prepared in a one-pot reaction *via* *N*-nitration followed by a ring closure reaction, which is similar to **10**. In addition, a series of salts **11-1** to **11-11** was prepared. Comparing the structures of **10** and **11** reveals that the only difference is that the pyrazole ring in **11** is replaced by the triazole ring in compound **10**, which makes it possible to introduce one more nitro group into compounds and to give **11** a higher oxygen balance and density. Among the energetic salts of **11**, the hydroxylammonium salt **11-2** exhibits the best detonation properties ($D = 9228$ m s^{-1} and $P = 39.4$ GPa) due to high density (1.92 g cm^{-3}), and low sensitivity (IS = 19 J, FS = 360 N) derived from the coplanar structure of its fused ring system (Scheme 9).[21]

2,5-Dinitramide-7-amino-[1,2,4]triazolo[1,5-a][1,3,5]triazine (**12**), which contains a fused framework of a triazolo-triazine ring with one amino and two nitramino groups (Scheme 10), was obtained.[22] Its nitrogen-rich energetic salts (**12-1** to **12-9**) were prepared through neutralization and metathesis reactions. Featuring a planar structure, a conjugated system and hydrogen bond interactions originating from the amino groups in the fused ring framework, most of the energetic salts of **12** have high thermal stability and with good detonation performance. In particular, compounds **12-2** and **12-3** exhibit high detonation performance ($D = 9313$, and 9088 m s^{-1}; $P = 33.9$, and 34.1 GPa) comparable to that of the high explosive HMX and with low sensitivity (IS > 40 J; FS > 360 N) similar to that of TATB, causing them to stand out as some of the few examples featuring a good balance between high energy level and stability (Table 8). Thus, **12-2** and **12-3** are promising candidates as insensitive HEDMs. Additionally, the good stabilities and detonation properties of these amino-nitramino fused heterocycles indicate a potential design strategy for insensitive HEDMs. The 1,2,4,5-tetrazine ring has a high nitrogen content and has been used as a building block in the design and synthesis of energetic

Table 7 Physicochemical and energetic properties of compounds **10**, **11** and their energetic salts

No.	T_m, °C	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
10-1	—	249	1.77	8252	29.0	180.6/0.84	−29.61	>40	324	20
10-2	—	197	1.97	9069	39.5	218.6/0.94	−20.68	>40	324	20
10-3	266	269	1.78	8113	27.1	151.8/0.59	−43.38	>40	324	20
10-4	—	252	1.89	8463	30.7	350.8/1.18	−48.29	>40	360	20
10-5	213	237	1.81	8374	29.2	475.6/1.52	−48.53	>40	324	20
10-6	208	241	1.80	7856	25.2	−55.6/−0.18	−45.16	>40	>360	20
11	—	243	2.02	8515	33.2	131.8/0.50	−16.45	2.5	144	21
11-1	—	237	1.88	8836	35.0	180.1/0.69	−24.60	7	360	21
11-2	—	171	1.95	9228	39.4	226.2/0.82	−17.38	19	360	21
11-3	—	207	1.79	8674	32.7	336.8/1.22	−26.17	6.5	168	21
11-4	—	201	1.68	8157	26.2	364.6/1.10	−38.53	18	252	21
11-5	—	183	1.68	8293	26.9	475.2/1.37	−39.17	8	216	21
11-6	—	217	1.74	8149	27.0	394.4/1.20	−41.57	9	360	21
11-7	—	212	1.82	8467	29.9	353.5/1.03	−42.08	25	360	21
11-8	—	207	1.80	8387	28.6	475.2/1.33	−42.55	18	360	21
11-9	—	184	1.76	8499	30.2	564.3/1.72	−29.25	4	240	21
11-10	—	232	1.80	8485	29.4	698.0/1.76	−46.32	15	360	21
11-11	—	315	1.97	8008	28.0	34.7/0.12	−11.38	10	240	21



Scheme 10 Synthesis of **12** and its energetic salts.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

materials. However, the tetrazine-fused ring system has been relatively unexploited for use in energetic materials. Recently, the groups of Shreeve and Chavez have synthesized and characterized the oxidation products of tetrazolo[1,5-*b*][1,2,4,5]-tetrazine-6-amine (**13**). The synthesis of 6-amino-tetrazolo[1,5-*b*]-1,2,4,5-tetrazine-5-oxide (**14**) through the oxidation of 6-amino-[1,5-*b*]tetrazolo-1,2,4,5-tetrazine (**13**) by the H_2O_2/$(CF_3CO)_2O$ system was realized (Scheme 11).[23] Following the study of the oxidation of **13**, treatment of **13** with hypofluorous acid (HOF), which is a stronger oxidant than the H_2O_2/$(CF_3CO)_2O$ system, was carried out, and it was found that in addition to **14**, 6-amino-[1,5-*b*]tetrazolo-1,2,4,5-tetrazine-2,5-dioxide (**15**) was also formed.[24] In terms of detonation properties, **14** ($D = 9326$ m s^{-1} and $P = 36.4$ GPa) is superior to RDX and **15** ($D = 9600$ m s^{-1} and $P = 41.3$ GPa) is superior to HMX (Table 9). For **15**, the addition of the second N-oxide group makes its impact sensitivity slightly higher than that of **14**. Compound **15** exhibits a good detonation velocity of 9600 m s^{-1} and a detonation pressure of 41.3 GPa. Because of the fused ring system and the N-oxide group in the molecules, the N-oxide derivatives of tetrazines **14** and **15** exhibit more promising energetic performances and better sensitivities than some of their known derivatives such as 3,6-diazido-1,2,4,5-tetrazine, 2,4,6-tri(azido)-1,3,5-triazine, and 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine. This result suggests the potential application of **14** and **15** as HEDMs. Accordingly, several N-oxide derivatives with fused tetrazine rings were synthesized recently, which include 3-nitro-6-amino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine-7-N-oxide (**19**),[25] 3,6-diamino-1,2,4-triazolo[4,3-*b*][1,2,4,5] tetrazine-7-N-oxide nitrate (**20**),[25] 3,6-diamino-1,2,4-triazolo [4,3-*b*][1,2,4,5]tetrazine-7-N-oxide (**21**)[25] and 6,6′-diamino-3,3′-azo-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine-7,7′-*N*,*N*-dioxide (**22**) (Scheme 11).[25]

Through using nitrate as a functional group to modify the fused tetrazine backbone, 6-[tris(hydroxymethyl)aminomethane trinitrate]-1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (**16**) was prepared by the nitration of the intermediate 6-[tris(hydroxymethyl)-aminomethane]-1,2,4-triazolo[4,3-*b*]1,2,4,5-tetrazine (Scheme 11).[26] Intermolecular hydrogen bonding with the N–H group in **16** leads to a relatively high density (1.79 g cm^{-3}). However, low thermal, impact and friction stabilities were observed because of the trinitrate group in the molecule (Table 9), which limits its practical application as an HEDM.[26]

Azide and nitramino groups were used to modify the fused tetrazine ring as well. 3-Amine-6-azido-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**23**),[26] 6,6′-diazide-3,3′-azo-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**24**),[26] and 3-nitroamino-6-azido-[1,2,4]triazolo [4,3-*b*][1,2,4,5]tetrazine (**25**)[26] were synthesized. 6-Nitroamino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**17**) (Scheme 11), 3,6-dinitramino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**18**) (Scheme 11), 6,6′-dinitramino-3,3′-azo-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**26**) and 3-nitroamino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (**29**) and their energetic salts were prepared (Scheme 12).[27]

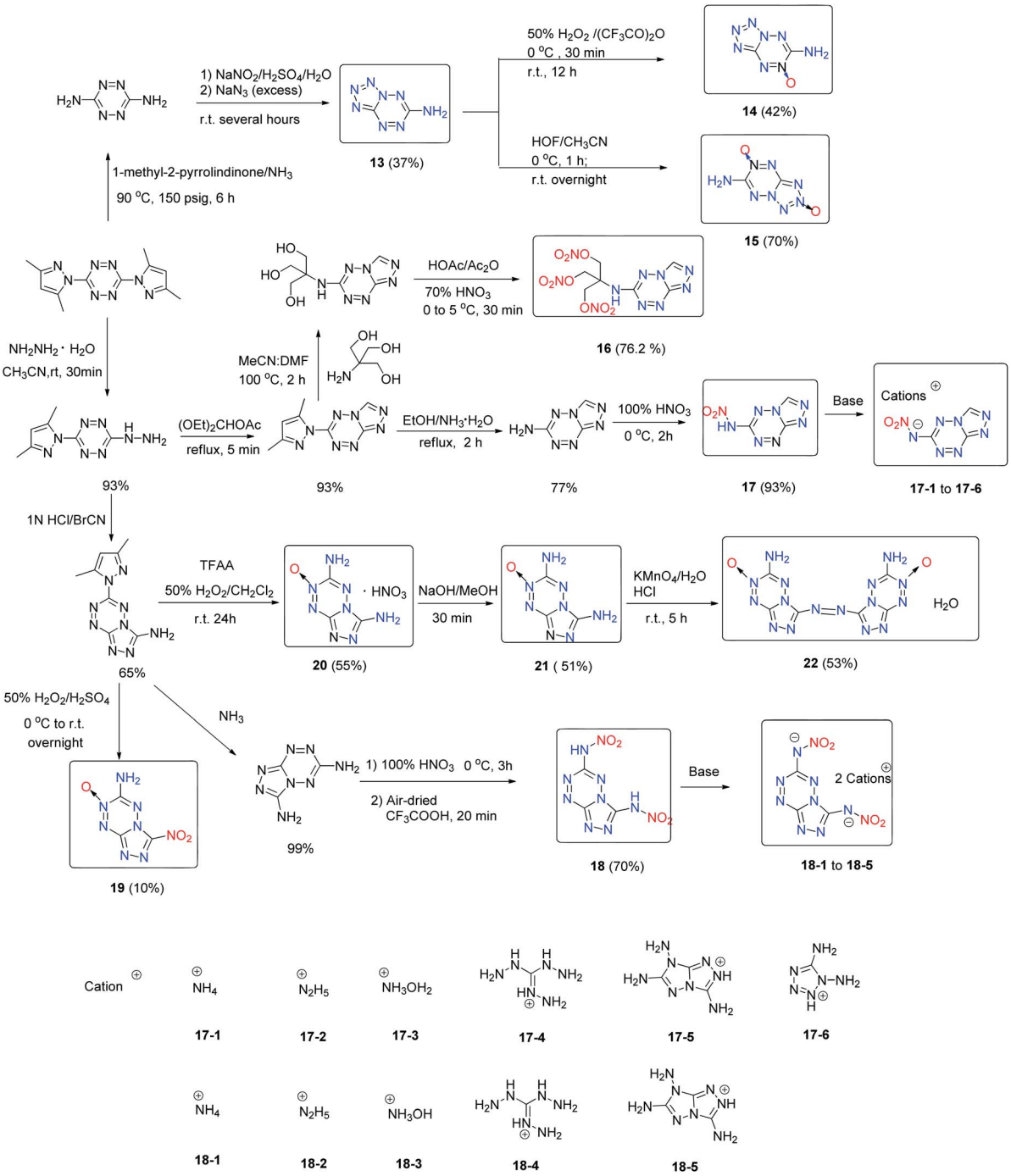
Some of these nitroamino-functionalized 1,2,4-triazolo[4,3-*b*][1,2,4,5]-tetrazine fused rings exhibit excellent detonation properties; for example, the sensitivities of all the hydroxylammonium salts are lower than those of their neutral precursors, such as compound **18** (3 J, >5 N) and compound **18-3** (25 J, 360 N) (Table 9). The detonation properties of **18-3** ($D =$ 9712 m s^{-1}, $P = 43$ GPa) and **26-2** ($D = 10\,233$ m s^{-1}; $P = 49$ GPa)

