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Russ. Chem. Rev., 2024, **93** (2) RCR5109

https://doi.org/10.59761/RCR5109

Energetic 1,2,4-oxadiazoles: synthesis and properties

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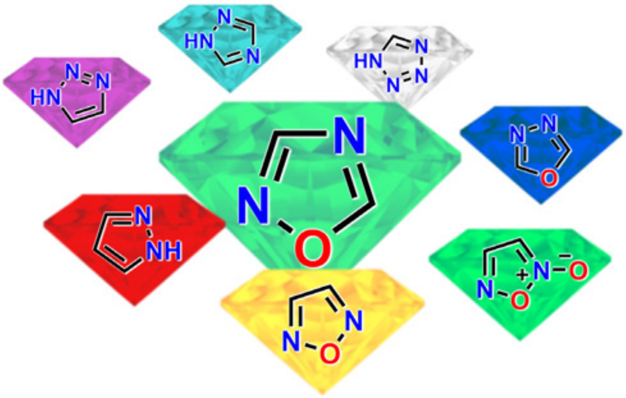

The study of high-energy materials based on polynitrogen- and nitrogen-oxygen-containing heterocycles is one of the most important and relevant modern interdisciplinary research areas at the intersection of organic and physical chemistry and materials science. Among such heterocycles, 1,2,4-oxadiazole ring is a rather interesting building block for the synthesis of new energetic compounds. Although the chemistry of 1,2,4-oxadiazoles has been developed for more than 100 years, high-energy materials based on these heterocycles have only recently become known and are currently one of the 'hot spots' in this field of science. This review systematizes recently published methods for the synthesis and features of the reactivity of 1,2,4-oxadiazole-based energetic compounds. Mono- and bis(1,2,4-oxadiazoles) as well as structures containing other azoles such as pyrazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-triazole, 1,2,4-triazole and tetrazole are considered. For the series of structurally similar compounds, their physicochemical properties are summarized and the factors affecting a particular parameter are considered. The bibliography includes 123 references.

Keywords: 1,2,4-oxadiazoles, *N*-oxides, nitrogen heterocycles, azoles, energetic compounds, thermal stability.

Contents

1. Introduction

The current state of scientific and technological development requires an ongoing search for materials with improved application properties. Recently, this problem has become particularly acute in the field of polynitrogen and nitrogen-oxygen energetic compounds, since traditional high-energy materials often prove unsuitable for solving new breakthrough scientific and technological challenges.[1–8] This is primarily due to the increased impact sensitivity of the most effective compounds and their non-compliance to modern requirements for energy efficiency and environmental safety. Moreover, the production of highly sensitive energetic substances inevitably entails an increase in anthropogenic risks, which is unacceptable for the development of advanced technologies in the XXI century.[9–12] Therefore, the search for an optimal balance between the physicochemical properties of energetic compounds and their impact sensitivity, taking into account the environmental safety of the synthesis methods, remains a pressing challenge.

The use of heterocyclic compounds as a synthetic platform for the construction of high-energy structures has significant advantages over the use of hydrocarbon frameworks. Such compounds have a high enthalpy of formation, higher density and high nitrogen content, which allows to reduce the amount of oxidant used in energetic compositions. At the beginning of the XXI century, a large number of high-energy materials based on various heterocycles were synthesized, new synthetic methods for their design have emerged, and nowadays, the trend in this field has completely shifted towards the application of heterocyclic derivatives.[13–24] In particular, 1,2,5-oxadiazole (furazan) and its *N*-oxide (furoxan) have the highest enthalpy of formation among isomeric oxadiazoles, which explains the extensive study of their derivatives as energetic materials of the new generation.[25,26] It was shown that the combination of

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Translation: N.M.Vinogradova.

Received 8 November 2023

different azole cores in a molecule provides balanced properties of the compound.[27–34] It is important to note that the introduction of the 1,2,4-oxadiazole moiety into the molecule is expected to increase the thermal stability of the compound as well as to reduce the impact sensitivity, *i.e.* in this case, a balance between safety and efficiency of the material is achieved. For this reason, an optimal way to design energetic materials is to combine the 1,2,4-oxadiazole ring with other azoles and various explosophoric substituents ($-NO_2$, $-ONO_2$, $-N-NO_2$, $-N=N-$, $-N=N(O)$, $-N_3$, $-CN$, $-C(NO_2)_3$).

The synthetic approaches to several energetic 1,2,4-oxadiazole derivatives are highlighted in a small review published in 2022.[35] However, since no comprehensive systematization of data on such derivatives has been carried out, the purpose of the present work was to summarize data on the synthesis and properties of high-energy compounds based on 1,2,4-oxadiazole. It considers both compounds based on mono- and bi(1,2,4-oxadiazoles) and structures containing other azoles, in particular pyrazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-triazole, 1,2,4-triazole and tetrazole, and systematizes their physicochemical and energetic performance. It is important to emphasize that the 1,2,4-oxadiazole ring has only recently been considered as a valuable building block in the design of energetic materials. As a result, almost all of the information on this topic presented in this review has been published over the last 15 years, indicating the extreme relevance of this research area.

2. Energetic mono- and bi(1,2,4-oxadiazoles)

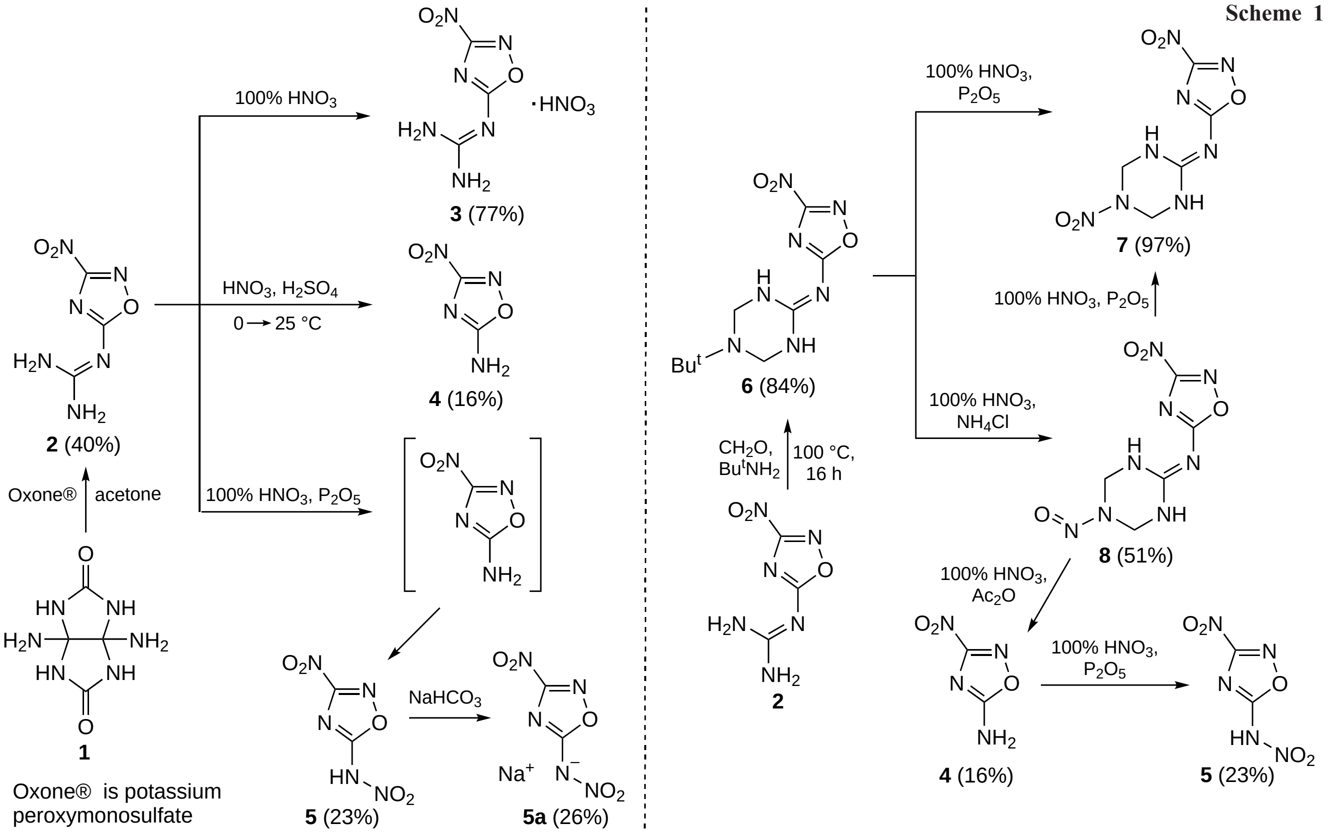
Energetic compounds based on 1,2,4-oxadiazole are generally under-represented in the literature compared to 1,2,5-oxadiazole-based structures, since the former compound has a relatively low enthalpy of formation (100 kJ mol^{-1}) in the series of isomeric nitrogen-containing heterocycles, whereas the enthalpies of formation of furazan and furoxan are 216 and 226 kJ mol^{-1}, respectively.[36] Nevertheless, examples of energetic compounds containing only 1,2,4-oxadiazole as the explosophoric group have been reported.

Thus, in 2012, diaminoglycoluril (**1**) was used as a starting material to produce 5-guanidino-3-nitro-1,2,4-oxadiazole (**2**), which then gave rise to a variety of energetic compounds (Scheme 1).[37] Attempts to nitrate compound **2** with concentrated nitric acid in the absence of any additives led only to the isolation of the corresponding salt **3**. At the same time, the use of a nitrating mixture consisting of sulfuric and nitric acids yielded 5-amino-3-nitro-1,2,4-oxadiazole (**4**), while the system $HNO_3-P_2O_5$ produced 5-nitramino derivative **5**, isolated both in the free form and in the form of salt **5a**. In addition, the Mannich reaction of 1,2,4-oxadiazole **2** with *tert*-butylamine gave compound **6**, the substitutive nitration of which with 100% HNO_3 and P_2O_5 produced nitramine **7**, while the use of 100% HNO_3 in the presence of NH_4Cl led to the isolation of the product of substitutive nitrolysis **8**.

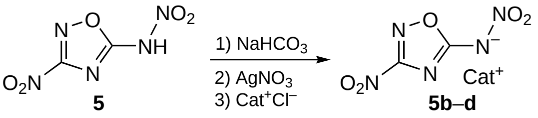
The difference in the action of different nitration systems on compound **8** should also be noted. The treatment of this compound with a mixture of 100% HNO_3 and P_2O_5 leads to oxidation to nitramine **7**, and in the presence of the system 100% HNO_3-Ac_2O, it undergoes cleavage to give oxadiazole **4** in low yield. Among the resulting compounds, 5-nitramino-3-nitro-1,2,4-oxadiazole (**5**) demonstrates detonation performance comparable to that of hexogen (cyclotrimethylene trinitramine, **RDX**) with comparatively lower impact sensitivity. Fu *et al.*[37] hypothesized that the nitro-1,2,4-oxadiazole core incorporated onto the molecule could improve the thermal stability of such a compound while reducing its impact sensitivity.

Based on 5-nitramino-3-nitro-1,2,4-oxadiazole (**5**) and guanidinium cations (Cat), a series of guanidinium energetic salts **5b**–**d** was obtained (Scheme 2, Table 1),[38] among which

Scheme 1



Scheme 2



Cat$^+$ = $(H_2N)_2C{=}\overset{+}{N}H_2$ (**5b**, 80%), $H_2NNHC(NH_2){=}\overset{+}{N}H_2$ (**5c**, 90%), $(H_2NNH)_2C{=}\overset{+}{N}HNH_2$ (**5d**, 85%)

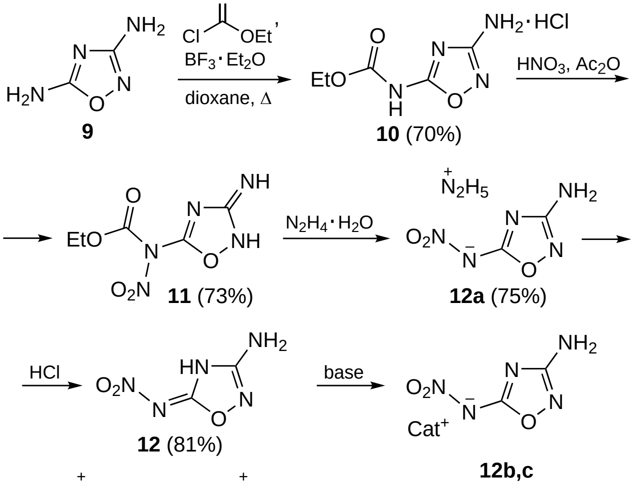
Table 1. Physicochemical properties of compounds **2**, **4**, **5**, **8** and **9** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	Ref.
2	290	1.77	235.1	28.2	8013	>40	37
4	265	1.72	177.0	30.3	8316	–	37
5	219	1.88	227.7	37.7	9095	15	37
5b	258	1.89	226.0	37.6	9319	>40	38
5c	205, 227	1.66	341.4	28.7	8526	>40	38
5d	155	1.77	554.1	35.0	9354	6	38
7	269	1.78	298.2	28.2	8013	10	37
8	252	1.77	354.5	26.4	7760	18	37
CL-20	210	2.04	397.8	45.2	9706	4	39
HMX	280	1.91	74.8	39.2	9144	7	39
RDX	204	1.80	70.7	34.9	8795	7.4	39
TNT	295	1.65	−59.3	21.3	7303	36.6	39

Note. The following designations are used: T_{dec} is decomposition temperature, ρ is density, ΔH_f^o is standard enthalpy of formation, P is detonation pressure, D is detonation velocity, IS is impact sensitivity, **CL-20** is 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, **HMX** is octogen, **RDX** is hexogen, **TNT** is trinitrotoluene. A dash indicates no data are available.

salt **5b** showed the best detonation performance (D = 9319 m s^{-1}; P = 37.6 GPa), while maintaining high thermal stability (T_{dec} = 258 °C).

Scheme 3



Cat$^+$ = $\overset{+}{N}H_4$ (**12b**, 72%), $\overset{+}{N}H_3OH$ (**12c**, 78%)

Acylation of 3,5-diamino-1,2,4-oxadiazole (**9**) with ethyl chloroformate yields the product **10**, the subsequent nitration of which gives the compound **11** as the single tautomer, the mononitration product being formed exclusively.[40] Further reaction with hydrazine hydrate affords the salt **12a**, which is converted to 3-amino-5-nitramino-1,2,4-oxadiazole (**12**) on acidification (Scheme 3). Ammonium and hydroxylammonium salts **12b**,**c** were obtained by the reaction of compound **12** with an appropriate base in methanol. Hydrazinium salt **12a**, with detonation performance comparable to that of hexogen (D = 8897 m s^{-1}; P = 30.6 GPa) and lower sensitivity (IS = 20 J, FS (friction sensitivity) = 240 N), is the most promising among the resulting structures (Table 2).[40]

Chaves *et al.*[41] studied the reactivity of 3,5-diamino-1,2,4-oxadiazole (**9**) in the Mannich condensation with trinitroethanol, since the trinitroethyl moity can significantly increase the oxygen balance of the compound. It was found that only 3-amino group of the heterocycle undergoes this reaction to give structure **13**. An attempt to use 2,2-dinitro-2-fluoroethanol in this process failed; the reaction product **14** was obtained only in trace amounts (Scheme 4). A complete characterization of the properties makes it possible to compare compounds **13** with hexogen, the former having a slightly better oxygen balance (–21.3% *vs* –21.6% for hexogen).

An accessible way of introducing a *gem*-dinitromethyl unit into an energetic compound is by oxidative nitration of the chloroxime group followed by the *in situ* reduction of the resulting chlorodinitromethyl intermediate.

Scheme 4

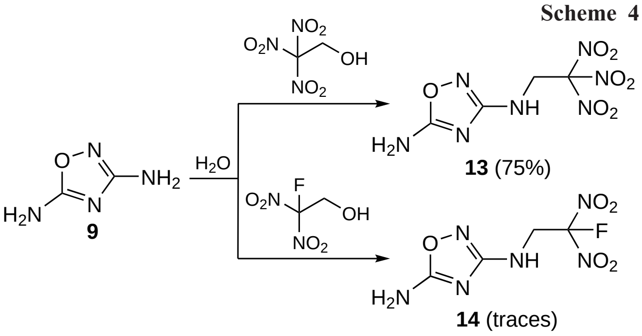


Table 2. Physicochemical properties of compounds **12** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
12 · H_2O	168	1.70	−196.3	25.6	8033	40	360	40
12a	152	1.70	271.2	30.6	8897	20	240	40
12b	214	1.68	116.7	27.5	8493	28	360	40
12c	144	1.73	179.0	32.5	8854	16	240	40
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

When treated with an orthoester, diaminoglyoxime **15** is cyclized to (5-methyl-1,2,4-oxadiazolyl)amidoxime **16**, and further diazotization in hydrochloric acid affords chloroxime **17**, which is nitrated to give 5-methyl-3-(chlorodinitromethyl)-1,2,4-oxadiazole (**18**).[42] The chlorodinitromethyl derivative **18** is then reduced with potassium iodide to produce the corresponding salt **19a**. Further acidification of salt **19a** generates compound **19**, which is neutralized, without isolation, with nitrogenous bases to prepare a series of energetic salts **19b–h** (Scheme 5). Such salts show good thermal stability, satisfactory impact and friction sensitivities (IS > 40 J, FS = 144–324 N) and superior detonation performance (D = 7845–8245 m s^{-1}; P = 22.9–28.4 GPa) compared to similar properties of trotyl (D = 7303 m s^{-1}; P = 21.3 GPa) (Table 3).[42]

A structurally similar chlorodinitromethyl derivative was obtained by nitration of compound **20** in a mixture of trifluoroacetic anhydride (TFAA) and $CHCl_3$; further treatment of the intermediate **21** with potassium iodide and acidification gave 3-dinitromethyl-1,2,4-oxadiazole **22**. Subsequent neutralization produced a series of salts **22b–d** (see Scheme 5).[43]

A series of trinitromethyl-substituted 1,2,4-oxadiazoles were obtained from amidoxime **23** (Scheme 6). In the reaction of substrate **23** with diphosgene, an oxadiazolone moiety is formed and ethyl-2-(4,5-dihydro-1,2,4-oxadiazol-5-one-3-yl)acetate (**24**) is obtained, whereas the reaction with acid chlorides gives the open-chain intermediates **25** and **26**, and subsequent heating

Scheme 5

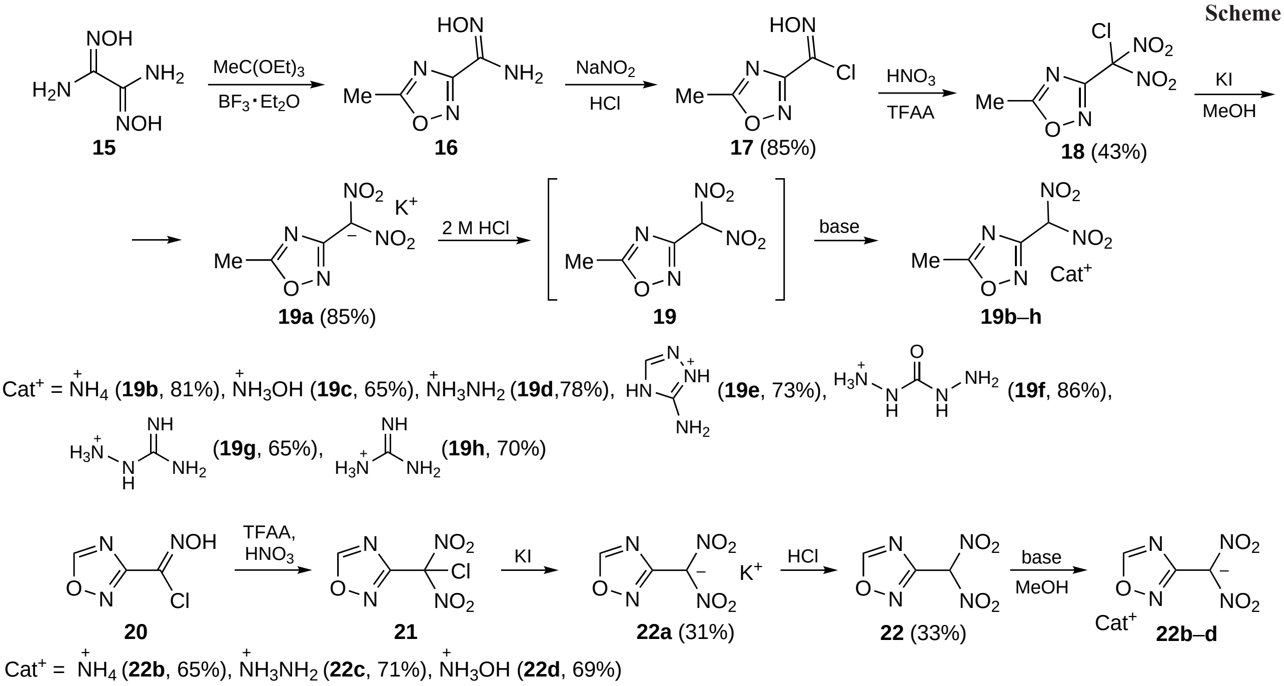
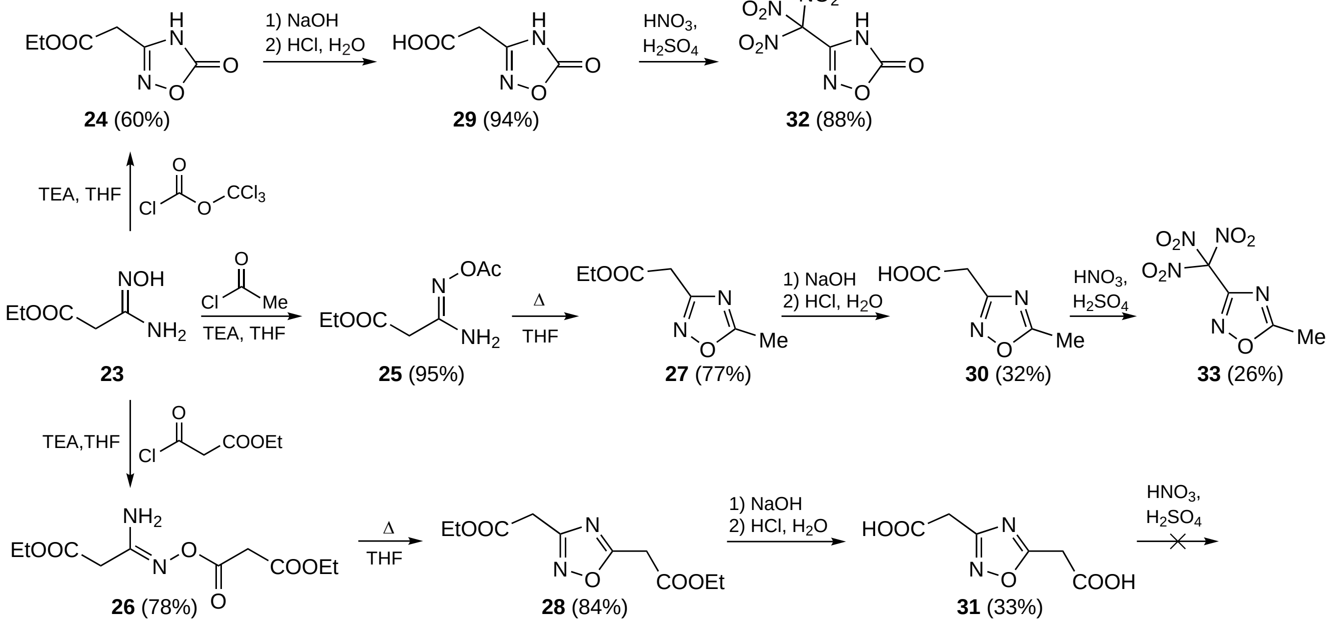


Table 3. Physicochemical properties of compounds **18**, **19**, **22** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
18	–	1.80	–	–	–	–	–	42
19a	178	1.86	−198.6	21.2	7125	>40	160	42
19b	161	1.67	−71.9	25.2	8002	>40	240	42
19c	146	1.70	–25.8	28.4	8239	>40	160	42
19d	166	1.67	81.2	26.6	8245	>40	144	42
19e	108	1.68	163.3	23.3	7845	>40	324	42
19f	137	1.67	4.0	24.8	8084	>40	240	42
19g	147	1.65	1.9	23.1	7920	>40	160	42
19h	185	1.68	−98.8	22.9	7861	>40	144	42
22	165	1.85	−20.6	32.3	8527	4	84	43
22a	176	2.07	−164.4	33.4	8880	0.6	36	43
22b	140	1.74	−29.7	29.4	8301	9	120	43
22c	132	1.81	118.8	34.3	8843	6	144	43
22d	156	1.84	16.7	35.5	8793	6	128	43
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 6



TEA is triethylamine

of the reaction mixture yields 1,2,4-oxadiazole ring in the corresponding oxadiazole acetic acid derivatives **27** and **28**. Acids **29**–**31**, obtained *via* further saponification, were nitrated, and trinitromethyl products **32** and **33** were isolated from compounds **29** and **30** respectively, while attempts to nitrate the diacid **31** lead to the decomposition of the starting compound.[44]