Table 8 Physicochemical and energetic properties of compounds **12** and its energetic salts

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
12	189	1.84	8787	34.2	544.9/2.13	−37.48	>40	>360	22
12-1	165	1.77	8791	29.7	386.1/1.33	−49.62	>40	>360	22
12-2	194	1.78	9313	33.9	754.6/2.36	−49.96	>40	>360	22
12-3	199	1.79	9088	34.1	528.8/1.64	−34.76	>40	>360	22
12-4	170	1.70	8445	27.0	1245.3/2.93	−67.87	>40	>360	22
12-5	221	1.60	7823	22.1	1002.3/2.36	−67.87	>40	>360	22
12-6	197	1.61	7824	21.5	396.5/1.06	−64.12	>40	>360	22
12-7	209	1.67	8500	26.3	797.6/1.97	−63.32	>40	>360	22
12-8	176	1.64	8440	25.6	854.8/1.97	−62.62	>40	>360	22
12-9	196	1.63	8546	26.4	1085.0/2.34	−62.02	>40	>360	22

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 11 Synthesis of **13** to **22** and energetic salts of **17**, **18**.

exceed those of the present high explosive benchmarks, such as HMX and CL-20. This result indicates that the fused 1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine ring system provides a balance between desirable detonation performances and acceptable stabilities and offers a promising approach to the design of low-sensitivity high-energy materials.

Similar to **24** and **26**, 1,2-bis([1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)diazene (**28**) was synthesized with an azo-bridge (Scheme 12). Compound **28** has a high measured density of 1.91 g cm^{-3}, an excellent thermal stability (T_d = 305 °C), and a very good calculated detonation performance (D = 9200 m s^{-1} and P = 34.8 GPa), which outperforms all current heat-resistant explosives. It has significant potential as a heat-resistant explosive. Azocoupling of diazopyrazole with nucleophiles is an efficient way to generate a fused ring and was studied in detail. This approach has proven to be an efficient way to generate amino-nitro fused systems with a pyrazolo-[5,1-*c*][1,2,4]triazine backbone for designing energetic materials.[27] 4-

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Table 9 Physicochemical and energetic properties of compounds 13 to 29 and energetic salts of 17, 18, 25, 26 and 29

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
13	200	1.68	8449	27.0	686.2/4.97	−57.93	1.5	15	23
14	185	1.87	9326	36.4	631.4/4.09	−41.53	10	60	23
15	150	1.93	9600	41.3	576.0/3.39	−28.22	6	109	24
16	155	1.79	8290	29.4	246.0/0.65	−38.28	3.9	94	26
17	148	1.76	8621	30.4	675.1/3.71	−43.93	20	>240	27
17-1	193	1.76	8937	31.6	649.1/3.26	−52.23	20	>240	27
17-2	133	1.77	9216	33.9	802.1/3.75	−52.30	12	240	27
17-3	156	1.82	9276	36.1	698.1/3.24	−40.91	28	>240	27
17-4	152	1.79	8748	28.4	959.5/3.35	−61.49	38	>360	27
17-5	155	1.76	9085	32.8	1233.6/3.67	−66.62	17	>360	27
17-6	248	1.80	8916	30.9	1176.4/4.17	−51.03	>40	>360	27
18	138	1.91	9301	38.3	740.9/3.06	−19.82	3	>5	27
18-1	213	1.84	9301	35.4	543.5/1.97	−34.76	32	>360	27
18-2	154	1.82	9625	37.9	871.8/2.85	−36.58	13	>240	27
18-3	154	1.92	9712	42.9	638.9/2.07	−20.77	25	>360	27
18-4	150	1.70	9061	30.8	1301.6/2.89	−53.29	30	>360	27
18-5	244	1.76	8792	29.8	1780.9/3.24	−61.05	>40	>360	27
19	220	1.86	9384	39.1	744.0/3.76	−32.31	25	240	25
20	191	1.81	8808	30.1	502.3/2.76	−31.15	>40	>40	25
21	196	1.82	9008	34.7	492.0/2.13	−66.62	>40	>360	25
22·H$_2$O	210	1.82	8542	28.8	1062/2.99	−57.79	22	40	25
23	165	1.74	8581	28.5	913.6/5.13	−62.88	30	>45	28
24	183	1.77	8690	30.2	2194.6/6.23	−54.51	1	<5	28
25	150	1.85	9236	36.3	951.8/4.27	−32.27	1	>40	28
25-1	180	1.77	9149	34.3	1055.6/4.40	−39.98	1	>160	28
25-2	170	1.76	8879	31.0	1026.0/3.64	−51.03	13	>160	28
25-3	156	1.79	9289	36.8	1106.3/4.32	−31.23	2	>100	28
25-4	129	1.74	9180	32.7	1352.6/4.13	−51.34	1	>40	28
26	170	1.85	9500	39.8	2037.8/5.22	−36.90	14	<5	27
26-1	240	1.84	9566	38.8	2014.7/4.75	−28.35	10	>40	27
26-2	185	1.99	10 233	48.6	2099.3/4.60	−35.07	14	>10	27
28	305	1.91	9200	34.8	1525.2/5.64	−76.99	16	>360	28
29	132	1.81	8880	33.2	647.8/3.56	−43.93	31	>240	28
29-1	193	1.79	9129	33.4	705.0/3.54	−52.23	33	>360	28
29-2	150	1.83	9408	37.8	751.2/3.49	−40.91	43	>360	28
29-3	280	1.79	8932	30.7	678.6/2.81	−63.03	50	>360	28
29-4	123	1.79	9416	35.7	858.4/4.01	−52.30	32	>360	28
29-5	156	1.78	8486	28.0	1009.7/3.10	−61.49	8	>240	28

Amino-3,7,8-trinitropyrazolo-[5,1-*c*][1,2,4]triazine (**30**) was obtained (Scheme 13).[29] The crystal density of compound **30** is 1.95 g cm^{-3} and it exhibits HMX-like performance with low sensitivity and good thermal stability, mainly due to the intra- and intermolecular hydrogen bonding in its structure. The notable combination of high calculated performance and low sensitivity makes **30** a promising explosive candidate (Table 10).[29]

Following the synthesis of **30**, 4-amino-3,7-dinitrotriazolo-[5,1-*c*][1,2,4]triazine (**31**) was obtained by reacting nitroacetonitrile with 5-amino-3-nitro-1*H*-1,2,4-triazole,[23,26] and further study by the oxidation of **31** with hypofluorous acid led to its oxidation product, 4-amine-3,7-dinitro-[1,2,4]triazolo[5,1-*c*][1,2,4]triazine-1-oxide (**32**) (Scheme 13). Compounds **31** and **32** display similar or better performance than RDX, and also show excellent insensitivity toward mechanical stimuli (Table 10).

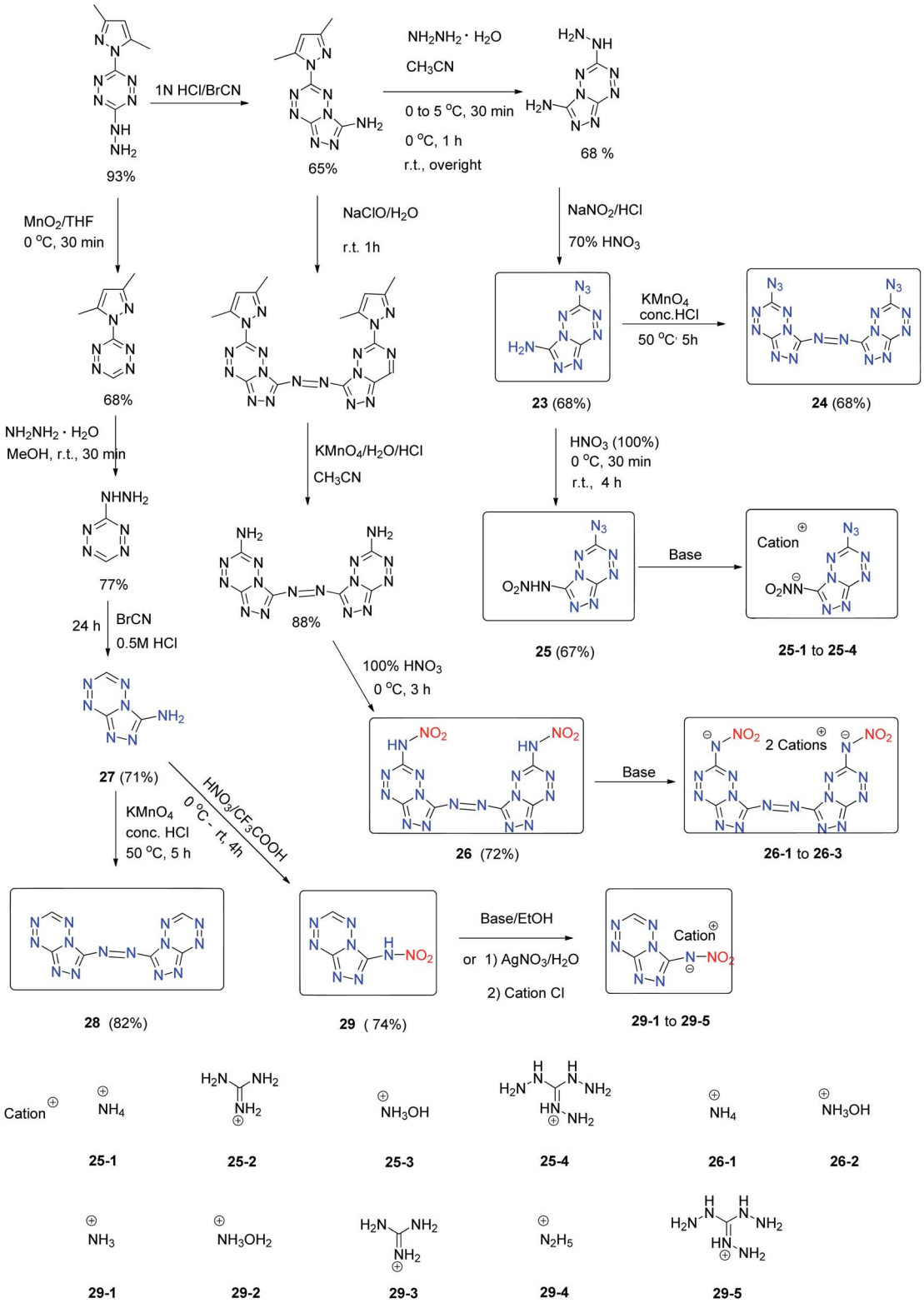
4-Amino-3-nitro-[1,2,4]triazolo[5,1-*c*][1,2,4]triazine-7-carbonitrile (**33**) was discovered by the diazotization of 3-amino-5-cyano-1,2,4-triazole followed by reaction with nitroacetonitrile (Scheme 13). The reaction of **33** with sodium azide resulted in the cyclization of the carbonitrile group to give 3-nitro-7-(1*H*-tetrazol-5-yl)-[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4-amine (**34**) (Scheme 13). Compound **34** is a thermally stable compound (T_d > 305 °C) with a density of 1.819 g cm^{-3}. It has good detonation properties (D = 8312 m s^{-1}, P = 27.04 GPa), and low sensitivity to impact, friction, and electrical discharge, making it an attractive candidate for replacing TATB (Scheme 13).

Using a similar strategy, 7,7′-bridged-bis-(4-amino-3,8-dinitropyrazolo-[5,1-*c*][1,2,4]triazine) (**35**) was synthesized from diethyl oxalate and acetone.[33] Compound **35** exhibits excellent thermal stability (T_d = 315 °C), high density (1.85 g cm^{-3}), good detonation properties and insensitivity to impact and friction with potential as a highly thermally stable HEDM.

Compared with [5,6]-bicyclic heterocyclic energetic materials, [6,6]-bicyclic heterocyclic energetic materials are limited, but earlier theoretical studies predict that [1,2,3,4]tetrazino[5,6-*e*][1,2,3,4]tetrazine-1,3,5,7-tetraoxide (**36**) and [1,2,3,4]tetrazino[5,6-*e*][1,2,3,4]tetrazine-1,3,6,8-tetraoxide (**37**) will match or

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

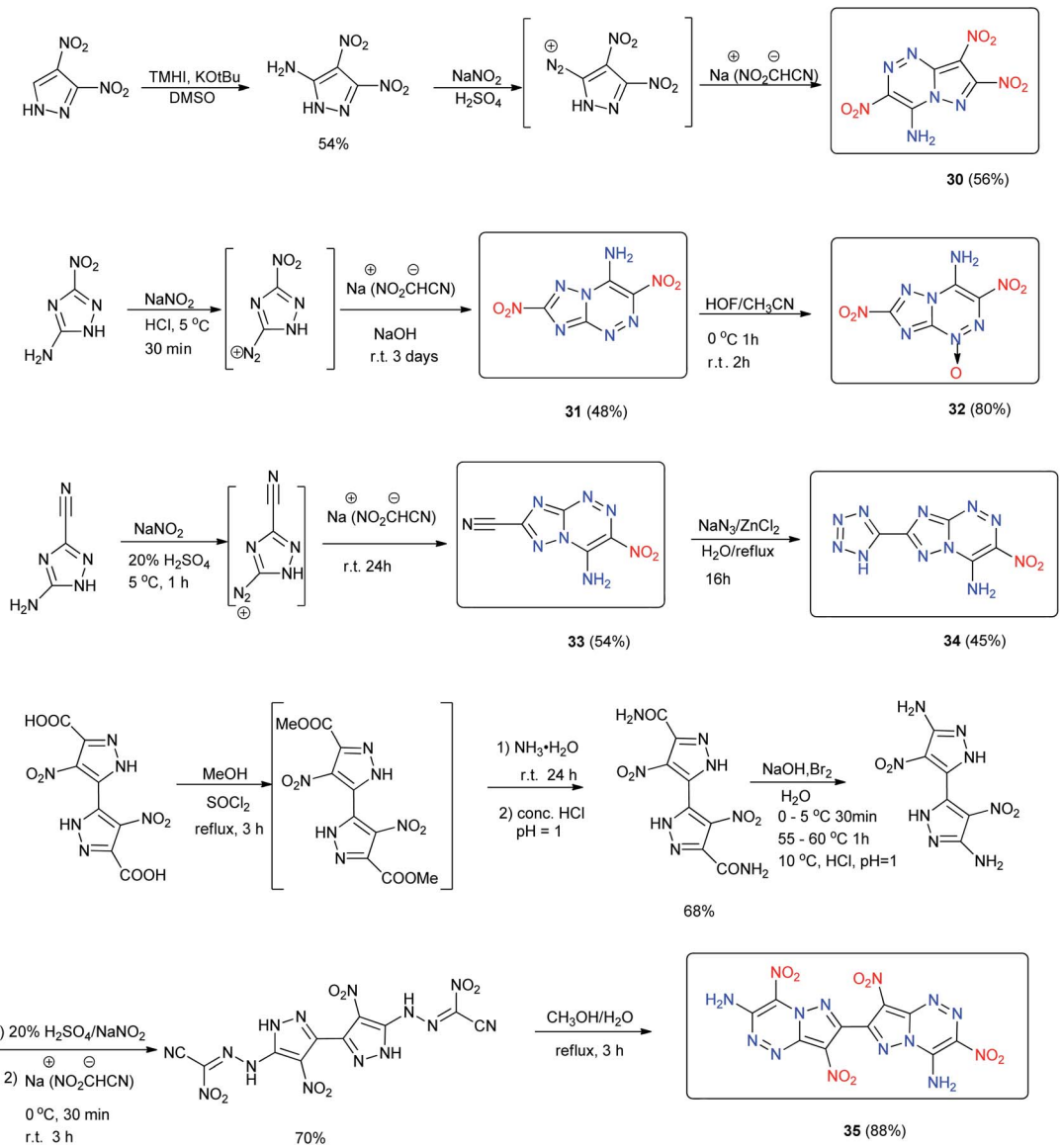


Scheme 12 Synthesis of 23 to 29 and energetic salts of 25, 26, 29.

substantially outperform CL-20 (Scheme 8).[34] Compound 37 has excellent theoretical detonation properties (D = 10 900 m s^{-1} and P = 60.0 GPa). As a result, their syntheses were desirable targets for chemists and have attracted considerable interest (Scheme 14).[35]

Compound 37 was prepared through a ten step series of reactions with 2,2-bis(*tert*-butyl-NNO-azoxy)acetonitrile as the starting material (Scheme 14).[36,37] 1*H*-1,2,3-triazolo[4,5-*e*][1,2,3,4]tetrazine-5,7-dioxide (38) was also found as an unexpected byproduct, which lowered the yield of compound 37 to

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 13 Synthesis of **30** to **35**.

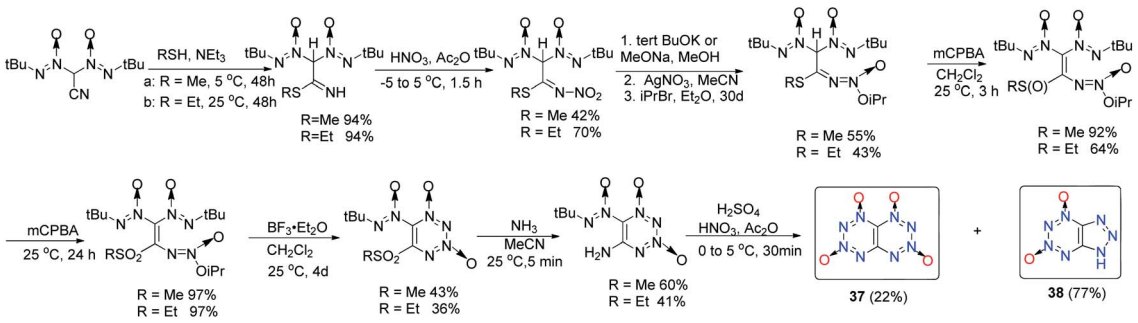
<1%. Compound **37** has acceptable thermal stability with a melting point between 183–186 °C (decomposition); however, its low hydrolytic stability may limit its potential application as a HEDM.[37]

Apart from its excellent detonation and safety properties and great promise for applications, 1,1-diamino-2,2-dinitroethene (FOX-7) also shows exciting and unpredictable reaction chemistry in building fused ring energetic materials. In 2019, Zhang's group synthesized a novel fused-ring polynitro compound 3,4,6,7,8,9-hexahydro-3,7,9,9-tetranitro-3,7,9,9-2*H*-pyrimido [1,6-*a*]-1,3,5-triazine (**39**) which features dinitromethylene through two-step reactions from FOX-7 (Scheme 15).[38]

Table 10 Physicochemical and energetic properties of compounds **30** to **35** and their energetic salts

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
30	246	1.95 (300 K)	8998	36.0	370.0/1.37	−29.62	58.4	324–360	29
31	232	1.86	8700	32	387.0/1.71	−35.38	29	>360	30
	272	1.82	8580	31.2	403.5/1.78		>60	>360	31
32	138	1.90 (predicted)	8970	35.4	378.0/1.56	−26.43	10.3	258	30
33	229	1.81	7763	23.1	533.5/3.25	−69.86	—	—	32
34	305	1.82	8312	27.0	752.7/3.02	−61.01	>80	>360	32
35	315	1.85	8572	31.4	899.0/2.01	−49.97	>60	>360	33

 This journal is © The Royal Society of Chemistry 2020



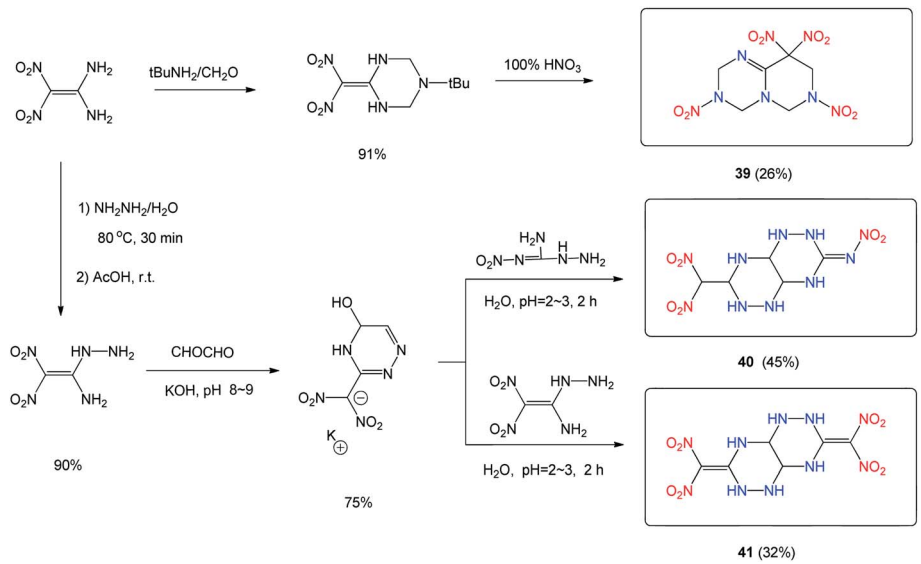
Scheme 14 Synthesis of **37** and **38**.