The oxadiazolone derivative **24** is further alkylated with dimethyl sulfate and ethyl bromoacetate to give the compounds **34** and **35**, which were hydrolyzed to give the corresponding acids **36** and **37**.[44] The nitration of the acid **37** delivers the trinitromethyl derivative **38**, while the diacid **36** decomposes under these conditions. Nitration of the oxadiazolylacetic acid esters **24**, **27** and **28** also yields the corresponding dinitro

Scheme 7

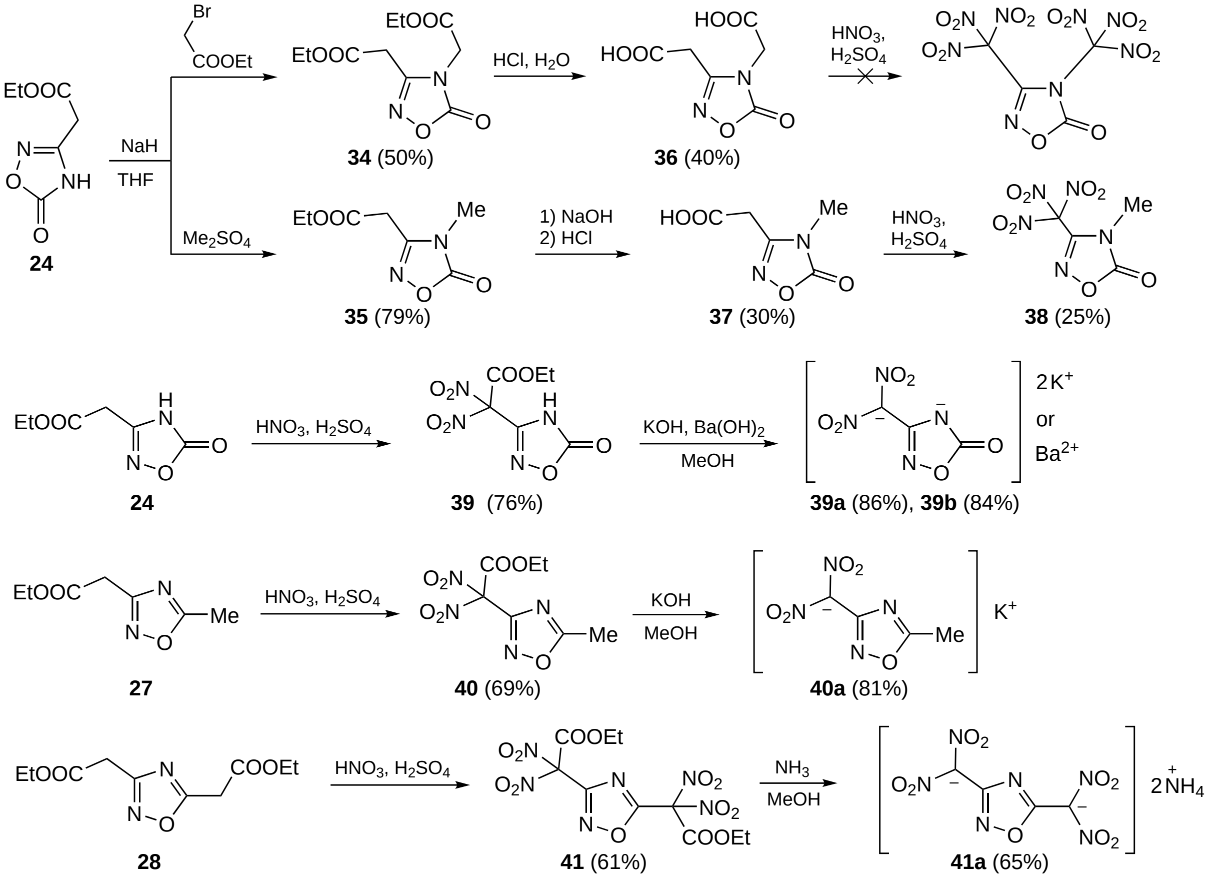


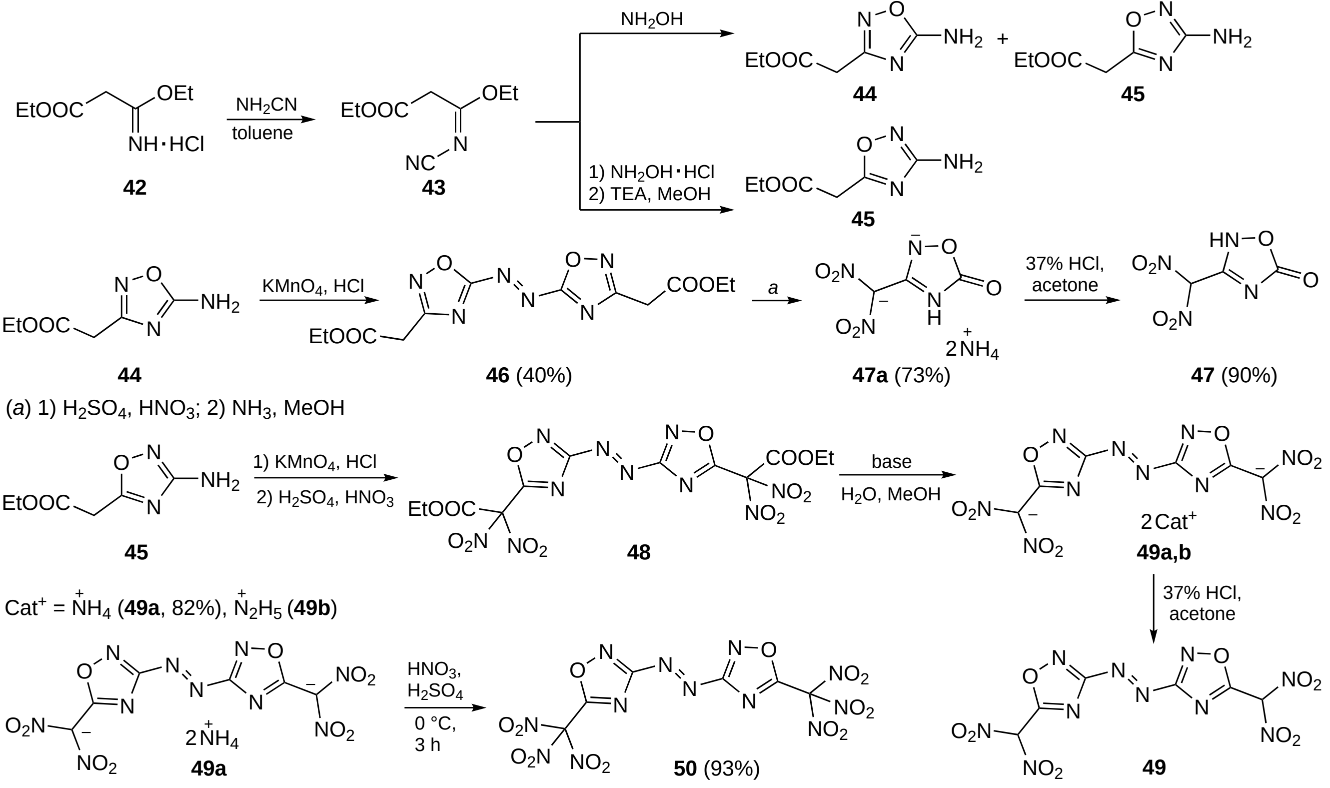
Table 4. Physicochemical properties of compounds **32**, **33**, **38**, **39**, **40a**, **41a**, **47**, **49**, **50** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
32	112	1.95	142.0	33.1	8798	25	324	44
33	148	1.84	43.0	34.6	8779	30	324	44
38	119	1.80	133.0	34.6	8804	30	324	44
39a	219	2.16	–	–	–	3	120	44
39b	145	2.07	–	–	–	10	160	44
40a	165	1.92	–	–	–	4	120	44
40a	130	1.75	–	–	–	3	120	44
47	76	1.85	−236.9	31.3	8454	6	40	45
47a	114	1.71	−477.3	24.5	7937	13	240	45
49	123	1.81	332.9	33.2	8764	6	120	45
49a	173	1.74	126.0	29.8	8348	12	240	45
49b	166	1.78	434.9	33.2	8724	10	240	45
50	125	1.85	461.4	33.2	8722	5	80	46
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39
PETN	202	1.75	480.0	31.6	8525	3	60	44

derivatives **39**–**41**, which are converted into the salts **39a**,**b**, **40a** and **41a** when reacted with potassium or barium hydroxide or when treated with an ammonia solution in methanol (Scheme 7). Trinitromethyl derivatives **32**, **33** and **38** have high positive oxygen balance and detonation performance ($D = 8779-8804$ m s^{-1}, $P = 33.1-34.6$ GPa), comparable with those of pentaerythritol tetranitrate (PETN): $D = 8525$ m s^{-1}, $P = 31.6$ GPa (Table 4).

The reaction between ethyl 3-imino-3-ethoxypropanoate hydrochloride **42** and cyanamide in toluene produced *N*-cyanoimidate **43**, which gave ethyl amino(1,2,4-oxadiazolyl) acetate in a similar manner. Depending on the order in which the reactants are mixed in this reaction, either the 5-amino isomer **44** or the 3-amino isomer **45** is formed.[45] Subsequent oxidation of amine **44** with potassium permanganate in acidic medium gives the corresponding azo derivative **46**, further nitration of which leads to the cleavage of the C–N bond to furnish 3-(dinitromethyl)-1,2,4-oxadiazol-5-one in the form of the ammonium salt **47a** (neutral compound **47** is obtained when treating salt **47a** with hydrochloric acid in acetone). At the same

Scheme 8



(a) 1) H_2SO_4, HNO_3; 2) NH_3, MeOH

Cat$^+$ = $\overset{+}{N}H_4$ (**49a**, 82%), $\overset{+}{N}_2H_5$ (**49b**) time, oxidation of the regioisomeric 3-amino-1,2,4-oxadiazole **45** followed by nitration affords bis(dinitromethyl) derivative **48** retaining the structure of the oxadiazole ring. The treatment action of compound **48** with bases leads to salts **49a,b** containing the dinitromethyl anion, and the neutral dinitromethyl derivative **49** is obtained upon acidification of salt **49a** in acetone (Scheme 8).

The hydrazinium salt **49b** has a rather high density of 1.78 g cm^{-3} and detonation performance comparable to that of hexogen ($D = 8724$ m s^{-1}; $P = 33.2$ GPa) (see Table 4).[45] Unfortunately, the original publication provided no data on the yields of compounds **44, 45, 48, 49** and **49b**. Nitration of ammonium salt **49a** gives compound **50**, containing six nitro groups and thereby having positive oxygen balance (+6.9% to CO_2) and detonation performance comparable to that of hexogen ($D = 8722$ m s^{-1}, $P = 33.2$ GPa).[46]

Diaminoglyoxime **15**, which can be cyclized to give both mono- and bi(oxadiazole) structures, is an important starting material for the synthesis of energetic 1,2,4-oxadiazole-based compounds. For example, condensation of diaminoglyoxime with diethyl malonate produces diethyl 2,2′-{[3,3′-bis(1,2,4-oxadiazole)]-5,5′-diyl}diacetate (**51**), which is further treated with a nitrating mixture to give diethyl 2,2′-{[3,3′-bis(1,2,4-oxadiazole)]-5,5′-diyl}bis(2,2-dinitroacetate) (**52**). The reaction of compound **52** with nitrogen-containing bases offers the potential for the synthesis of energetic dinitromethyl-1,2,4-oxadiazole salts **53a–j** (Scheme 9).[47] Hydroxylammonium salt **53b** has the highest density (1.95 g cm^{-3}) among the above compounds (Table 5).

Hydrolysis of diester **51** produces the corresponding diacid **54**; attempts to crystallize it from DMF led to its decarboxylation to give dimethyl derivative **55**. Substitutive nitration of diacid **54** proceeds as completely as possible to afford bi(trinitromethyl-1,2,4-oxadiazole) **56**. It should be noted that nitration of the diamonium salt **53** with NO_2BF_4 also gives compound **56**, but in lower yield.[48] The reaction of salt **53a** with 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (trade name Selectfluor®) proceeds differently depending on the solvent: carrying out the process in water leads to the cleavage of the bond between the oxadiazole ring and the dinitromethyl anion to form bis(oxadiazolone) **57**, whereas running the reaction in acetonitrile leads to the incorporation of the fluorine atom into the dinitromethyl anion to provide bis(fluorodinitromethyl) derivative **58**.[49] It is also worth noting that the introduction of the fluorine atom instead of one of the nitro groups significantly increases the thermal stability of the compound and reduces its friction sensitivity (see Table 5).

The reaction of amidoxime **23** with oxalyl chloride gives diethyl 2,2′-{[5,5′-bis(1,2,4-oxadiazole)]-3,3′-diyl}diacetate **59**, which is isomeric to compound **51**. Its subsequent hydrolysis leads to a diacid **60**, the nitration of which affords 3,3′-bis(trinitromethyl)-5,5′-bis(1,2,4-oxadiazole) **61**, the regioisomer of structure **56**.[50] When comparing the properties of the two regioisomers, compound **61** was found to have a slightly

Scheme 9

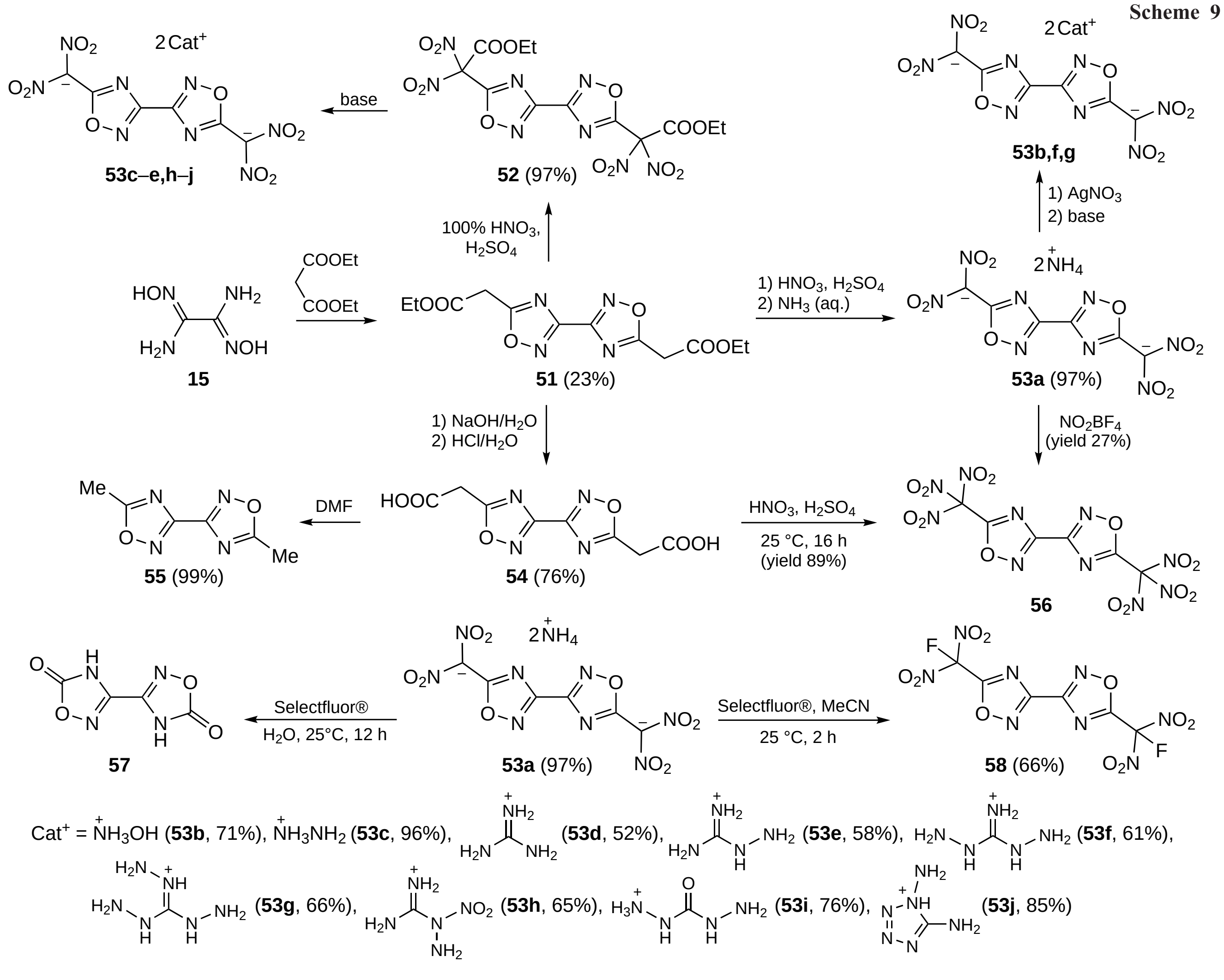
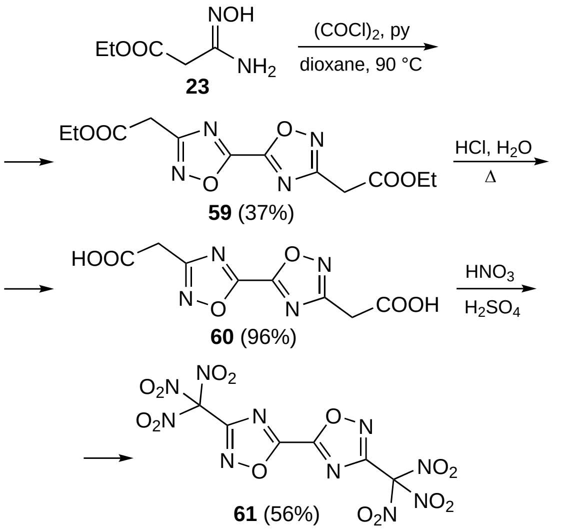


Table 5. Physicochemical properties of compounds **53**, **56**, **58**, **61** in comparison with similar parameters of known explosives.

Compound	$T_{\text{dec,}}$ °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
53a	223	1.90	−91.6	35.0	8618	6	252	47
53b	156	1.95	41.1	39.4	8935	4	108	47
53c	135	1.76	–	–	–	40	288	47
53d	239	1.75	−73.4	27.0	8038	35	360	47
53e	141	1.70	148.6	26.6	8078	6	360	47
53f	197	1.66	386.3	26.3	8108	20	288	47
53g	204	1.73	595.1	29.8	8513	2	216	47
53h	149	1.85	593.1	36.6	8872	7	120	47
53i	197	1.79	188.5	31.6	8508	5	252	47
53j	178	1.84	920.5	34.3	8744	2	108	47
56	124	1.936	61.9	34.5	8814	10	80	49
58	151	1.96	−362.4	30.1	8367	10	192	49
61	142.8	1.942	165.5	34.3	8882	12	360	50
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

higher density, a higher decomposition temperature (142.8 °C) and friction insensitivity (Scheme 10).

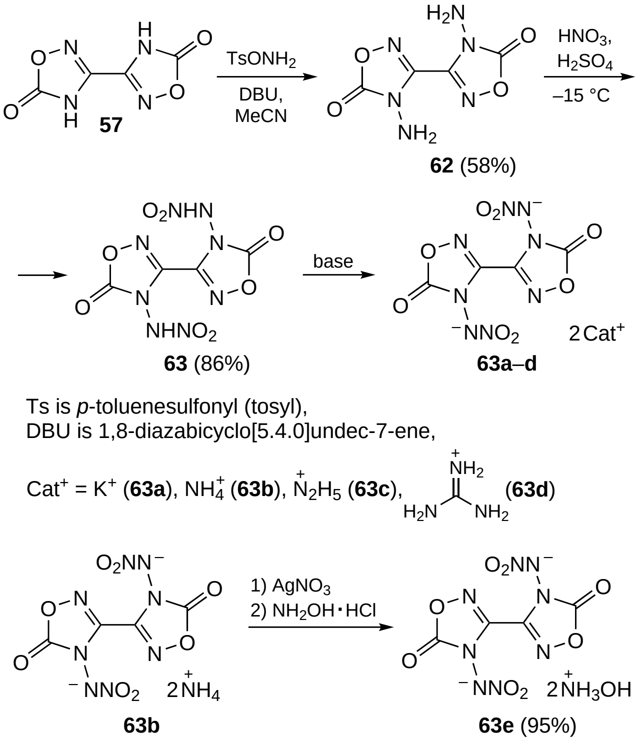
Scheme 10



Compound **57** was aminated to give structure **62**, the nitration of which gives dinitramide **63**, which has high density (1.932 g cm^{-3}), moderate thermal stability and detonation characteristics comparable to those of octogen (D = 9106 m s^{-1}, P = 36.6 GPa).[51] When treated with bases, nitramide **63** delivers a number of energetic salts **63a–e** (Scheme 11). Hydroxylammonium salt **63e** shows detonation velocity and pressure (D = 9507 m s^{-1}, P = 40.1 GPa) comparable to those of isowurtzitane **CL-20**, and also high density (1.929 g cm^{-3}) (Table 6).

Cyclization of diaminoglyoxime **15** with chloroxoethyl acetate gave bis(oxadiazole) derivative **64**, which was further hydrolyzed to give alcohol **65**. Subsequent nitration of compound **65** led to bis(1,2,4-oxadiazole)bis(methylene)dinitrate **66** (Scheme 12). By optimizing the synthesis conditions, the yield of the target compound was improved more than five-fold.[52] The resulting material is proposed to be used as a potential melt-castable explosive as well as an energetic plasticizer.

Scheme 11



Ts is *p*-toluenesulfonyl (tosyl),
DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene,

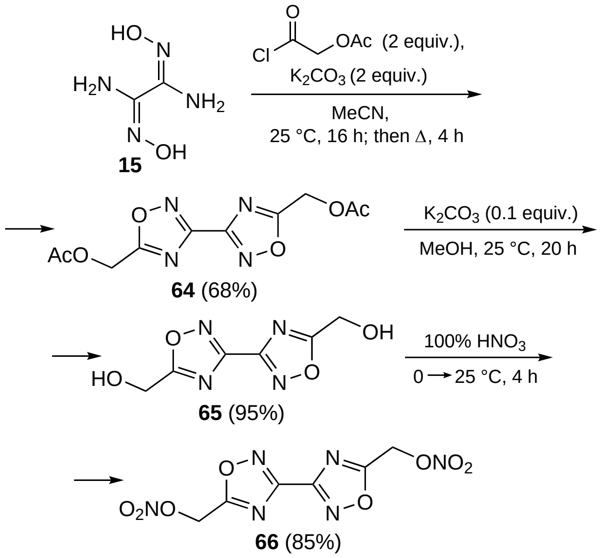
Cat$^+$ = K$^+$ (**63a**), NH_4^+ (**63b**), $N_2H_5^+$ (**63c**), $C(NH_2)_3^+$ (**63d**)

The reaction of diaminoglyoxime **15** with chloroacetyl chloride followed by boiling in dimethylformamide gave bis(chloromethyl-1,2,4-oxadiazole) **67**, after which the chlorine atoms in the product were successfully replaced by azido groups to furnish bis(azidomethyl-1,2,4-oxadiazole) **68** (Scheme 13).[53] Similarly, bis(amidoxime)furoxan **69** was converted to the dichloromethyl derivative **70**, which was further reduced with tin(II) chloride in hydrochloric acid to give furazan **71**. Treatment of compounds **70** and **71** with sodium azide in acetonitrile provided the corresponding azidomethyl derivatives **72** and **73**. These compounds are liquid at room temperature, have high enthalpies of formation (1072.9–1079.9 kJ mol^{-1}), and also

Table 6. Physicochemical properties of compounds **62** and **63** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
62	198	1.832	–87.4	23.6	7783	40	360	51
63	105	1.932	51.5	36.6	9106	10	160	51
63a	178	2.180	–252.3	33.0	8494	3	20	51
63b	205	1.827	25.6	32.8	8796	25	240	51
63c	118	1.829	355.7	35.5	9166	22	180	51
63d	167	1.563	104.9	23.4	7969	40	360	51
63e	134	1.929	131.5	40.1	9507	13	120	51
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

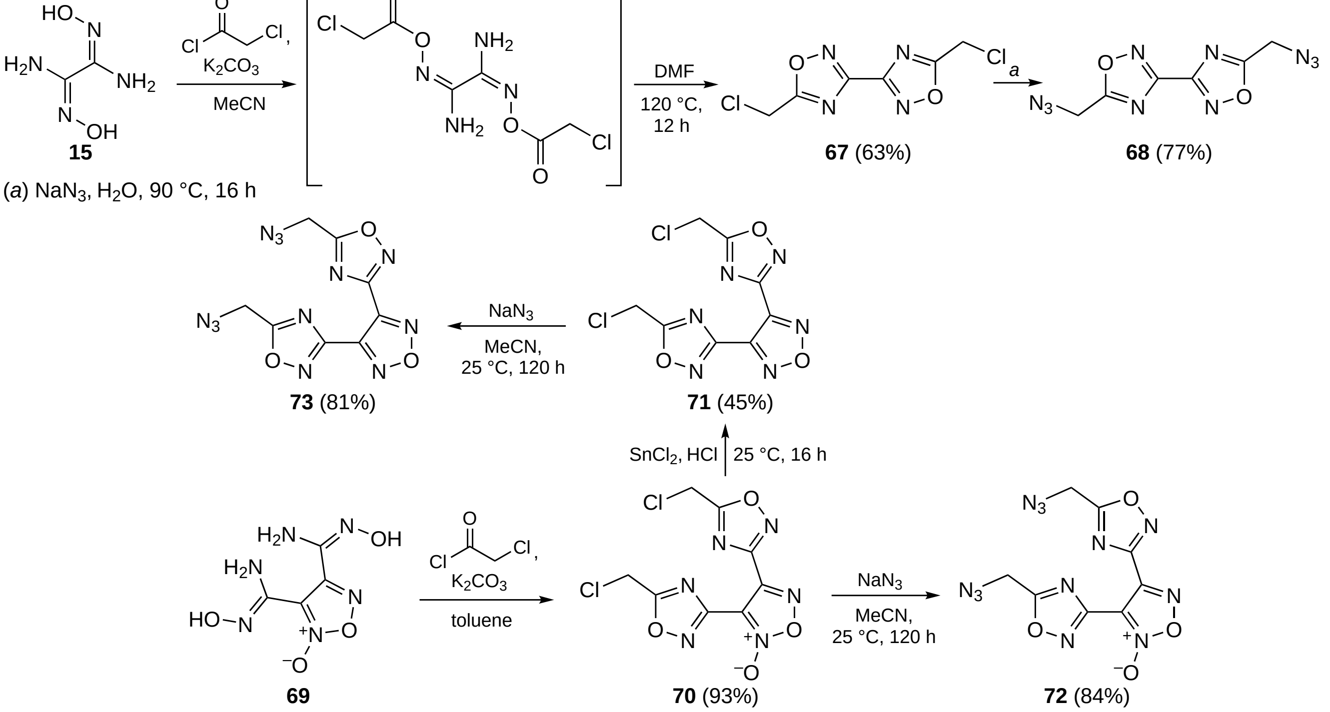
Scheme 12



show lower impact sensitivity compared to trinitrotoluene, while having similar detonation properties ($D = 7672-8071$ m s^{-1}; $P = 22.7-26.1$ GPa) (Table 7).