Compound **39** exhibits a high crystal density of 1.86 g cm^{-3}, a good thermal decomposition temperature of 176 °C, high detonation performances comparable to RDX, and low mechanical sensitivities.[38]

The condensation of the hydrazine derivative of FOX-7, (1-amino-1-hydrazino-2,2-dinitroethene, H-FOX) with glyoxal in aqueous KOH solution gives the 3-(dinitromethyl)-1,2,4-triazine potassium salt, which when reacted with 1-nitro-3-aminoguanidine, forms the 3-nitrimino-7-dinitromethylene-octahydro-[1,2,4]triazino-[6,5-*e*][1,2,4]triazine (**40**).[39] A similar reaction of 3-(dinitromethyl)-1,2,4-triazine potassium salt with 1-amino-1-hydrazino-2,2-dinitroethene led to 3,7-bis(dinitro-methylene)-octahydro-[1,2,4]triazino-[6,5-*e*][1,2,4]triazine (**41**),[39] which exhibits better detonation properties (density 1.85 g cm^3; pressure, 35.2 GPa, velocity, 8862 m s^{-1}, IS = 7.5 J) than **40**, and compares favorably with (RDX), and thus may have potential as a HEDM (Table 11).

[5,6,5]- or [5,7,5]-Tricyclic heterocycle-based energetic materials

Tricyclic heterocycle-based energetic materials have a greater scope in selecting different rings in their backbones. Usually, the generation of the third ring through a ring closure reaction is the main method in building the tricyclic backbones of these compounds, which makes most of them symmetric (Scheme 16). 4,4′,5,5′-Tetranitro-2*H*,2′*H*-3,3′-bipyrazole, 5,5′-dinitro-



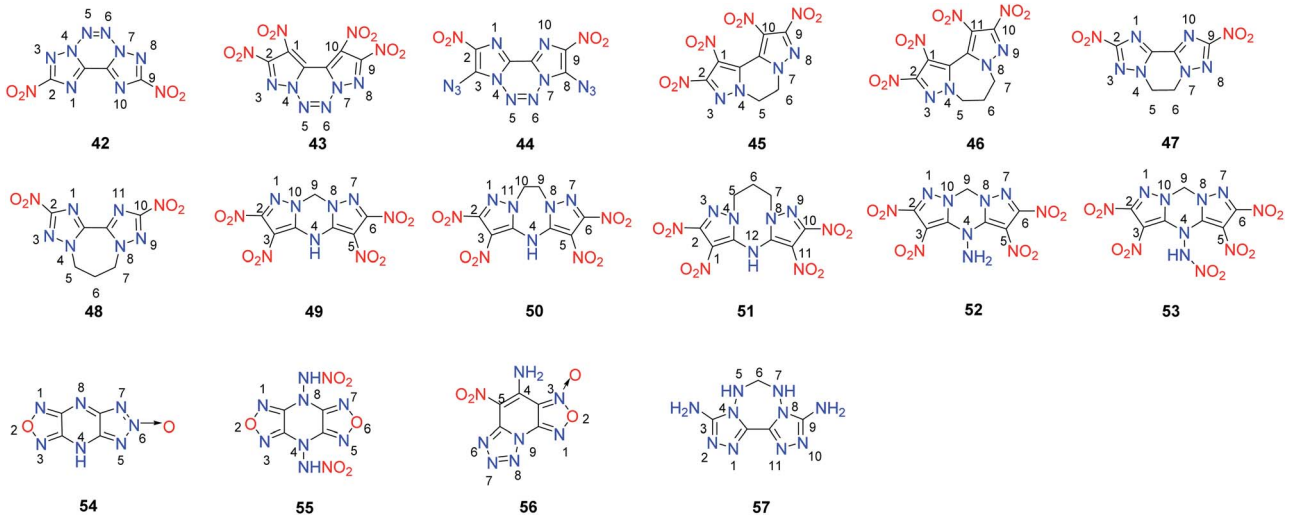
Scheme 15 Synthesis of **39** to **41**.

Table 11 Physicochemical and energetic properties of compounds **39** to **41**

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
39	176	1.86	8798	33.87	124.76/0.39	−39.98	12	216	38
40	124	1.73	8492	29.4	304.2/1.30	−47.03	8	360	39
41	126	1.85	8862	35.2	348.2/1.04	−36.76	7.5	160	39

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

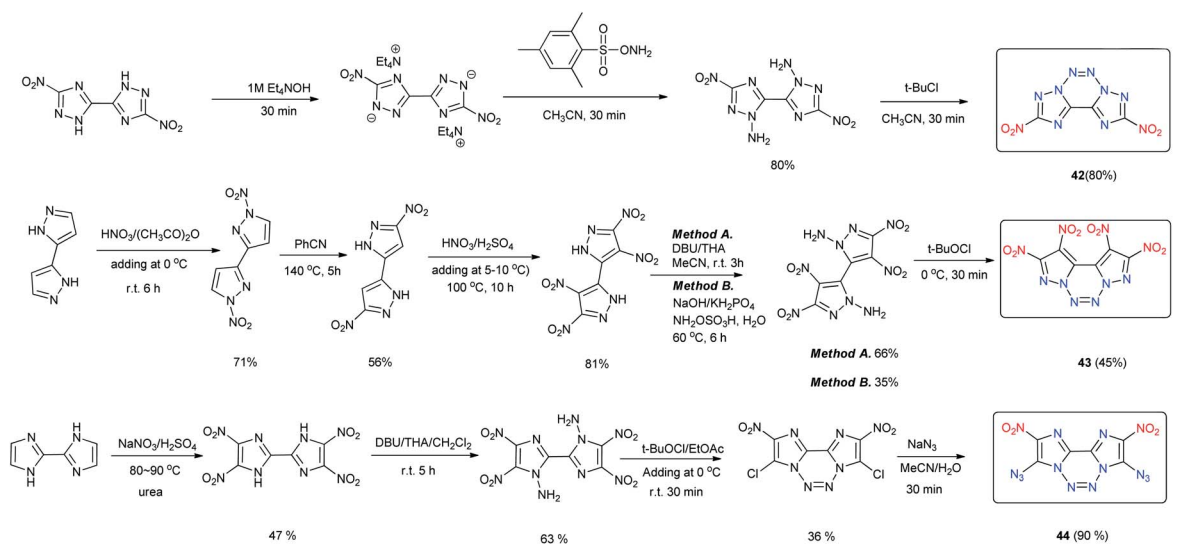
Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 16 [5,6,5]-Tricyclic, [5,7,5]-tricyclic and [5,8,5]-tricyclic heterocyclic energetic materials.

2*H*,2′*H*-3,3′-bi-1,2,4-triazole,4,4′,5,5′-tetranitro-2*H*,2′*H*-bisimidazole and their derivatives were synthesized as energetic materials. Recently, these compounds have become attractive building blocks for fused tricyclic energetic compounds containing the 1,2,3,4-tetrazine unit.

The fused tricyclic compound, 2,9-dinitro-bis[1,2,4]triazolo[1,5-*d*:5′,1′-*f*][1,2,3,4]tetrazine (**42**) was synthesized through the amination of 5,5′-dinitro-2*H*,2′*H*-3,3′-bi-1,2,4-triazole followed by N-azo coupling by oxidizing the product with *tert*-butyl hypochlorite (*t*-BuOCl) (Scheme 17).[40] Calculations indicate that **42** is a highly energetic material that is similar to RDX with respect to its sensitivity properties. However, its low thermal stability (T_d = 138 °C) limits its practical application (Table 12). The low thermal stability of **42** may be the result of the conjugation of the fused backbone and the nature of the pyrazole ring. Using a similar strategy as that employed for **42**, 4,4′,5,5′-tetranitro-2*H*,2′*H*-3,3′-bipyrazole was converted into 1,2,9,10-tetranitro-dipyrazolo[1,5-*d*:5′,1′-*f*][1,2,3,4]tetrazine (**43**) (Scheme 17).[41] Compound **43** exhibited good thermal stability (T_d = 233 °C) and high density (d = 1.96 g cm^{-3}). Its detonation properties (D = 9631 m s^{-1}; P = 44.0 GPa) are superior to those of RDX and HMX and comparable to those of CL-20. Furthermore, **42** is more stable toward impact and friction than CL-20. The excellent properties of **43** indicate that it is a superior HEDM, and the method for building the backbone of **43** provides a potential design concept for introducing the 1,2,3,4-tetrazine moiety into a fused ring system. Attempts to design and synthesize different conjugated tricyclic fused energetic molecules by using 4,4′,5,5′-tetranitro-2*H*,2′*H*-bisimidazole as the starting material have been made. In contrast to the synthesis of **43**, the oxidation reaction of 4,4′,5,5′-tetranitro-2,2′-diamino-bisimidazole with *t*BuOCl led to a dichloro-substituted tricyclic fused ring product



Scheme 17 Synthesis of compounds **42** to **44**.

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Table 12 Physicochemical and energetic properties of compounds 42 to 44

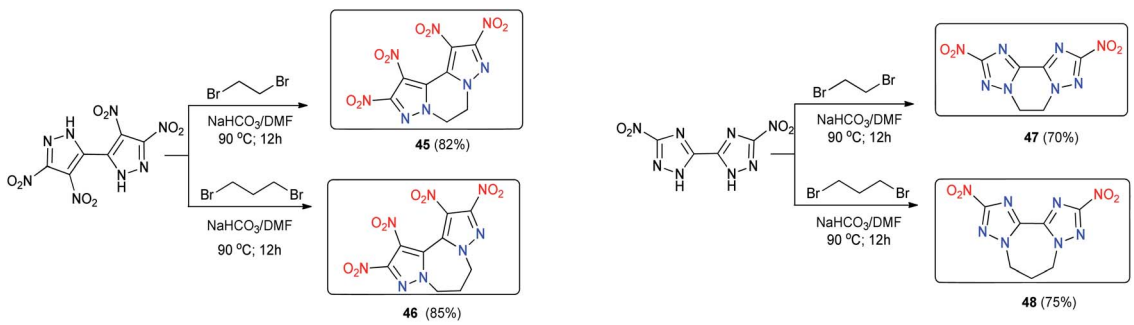
No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
42	138	1.91(α)/1.901(β) (294 K)	9400	38.0	787.0/3.12	−25.39	5.3	92	40
43	233	1.96	9631	44.0	758.5/2.23	−18.82	10	240	41
44	111	1.89	9256	36.7	1318.8/3.97	−38.54	2	20	42

with an N-azo structure.[42] When the chlorine atom was replaced with an azide group, 3,8-diazido-2,9-dinitrodiimidazo[1,2-*d*:2′,1′-*f*]-[1,2,3,4]tetrazine (**44**) was formed (Scheme 17). It exhibits high density (1.89 g cm^{-3}) and excellent detonation properties (D = 9256 m s^{-1}; P = 36.7 GPa). The high sensitivities of **44** toward impact and friction suggest it as a promising primary explosive.

The tricyclic energetic molecules 1,2,9,10-tetranitro-5,6-dihydro-dipyrazolo[1,5-*a*:50,10-*c*]pyrazine (**45**), 1,2,10,11-tetranitro-6,7-dihydro-5*H*-dipyrazolo[1,5-*a*:5′,1′-*c*][1,4]diazepine (**46**), 2,9-dinitro-5,6-dihydro-bis([1,2,4]triazolo)[1,5-*a*:5′,1′-*c*]pyrazine (**47**), and 2,10-dinitro-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[1,5-*a*:50,10-*c*][1,4]diazepine (**48**) were prepared through the ring closure of the sodium salts of 4,4′,5,5′-tetranitro-2*H*,2′*H*-3,3′-bipyrazole and 5,5′-dinitro-2*H*,2′*H*-3,3′-bi-1,2,4-triazole with an *N*,*N*′-ethylene bridge (**45** and **47**) or an *N*,*N*′-propylene bridge (**46** and **48**) (Scheme 18).

The new compounds have excellent thermal stabilities, with **48** having the highest decomposition temperature at 328 °C (Table 13). The incorporation of an *N*,*N*′-ethylene/propylene bridge into polynitroazoles improves their thermal stabilities. These compounds exhibit better detonation performance than TNT, and the performance of **45** is comparable to that of TATB. Their sensitivities toward impact and friction are also better than TNT. Their good detonation performance and, remarkable high thermal stability and "green" nitrogen-rich backbone make them potential candidates in the field of HDEMs. This ring closure strategy may open a route to the design of highly thermally stable energetic compounds.

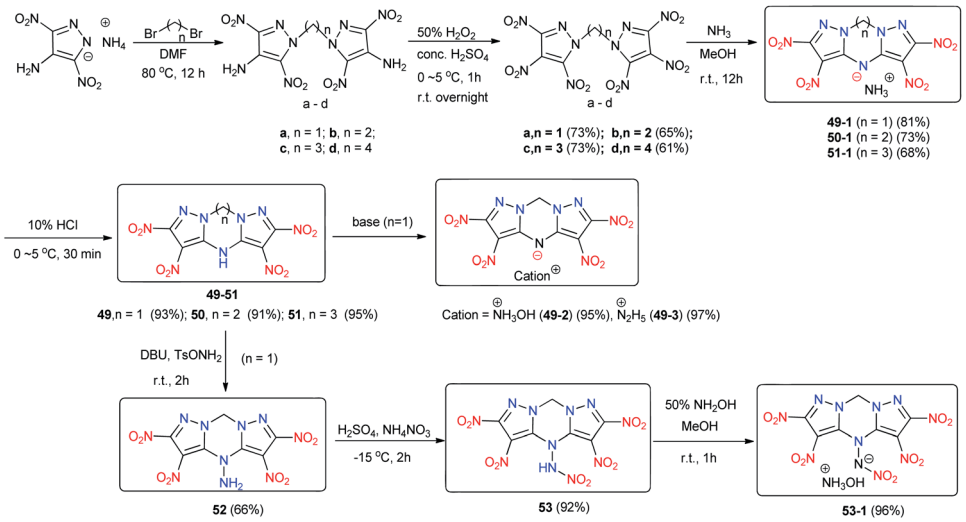
A concise methodology for constructing the fused compounds 2,3,5,6-tetranitro-4*H*,9*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazine (**49**), 2,3,5,6-tetranitro-9,10-dihydro-4*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazepine (**50**) and 1,2,10,11-tetranitro-6,7-dihydro-5*H*,12*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazocine (**51**) was reported.[43] These compounds contain tricyclic frameworks of dipyrazolo-1,3,5-triazinane, dipyrazolo-1,3,5-triazepane, and dipyrazolo-1,3,5-triazocane, respectively (Scheme 19) and were easily obtained by treating the corresponding *N*,*N*′-alkylene-bridged polynitropyrazoles with ammonia–methanol solution followed by acidification with hydrochloric acid. This approach is a facile and concise cyclization strategy for building the seven-membered 1,3,5-triazepane and eight-membered 1,3,5-triazocane rings. The deprotonation of **49** in 50% hydroxylamine solution or hydrazine monohydrate solution yields hydroxylammonium 2,3,5,6-tetranitro-9*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazin-4-ide (**49-2**) or hydrazinium 2,3,5,6-tetranitro-9*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazin-4-ide (**49-3**), respectively. The amination of **49** gave 2,3,5,6-tetranitro-4-amine-4*H*,9*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazine (**52**), which was nitrated to obtain 4-nitroamino-



Scheme 18 The synthesis of **45** to **48**.

Table 13 Physicochemical and energetic properties of compounds 45 to 48

No.	T_m, °C	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
45	233	261	1.76	8135	28.1	326.6/0.96	−47.04	15	>360	44
46	278	280	1.68	7700	24.1	280.1/0.79	−58.72	28	>360	44
47	304	307	1.73	7838	24.1	345.3/1.37	−63.45	22	>360	44
48	325	328	1.63	7336	19.7	307.2/1.15	−78.14	30	>360	44



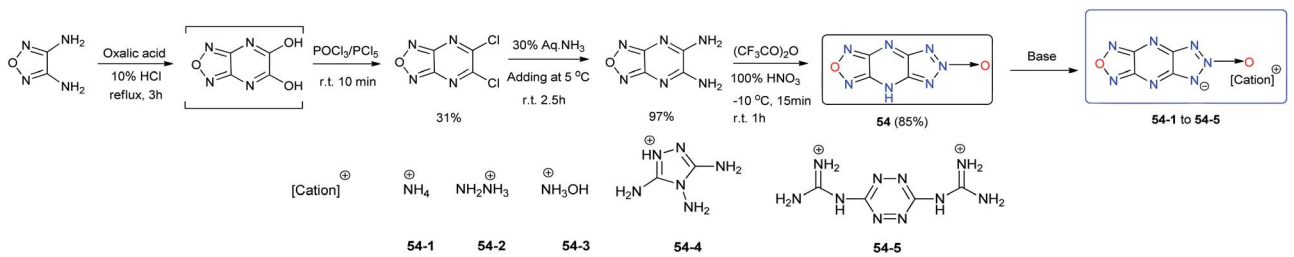
Scheme 19 Synthesis of **49** to **53** and energetic salts of **49** and **53**.

2,3,5,6-tetranitro-4*H*,9*H*-dipyrazolo[1,5-*a*:5′,1′-*d*][1,3,5]triazine (**53**). Similar to **50**, the deprotonation of **53** was carried out to yield the hydroxylammonium salt **53-1**.

Among these new energetic tricyclic compounds, **50** and **53** exhibit high densities (1.90 and 1.94 g cm^{-3}) comparable to that of HMX. These high densities arise because the dipyrazolo-1,3,5-triazinane backbone has a nearly planar structure that enhances the density and thermal stability of **50** and its derivatives (Table 14). Regarding detonation performance, some representative compounds (**49-2**, $D = 8893$ m s^{-1}, $P = 35.9$ GPa; **53**, $D = 9226$ m s^{-1}, $P = 38.8$ GPa; **53-1**, $D = 9034$ m s^{-1}, $P = 37.1$ GPa) are comparable to RDX or HMX. Most of the compounds exhibit favorable thermal stability, and their T_d values range from 207 to 307 °C, except for the nitramine **53** ($T_d = 117$ °C) and its hydroxylammonium salt **53-1** ($T_d = 138$ °C). In addition, **53** and **53-1** exhibit sensitivity toward mechanical stimuli, limiting their application as HEDMs. Considering both detonation properties and sensitivity, **49-2** is characterized by a promising overall energetic performance (**49-2**, $D = 8893$ m s^{-1}, $P = 35.9$ GPa, IS = 35 J, FS = 360 N) exceeding that of the benchmark explosive RDX.