Johnson *et al.*[54] managed to combine the 1,2,4-oxadiazole ring and the nitratomethyl-substituted isoxazole core in a molecule. In an attempt to obtain the starting compound **74** by cyclization of diaminoglyoxime with triethyl orthoformate, a mixture of mono- (**74**) and bicyclization products (**75**) was isolated in the form of a co-crystallisate. However, treatment of such a co-crystallisate with sodium nitrite in concentrated HCl leads to the precipitation of pure hydroxymoyl chloride **20**. The formation of the isoxazole ring in structure **76** is achieved by [3+2]-cycloaddition of propargyl alcohol to nitrile oxide generated from hydroxymoyl chloride **75** (Scheme 14). Further nitration of the hydroxymethyl group in compound **76** gives the product **77**, which has detonation properties comparable to those of trinitrotoluene ($D = 7087$ m s^{-1}, $P = 21.0$ GPa) and also melts without decomposition at 76.6 °C ($T_{dec} = 184.5$ °C) (Table 8), allowing its use as a melt-castable explosive.

Scheme 13

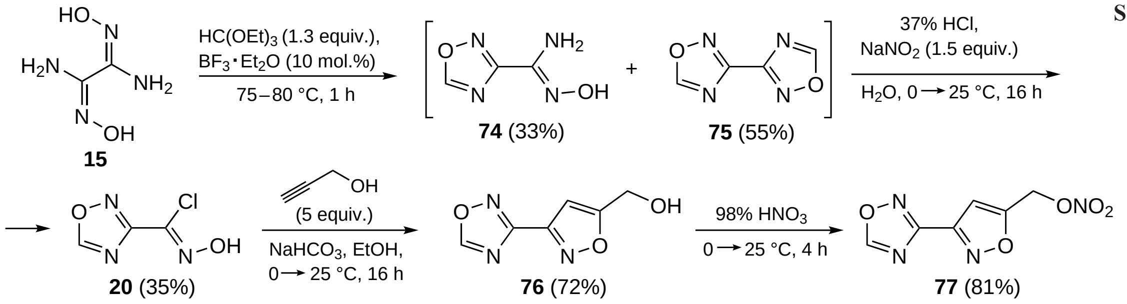


(*a*) NaN_3, H_2O, 90 °C, 16 h

Table 7. Physicochemical properties of compounds **66**, **68**, **72**, **73** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
66	183.4	1.83	−79.4	29.4	8180	8.7	282	52
68	209	1.65	781.5	19.2	7221	>40	>360	53
72	210	1.80	1079.9	26.1	8071	20	–	53
73	193	1.75	1072.9	22.7	7672	40	–	53
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 14



Cao *et al.*[55] proposed a convenient synthetic approach to 5,5′-diamino-3,3′-bi(1,2,4-oxadiazole) based on the cyclization of diaminoglioxime **15** and trichloroacetic anhydride (TCAA) to form the compound **78** and the substitution of the amino functionality by the trichloromethyl group using ammonia solution in methanol. Subsequent nitration of the diaminooxadiazole **79** gives dinitramine **80**, which can be neutralized with various nitrogen-rich bases to deliver a series of energetic salts **80a–g** (Scheme 15). Among these compounds, the hydroxylammonium salt **80b** has the best detonation performance (D = 8916 m s^{-1}, P = 36.2 GPa), exceeding that of hexogen (see Table 8).

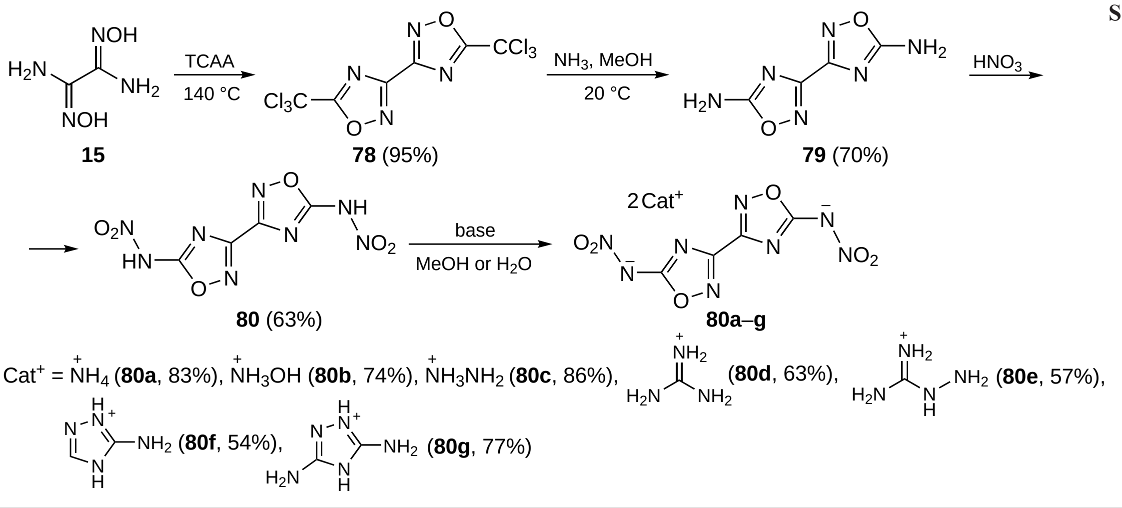
A similar synthetic scheme was used to obtain energetic structures of a new type, consisting of two 1,2,4-oxadiazole rings bridged with a methylene unit so as to desensitize the resulting structure (Scheme 16).[56] Replacing the trichloromethyl group in the derivative **81** with an amino group affords methylenebis(amino-1,2,4-oxadiazole) **82**. When compound **82** was nitrated with nitric acid, the authors failed to extract dinitramine **83** from the aqueous fraction. However, the use of N_2O_5 as a nitrating agent greatly simplifies isolation and purification of product **83**, the neutralization of which produced a series of energetic salts.[56] Such compounds have good thermal stabilities and moderate impact sensitivities. Among salts **83a–f**, the hydrazinium salt **83b** has the highest detonation performance (D = 7962 m s^{-1}, P = 27.1 GPa) (Table 9).

An important class of high-energy materials are compounds containing an azo functionality (–N=N–) which acts as a linker to connect azole rings in the molecule. It was shown that the presence of the azo moiety significantly increases the enthalpy of formation of the molecule and reduces its impact sensitivity. For example, Thottempudi *et al.*[57] report the synthesis of azo-coupled 5-amino-1,2,4-oxadiazole **84** using sodium dicyanoamide (Scheme 17). However, an attempt to nitrate the amino groups of compound **84** with nitric acid in acetic anhydride only led to azobis(1,2,4-oxadiazolone) **85** isolated in 54% yield. It was suggested that the intermediate dinitramide decomposes during the aqueous work-up of the reaction mixture, with the nitro group being replaced by the hydroxyl group, thereby affording compound **85**. Due to the presence of the N–H bond in the azobis(oxadiazolone) structure,

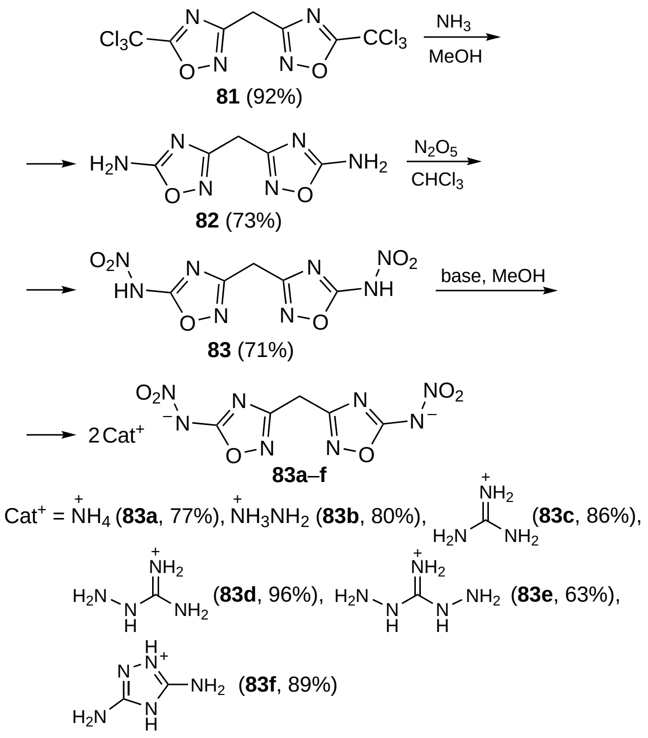
Table 8. Physicochemical properties of compounds **77** and **80** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
77	185	1.64	−5.8	21.0	7087	>15	>360	54
80	137	1.86	175.8	31.8	8388	8	128	55
80a	245	1.73	−3.0	26.9	7881	44	240	55
80b	190	1.88	110.0	36.2	8916	4	192	55
80c	223	1.79	304.6	31.4	8421	3	160	55
80d	317	1.65	−3.4	21.5	7154	10	>360	55
80e	237	1.63	230.6	22.6	7369	13	>360	55
80f	248	1.76	508.8	25.1	7562	5	240	55
80g	195	1.80	410.0	25.3	7553	5	252	55
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

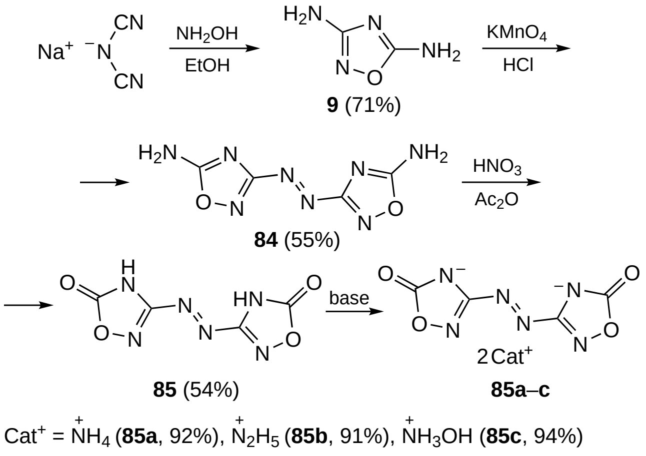
Scheme 15



Scheme 16



Scheme 17



85 reacts with basic amines to give a series of energetic salts **85a–c** in high yields. These compounds show lower impact sensitivities than trinitrotoluene (Table 10).

Triazene (–NH–N=N) and amino (–NH–) functionalities can also be used as bridging groups for azoles, as the presence of the N–H linkage makes them excellent precursors for energetic salts. Oxidation of 5-amino-3-nitro-1,2,4-oxadiazole (**4**) with sodium dichloroisocyanurate (SDIC) gave a mixture of amino- and triazene-bridged derivatives **86a** and **87a** (Scheme 18). After separation of the mixture, individual products were

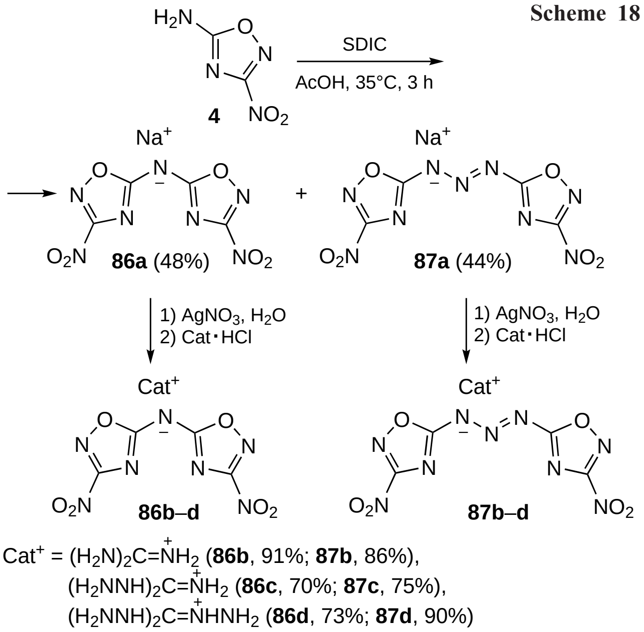
Table 9. Physicochemical properties of compounds **83** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
83	152	1.74	115.9	26.4	7787	5	160	56
83a	209	1.76	−39.1	26.5	7775	8	324	56
83b	148	1.69	300.5	27.1	7962	3	96	56
83c	195	1.57	−14.8	19.1	6845	11	>360	56
83d	199	1.61	198.9	23.4	7511	9	192	56
83e	183	1.68	429.3	24.9	7661	7.5	128	56
83f	192	1.73	389.1	23.0	7291	14	168	56
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Table 10. Physicochemical properties of compounds **84**–**87** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	Ref.
84	355	1.73	334.3	23.4	7980	>40	57
85	123	1.70	−80.8	20.7	7363	>40	57
85a	237	1.68	−463.9	16.7	7006	>40	57
85b	140	1.69	−115.4	22.1	7875	>40	57
85c	112	1.67	−306.3	22.7	7222	>40	57
86a	249	1.80	126.0	25.0	7701	20	58
86b	241	1.80	124.0	29.0	8351	>40	58
86c	197	1.69	347.3	26.5	8205	>40	58
86d	171	1.74	470.7	29.4	8542	30	58
87a	227	1.85	405.2	29.0	8180	>40	58
87b	206	1.62	416.1	24.2	7894	>40	58
87c	189	1.62	628.2	25.4	8084	>40	58
87d	166	1.60	758.4	25.3	8118	25	58
CL-20	210	2.04	397.8	45.2	9706	4	39
HMX	280	1.91	74.8	39.2	9144	7	39
RDX	210	1.80	70.7	34.9	8795	7.4	39
TNT	295	1.65	−59.3	21.3	7303	36.6	39

Scheme 18



subjected to the two-step cation metathesis, which provided a series of the corresponding energetic salts **86b–d** and **87b–d**.[58] Detonation performance parameters of these compounds ($D = 7701–8542$ m s^{-1}; $P = 24.2–29.4$ GPa) are comparable to those of trinitrotoluene (see Table 10) and these molecules show much lower impact sensitivities. Nitration of both amino groups in the azo compound **84** furnished the dinitramide azobis(oxadiazole) **88**, and subsequent metathesis with nitrogen-containing bases gave rise to a series of energetic salts **88a–h** (Scheme 19). Among these derivatives, the hydroxylammonium salt **88a** is the most promising compound, combining high detonation properties ($D = 9243$ m s^{-1}; $P = 39.2$ GPa) with acceptable thermal stability ($T_{\text{dec}} = 169$ °C) and sensitivity (Table 11).[59]

In addition to azo functionalities and methylene bridges, it is possible to use an ethene unit as a linker between nitrogen-

Scheme 19

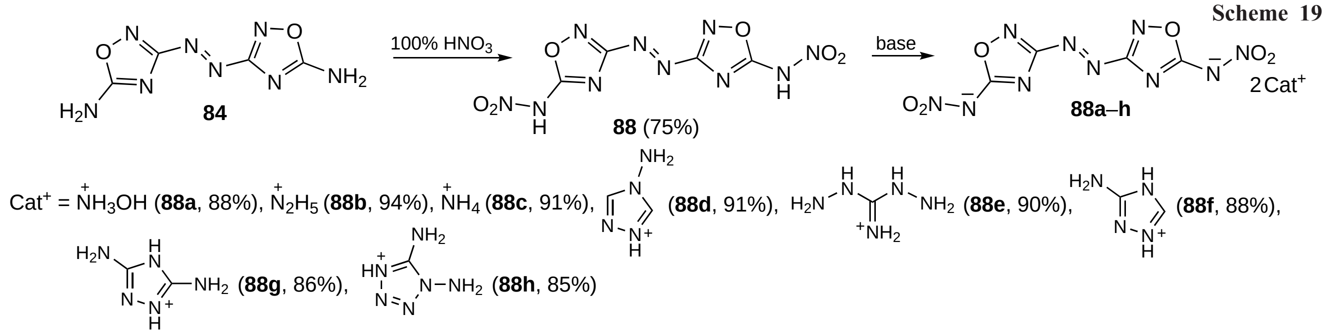


Table 11. Physicochemical properties of compounds **88** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
88	140	1.90	487.2	37.5	9190	2	10	59
88a	169	1.86	514.2	39.2	9243	10	160	59
88b	175	1.81	726.5	35.8	9240	8	120	59
88c	261	1.75	411.8	31.1	8670	12	240	59
88d	213	1.74	1220.0	29.2	8557	20	240	59
88e	160	1.71	711.5	27.6	8570	17	160	59
88f	241	1.74	938.6	27.5	8381	18	160	59
88g	183	1.76	904.8	27.7	8466	16	160	59
88h	188	1.74	1685.6	32.8	8955	12	120	59
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 20

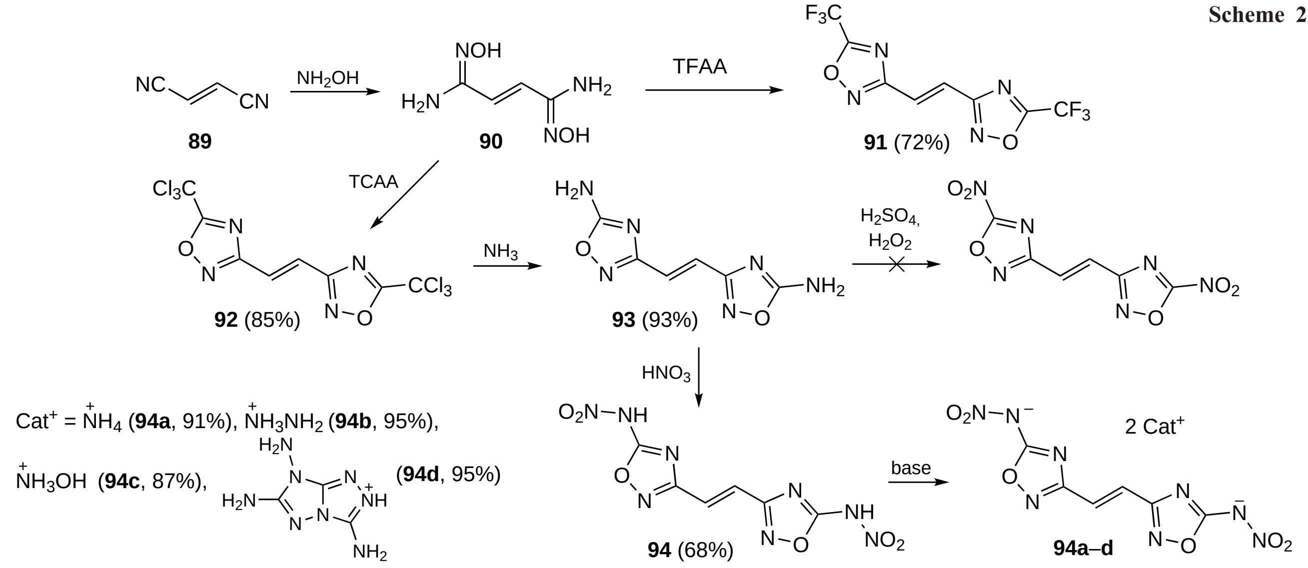


Table 12. Physicochemical properties of compounds **91**, **94** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
91	143	1.83	−1041.7	11.5	5535	40	360	61
94	153	1.81	482.4	29.9	8382	13	240	61
94a	249	1.70	260.1	24.7	8037	18	360	61
94b	204	1.72	585.0	28.3	8548	18	360	61
94c	195	1.81	365.0	32.2	8778	15	360	61
94d	267	1.78	1444.9	33.4	9305	20	360	61
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

containing heterocycles.[60] In this case, the overall planar structure of the target compound makes it possible to reduce its impact and friction sensitivities compared to similar structures containing an azo group, as well as to increase its density. The addition of hydroxylamine to fumaronitrile **89** afforded the starting compound **90**, which was cyclized with trifluoro- and trichloroacetic anhydrides to give products **91** and **92** respectively. Replacement of the CCl_3 moiety with an amino group by reaction with gaseous NH_3 yields compound **93**, and further nitration and metathesis with bases provided dinitramine **94** and its energetic salts **94a–d** (Scheme 20). Among the structures obtained, the salts **94c,d** have acceptable sensitivities (IS = 15–20 J, FS = 360 N) and good detonation performance ($D = 8778-9305$ m s^{-1}, $P = 32.2-33.4$ GPa) (Table 12), which allow their use as energetic materials. It is also worth noting that an attempt to oxidize the amino groups in compound **93** with hydrogen peroxide resulted in the decomposition of the starting compound.[61]

3. 1,2,4-Oxadiazole/pyrazole-based energetic compounds

The pyrazole ring has long attracted the attention of researchers due to its high thermal stability, as well as the possibility of chemical modification and introduction of various functional groups into the molecule, including amino, nitramino and nitro groups.[62,63] In particular, a number of energetic compounds containing pyrazole and 1,2,4-oxadiazole heterocycles have been synthesized from commercially available 1*H*-pyrazole-3-carboxylic acid (**95**). The polycyclic precursors **96** and **97** were obtained by cyclization of the acid chloride **98** with pyrazolyl amidoxime and diaminoglyoxime respectively. Further nitration of the pyrazole ring at the C(3) and C(4) positions was carried out under different conditions. For example, when treated with excess nitric acid and acetic anhydride, *N*-nitro derivatives are formed which, when heated to 140 °C in benzonitrile, are rearranged to the corresponding 3-nitro derivatives **99** and **100** (Scheme 21).[64] Further nitration of compounds **99** and **100** gives dinitropyrazoles **101** and **102**. On the other hand, the use of a nitrating mixture consisting of sulfuric and nitric acids leads to 4-nitro derivatives **103** and **104**, which were further nitrated with a mixture of nitric acid and acetic anhydride to yield compounds **105** and **106** containing a nitro group at the heterocyclic nitrogen atom. Among the compounds obtained, products **101** and **102** have comparable detonation velocities and pressures ($D = 8685-8741$ m s^{-1}, $P = 33.4-34.0$ GPa), while being less sensitive to impact and friction (Table 13), and structures **105** and **106** have the best detonation performances ($D = 8867-8904$ m s^{-1}, $P = 34.5-35.1$ GPa).

In 2022, high-energy molecules were synthesized containing three different azoles: pyrazole, furazan and 1,2,4-oxadiazole.[65] The first cyclization of amidoxime **107** with 1*H*-pyrazole-3-carbonyl chloride affords the tricyclic derivative **108**, which is oxidized with a mixture of 98% sulfuric acid and 30% hydrogen peroxide to give the nitro compound **109** in 68% yield. A

Scheme 21

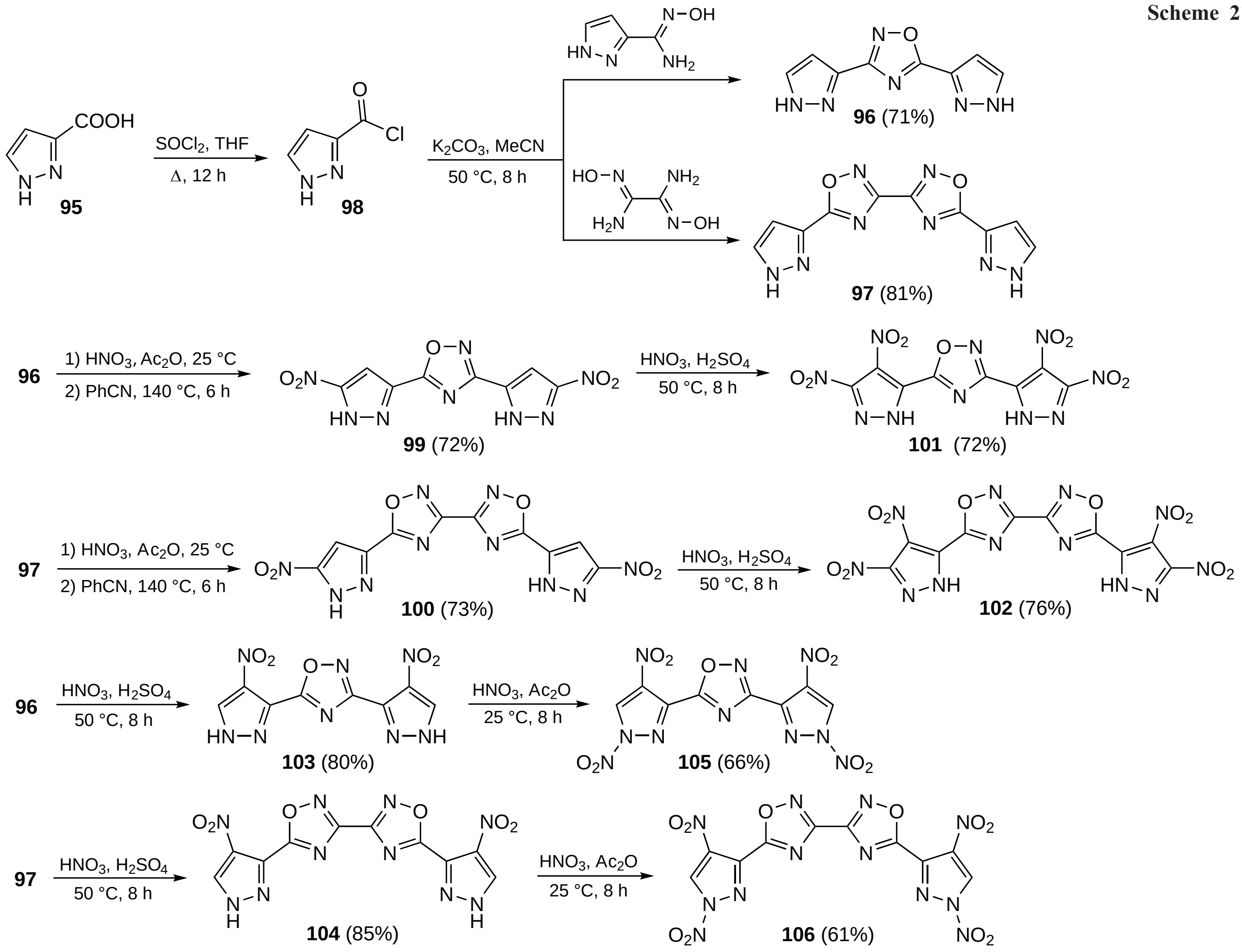


Table 13. Physicochemical properties of compounds **101–106** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
101	274	1.84	659.8	34.0	8741	33	>360	64
102	272	1.86	789.3	33.4	8685	31	>360	64
103	314	1.77	548.5	26.4	8027	>40	>360	64
104	317	1.78	676.9	25.2	7991	>40	>360	64
105	156	1.82	825.4	35.1	8904	17	250	64
106	172	1.83	992.5	34.5	8867	8	160	64
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

sequential introduction of nitro groups into the pyrazole ring is then carried out using different synthetic strategies. First, the dinitro derivatives **110** and **111** (the latter was not isolated in the individual state) were prepared and subjected to additional nitration to isomers **112** and **113** (Scheme 22).[65] Compound **113** has a high density (1.876 g cm^{-3}), good detonation velocities and pressures ($D = 9094$ m s^{-1}, $P = 36.7$ GPa) exceeding those of hexogen, as well as acceptable sensitivity values (IS = 24 J, FS = 300 N) and satisfactory thermal stability ($T_{dec} = 265$ °C) (Table 14).

Since the NH functionality in compound **113** is rather acidic due to the presence of two electron-withdrawing nitro groups in the pyrazole ring, an attempt was made to convert this compound to the salt form by the action of a weak base (aqueous ammonia solution). Instead, a chemoselective substitution of the nitro group in the furazan ring by an amino group was observed, and energetic salts were obtained by nitration of product **114** with fuming nitric acid followed by the treatment with an aqueous ammonia solution, hydrazine hydrate or hydroxylamine (Scheme 23). The salts **115a–c** have detonation properties corresponding to the neutral compound ($D = 8618–8996$ m s^{-1}, P = 32.0–36.3 GPa).

A series of isomeric 3,5-bis(nitropyrazolyl)-1,2,4-oxadiazoles were prepared using a strategy of acylation of the corresponding

Scheme 22

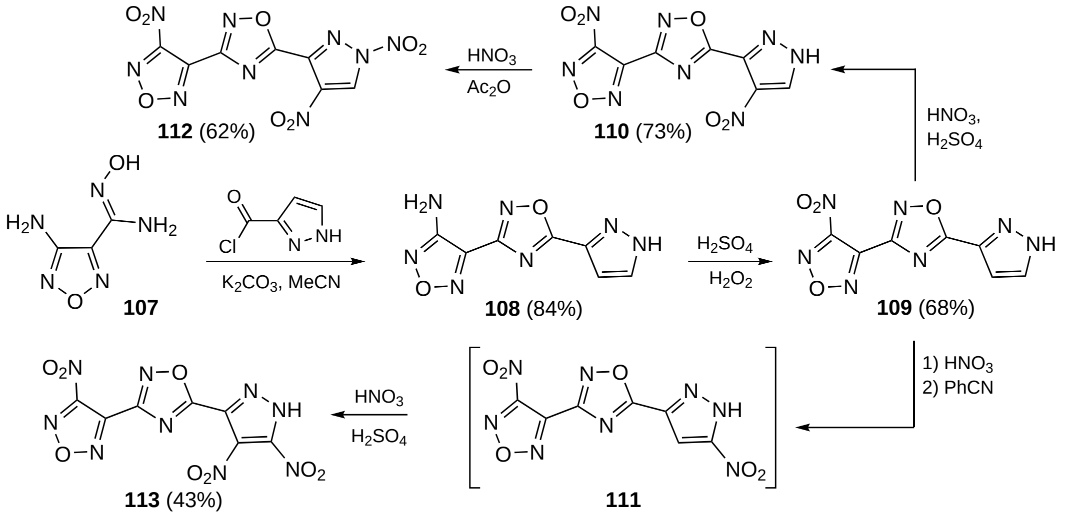


Table 14. Physicochemical properties of compounds **110**, **112** – **115** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
110	172	1.85	773.0	36.4	9067	18	200	65
112	272	1.85	648.0	32.5	8665	35	>360	65
113	265	1.88	707.0	36.7	9094	24	300	65
114	215	1.84	636.0	32.2	8609	28	320	65
115a	197	1.79	563.0	32.0	8618	30	360	65
115b	181	1.83	841.0	35.0	8996	22	240	65
115c	182	1.83	699.0	36.3	8942	26	300	65
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

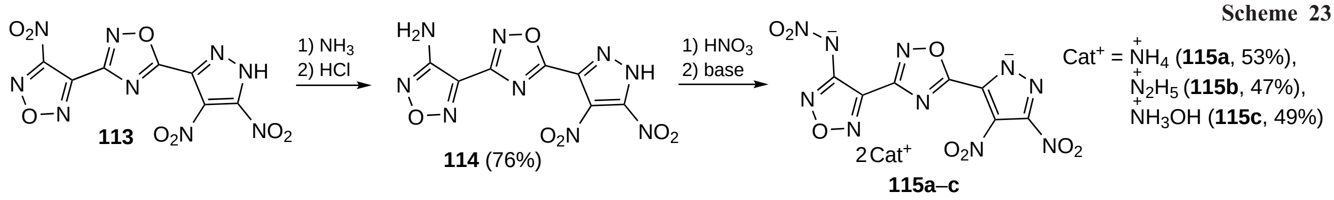
amidoximes **116** with pyrazole carboxylic acid chlorides **117** in acetonitrile in the presence of triethylamine to give derivatives **118** and subsequent closure of the 1,2,4-oxadiazole ring in boiling acetic acid. This furnished the target products **119a–i**. The combination of regioisomeric nitropyrazoles as starting compounds allows a wide range of isomeric structures to be obtained in sufficiently high yields (Scheme 24).[66] Such compounds have high decomposition temperatures and moderate to high densities. In the range of isomeric structures, heterocycle **119b** has the highest density (1.804 g cm^{-3}) and excellent thermal stability (T_{dec} = 343 °C), as well as detonation properties comparable to those of trotyl (D = 7670 m s^{-1}, P = 27.5 GPa) (Table 15).

A similar synthetic methodology has been used for the oxadiazole ring closure in compounds **120a**,**b**.[67] Further oxidation of the amino group in the 1,2,5-oxadiazole moiety of tricyclic energetic structures **121a**,**b** yields nitro derivatives **122a**,**b** or azo compounds **123a**,**b** (Scheme 25).[67] These heterocycles have detonation properties (D = 7800 – 8100 m s^{-1}, P = 30 – 32 GPa) exceeding those of **TNT**, while exhibiting comparable impact sensitivities (Table 16).

Energetic structures containing methylene-bridged 5-nitramino-3,4-dinitropyrazole and 5-nitrosamino-1,2,4-oxadiazole moieties were constructed using a similar synthetic approach (Scheme 26).[68] The nitro group at the pyrazole ring in heterocycle **124** is replaced by an amino group when treated with ammonia to give compound **125**, and further nitration affords dinitramine **126**. The action of alkali on compounds **125** and **126** affords the corresponding potassium salts **127** and **128**. A study of the physicochemical properties shows that compound **128** is extremely impact sensitive and has good detonation performance (D = 8059 m s^{-1}, P = 30.9 GPa) (Table 17), which allows it to be considered as a primary explosive.

Previously, the same research group[69] obtained similar energetic compounds differing in the set of substituents in polynitropyrazole (Scheme 27). The addition of hydroxylamine to nitrile **129** leads to the corresponding amidoxime **130**, and the 5-amino-1,2,4-oxadiazole ring in compound **131** is constructed *via* cyclization of substrate **130** with cyanogen bromide in the presence of sodium bicarbonate. Attempted nitration of the amino group at the pyrazole ring in compound **131** gave unexpectedly the internal diazonium salt **132** instead of nitramine, and the action of 30% hydrogen peroxide in sulfuric acid allowed the chemoselective oxidation of the amino group at the pyrazole ring to afford three nitropyrazoles **133**. Subsequent oxidative coupling afforded a tetracyclic azo derivative **134** and nitration with nitric acid furnished nitramine **135**. It is worth noting that when neutralizing compound **135** with excess ammonia, a nucleophilic substitution of one of the nitro groups in the pyrazole rings occurs, leading to the salt **136**. Among the structures obtained, the azo compound **134** has the best thermal stability (T_{dec} = 250 °C), good detonation performance (D = 8897 m s^{-1}, P = 35.2 GPa) and moderate sensitivity to mechanical stimuli (IS = 10 J, FS = 120 N) (Table 18). (Heterocycle **135** has detonation characteristics comparable to

Scheme 23



Scheme 24

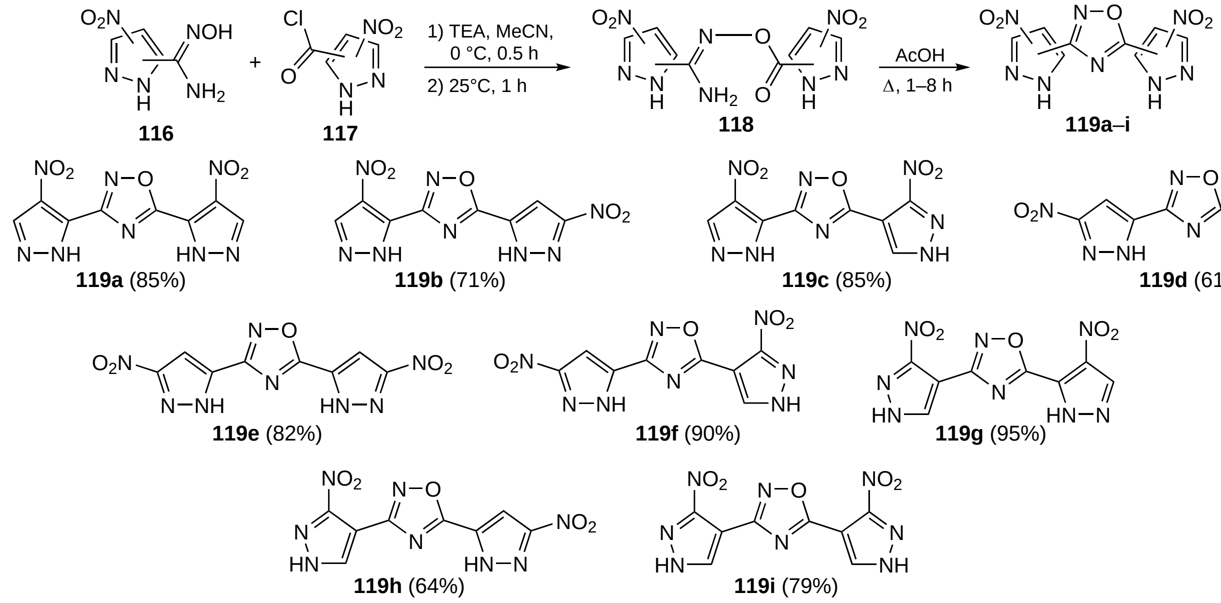


Table 15. Physicochemical properties of compounds **119** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
119a	335	1.699	444	24.1	7350	60±20	>360	66
119b	343	1.804	435	27.5	7670	12±4	>360	66
119c	313	1.741	451	25.5	7490	23±10	>360	66
119d	312	1.770	441	26.4	7570	35±9	>360	66
119e	312	1.759	448	26.0	7540	15±3	>360	66
119g	288	1.637	459	22.3	7180	60±20	>360	66
119h	295	1.787	444	27.0	7630	11±6	>360	66
119i	263	1.679	456	23.5	7290	44±13	>360	66
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 25

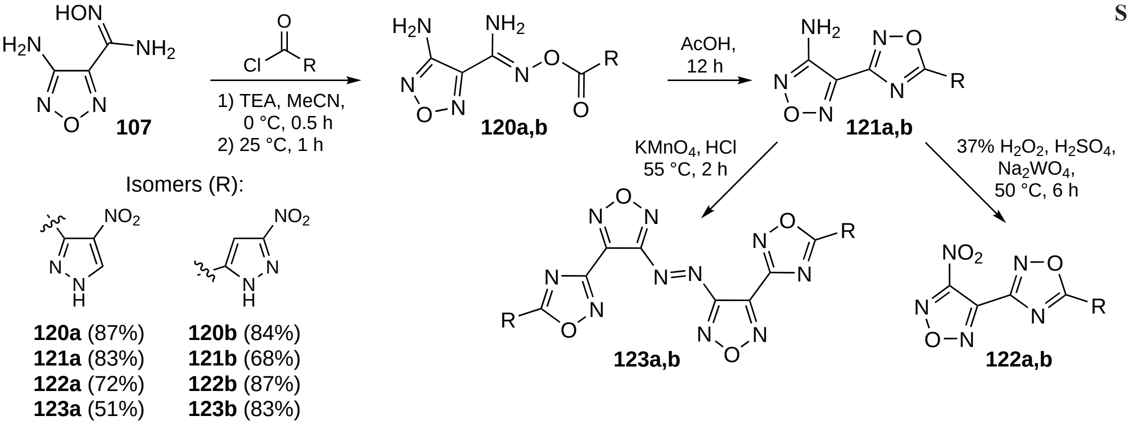


Table 16. Physicochemical properties of compounds **122**, **123** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
122a	256	1.814	520	32	8100	25	360	67
122b	260	1.749	534	30	7900	6	270	67
123a	229	1.738	1362	30	7800	21	>360	67
123b	231	1.75	1370	30	7800	29	>360	67
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 26

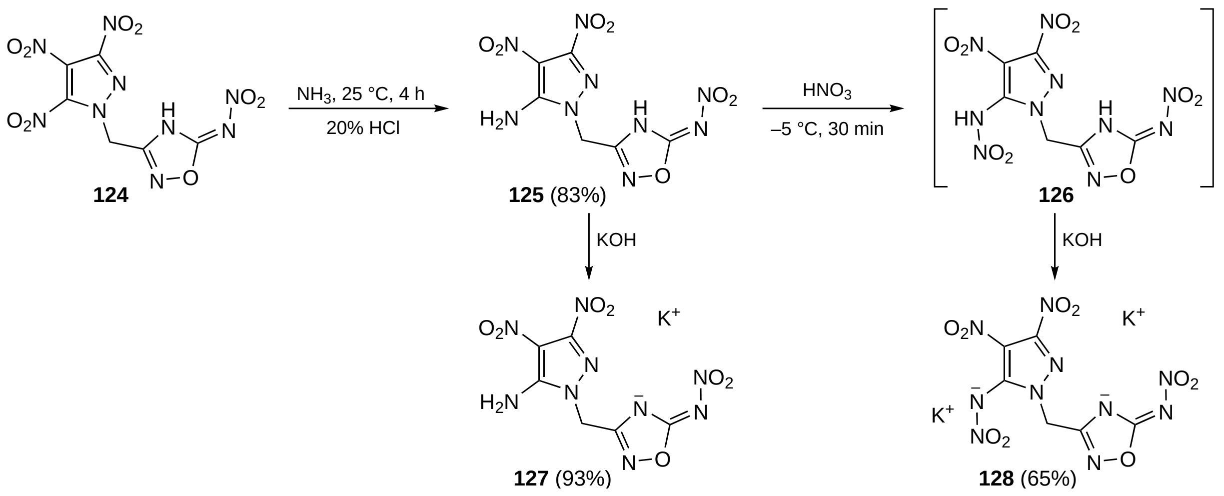


Table 17. Physicochemical properties of compounds **125**, **127**, **128** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
125	201.0	1.80	502.9	32.0	8402	12	200	68
127	199.7	1.93	252.1	26.9	7704	6	100	68
128	230.8	2.04	685.6	30.9	8059	1.2	40	68
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

those of hexogen ($D = 9014$ m s^{-1}, $P = 36.7$ GPa), but is extremely impact sensitive (IS = 1.5 J).

4. 1,2,4-Oxadiazole/1,2,5-oxadiazole-based energetic compounds

Energetic compounds based on a combination of 1,2,4- and 1,2,5-oxadiazole rings have been thoroughly studied. The introduction of the 1,2,5-oxadiazole core into the molecule makes it possible to significantly increase the enthalpy of formation, detonation rate and density,[70] so its combination with the 1,2,4-oxadiazole ring, which reduces impact sensitivity, is a promising approach to the design of new high-energy materials.

An extremely valuable and commonly used starting compound for the preparation of energetic materials is 4-amino-3-furazancarboxamidoxime (**107**), which is readily synthesized from commercially available malononitrile.[71] Condensation with diethyl oxalate gives 3,3′-bis(4-aminofurazan-3-yl)-5,5′-bis(1,2,4-oxadiazole) **137**, oxidation of the amino groups provides dinitro derivatives **138** (Scheme 28).[71] Similar cyclization with cyanogen bromide leads to 3-(4-aminofurazan-3-yl)-5-amino-1,2,4-oxadiazole **139**, which further undergoes chemoselective oxidation to form the nitrofurazan moiety in compound **140**. Furthermore, the reaction between amidoxime **107** and 3-amino-4-cyanofurazan **141** in the presence of zinc chloride as a Lewis acid opens the way to the synthesis of 3,5-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazole **142**,[72, 73] which is further oxidized with 70% hydrogen peroxide to the dinitro derivative **143** or nitrated. In the latter case, the dinitramino derivative **144** is formed, which is isolated as ammonium and hydrazinium salts **144a**,**b**.

Nitration of diamine **139** with nitric acid and subsequent treatment of the dinitramine intermediate with gaseous ammonia gives ammonium salt **145a**, which is further subjected to metathesis with silver nitrate and nitrogen-containing bases to afford the energetic salts **145b–g** (Scheme 29).[73] Compounds **144a**,**b**, **145a–g** show good thermostabilities, have a high enthalpies of formation (Table 19) and acceptable densities. These salts have lower impact and friction sensitivities compared

Scheme 27

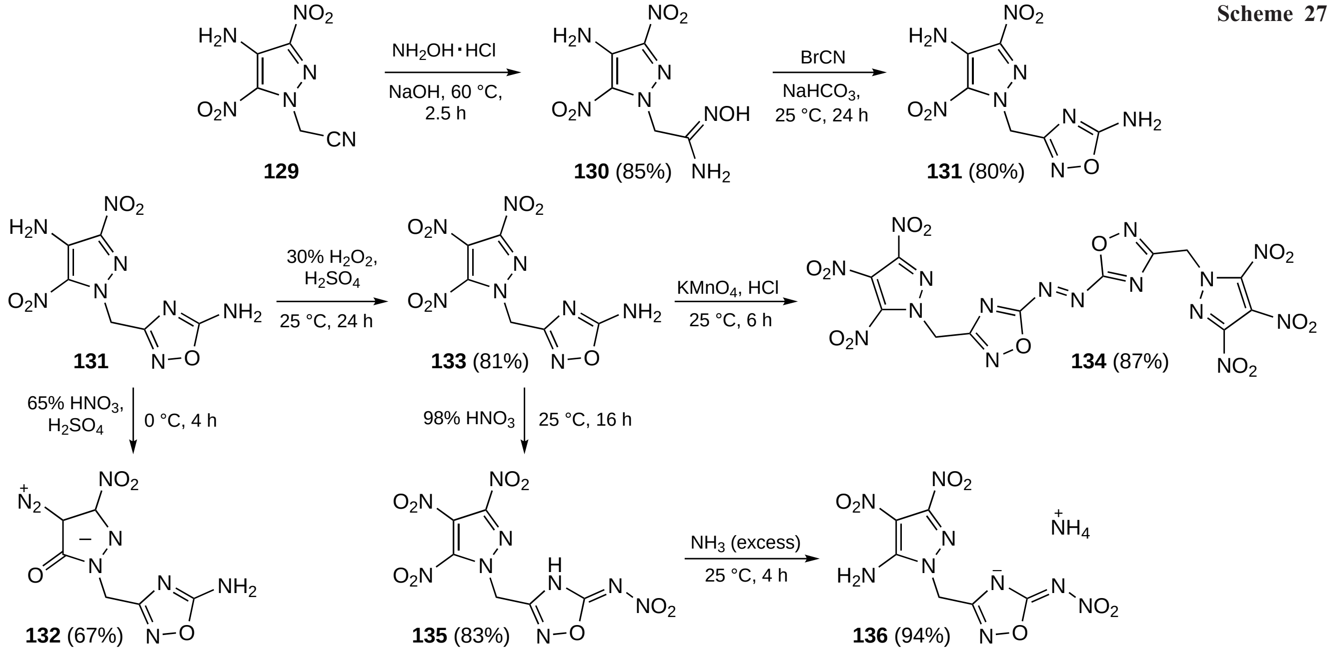
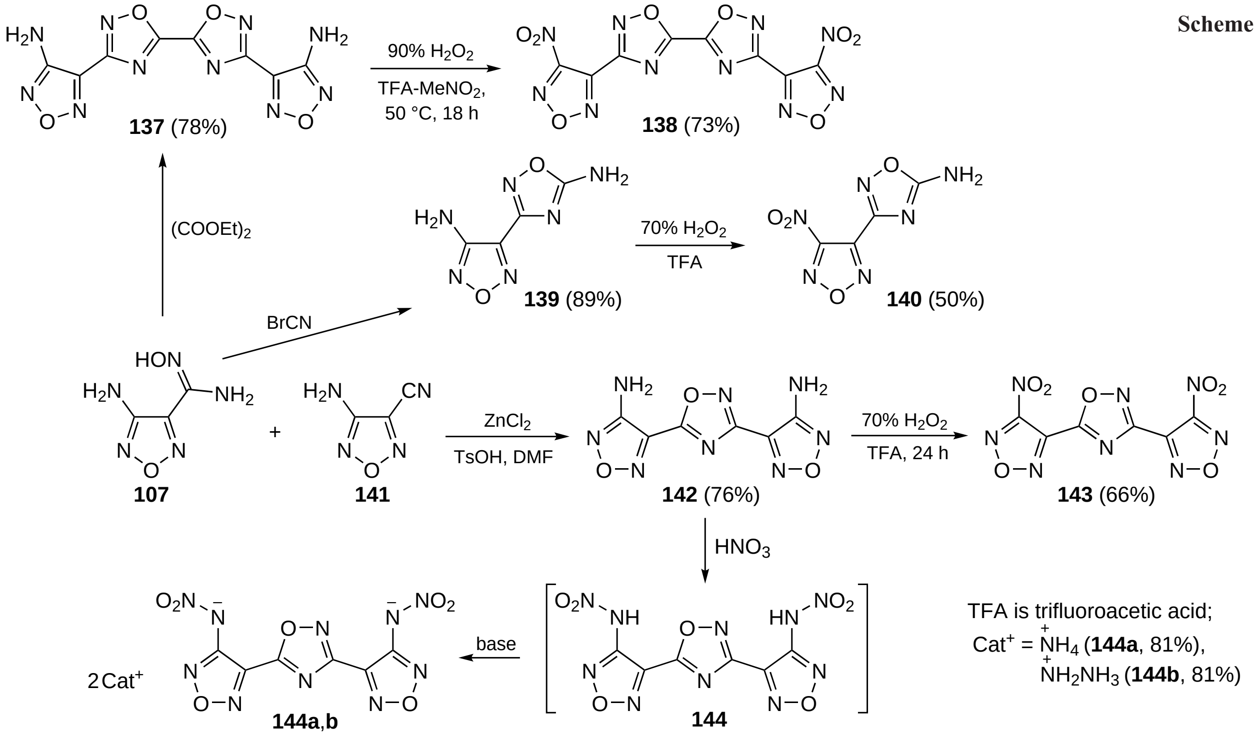