Table 14 Physicochemical and energetic properties of compounds **49** to **53** and energetic salts of **49** and **53**

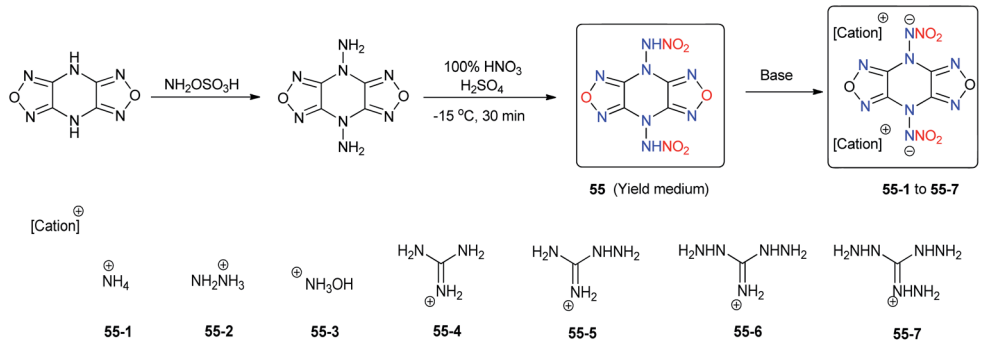
No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
49	261	1.90	8792	34.3	375.3/1.10	−35.17	15	240	43
50	307	1.80	8257	29.2	301.9/0.85	−47.30	25	240	43
51	276	1.76	8051	27.2	299.1/0.81	−58.50	30	360	43
49-1	220	1.82	8518	31.7	347.4/0.97	−40.20	40	360	43
49-2	221	1.86	8893	35.9	392.9/1.05	−34.21	35	360	43
49-3	207	1.83	8690	33.2	496.4/1.33	−40.73	25	360	43
52	242	1.79	8356	29.6	341.9/0.96	−35.94	15	160	43
53	117	1.94	9226	38.8	521.5/1.30	−21.94	3	20	43
53-1	138	1.87	9034	37.1	573.1/1.32	−22.11	10	80	43



Scheme 20 Synthesis of **54** and its energetic salts.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

 This journal is © The Royal Society of Chemistry 2020

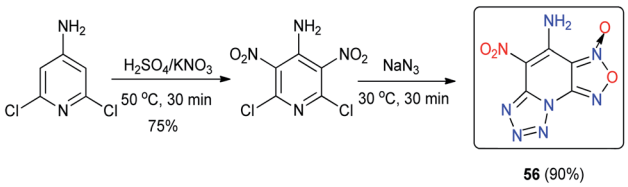


Scheme 21 Synthesis of 4,8-dinitraminodifurazano[3,4-*b*,*e*]pyrazine (**55**) and its salts.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Furazano-[3,4-*b*]pyrazine is considered an attractive fragment for the construction of planar polycondensed molecules to produce polynitrogen compounds with unique energy characteristics. 1*H*-[1,2,5]oxadiazolo[3,4-*b*][1,2,3]triazolo[4,5-*e*]pyrazine, 6-oxide (**54**) was prepared using a straightforward method starting from the diamino furazan (Scheme 20),[45] and its energetic salts **54-1** to **54-5** were prepared by neutralization reactions. As seen in Table 16, the introduction of an N-oxide into the fused 1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine ring results in an increase in the density of **54** (d = 1.85 g cm^{-3}), which contributes to the high performance of **54** and its energetic salts. Compared to their precursor, most of the energetic salts of **54** are less sensitive to impact and exhibit prominent physical and detonation properties, such as high thermal stability, good density, and good detonation properties, which are comparable to those of explosives such as TNT, and RDX. These results suggest that they might have potential as insensitive nitrogen-rich HEDMs for future applications.

In contrast to **54**, which has an asymmetric structure, 4,8-dinitraminodifurazano[3,4-*b*,*e*]pyrazine (**55**) was obtained by treating 4,8-dihydrodifurazano[3,4-*b*,*e*]pyrazine with NH_2OSO_3-H followed by nitration with HNO_3 (100%) (Scheme 21).[46] A series of new energetic salts (**55-1** to **55-7**) based on **55** were further synthesized by neutralization or metathesis reactions. The introduction of highly energetic nitramino moieties into the nitrogen-rich 4,8-dihydrodifurazano[3,4-*b*,*e*]pyrazine backbone obviously resulted in significant detonation properties. Among these compounds, energetic salts **55-1**, **55-2**, **55-3** and **55-7** exhibited satisfactory detonation performances (8921 m s^{-1} < D < 9413 m s^{-1}, 32.8 GPa < P < 36.8 GPa), which are close to or exceed that of RDX. However, these salts are highly sensitive (Table 15). Notably, the detonation velocity of **55-6** is superior to that of RDX, while the mechanical stability is similar to that of RDX. The prominent detonation performance along with moderate sensitivity indicates that compound **55-6** has the potential to compete with traditional high explosives and serve as a new !synthesis of 4-amino-5-nitro-[1,2,5]oxadiazolo-[3,4-*e*]tetrazolo[1,5-*a*]pyridine-3-oxide (**56**) from 4-amino-2,6-dichloropyridine in a short reaction time using a step-economical fashion (Scheme 22) has been reported.[47] Compound **56** is a tricyclic fused energetic material containing vicinal amino and nitro moieties. The facile synthetic approach was shown to be a successful method to build tricyclic



Scheme 22 Synthesis of **56**.

Table 15 Physicochemical and energetic properties of compounds **54**, **55** and their energetic salts

No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
54	281	1.85	8532	32.4	597/3.3	−58.07	32	—	45
54-1	270	1.73	8079	26.3	476/2.4	−65.26	>40	—	45
54-2	141	1.76	8378	30.0	641/3.0	−64.41	38	—	45
54-3	157	1.74	8518	30.3	542/2.5	−52.80	35	—	45
54-4	274	1.70	7972	25.0	794/2.7	−73.67	>40	—	45
54-5	301	1.69	7871	24.0	1070/2.8	−72.15	>40	—	45
55-1	208	1.76	8921	32.8	558.6/1.75	−29.98	2	42	46
55-2	189	1.78	9378	36.0	882.8/2.52	−31.98	1	24	46
55-3	155	1.80	9156	36.8	680.0/1.93	−18.17	1	28	46
55-4	232	1.61	8135	24.1	607.0/1.50	−47.49	8	120	46
55-5	190	1.64	8509	26.4	828.0/1.91	−47.89	10	112	46
55-6	187	1.72	9166	31.4	1045.5/2.25	−48.24	8	108	46
55-7	207	1.71	9413	33.0	1380.5/2.79	−48.55	3	54	46

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Table 16 Physicochemical and energetic properties of compounds **56** to **63** and energetic salts of **58**

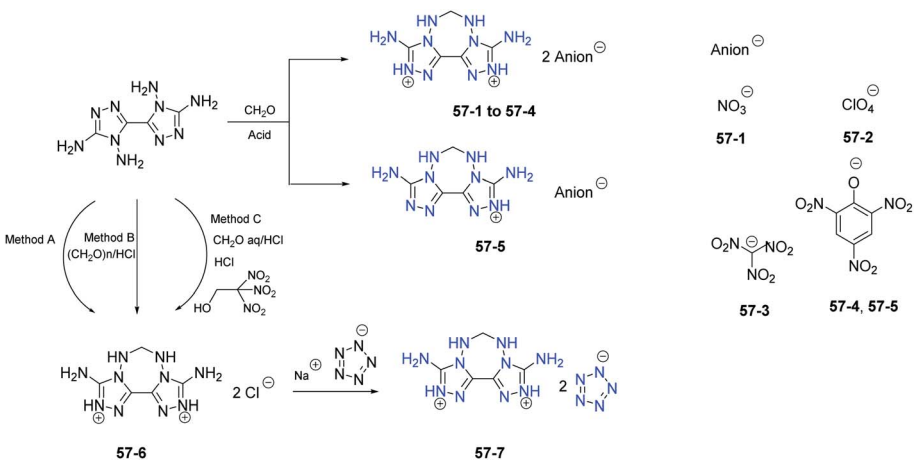
No.	T_d, °C	d, g cm^{-3}	D, m s^{-1}	P, GPa	HOF, kJ mol^{-1}/kJ g^{-1}	OB, %	IS, J	FS, N	Ref.
56	134	1.92	8838	36.0	908.0/3.81	−47.04	3	100	47
57-1	203	1.79	8073	29.6	222.8/0.67		16	360	48
57-2	278	1.92	8622	34.6	305.4/0.75		12	240	48
57-3	142	1.85	8942	37.4	715.5/1.40		10	160	48
57-4	206	1.77	7694	27.9	705.2/1.06		22	300	48
57-5	262	1.76	7862	26.9	890.0/2.04		28	360	48
57-7	100		7615	23.6	1341.2/3.83		10	120	49 and 50
58	400	1.69	7032	19.9	695.0/0.9	−92.65	19.0	—	51
59	356	1.77	7160	19.4	463.0/2.3	−107.38	18.0	—	51
59-1	162	2.10	—	—	—	−71.88	7.5	—	51
59-2	283	2.41	—	—	—	−60.87	5.0	—	51
59-3	391	2.80	—	—	—	−36.80	3.5	—	51
60	38	1.82	8376	31.2	710.0/2.1	−28.56	3.0	—	51
61	207	1.80	6234	13.7	711.0/2.3	−55.18	5.0	—	51
62·2H_2O	129	1.79	7946	26.9	618.0/2.1	−46.71	5.5	—	51
63	128	1.96	—	—	—	−9.60	11	130	52
64	157	1.97	—	—	—	−21.52	14	190	52

heterocyclic backbones with adequate purity, easy operation, and mild reaction conditions and allows further scale-up to mass production level. It has a high density (1.92 g cm^{-3}), which is much higher than those of known polynitro energetic materials, such as TNT, RDX and TATB. As shown in Table 16, the high density of **56** is associated with high detonation properties (P = 36.01 GPa, D = 8838 m s^{-1}), which are superior to those of TNT. In addition to the detonation properties, **56** with an impact sensitivity of 3 J and a friction sensitivity of 100 N is more sensitive than RDX and HMX (7.4 J, 120 N). It also has a low thermal stability decomposing at 134 °C.

Most of the above tricyclic heterocycle-based energetic materials are neutral compounds, some of them have a tendency to lose one or two protons and their negative ions (anions) were prepared.[43,45,46] However, none of them exhibits a strong tendency to gain a proton to form a cation. In 2018, through the cyclization condensation of the 4,4′,5,5′-tetraamino-3,3′-bi-1,2,4-triazole with 37% HCHO solution, a new family of 3,9-diamino-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[4,3-*e*:3′,4′-*g*][1,2,4,5]tetrazepine-2,10-diium salts with a fused tricyclic backbone in the cation was synthesized. Through reaction with a variety of energetic acids or metathesis reactions, a series of energetic salts were obtained (Scheme 23).[48–50] The fused tricyclic energetic salts **57-2** (d: 1.92 g cm^{-3}; D: 8622 m s^{-1}; P: 34.6 GPa) and **57-3** (d: 1.85 g cm^{-3}; D: 8942 m s^{-1}; P: 37.4 GPa) display interesting thermal behaviour and are predicted to be high-performance energetic materials. This work highlights ([1,2,4]triazolo)[4,3-*e*:3′,4′-*g*][1,2,4,5] tetrazepine-2,10-diium cation as a promising energetic building block that may provide new inspiration for fused heterocyclic chemistry.