Table 18. Physicochemical properties of compounds **131**–**136** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
131	211	1.75	378.5	27.5	8027	22	240	69
132	121	1.76	380.7	28.1	8016	9.8	120	69
133	202	1.76	417.0	30.6	8375	16	200	69
134	250	1.64	1090.7	35.2	8897	10	120	69
135	170	1.84	480.3	36.7	9014	1.5	80	69
136	174	1.74	448.5	31.2	8392	22	260	69
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 28



TFA is trifluoroacetic acid;
Cat$^+$ = $\overset{+}{N}H_4$ (**144a**, 81%), $\overset{+}{N}H_2NH_3$ (**144b**, 81%)

Scheme 29

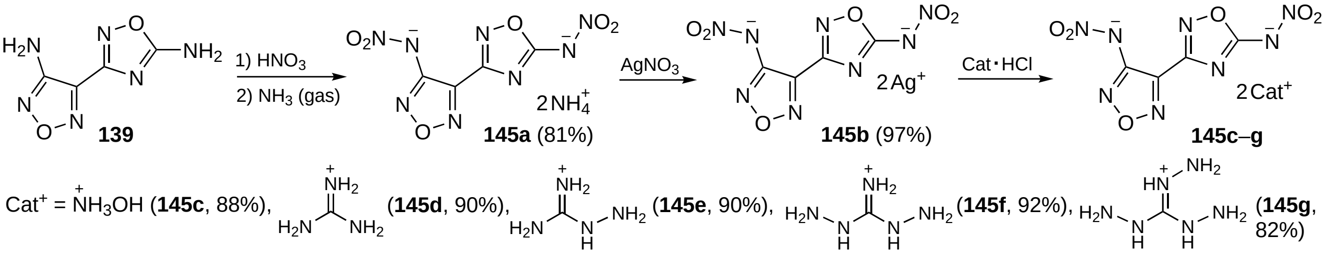


Table 19. Physicochemical properties of compounds **138**, **140**, **143** – **145** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
138	295	1.94	891.0	–	–	15	250	71
140	289	1.74	190.0	–	–	36	360	71
143	261	1.91	687.0	–	–	10	148	72
144a	231	1.71	425.1	27.9	8271	16	120	73
144b	234	1.71	752.1	30.1	8603	19	240	73
145a	218	1.70	154.9	27.6	8102	14	120	73
145c	193	1.85	250.8	37.4	9046	16	160	73
145d	269	1.71	172.9	25.0	8147	26	240	73
145e	208	1.71	425.1	26.6	8426	21	160	73
145f	172	1.74	618.3	29.3	8764	15	120	73
145g	210	1.67	894.3	28.0	8563	14	160	72
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 30

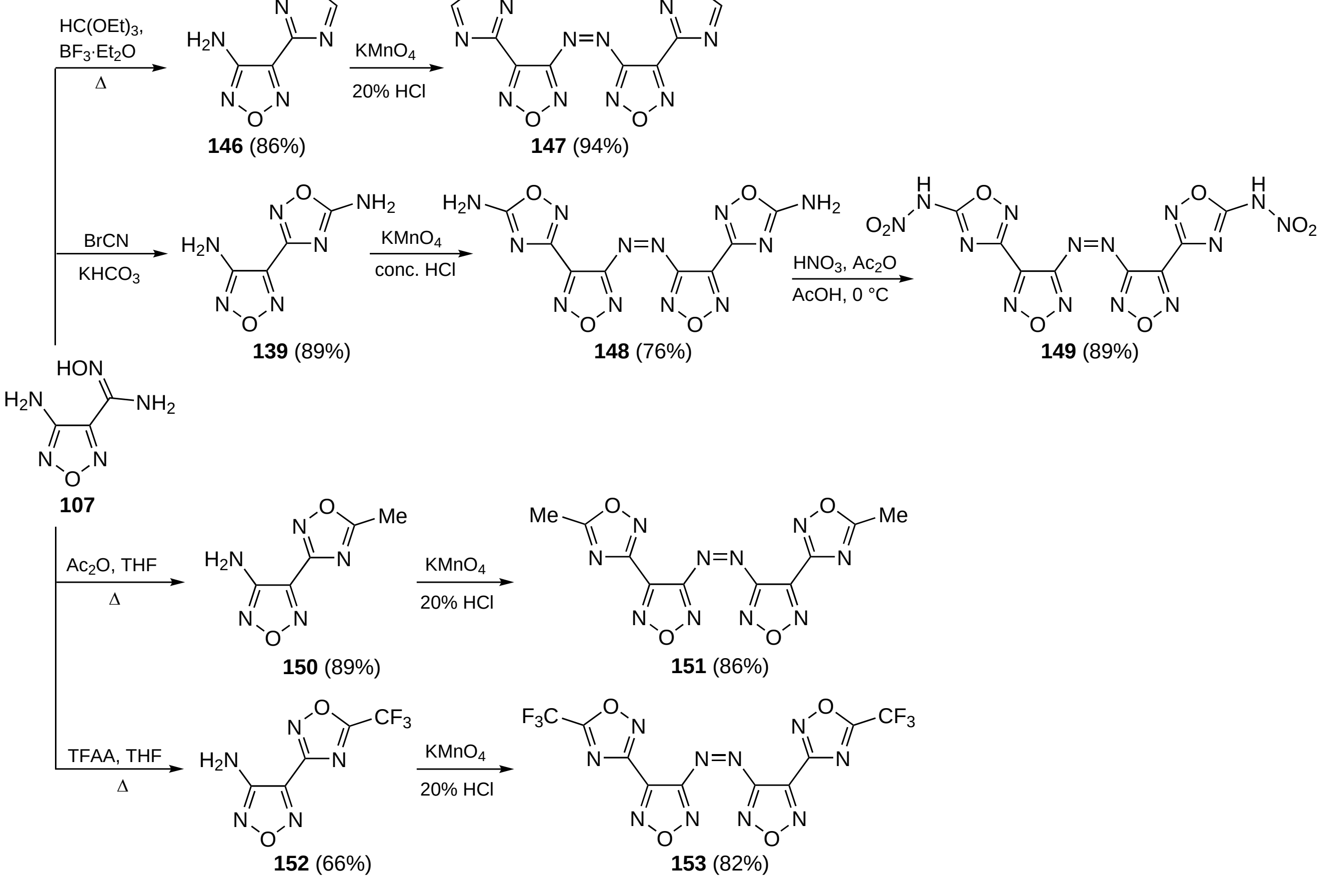


Table 20. Physicochemical properties of compounds **147**–**149**, **151**, **153** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
147	259	1.79	832.9	22.7	7685	12.5	⩾360	74
148	267	1.85	711.2	28.3	8445	⩾80	⩾360	74
149	317	2.12	1038.0	46.1	10114	6.0	80	74
151	271	1.75	696.5	22.6	7781	⩾80	80	74
153	240	1.94	−488.6	24.3	6602	⩾80	⩾360	74
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

to hexogen, and salt **145c** has the best detonation performance in this series of compounds (D = 9046 m s^{-1}, P = 37.4 GPa).

Aminofurazanylamidoxime was also used as a starting material for the synthesis of a number of tetracyclic azo derivatives combining 1,2,4-oxadiazole and furazan cores. Oxidation of oxadiazolylaminofurazans **139** and **146** with potassium permanganate in hydrochloric acid gave the azo compounds **147** and **148** (Scheme 30).[74] Subsequent nitration of the heterocycle **148** in acetic acid furnishes the dinitramine derivative **149**. Oxidation of compound **150** leads to the azo

Scheme 31

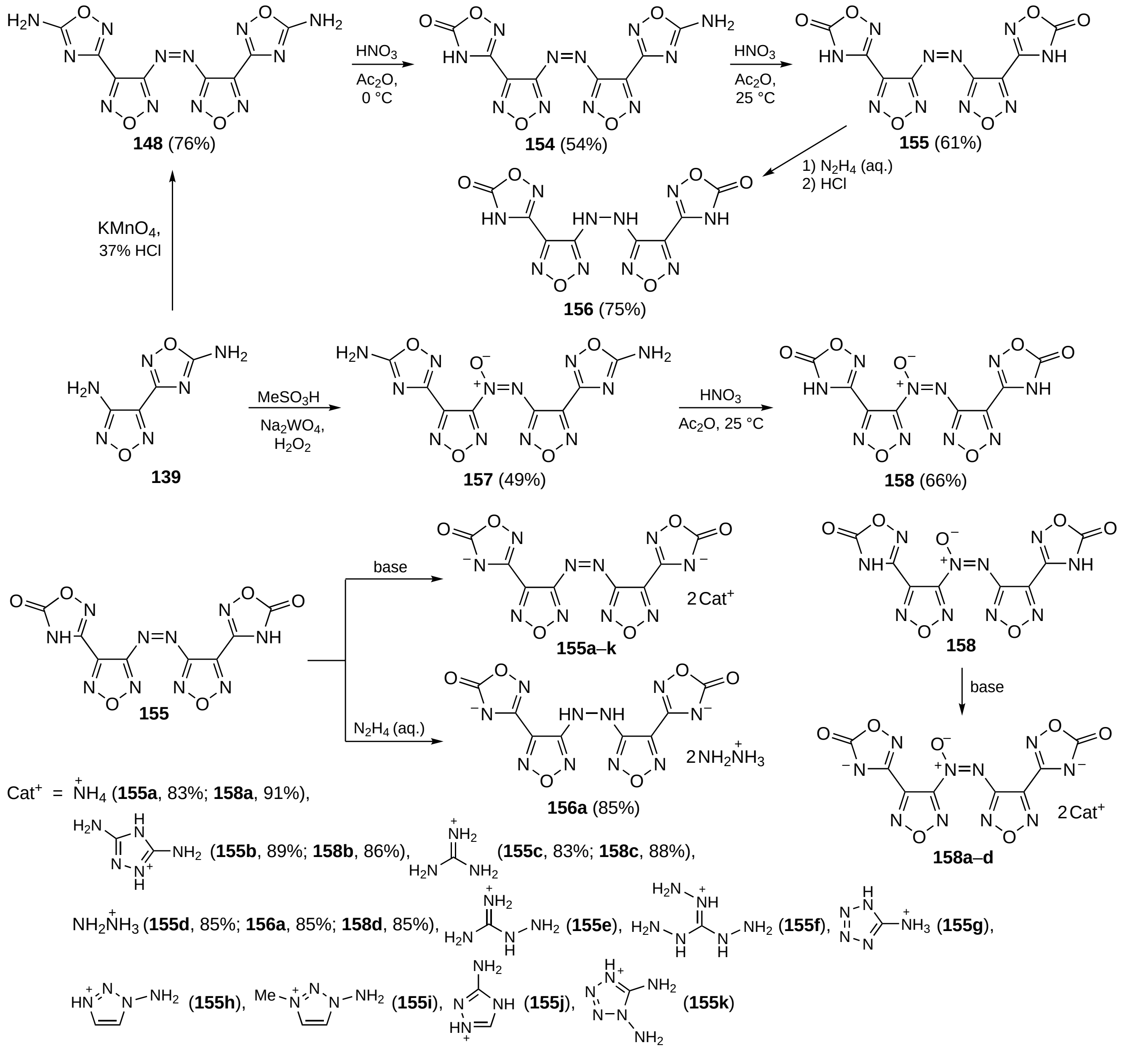


Table 21. Physicochemical properties of compounds **154–158** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
154	270	1.80	942.6	29.6	8419	26	240	75
155	322	1.89	529.7	30.7	8507	16	160	75
155a	318	1.71	1111.9	29.4	8464	>40	>360	75
155b	239	1.71	1181.2	24.5	8013	>40	>360	75
155c	262	1.83	1112.8	31.4	8853	>40	>360	75
155d	219	1.77	1201.2	32.0	8914	>40	>360	76
156	271	1.86	289.3	27.9	8209	30	240	75
156a	219	1.76	1201.2	32.0	8914	>40	>360	75
157	264	1.80	1108.1	30.8	8568	24	220	75
158	307	1.95	493.4	34.4	8844	13	160	75
158a	207	1.74	1078.3	31.1	8604	>40	>360	75
158b	204	1.73	1129.9	25.5	8125	>40	>360	75
158c	227	1.84	1067.1	32.5	8892	>40	>360	75
158d	215	1.79	1378.9	35.0	9042	>40	>360	75
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

compound **151**, and oxadiazolylaminofurazan **152** gives the product **153**. These compounds decompose at temperatures above 240 °C (Table 20). It is worth noting that heterocycle **149** has a high density (2.12 g cm^{-3}) and enthalpy of formation (1038 kJ mol^{-1}), as well as excellent detonation properties (D = 10114 m s^{-1}, P = 46.1 GPa), exceeding those of **CL-20** and octogen, but the sensitivity of this compound is slightly lower than that of **CL-20**.

An azo group can be further reduced or oxidized to extend a pool of energetic structures. In order to study the influence of the azo group on the performance of energetic materials, a series of molecules based on 1,2,4-oxadiazole and furazan, bearing different linker groups, have been synthesized (Scheme 31).[75] The oxidative coupling of diamine **139** gives the azo structure **148** comprising two azo-bridged furazan rings. The subsequent nitration of compound **148** with nitric acid in acetic anhydride leads to the sequential formation of the first one and then another oxadiazolone moiety to give structures **154** and **155** respectively. It should be noted that in an attempt to obtain the hydrazinium salt **155**, the reduction of the N=N double bond to a single bond is observed to produce the hydrazo derivative **156a**, which on acidification gives a neutral compound **156**. The oxidation of diamine **139** leads to heterocycle doubling to form the azo structure **157**, which, under similar conditions, is converted to the dioxadiazolone derivative **158**. Energetic salts **155a–d**, **158a–d** were derived from the above compounds and their energetic performance was studied in detail. The library of energetic salts was further extended in a patent,[76] but the authors provide no information on the yields of compounds **155e–k**. These compounds have high densities and enthalpies of formation, good detonation performance; they are also thermally stable (T_{dec} = 204–322 °C) and insensitive to friction and impact (Table 21). The neutral azo derivative **155** decomposes at 322 °C, this temperature being significantly higher than that of the hydrazine derivative **156** (271 °C) and the azo derivative **158** (307 °C). The same regularity is followed in the series of the corresponding salts, showing the advantage of the azo group present in the structure of the energetic compound in terms of thermal stability. Compound **155** also gave rise to a number of energetic salts insensitive to impact and friction. The azoxy derivative **158** shows superior detonation characteristics (D = 8844 m s^{-1}, P = 34.4 GPa) than azo or hydrazo compounds; a similar pattern is observed when comparing the salts with corresponding cations.

Various *N*-alkyl moieties can be used as linkers for the azole rings. For example, the amino derivative **146** reacts with formaldehyde to give the product **159**. Oxidation of substrate **146** to nitro derivative **160** and subsequent nucleophilic substitution of the nitro group by ethylenediamine affords the diamine-bridged heterocycle **161** (Scheme 32). These compounds were nitrated with a mixture of acetic anhydride and 100% nitric acid to give the dinitramine derivatives **162** and **163**, which were further reacted with hydrazine hydrate to undergo the opening of the oxadiazole ring and to afford the corresponding products **164** and **165**.[77]

These compounds are characterized by moderate thermal stability, acceptable density, high values of enthalpy of formation and detonation velocity, and low impact sensitivity. It should be noted that for compounds **164** and **165**, which are free from the 1,2,4-oxadiazole ring, the values of density and thermostability are significantly reduced (Table 22).

Amidoxime **107** reacts with acetamide at high temperature to give 3-amino-4-(5-methyl-1,2,4-oxadiazol-3-yl)furazan **150**.[78] Subsequent reaction of the latter with trinitroethanol gives the product **166**, which is further nitrated with a mixture of 100% HNO_3 and Ac_2O to produce the polynitro derivative **167**. Compound **150** was also nitrated with fuming nitric acid and its further reaction with a number of bases gave salts **168a–i** (Scheme 33). It should be noted that when the ether solution of compound **168** is washed with brine during the purification process, the sodium salt **168d** is formed, the properties of which have been studied together with the corresponding organic salts. The resulting compounds are insensitive to impact and friction (except for nitramine **167**), and the hydroxylammonium salt **168a** has the best detonation performance in this series

Scheme 32

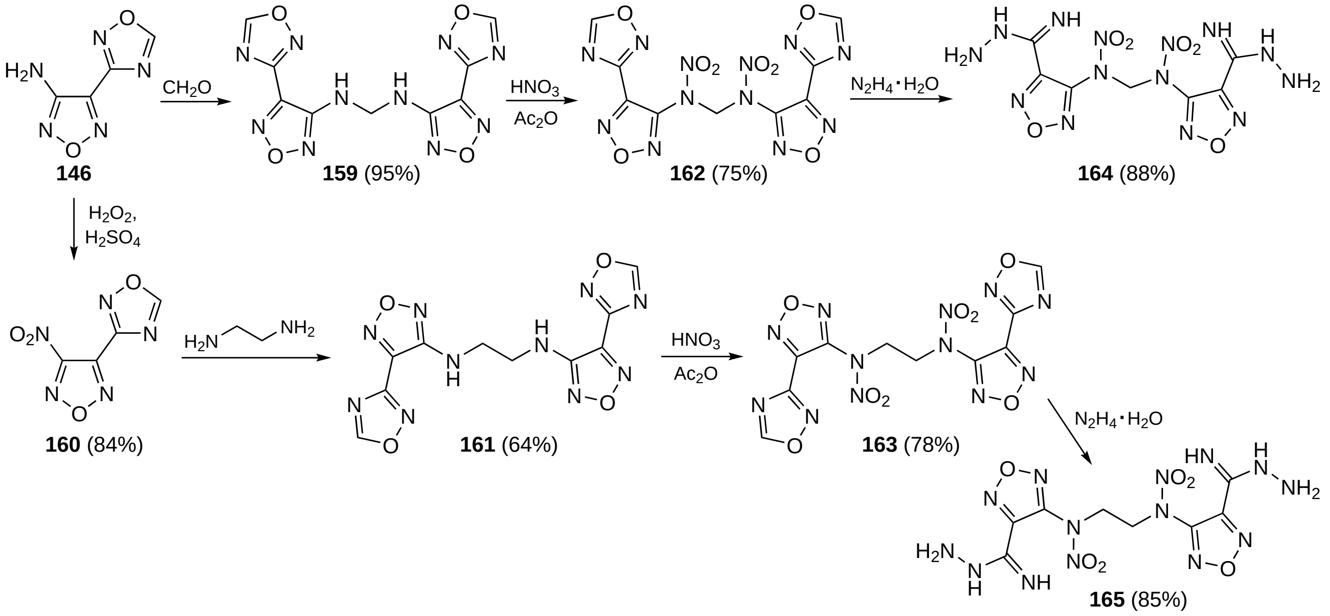


Table 22. Energetic and physicochemical properties of compounds **162–165** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
162	149	1.77	586.2	27.7	8182	27	240	77
163	175	1.75	785.8	27.9	8185	31	240	77
164	138	1.64	810.7	25.3	8126	>40	>360	77
165	145	1.60	797.6	23.3	7914	>40	>360	77
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

($D = 8545$ m s^{-1}, $P = 30.2$ GPa), close to that of hexogen (Table 23).[73,78]

Compound **137** undergoes the Mannich reaction with trinitroethanol and then the NH groups of the intermediate **169** can be nitrated to form compound **170** (Scheme 34).[79] In addition, nitration of the amino groups in compound **137** gives dinitramine **171**. Treatment of the latter with bases, both directly and after the intermediate formation of the silver salt **172a**, produces energetic salts **171a–q**.[79,80] These salts are thermally

Scheme 33

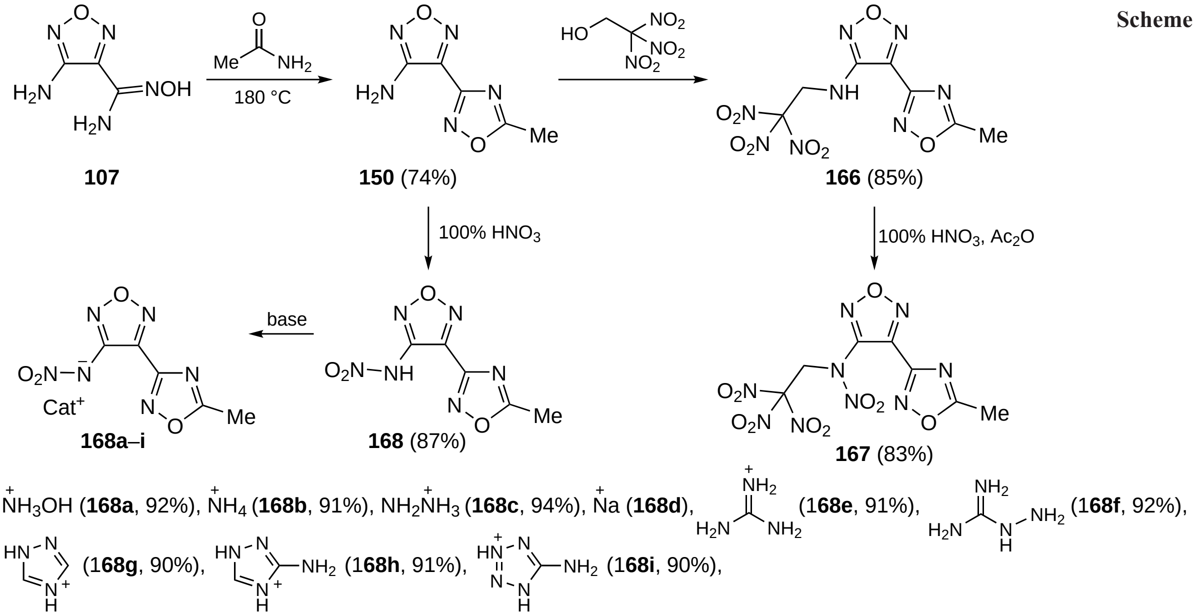


Table 23. Physicochemical properties of compounds **166–168** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
166	200	1.71	295.1	27.7	8118	>40	>360	78
167	172	1.78	412.7	32.8	8602	–	–	78
168	159	1.65	355.8	24.1	7810	37.8	360	78
168a	255	1.75	370.3	30.2	8545	>40	>360	78
168b	203	1.73	310.2	27.0	8317	>40	>360	78
168c	215	1.72	444.6	28.0	8495	>40	>360	78
168d	246	1.77	258.3	20.8	7143	>40	>360	78
168e	224	1.67	478.0	22.8	7885	>40	>360	78
168f	200	1.63	456.1	23.2	7968	>40	>360	78
168g	208	1.72	523.0	24.8	8024	>40	>360	78
168h	219	1.74	552.8	25.9	8204	>40	>360	78
168i	212	1.73	686.9	27.3	8350	>40	>360	78
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 34