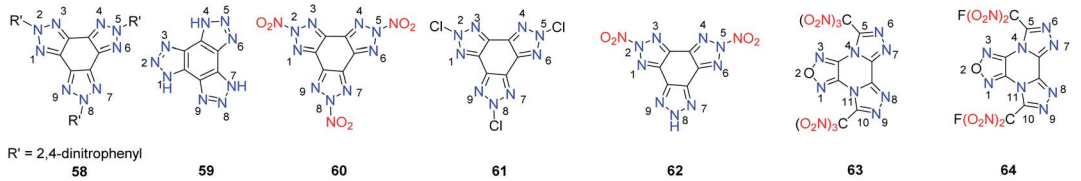
Tetracyclic heterocycle-based energetic materials

Compared with bicyclic or tricyclic heterocycle-based energetic materials, tetracyclic heterocycle-based energetic materials are more difficult to synthesize, and few backbones containing tetracyclic heterocycles have been reported in



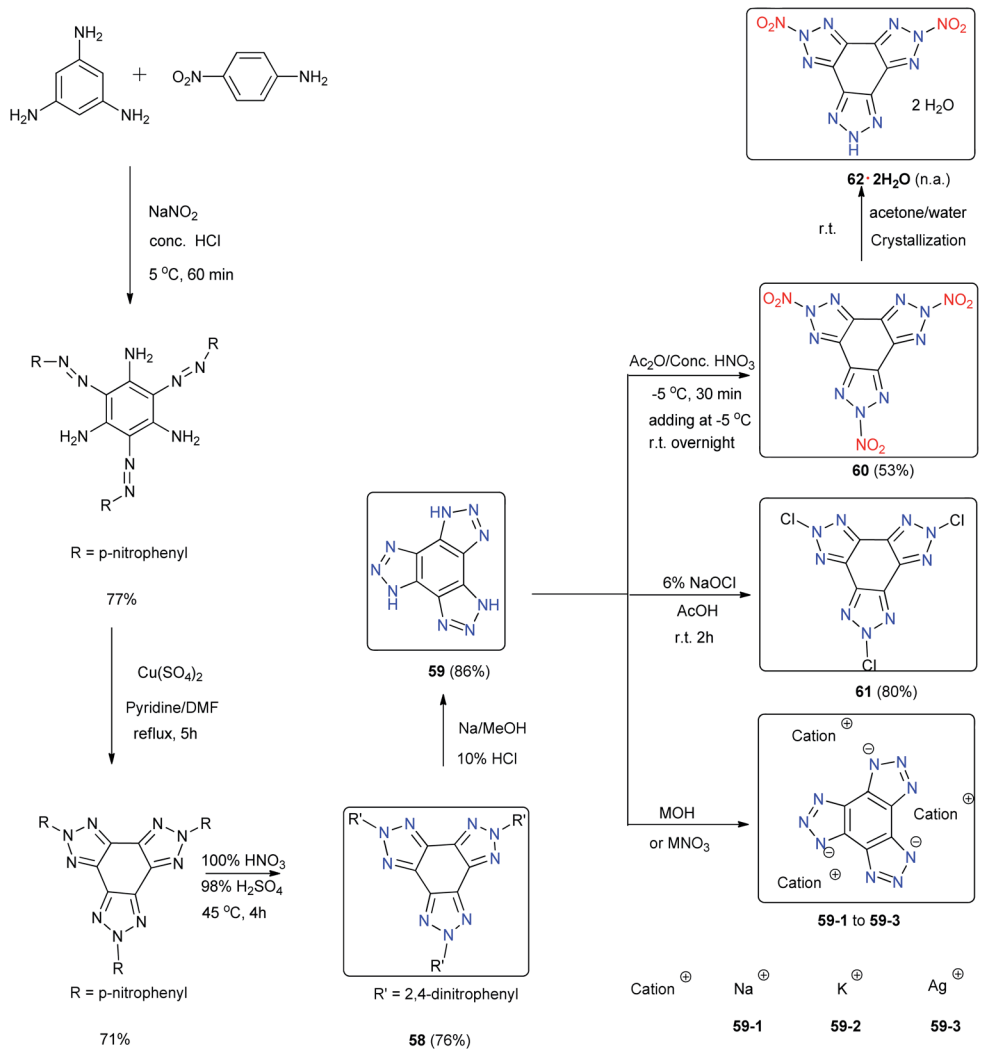
Scheme 23 Synthesis of energetic salts of **57-1** to **57-7**.

 This journal is © The Royal Society of Chemistry 2020



Scheme 24 Tetracyclic heterocycle-based energetic materials.

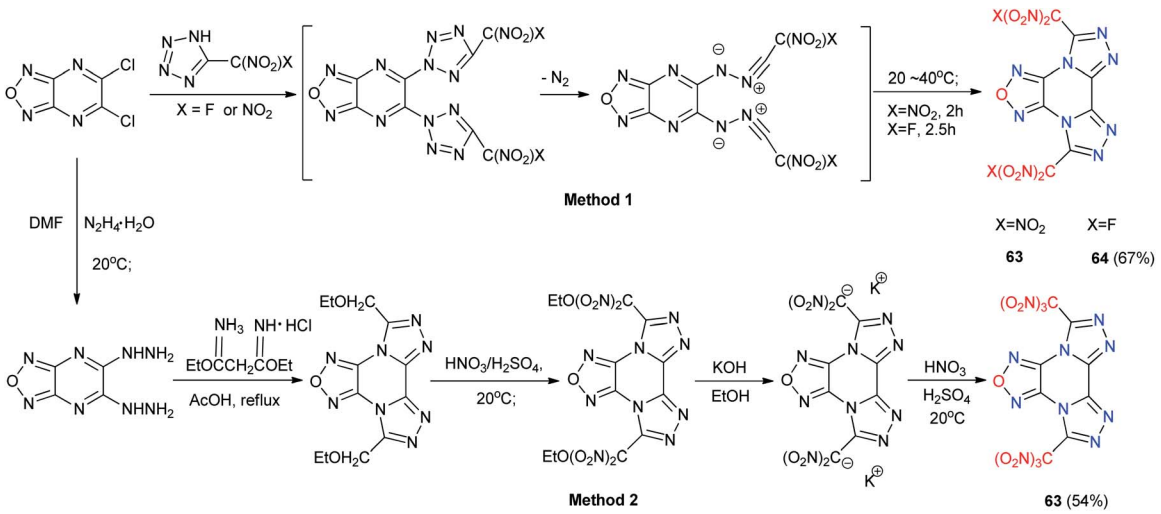
recent years (Scheme 24). 1,4,7-Trihydro-benzo[1,2-*d*:3,4-*d*′:5,6-*d*′]tris[1,2,3]triazole (**59**) is a fused ring system with three triazole units on one benzene ring. An improved synthesis of **59** and its derivatives from 1,3,5-triaminobenzene trihydrochloride, an easily accessible starting material, by using reported methods of treating the 2,5,8-tris(2,4-dinitrophenyl)-5,8-dihydro-2*H*-benzo[1,2-*d*:3,4-*d*′:5,6-*d*″]tris[1,2,3]triazole (**58**) with sodium followed with acidification produced **59**.[51] Metal salts (**59-1**, **59-2** and **59-3**) and 2,5,8-trinitro-benzo[1,2-*d*:3,4-*d*′:5,6-*d*″]tris[1,2,3]triazole (**60**) and 2,5,8-trichloro-benzo[1,2-*d*:3,4-*d*′:5,6-*d*″]tris[1,2,3]triazole (**61**) were synthesized with good yields (Scheme 25). Attempts to crystallize the trinitro compound **60** in acetone/water led to single crystals of the hydrate of 5,8-dihydro-2,5-dinitro-2*H*-benzo[1,2-*d*:3,4-*d*′:5,6-*d*″]tris[1,2,3]triazole (**62**·**2H$_2$O**). The trinitro compound **59** could not be recrystallized because it decomposed and only **62**·**2H$_2$O** was obtained. The single-crystal X-ray analysis shows that the structure of **62**·**2H$_2$O** is influenced by strong hydrogen bonds between H_2O and **62** with the triazole rings being nearly planar. Because tris(triazolo) benzene has the advantage of having high thermal tolerance and being rich in nitrogen, these derivatives exhibit good physical and detonation



Scheme 25 Synthesis of **57** to **61** and energetic salts of **58**.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.



Scheme 26 Synthesis of 5,10-bis(trinitromethyl)furazano[3,4-*e*]di([1,2,4]triazolo)[4,3-*a*:3′,4′-*c*]pyrazine (**63**) and 5,10-bis(fluorodinitromethyl) furazano[3,4-*e*]di([1,2,4]triazolo)[4,3-*a*:3′,4′-*c*]pyrazine (**64**).[52]

properties, including high stabilities, high densities, and high HOF. These explosives exhibit calculated detonation values comparable to those of TNT and PETN, which suggests that they might be of interest for future applications as environmentally friendly HDEMs (Table 16). Compound **61** was found to be a powerful hypergolic oxidizer with various commonly used fuels, resulting in better ignition delay times than those with white fuming nitric acid (WFNA).

Another example of a tetracyclic heterocycle-based energetic material is a one-pot method utilized for the synthesis of 5,10-bis(trinitromethyl)furazano[3,4-*e*]di([1,2,4]triazolo)[4,3-*a*:3′,4′-*c*] pyrazine (**63**) and its fluorinated analogue 5,10-bis(-fluorodinitromethyl) furazano[3,4-*e*]di([1,2,4]triazolo)[4,3-*a*:3′,4′-*c*]pyrazine (**64**). The synthesis was performed at low temperature, and the product was obtained in only two steps (Scheme 26).[52,53] Compounds **62** and **63** are tetracyclic hybrids of the dense 1,2,4-triazole and furazano[3,4-*b*]pyrazine backbones, which ensures good density and acceptable thermal stability (Scheme 26). These compounds are much less sensitive to impact and friction than HMX and are predicted to be HEDMs (Table 16). The trinitromethyl groups in **63** are on the structurally rigid backbone. The oxygen-rich character of **63** makes it useful in the processing of energetic formulations.