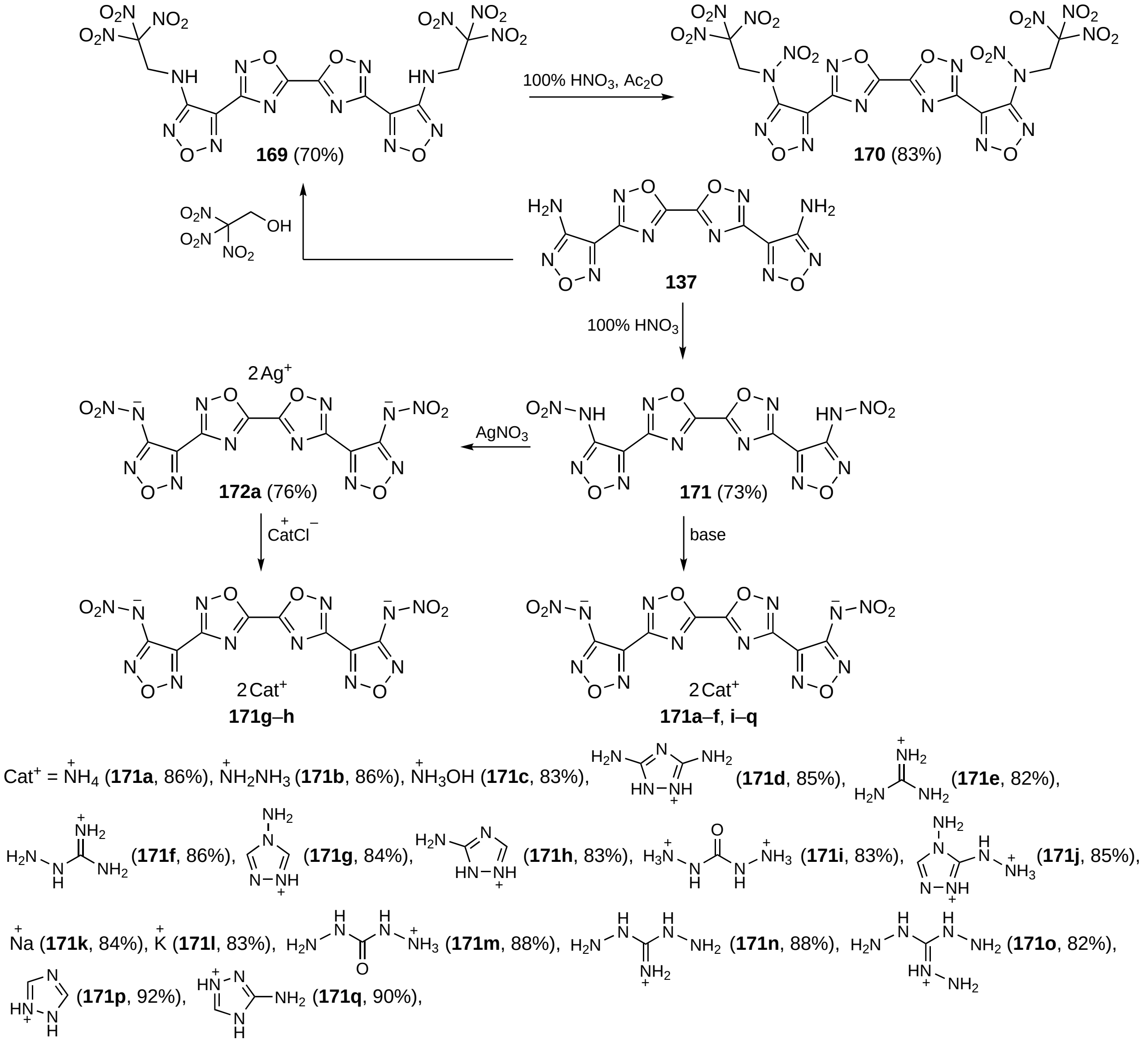


Table 24. Physicochemical properties of compounds **169**–**171**, **174** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
169	188	1.90	897.9	37.2	9062	10.5	240	80
170	152	1.93	1369.4	41.9	9550	4.5	120	80
171	84	1.85	786.3	33.3	8793	16	180	79
171a	215	1.76	614.9	28.8	8343	20	240	79
171b	225	1.82	910.5	33.0	8836	12	160	79
171c	187	1.87	699.8	36.0	9030	12	180	79
171d	225	1.79	1014.6	27.2	8315	>40	>360	79
171e	263	1.67	607.5	23.2	7838	36	360	79
171f	228	1.70	804.9	25.5	8151	40	>360	79
171g	221	1.76	1345.2	27.9	8325	14	160	79
171h	218	1.73	1087.9	25.7	8078	22	220	79
171i	191	1.80	487.3	29.2	8339	20	180	79
171j	198	1.77	553.0	26.0	8080	18	180	79
171k	303	1.89	511.1	–	–	20	280	79
171l	274	1.97	355.2	–	–	36	>360	79
171m	209	1.81	1083.4	32.6	8831	>40	>360	80
171n	205	1.73	1178.1	28.1	8515	>40	>360	80
171o	183	1.72	1401.0	29.3	8688	>40	>360	80
171p	176	1.75	1363.5	28.1	8287	>40	>360	80
171q	211	1.75	1332.6	28.2	8343	>40	>360	80
174a	161	1.80	145.0	32.8	8652	23	>360	81
174b	190	1.86	259.9	38.0	9028	22	>360	81
174c	210	1.83	466.9	36.0	9064	19	>360	81
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

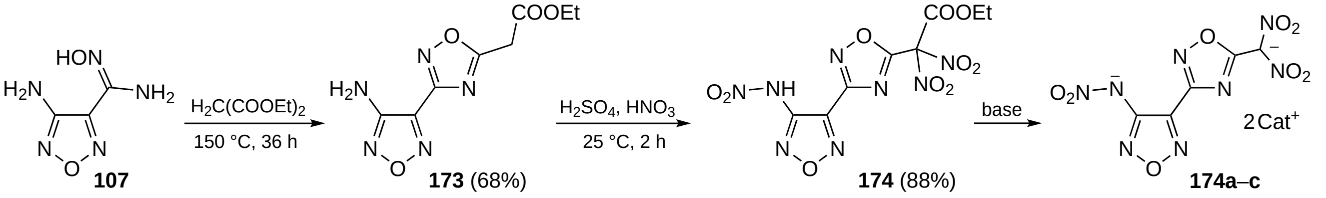
stable (Table 24), in contrast to their precursor **171**, which has a decomposition temperature of as low as 84 °C.

He *et al.*[81] explored optimum conditions for cyclocondensation as an approach to compound **173**, which is nitrated to afford the nitramine derivative **174** and reacts with bases to give the energetic salts **174a–c** (Scheme 35). The densities of the products exceed those of hexogen and the detonation performance (D = 8652–9064 m s^{-1}, P = 32.8–38.0 GPa) are close to that of octogen (see Table 24). It should be noted that these salts are relatively insensitive to mechanical stimuli, making them potential secondary explosives.

Oxadiazolone **175** was obtained *via* oxidative cleavage of the 5-methyl-1,2,4-oxadiazole moiety in compound **150**.[82] Oxadiazolone **175** was further subjected to azo coupling, nitration and oxidation under various conditions to give the corresponding products **176**, **177** and **178**. The Mannich reaction of compound **175** with trinitroethanol produces the derivative **179**, and neutralization of the heterocycles **177** and **178** with nitrogen-containing bases furnishes the energetic salts **177a–c** and **178a–c** (Scheme 36).[82] Among these compounds, the neutral compounds have densities higher than those of the corresponding salts (Table 25), and compound **179**, which has an acceptable sensitivity (IS = 16 J, FS = 240 N) with good detonation performance (D = 8637 m s^{-1}; P = 32.2 GPa), proved to be the closest to practical use as an alternative to hexogen.

According to literature data,[83–85] energetic salts of nitrogen-containing heterocycles usually have higher thermal stability compared to neutral precursors. Based on these considerations, we studied the properties of a series of nitrogen-rich energetic salts **180a–f**, obtained by chemoselective nitration of compound **139** with subsequent neutralization of the reaction product **180** (Scheme 37).[86] Only one amino group in the furazan heterocycle is nitrated, since the strong inductive effect of the oxygen atom of the 1,2,4-oxadiazole ring significantly reduces the reactivity of the second amino group in the molecule. Salts **180–f** have

Scheme 35



Cat$^+$ = $\overset{+}{N}H_4$ (**174a**, 95%), $\overset{+}{N}H_3OH$ (**174b**, 95%), $\overset{+}{N}H_3NH_2$ (**174c**, 98%)

Scheme 36

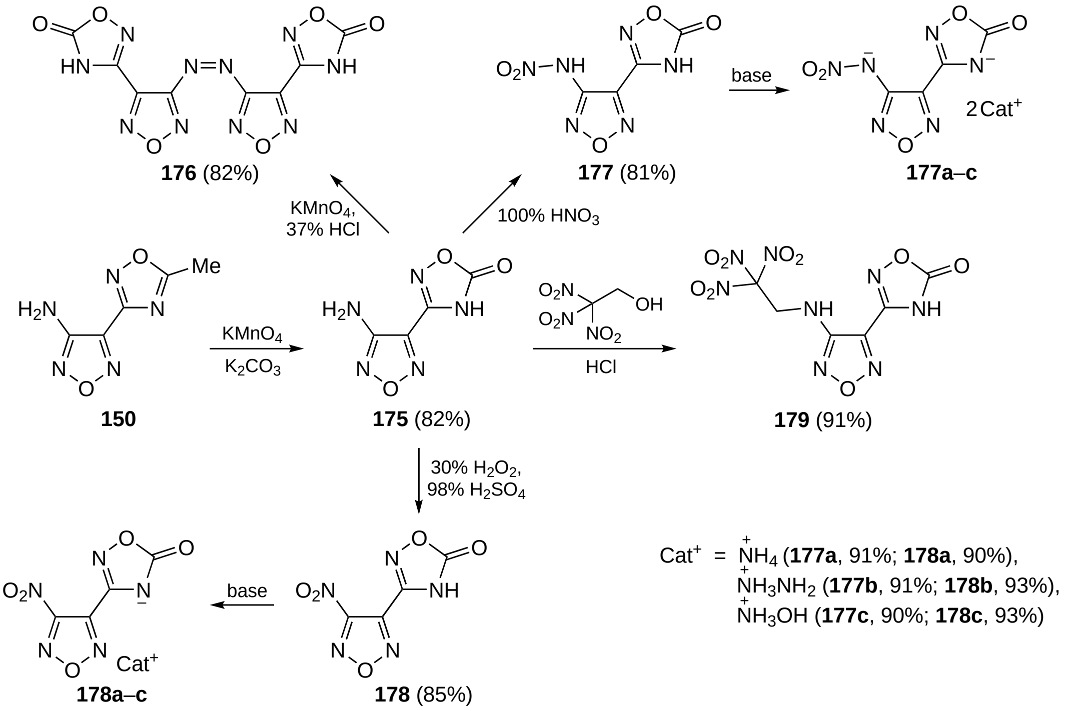


Table 25. Physicochemical properties of compounds **177**–**179** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
177	127	1.83	245.2	32.5	8644	15	240	82
177a	212	1.64	−94.1	22.3	7749	>40	>360	82
177b	190	1.61	284.2	26.1	8067	>40	>360	82
177c	184	1.68	51.6	28.3	8283	>40	>360	82
178	162	1.89	218.4	35.8	8892	8	240	82
178a	202	1.68	152.4	26.7	8031	>40	>360	82
178b	192	1.71	300.9	29.1	8352	>40	>360	82
178c	230	1.76	192.6	31.7	8494	>40	>360	82
179	222	1.80	222.8	32.2	8637	16	240	82
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

considerably higher decomposition temperatures (175–235 °C), than the neutral compound **180** (111 °C), and also excellent detonation performance ($D = 8191-8838$ m s^{-1}, $P = 26.0-33.3$ GPa) (Table 26).

One way to improve the oxygen balance in the target energetic molecules is the introduction of a nitramine or nitroether moiety into nitrogen-rich heterocyclic frameworks. This approach was tested on the example of compound **181** obtained by the reaction of 2-oxoethyl-2-chloroacetate with amidoxime **107**.[87] Direct nitration of the heterocycle **181** produces nitramine **182**, which is converted to the ammonium salt **182a** (Scheme 38). At the same time, the preliminary hydrolysis of the substrate **181** to the compound **183**, followed by nitration, gives the nitroether **184**, which is further converted into the salt forms **184a–c** by two-step metathesis. Compound **181** is also subjected to the oxidative coupling with simultaneous hydrolysis of the acetyl groups to afford the azo structure **185**, which is converted into nitroether **186** when treated with nitric acid. The resulting compounds show good thermal stabilities

Scheme 37

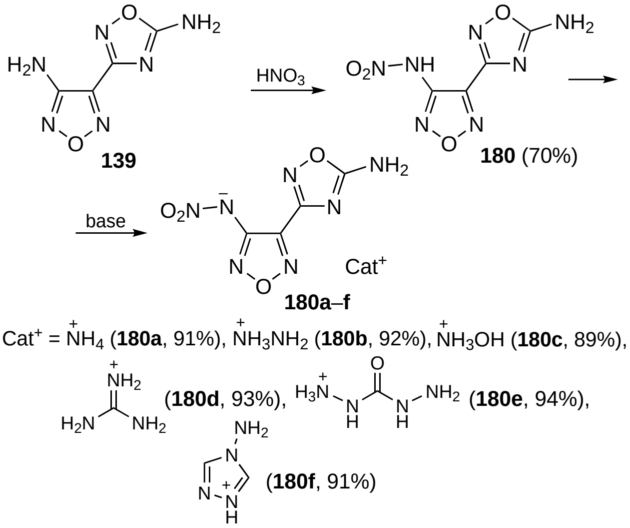


Table 26. Physicochemical properties of compounds **180** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	$\Delta H^{\circ}_{\mathrm{f}}$, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
180	111	1.82	226.0	29.7	8398	25	240	86
180a	206	1.78	307.0	30.1	8602	>40	>360	86
180b	192	1.78	461.6	31.7	8838	>40	>360	86
180c	175	1.80	363.3	33.3	8807	>40	>360	86
180d	235	1.76	273.9	26.6	8357	>40	>360	86
180e	190	1.78	381.5	30.0	8687	>40	>360	86
180f	191	1.70	657.4	26.0	8191	>40	>360	86
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

(except for the neutral compound **184**) and good detonation performance ($D = 7809 - 8822$ m s^{-1}, $P = 27.2 - 35.2$ GPa) (Table 27).

Similarly, the azido derivative **187** was derived from aminofurazanylamidoxime **107**, which was further subjected to nitration with the reaction product being isolated in the form of silver salt **187a**, followed by metathesis to afford salts **187b–e** (Scheme 39).[88] The authors also carried out the oxidation of the aminofurazan functionality in compound **187** to the nitrofurazan moiety. Oxidation product **188** is a liquid at room temperature and has acceptable detonation properties ($D = 8290$ m s^{-1}; $P = 28.6$ GPa) (see Table 27).

1,2,5-Oxadiazole *N*-oxide (furoxan) containing a ‘hidden nitro group’ due to the presence of two active oxygen atoms, which makes it possible to improve the oxygen balance of the compound and increase the density and detonation efficiency of the material, is a valuable structural building block for the design of energetic materials.[25,89]

In 2015, the conditions for the synthesis of the 1,2,4-oxadiazole ring attached to furoxan were optimized. 3-Methyl-4-cyanofuroxane **189** was converted to amidoxime **190**, which was further condensed with an excess of trimethyl orthoformate in the presence of scandium trifluoromethanesulfonate (triflate, OTf) (10 mol.%) as a Lewis acid (Scheme 40).[90] The reaction proceeds in 1 min to give rather high yield of the product **191** (86%). Using the same procedure, dicyanofuroxane **192** gave bis(amidoxime) **193** and 3,4-bis(1,2,4-oxadiazol-3-yl)furoxane **194** in 82% yield. This method was scaled up in 2019 and optimized by replacing the Lewis acid with $BF_3 \cdot Et_2O$, resulting in an increase in the overall product yield.[91] Compound **194** has a high density (1.79 g cm^{-3}) and enthalpy of formation (357 kJ mol^{-1}), as well as good detonation performance ($P = 24.1$ GPa, $D = 7577$ m s^{-1}) and low sensitivity to

Scheme 38

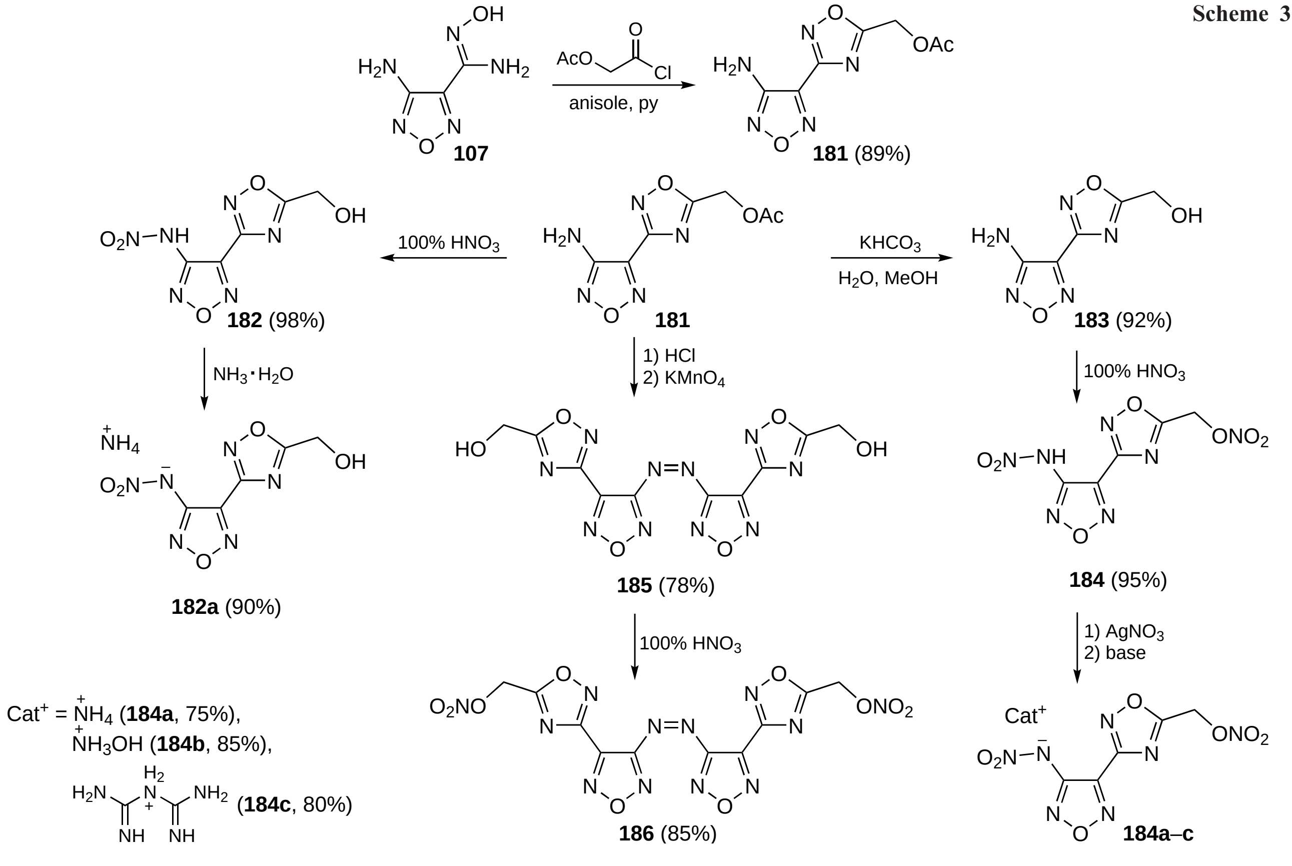
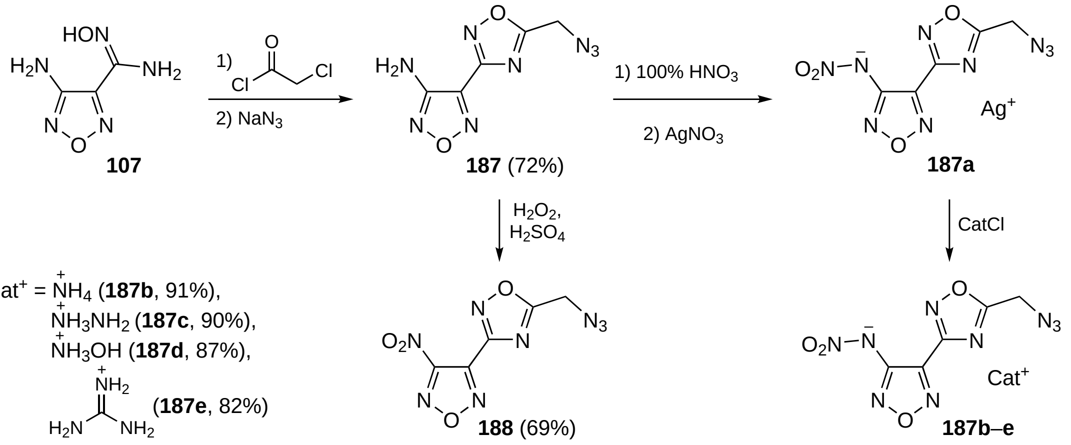


Table 27. Physicochemical properties of compounds **184**, **186**–**188** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
184	60	1.83	237.8	31.1	8451	10	–	87
184a	135	1.79	253.5	32.0	8428	35	>360	87
184b	148	1.82	309.1	35.2	8822	40	>360	87
184c	135	1.75	263.1	27.2	7809	>40	>360	87
186	200	1.78	650.7	27.4	8081	35	>360	87
187	183	1.66	651.3	21.0	7471	20	160	88
187b	122	1.64	1070.4	28.7	8416	25	360	88
187c	159	1.72	1192.0	32.3	8888	15	160	88
187d	159	1.79	1112.1	35.8	9090	15	120	88
187e	167	1.71	1007.9	27.7	8399	25	240	88
188	158	1.75	705.2	28.6	8290	20	360	88
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 39

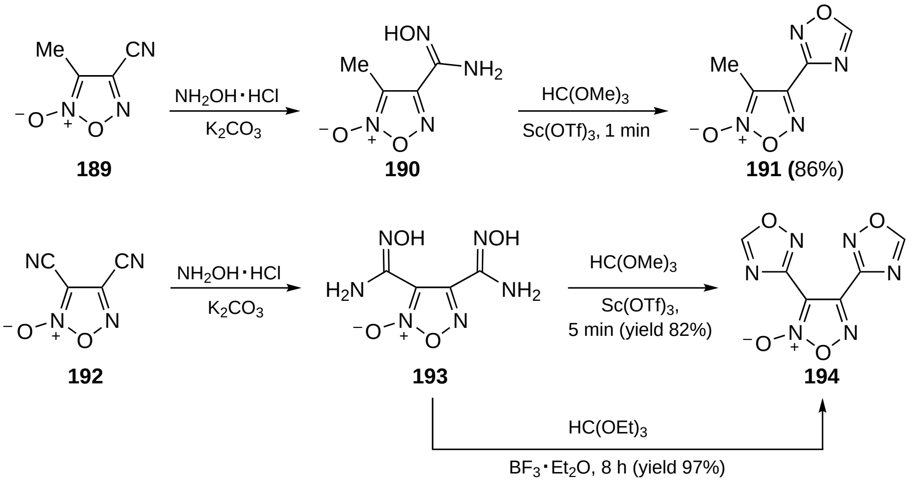


mechanical (IS > 34.7 J, FS > 360 N) and electrostatic (ESD > 0.25 J) stimuli.

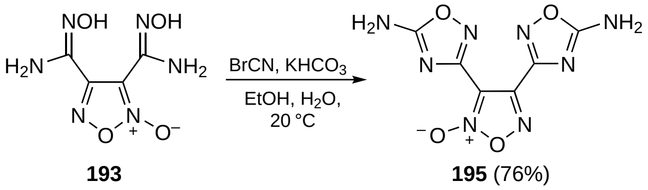
A similar method was used to prepare the tricyclic furoxan derivative **195** containing directly linked 5-amino-1,2,2-oxadiazole rings.[92] The synthesis of bis(1,2,4-oxadiazol-3-yl) furoxan **195** was carried out *via* cyclization of bis(amidoxime) **193** with cyanogen bromide (Scheme 41). This procedure was modified in work,[32] where the authors managed to increase the yield of the target product and studied its physicochemical and energetic properties. Compound **195** is characterized by high thermal stability, decomposing at 269 °C, and also has a detonation velocity and pressure (D = 7280 m s^{-1}, P = 23.7 GPa) comparable to those of trotyl.

Chemoselective addition of hydroxylamine to dicyanofuroxan **192** gives amidoxime **196**, and subsequent cyclization with cyanogen bromide delivers 4-(5-amino-1,2,4-oxadiazol-3-yl)-3-

Scheme 40



Scheme 41



cyanofuroxane (**197**).[93] Upon addition of sodium azide to cyanofuroxan in the presence of zinc bromide, tetrazole ring is formed in the structure **198**, further nitration of which gives the nitramino derivative **199**. The two-step synthesis of chloroxime **200** followed by nitration with nitric acid in trifluoroacetic anhydride affords a dinitromethyl derivative isolated as the potassium salt **201a**. The corresponding energetic salts **199a–e** and **201b,c** were also obtained by the metathesis reaction (Scheme 42). (It should be noted that the metathesis of potassium salt **201a** leads to a double salt with only 1 equiv. of potassium being substituted).

The salts **199a–c,e** are characterized by a relatively higher thermal stability (179–234 °C) compared to the neutral compound **199**, which decomposes at 121.2 °C (Table 28). In this series, the highest densities are observed for compounds **199** and **199c** (1.86 and 1.84 g cm^{-3}), while the hydrazinium salt **199b**, despite its comparatively low density, has an extremely high enthalpy of formation (702.9 kJ mol^{-1}) and consequently a high detonation velocity ($D = 8713$ m s^{-1}, $P = 29.7$ GPa), comparable to that of hexogen. Salt **201a** has the following detonation properties: $D = 8076$ m s^{-1}, $P = 29.8$ GPa, exceeding similar parameters of lead azide ($Pb(N_3)_2$), and it is extremely sensitive to impact (IS = 3 J) but not to friction (FS = 60 H). This allows us to consider structure **201a** as a potent ‘green’ alternative to toxic primary lead azide-based explosive compositions.

As mentioned above, the reactivity of the amino group in the 1,2,4-oxadiazole ring is often greatly reduced because of the

Scheme 42

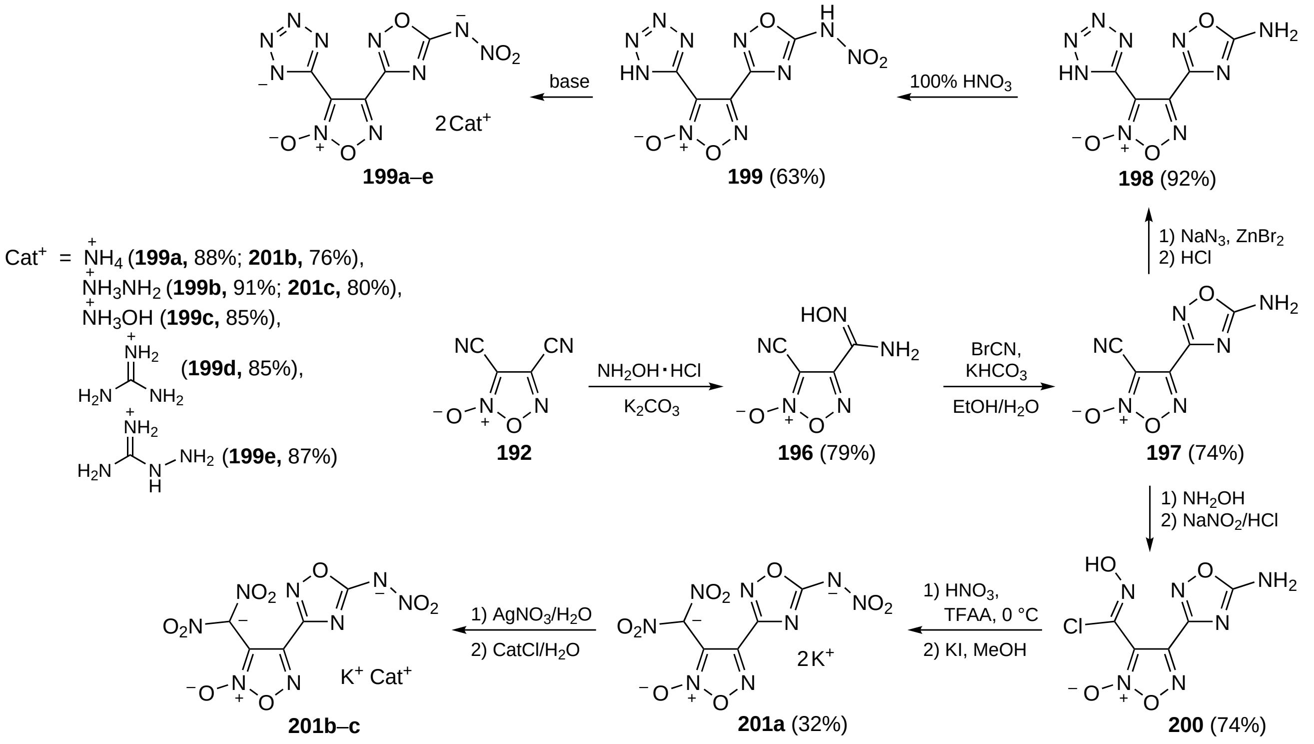


Table 28. Physicochemical properties of compounds **194**, **195**, **199**, **201** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
194	227	1.79	357.0	24.1	7577	>34.7	>360	91
195	269	1.71	178	23.7	7280	>100	>360	32
199	121	1.86	441.3	31.8	8639	11	160	93
199a	234	1.75	369.1	27.5	8373	32	>360	93
199b	205	1.74	702.9	29.7	8713	15	280	93
199c	179	1.84	475.8	35.3	8977	13	>360	93
199e	197	1.66	650.7	24.2	8131	>40	>360	93
201a	186	2.14	−376.9	29.8	8076	3	60	93
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 43

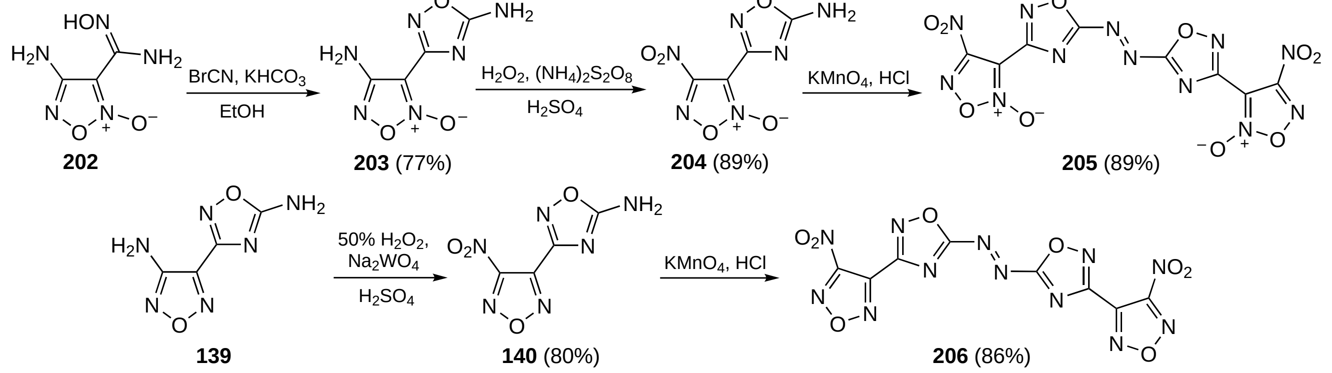
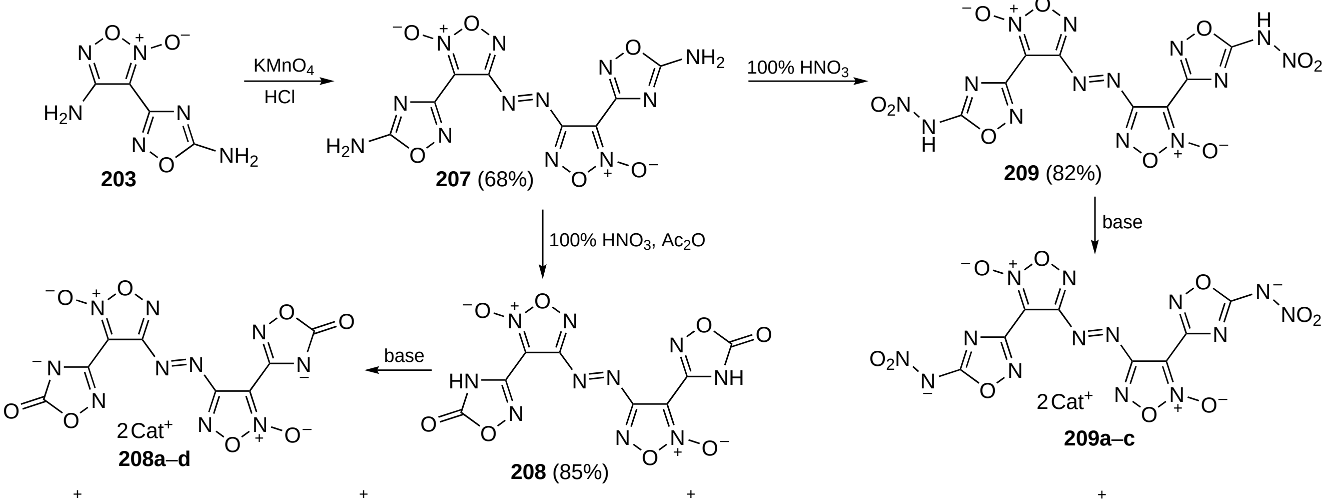


Table 29. Physicochemical properties of compounds **204**–**206**, **208**, **209** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
204	176	1.85	411.7	33.7	8651	20	240	94, 95
205	180	1.92	1188.8	42.8	9666	12	180	94, 95
206	256	1.92	962.4	37.5	9240	18	220	94, 95
208	189	1.90	633.4	34.7	8891	10	120	96
208a	180	1.65	534.9	273.	8234	18	180	96
208b	174	1.71	887.2	29.3	8453	15	120	96
208c	161	1.72	666.6	30.7	8445	17	120	96
208d	168	1.65	504.8	26.7	8150	22	180	96
209	126	1.92	1241.1	41.3	9505	4	80	96
209a	180	1.66	1060.9	28.9	8357	14	120	96
209b	165	1.74	1187.5	31.9	8860	10	120	96
209c	168	1.72	1405.6	34.3	8846	12	120	96
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

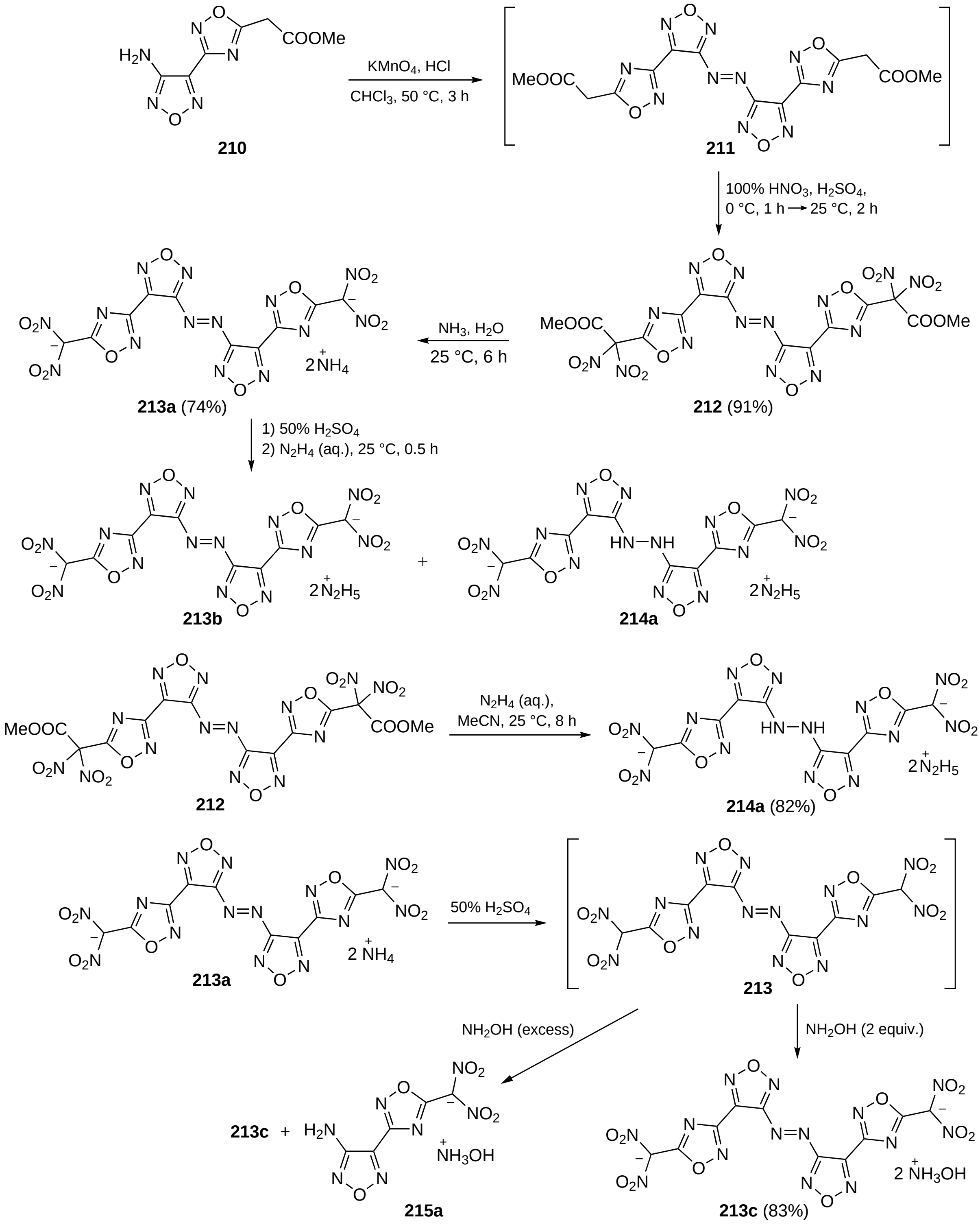
lack of electron density due to the strong electron-withdrawing effect of the intracyclic oxygen atom.[92] Based on these data, we developed a method for the synthesis of tetracyclic energetic molecules containing 1,2,5- and 1,2,4-oxadiazole rings. First, cyclization of aminofuroxanylamidoxime **202** with cyanogen bromide gave 5-amino-3-(4-aminofuroxanil)-1,2,4-oxadiazole **203**, in which the amino groups at the furoxan ring were selectively oxidized to give the product **204**. Further oxidative coupling under the action of the $KMnO_4$–HCl system produced the tetracyclic azo derivative **205** (Scheme 43). Compounds **140** and **206** containing the furazan ring were obtained in a similar way.[94,95] When comparing the energetic properties of the obtained products, it was found that the densities, enthalpyiesof formation and detonation performance

Scheme 44

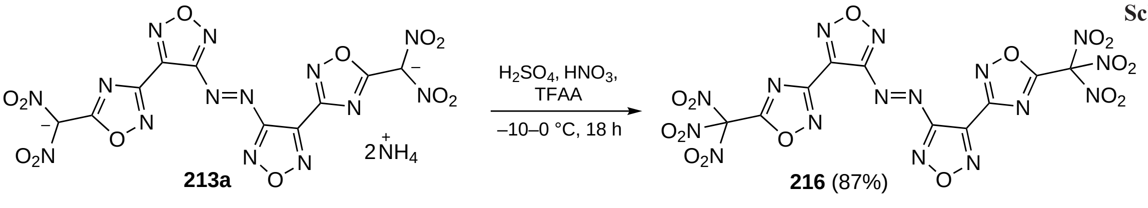


Cat$^+$ = $\overset{+}{N}H_4$ (**208a**, 78%; **209a**, 76%), $\overset{+}{N}H_3NH_2$ (**208b**, 81%; **209b**, 81%), $\overset{+}{N}H_3OH$ (**208c**, 76%; **209c**, 85%), $(H_2N)_2C{=}\overset{+}{N}H$ (**208d**, 85%)

Scheme 45



Scheme 46



of the azo derivatives were significantly superior to those of the precursors. When comparing furazan and furoxan derivatives, their *N*-oxides were found to have higher densities, enthalpies of formation and detonation properties than furazan derivatives bearing no *N*-oxide functionality. All the heterocycles obtained show acceptable impact and friction sensitivities. Compound

Scheme 47

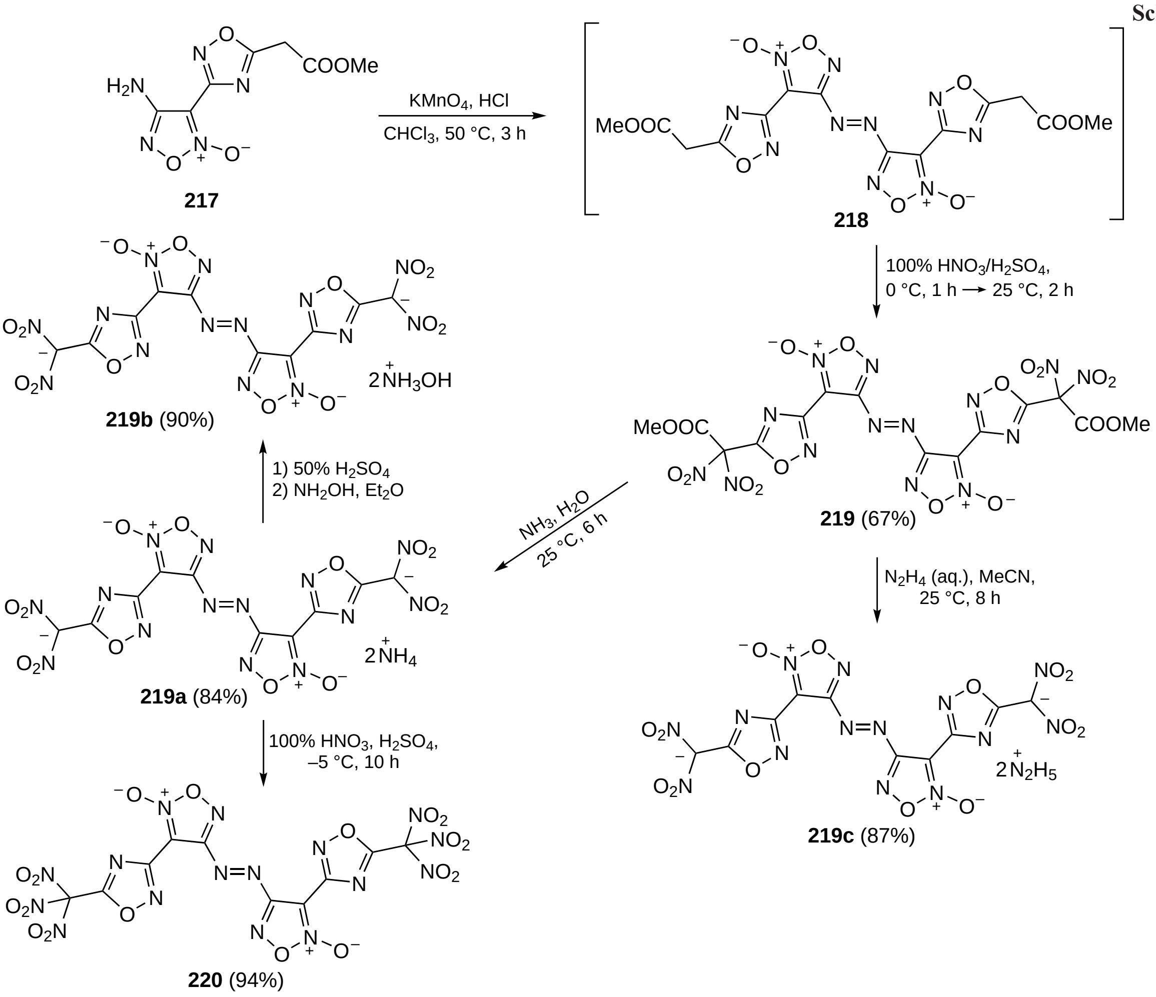


Table 30. Physicochemical properties of compounds **213**–**215**, **216**, **219**, **220** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
213a	154.2	1.836	1176	34.17	8824	24	144	97
214a	208.8	1.832	1159	33.86	8850	>40	>360	97
215a	182.8	1.885	1261	38.62	9196	18	144	97
216	115.9	1.897	985	37.46	9351	3	40	98
219a	172	1.86	785.6	34.6	8841	14	192	99
219b	145	1.90	861.5	38.3	9167	12	168	99
219c	187	1.81	862.5	33.1	8731	19	280	99
220	119	1.93	993.5	39.0	9411	3	54	99
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

205 is less impact sensitive than hexogen, and its detonation performance parameters ($D = 9666$ m s^{-1}, $P = 42.8$ GPa) are comparable to those of **CL-20**, which allows us to recommend this heterocycle as a promising explosive (Table 29).

The amino group at the furoxan ring of compound **203** can be also involved in the azo coupling to give the azo derivative **207**, which was further nitrated with different reagents to give the oxadiazolone or nitraminooxadiazole derivatives **208** and **209** (Scheme 44).[96] Two series of energetic salts (**208a–c** and **209a–c**) were obtained by metathesis with different nitrogen-containing amines. Among these compounds, heterocycle **209** has the highest density (1.92 g cm^{-3}) and high detonation performance ($D = 9505$ m s^{-1}, $P = 41.3$ GPa), while having a sensitivity (IS = 4 J, FS = 80 N) comparable to that of **CL-20** (see Table 29).

A similar strategy was used to synthesize tetracyclic azo derivatives bearing explosophoric substituents. The oxidative coupling of aminofurazan **210** followed by nitration of the azo structure **211** leads to a dinitromethyl derivative **212** which is further converted to the bis(dinitromethyl) ammonium salt **213a** by the reaction with an aqueous ammonia solution.[97] An attempt to obtain the hydrazinium salt in a similar way resulted in a

Scheme 48

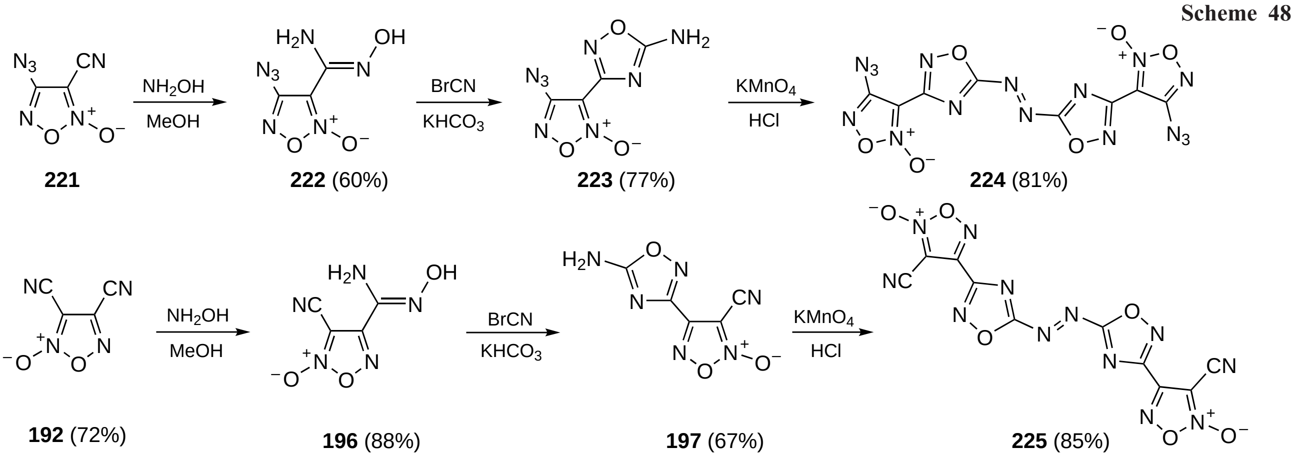
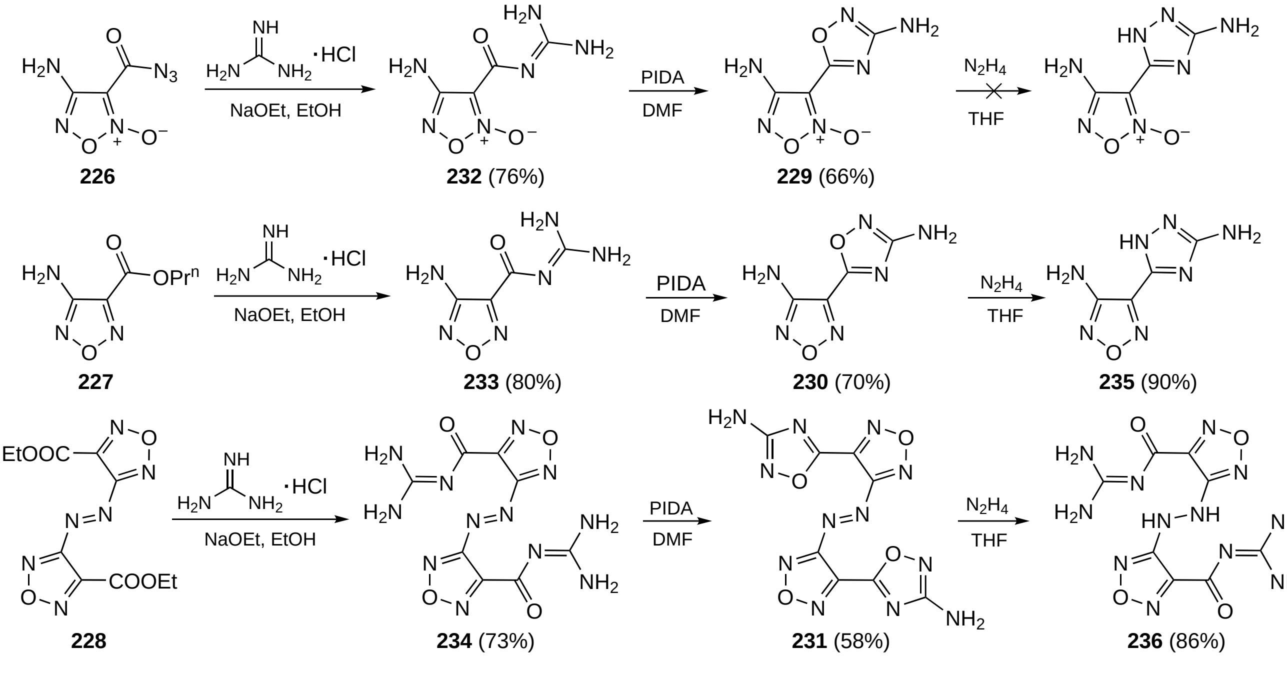