Conclusion

The chemistry of fused heterocyclic compounds which represent valuable scaffolds for constructing more powerful and less sensitive eco-friendly energetic materials is reviewed. The reactions that are presented and discussed illustrate the versatility of 64 different fused heterocycles designed as building blocks for the synthesis of a wide range of high-performance energetic materials. The key contributions of these fused backbones, which strongly regulates their energetic performance, are enhanced thermal stability and low sensitivity toward destructive mechanical stimuli. Additionally, these results exemplify the rational design and discovery of new fused heterocycle-based explosive molecules *via* the construction of the fused ring skeleton and subsequent improvements in their energetic performance by adding energetic groups to the backbones. These lead to novel energetic compounds with a combination of features that enhance performance (high density and good oxygen balance) while preserving molecular stability (hydrogen bonding, planar geometries, and π–π interactions). Thus far, some of the processes have been found to be straightforward, practical and easily scalable, such as those for compounds **1**, **10**, **11**, **12** and **55**; however, the design and syntheses of the backbones of most fused heterocyclic energetic materials are difficult. The authors believe that a more reasonable procedure for searching for fused heterocyclic energetic materials with the desired detonation properties includes two steps. The first step is the selection of possible backbones to ensure the necessary properties of the target molecules, where developing a more efficient way of building the backbones should be key. The second step is the estimation of properties for the selected backbones and selection of the energetic groups to modify these moieties, which then become the targets of a subsequent synthetic search.

It is necessary to clarify that the heat of formation and detonation performance of all the compounds in this review are obtained by theoretical calculations, and it is practically used in current research of design and synthesis of new energetic materials.[54] The main reason for using this method is that the synthesis of new energetic materials is difficult and risky. Usually, the amount of the new energetic materials is limited, and, in most cases, there is only enough to measure spectral data (infrared, nuclear magnetic resonance), elemental analysis, decomposition temperature, and single crystal diffraction data, *etc.* To obtain the standard molar formation enthalpy and detonation performance by experimental methods, a larger amount (few grams or even few hundred grams) is required. Considering that not all compounds have excellent detonation

 This journal is © The Royal Society of Chemistry 2020

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

performance, in order to avoid a large number of synthetic experiments, potential risk of explosion and cost reduction must be considered. We found that the combination of empirical and theoretical calculations are powerful tools in predicting HOF of energetic materials. In addition, the studies show that the difference between the calculated detonation performance (D, P) by EXPLO5 (ref. 1 and 55) and experimental values of is less than 5% (for D) and 10% (for P), respectively. Different theoretical models are effective methods to study the new energetic materials using this model of theoretical calculation; they have time-saving capabilities and they can reduce costs and inherent danger of synthesis associated with tests.[56]

From the above results, it is shown clearly that considerable effort has been devoted to the research and development of fused energetic materials over the past several years. The number of publications relating to fused energetic materials studies reveals that this field is an interesting area that requires further exploration because it is particularly relevant to the target-oriented synthesis of energetic materials featuring integrated properties. This research area will become a major focus in the pursuit of the next generation of HEDMs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the support of the Science Challenge Project (TZ2018004).

Notes and references

1 M. Sućeska, *EXPLO5, Version 6.01*, Brodarski Institute, Zagreb, Croatia, 2013.
2 T. Brinck, *Green Energetic Materials*, John Wiley & Sons, New York, NY, 2014, vol. 1, pp. 1–13.
3 Q. Zhang and J. M. Shreeve, *Chem. Rev.*, 2014, **114**, 10527–10574.
4 Y. Qu and S. P. Babailov, *J. Mater. Chem. A*, 2018, **6**, 1915–1940.
5 P. He, J.-G. Zhang, X. Yin, J.-T. Wu, L. Wu, Z.-N. Zhou and T.-L. Zhang, *Chem.–Eur. J.*, 2016, **22**, 7670–7685.
6 R. P. Singh, H. Gao, D. T. Meshri and J. M. Shreeve, *Struct. Bonding*, 2007, **125**, 35–83.
7 S. Zhang, Q. Yang, X. Liu, X. Qu, Q. Wei, G. Xie, S. Chen and S. Gao, *Coord. Chem. Rev.*, 2016, **307**, 292–312.
8 T. M. Klapötke, P. C. Schmid, S. Schnell and J. Stierstorfer, *Chem.–Eur. J.*, 2015, **21**, 9219–9228.
9 P. Yin, C. He and J. M. Shreeve, *J. Mater. Chem. A*, 2016, **4**, 1514–1519.
10 T. M. Klapötke, M. Leroux, P. C. Schmid and J. Stierstorfer, *Chem.–Asian J.*, 2016, **11**, 844–851.
11 J. Zhang, D. A. Parrish and J. M. Shreeve, *Chem. Commun.*, 2015, **51**, 7337–7340.
12 J. Zhang, D. A. Parrish and J. M. Shreeve, *Chem.–Asian J.*, 2014, **9**, 2953–2960.
13 P. Yin, J. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2015, **3**, 8606–8612.
14 Q. Ma, G. Fan, L. Liao, H. Lu, Y. Chen and J. Huang, *ChemPlusChem*, 2017, **82**, 474–482.
15 Y. Xu, L. Tian, D. Li, P. Wang and M. Lu, *J. Mater. Chem. A*, 2019, **7**, 12468–12479.
16 P. Yin, C. He and J. M. Shreeve, *Chem.–Eur. J.*, 2016, **22**, 2108–2113.
17 P. Yin, J. Zhang, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, **55**, 12895–12897.
18 C. He, J. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2013, **1**, 2863–2868.
19 Y. Tang, C. He and J. M. Shreeve, *J. Mater. Chem. A*, 2017, **5**, 4314–4319.
20 C. Bian, X. Dong, X. Zhang, Z. Zhou, M. Zhang and C. Li, *J. Mater. Chem. A*, 2015, **3**, 3594–3601.
21 B.-J. Zhao, P. Wang, W. Fu, C. Li and Z.-M. Zhou, *ChemistrySelect*, 2018, **3**, 4797–4803.
22 J. Ma, G. Cheng, X. Ju, Z. Yi, S. Zhu, Z. Zhang and H. Yang, *Dalton Trans.*, 2018, **47**, 14483–14490.
23 H. Wei, J. Zhang and J. M. Shreeve, *Chem.–Asian J.*, 2015, **10**, 1130–1132.
24 D. E. Chavez, D. A. Parrish, L. Mitchell and G. H. Imler, *Angew. Chem., Int. Ed.*, 2017, **56**, 3575–3578.
25 L. Hu, P. Yin, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *Chem. Commun.*, 2019, **55**, 8979–8982.
26 T. W. Myers, C. J. Snyder, D. E. Chavez, R. J. Scharff and J. M. Veauthier, *Chem.–Eur. J.*, 2016, **22**, 10590–10596.
27 L. Hu, P. Yin, G. Zhao, C. He, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *J. Am. Chem. Soc.*, 2018, **140**, 15001–15007.
28 Y. Liu, G. Zhao, Y. Tang, J. Zhang, L. Hu, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2019, **7**, 7875–7884.
29 M. C. Schulze, B. L. Scott and D. E. Chavez, *J. Mater. Chem. A*, 2015, **3**, 17963–17965.
30 D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler and D. A. Parrish, *Angew. Chem., Int. Ed.*, 2016, **55**, 15315–15318.
31 D. Kumar, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem.–Eur. J.*, 2017, **23**, 1743–1747.
32 C. J. Snyder, T. W. Myers, G. H. Imler, D. E. Chavez, D. A. Parrish, J. M. Veauthier and R. J. Scharff, *Propellants, Explos., Pyrotech.*, 2017, **42**, 238–242.
33 Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem. Commun.*, 2018, **54**, 10566–10569.
34 P. Politzer, P. Lane and J. S. Murray, *Cent. Eur. J. Energ. Mater.*, 2013, **10**, 37–52.
35 K. O. Christe, D. A. Dixon, M. Vasiliu, R. I. Wagner, R. Haiges, J. A. Boatz and H. L. Ammon, *Propellants, Explos., Pyrotech.*, 2015, **40**, 463–468.
36 M. S. Klenov, O. V. Anikin, A. M. Churakov, Y. A. Strelenko, I. V. Fedyanin, I. V. Ananyev and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2015, **2015**, 6170–6179.
37 M. S. Klenov, A. A. Guskov, O. V. Anikin, A. M. Churakov, Y. A. Strelenko, I. V. Fedyanin, K. A. Lyssenko and V. A. Tartakovsky, *Angew. Chem., Int. Ed.*, 2016, **55**, 11472–11475.

Published on 06 februar 2020. Downloaded on 9. 10. 2024 06:54:24.

38 C. Yan, X. Qi, K. Wang, Y. Jin, G. Cheng, T. Liu, H. Yang and Q. Zhang, *Chem. Commun.*, 2019, **55**, 3497–3500.
39 H. Gao and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2015, **54**, 6335–6338.
40 D. E. Chavez, J. C. Bottaro, M. Petrie and D. A. Parrish, *Angew. Chem., Int. Ed.*, 2015, **54**, 12973–12975.
41 Y. Tang, D. Kumar and J. M. Shreeve, *J. Am. Chem. Soc.*, 2017, **139**, 13684–13687.
42 Y. Tang, C. He, P. Yin, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Eur. J. Org. Chem.*, 2018, **2018**, 2273–2276.
43 P. Yin, J. Zhang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2017, **56**, 8834–8838.
44 Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2018, **6**, 8382–8387.
45 V. Thottempudi, P. Yin, J. Zhang, D. A. Parrish and J. M. Shreeve, *Chem.–Eur. J.*, 2014, **20**, 542–548.
46 W. Li, J. Tian, X. Qi, K. Wang, Y. Jin, B. Wang and Q. Zhang, *ChemistrySelect*, 2018, **3**, 849–854.
47 C. Ma, Y. Pan, J. Jiang, Z. Liu and Q. Yao, *New J. Chem.*, 2018, **42**, 11259–11263.
48 Y. Xu, Z. Zhu, C. Shen, Q. Lin and M. Lu, *Propellants, Explos., Pyrotech.*, 2018, **43**, 595–601.
49 Y. Xu, Q. Lin, P. Wang and M. Lu, *Chem.–Asian J.*, 2018, **13**, 924–928.
50 Y. Xu, L. Tian, P. Wang, Q. Lin and M. Lu, *Cryst. Growth Des.*, 2019, **19**, 1853–1859.
51 V. Thottempudi, F. Forohor, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2012, **51**, 9881–9885.
52 A. B. Sheremetev, V. L. Korolev, A. A. Potemkin, N. S. Aleksandrova, N. V. Palysaeva, T. H. Hoang, V. P. Sinditskii and K. Y. Suponitsky, *Asian J. Org. Chem.*, 2016, **5**, 1388–1397.
53 D. B. Lempert and A. B. Sheremetev, *Russ. Chem. Bull.*, 2018, **67**, 2065–2072.
54 H. Gao, C. Ye, C. Piekarski and J. M. Shreeve, *J. Phys. Chem. C*, 2007, **111**, 10718–10731.
55 M. Sućeska, *Mater. Sci. Forum*, 2004, 325–330.
56 H. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377–7436.

 This journal is © The Royal Society of Chemistry 2020