Table 31. Physicochemical properties of compounds **197, 223–225** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
197	133	1.66	638.6	27.0	7900	5	260	100
223	150	1.79	536.2	28.0	7980	3	110	100
224	155	1.82	1720.0	37.4	9090	3	30	100
225	223	1.62	1221.9	25.0	7660	7	300	100
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39
PETN	202	1.75	480.0	31.6	8525	3	60	43

Scheme 49



PIDA is di(acetoxy)iodobenzene

mixture of salts of azo (**213b**) and hydrazino derivatives (**214a**) and, using acetonitrile as a solvent, the azo group is reduced to the hydrazinium moiety and salt **214a** is isolated in a good yield (Scheme 45). The pathway of the reaction of compound **213** with an aqueous solution of hydroxylamine depends on the amount of the reagent: with an equimolar amount of hydroxylamine, the hydroxylammonium salt **213c** is formed, while using an excess leads to the complete destruction of the azo-bridge to afford the amino derivative **215a** in the form of an ammonium salt in a mixture with the product **213c**. Nitration of the ammonium salt **213a** also gives the bis(trinitromethyl)azo compound **216** (Scheme 46).[98]

Using aminofuroxan **217** as a starting compound, an azo derivative **218** was obtained from which tetracyclic azo

Table 32. Physicochemical properties of compounds **232**–**235** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
229	219	1.79	186.0	26.8	8193	>40	>360	102
230	249	1.68	186.6	20.4	7495	>40	>360	102
231	213	1.65	780.7	21.6	7547	>40	>360	102
235	245	1.72	289.1	21.5	7798	>40	>360	102
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 50

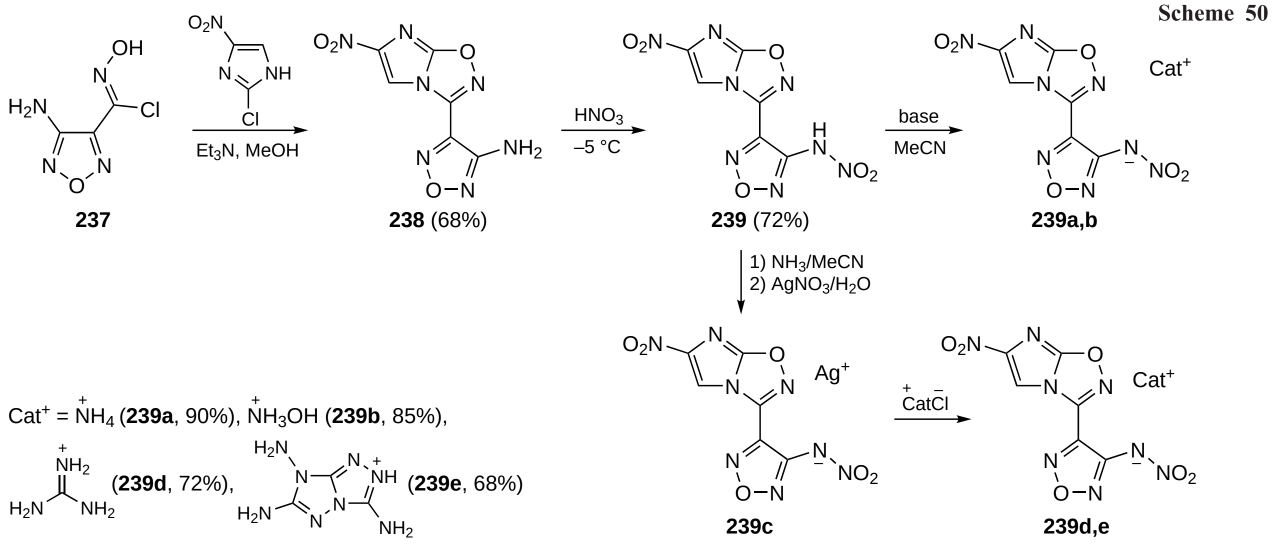


Table 33. Physicochemical properties of compounds **238** and **239** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
238	189	1.78	465.3	25.0	7840	>40	>360	103
239	128	1.80	600.8	30.4	8439	12	160	103
239a	171	1.76	469.5	27.5	8152	24	240	103
239b	160	1.85	506.6	32.8	8682	>40	>360	103
239d	187	1.78	185.0	25.5	8051	25	240	103
239e	158	1.83	952.1	27.4	8303	20	216	103
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

compounds **219** and **220** containing di- and trinitromethyl groups were synthesized similar to compounds **213** and **216**.[99] It should be noted that, unlike the furazan-containing analogues, the synthesis of the energetic salts **219a**–**c** produces no products of the azo group reduction (Scheme 47). The detonation performance parameters of all the above compounds are comparable to those of hexogen, and the bis(trinitromethyl) derivatives **216** ($D = 9351$ m s^{-1}; $P = 37.46$ GPa) and **220** ($D = 9411$ m s^{-1}; $P = 39.0$ GPa) show detonation velocities and pressures comparable to those of octogen (Table 30). The hydrazinium salt **214a** is impact insensitive.

The library of energetic tetracyclic oxadiazoles has been extended by combining various explosophoric substituents with azo-bridged oxadiazole rings.[100] Addition of hydroxylamine to the cyano group of compounds **221** and **192** followed by condensation of the resulting amidoximes **222** and **196** with BrCN gave 4-azido-3-(5-amino-1,2,4-oxadiazolyl)furoxan **223** (see [101]) and 4-(5-amino-1,2,2-oxadiazolyl)-3-cyanofuroxan **197** respectively.[93] The target energetic azo-bridged tetracycles **224** and **225** were synthesized by oxidative coupling of compounds **223** and **197** using $KMnO_4$ in hydrochloric acid (Scheme 48).

Azo structures **224** and **225** have high nitrogen and oxygen contents (>68%) and, due to the presence of different azole rings in the molecule, high enthalpies of formation (1720.0 and 1221.9 kJ mol^{-1}), significantly exceeding those of hexogen and octogen (Table 31). In addition, the detonation parameters of these compounds exceed those of trinitrotoluene, while the first compound ($D = 9090$ m s^{-1}, $P = 37.4$ GPa) is also superior to hexogen.

Using the precursors **226–228**, Tang *et al.*[102] synthesized bicyclic 3-amino-1,2,4-oxadiazoles **229–231**. The key step of the process is the oxidative cyclization of *N*-carbamoyl-substituted 1,2,5-oxadiazoles **232–234**, initiated by $PhI(OAc)_2$ (Scheme 49). The compounds **229–231** react differently with hydrazine monohydrate depending on their structure: furoxan **229** does not undergo this reaction, whereas furazan **230** gives the aminotriazole **235**, and in the case of the tetracyclic azo compound **231**, both the reduction of the azo-bridge and the opening of the aminooxadiazole ring to afford the heterocycle **236** are observed. The detonation performance of these compounds exceed that of trinitrotoluene (Table 32).[102]

An effective method for constructing an energetic molecule is the use of fused polyazole frameworks. Dou *et al.*[103] have succeeded in synthesizing energetic compounds based on imidazo[1,2-*d*][1,2,4]oxadiazole, which is additionally fused to the nitraminofurazan ring *via* the C–C bond. The key step in the synthesis is the annulation of 4-nitro-2-chlorimidazole to amidoxime **237** in the presence of triethylamine as a base (Scheme 50). Next, the amino group of intermediate **238** is nitrated. The product **239** and its energetic salts **239a–e** have detonation properties comparable to those of hexogen ($D = 8051–8682$ m s^{-1}, $P = 25.5–32.8$ GPa) (Table 33), being less impact sensitive.

5. 1,2,4-Oxadiazole/1,3,4-oxadiazole-based energetic compounds

Among isomeric azoles containing nitrogen and oxygen atoms, 1,3,4-oxadiazole has the lowest enthalpy of formation, and chemical modification of the substituents at the carbon atoms in the ring is rather difficult and requires strict conditions. Nevertheless, a number of energetic 1,3,4-oxadiazole-based compounds are known that combine low impact sensitivity with increased thermal stability, such as 5,5′-bis(2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole) (TKX-55) with a decomposition temperature >335 °C.[104] The use of quantum chemical calculations using the Density Functional Theory (DFT) method[105] allowed us to determine the potential properties of compounds containing 1,2,4- and 1,3,4-oxadiazole rings. The calculated detonation parameters exceed those of hexogen, so that the incorporation of the 1,3,4-oxadiazole fragment into the energetic structure may help to achieve a balance between the stability of the compound and its detonation performance.

To date, a small number of energetic compounds containing 1,2,4- and 1,3,4-oxadiazoles with good detonation properties have been synthesized. For example, cyclization of diaminoglyoxime **15** with ethyl chlorooxoacetate gives bi(1,2,4-oxadiazole) **240**, which is then sequentially reacted with hydrazine to give hydrazide **241** and with cyanogen bromide to give the tetracyclic structure **242**. Further nitration and reaction with bases produces compound **243** and its salts **243a–c** (Scheme 51). In this series, compound **243** has the highest density (1.90 g cm^{-3}), comparable to that of hexogen. Among the salts, the hydrazinium salt **243c** has the highest detonation velocity ($D = 8648$ m s^{-1}) and the hydroxylammonium salt **243b** has the highest detonation pressure ($P = 31.7$ GPa) (Table 34). The resulting structures show acceptable impact sensitivities (IS = 10–20 J, FS = 110–240 N), and together with high thermal stability and high detonation performance, they can be considered as a new generation of energetic materials.[106]

Similarly, it is possible to carry out the sequential construction of isomeric oxadiazole rings in ethyl cyano formate **244**.[107] Addition of hydroxylamine gives amidoxime **245**, further cyclization with cyanogen bromide gives aminooxadiazole **246**, which is further converted to hydrazide **247**. Closure of the 1,3,4-oxadiazole ring affords compound **248**, subsequent

Scheme 51

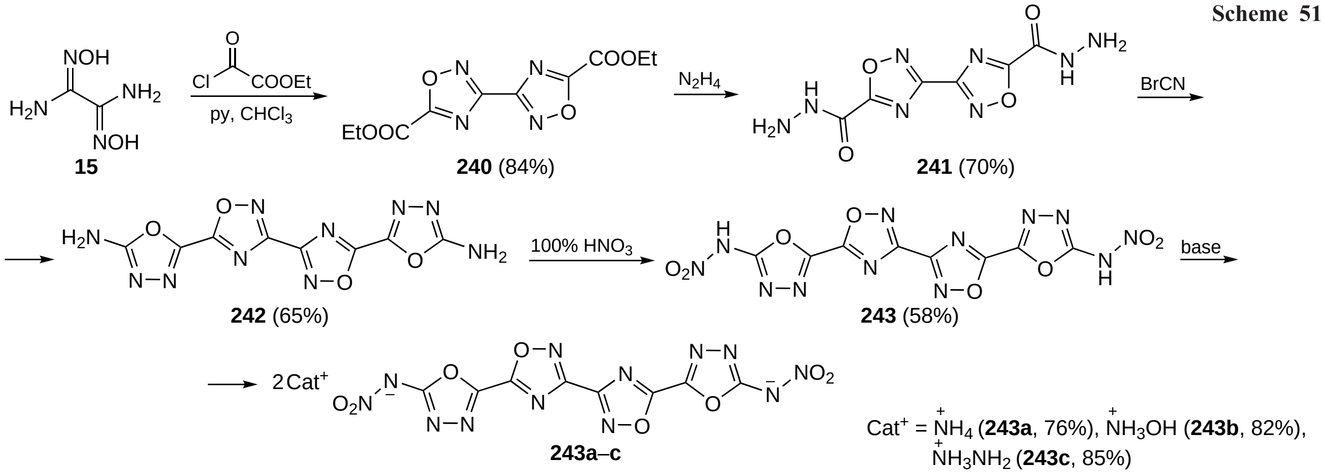


Table 34. Physicochemical properties of compounds **243** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
243	215	1.90	418.9	32.7	8789	10	110	106
243a	212	1.81	185.4	27.8	8340	>20	220	106
243b	169	1.84	302.0	31.7	8644	>20	200	106
243c	203	1.79	514.5	30.6	8648	>20	240	106
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	–59.3	21.3	7303	36.6	353	39

Scheme 52

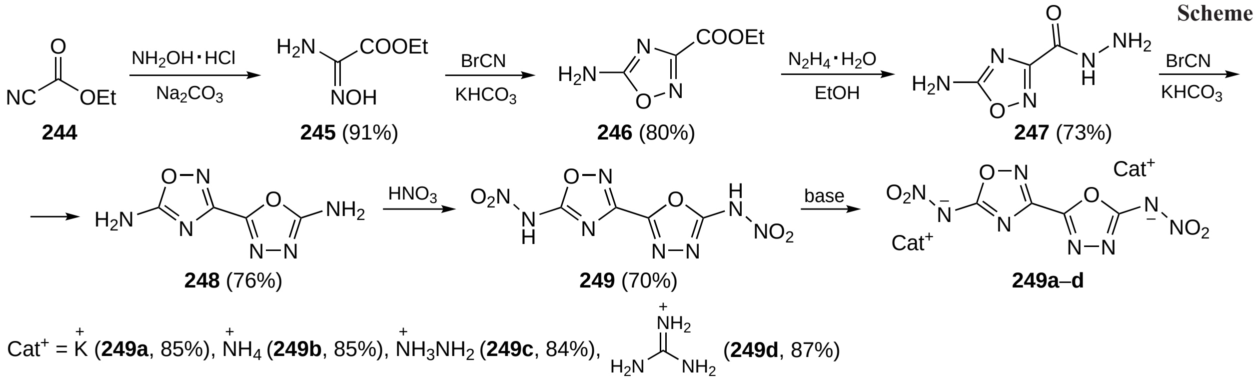


Table 35. Physicochemical properties of compounds **249** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
249	176	1.86	267.7	34.1	8888	10	108	107
249a	267	2.04	−285.7	27.3	8637	2	40	107
249b	207	1.75	−25.3	27.0	8318	18	160	107
249c	170	1.70	324.9	29.2	8663	14	120	107
249d	292	1.71	7.4	23.6	8080	25	240	107
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

nitration gives dinitramine **249**, and metathesis involving its produces a series of energetic salts **249a–d** (Scheme 52). The study of the energetic properties of the above compounds shows that product **249** and its non-metallic salts **249b–d** are significantly less sensitive to mechanical stimuli than hexogen, with comparable detonation parameters (D = 8080–8888 m s^{-1}, P = 23.6–34.1 GPa) (Table 35).[107]

6. 1,2,4-Oxadiazole/1,2,3- (or 1,2,4)-triazole-based energetic compounds

The combination of 1,2,4-oxadiazole and triazole heterocycles is quite rare in energetic materials. In 2020, a number of structures based on the 1,2,3-triazole/1,2,4-oxadiazole combination were synthesized.[108] Using 5-amino-1*H*-1,2,3-triazole (**250**) as a starting compound, amidoxime **251** and bicyclic precursor **252** were obtained by a tandem addition–cyclization, followed by ammonolysis to provide 5-amino-3-(5-amino-1*H*-1,2,3-triazol-4-yl)-1,2,4-oxadiazole (**253**) (Scheme 53). Subsequent nitration with various reagents gives the mononitration product **254** and (mediated by carbamate **255**) dinitration product **256**, isolated in the form of the corresponding energetic salts **254a–c** и **256a–d**. The preliminary reaction of the heterocycle **253** with ethyl chlorophormate to form the structure **255** enables the amino group in the 1,2,4-oxadiazole ring, which reactivity is significantly reduced, to be nitrated. The resulting salts have high enthalpies of formation and acceptable impact sensitivities (Table 36). It was shown that the salts **254a–c** bearing one nitramine group are more thermally stable but have lower detonation performance compared to the characteristics of the corresponding analogues **256a–d** with two nitramine groups.

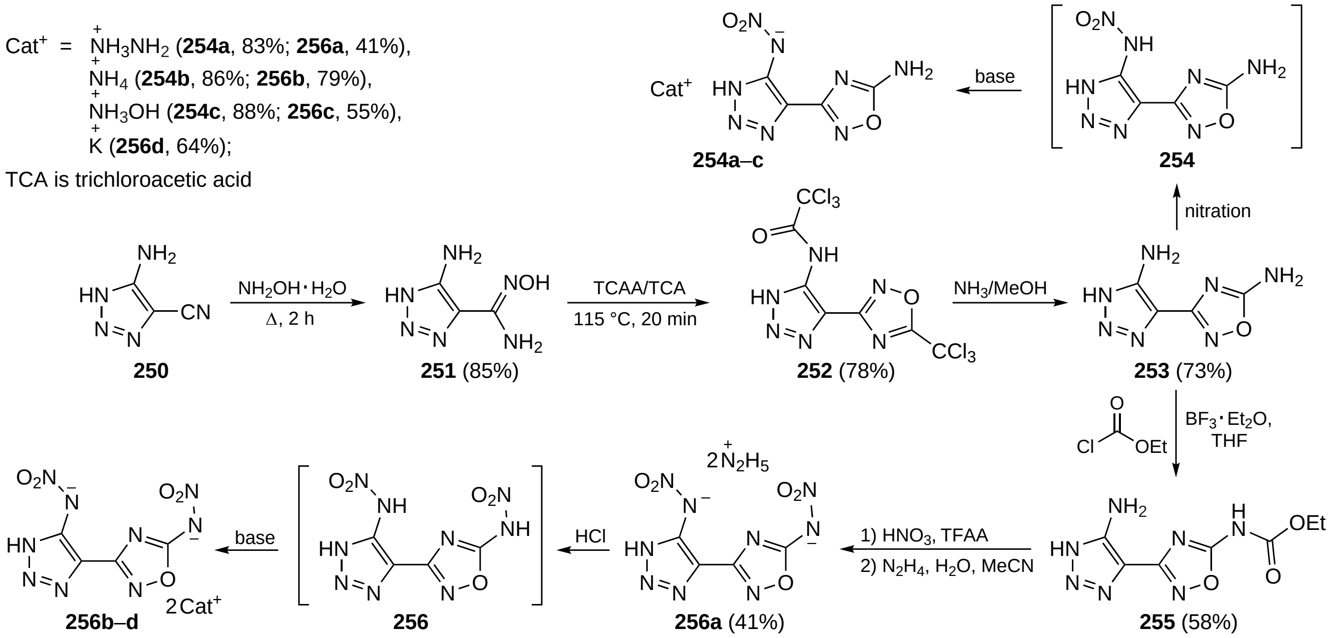
A similar strategy was used to obtain the 1,2,4-triazole isomer.[109] 5-Amino-3-cyano-1,2,4-triazole (**257**) was treated with hydroxylamine, the intermediate amidoxime **258** was then reacted with trichloroacetic anhydride to give the product **259**. Further treatment with methanolic ammonia leads to the replacement of the trichloromethyl group with the amino group to give 5-amino-3-(5-amino-1H-1,2,4-triazol-3-yl)-1,2,4-oxadiazole (**260**). Nitration under different conditions gives mono- (**261**) and dinitration products (**262**), which are used to prepare a wide range of energetic nitrogen-containing salts **261a–n** and **262a–n** (the original publication provided no yields of these salts) (Scheme 54).[109] In this series, products **262** and **262c** have comparable detonation performance (D = 9087–9135 m s^{-1}, P = 35.3–35.9 GPa) (see Table 36) and lower sensitivities (IS = 16–20 J, FS = 252–288 N), making them safer substitutes for hexogen and octogen.

Detailed studies of energetic compounds based on the combination of triazole and 1,2,4-oxadiazole heterocycles have not been carried out. Nevertheless, a number of compounds combining triazole and furazane rings, as well as explosophoric groups, in particular nitro and nitramino functionalities,[110] have been described.[111–114] This approach to the design of nitrogen-containing high-energy structures is the most common and effective.

7. 1,2,4-Oxadiazole/tetrazole-based energetic compounds

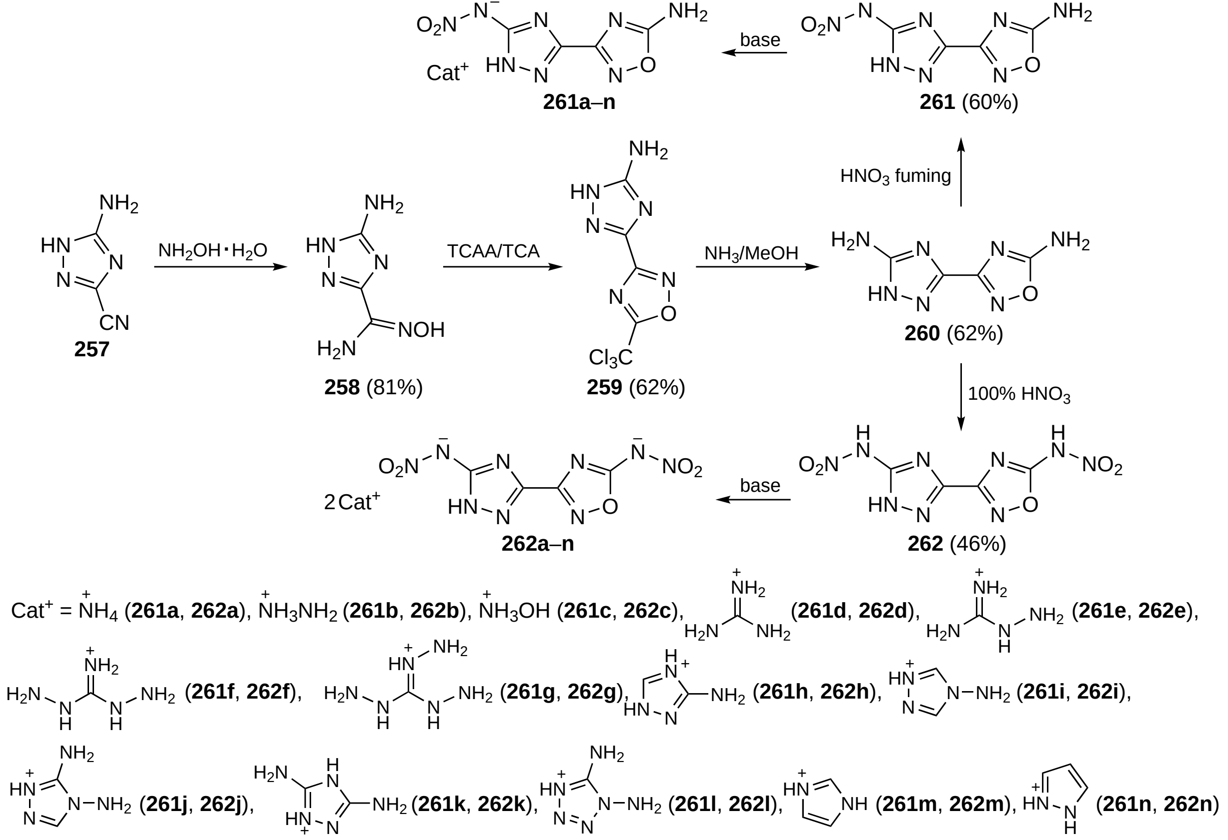
Tetrazole stands out among energetic compounds due to its high nitrogen content and high enthalpy of formation (237 kJ mol^{-1}).[115] The combination of tetrazole and 1,2,4-oxadiazole in a molecule significantly improves the enthalpy of formation of the energetic material, and the additional introduction of a hydroxyl group into the tetrazole ring increases the density of the compound and improves its detonation performance.[116] In addition, deprotonation of

Scheme 53



Cat^+ = $\overset{+}{N}H_3NH_2$ (**254a**, 83%; **256a**, 41%),
$\overset{+}{N}H_4$ (**254b**, 86%; **256b**, 79%),
$\overset{+}{N}H_3OH$ (**254c**, 88%; **256c**, 55%),
$\overset{+}{K}$ (**256d**, 64%);
TCA is trichloroacetic acid

Scheme 54



hydroxytetrazole or tetrazole opens the way to the preparation of energetic salts. At present, only a few energetic compounds combining 1,2,4-oxadiazole and tetrazole rings are known. The first examples of such structures were described in 1989.[117] The authors found that heating azidoximes **263**, derived from halooximes **264**, in ether, leads to the closure of the tetrazole ring in compound **265** instead of the expected product of the azole-azole rearrangement **266** (Scheme 55).

Zhang *et al.*[118] reported examples of melt-castable energetic materials containing methylene-bridged 5-nitrotetrazole and 1,2,4-oxadiazole rings for the first time. The starting 2-(5-nitro-2H-tetrazol-2-yl)acetonitrile (**267**) reacts with hydroxylamine hydrochloride in the presence of sodium bicarbonate to give the compound **268** and then, depending on the electrophilic agent in choice, the closure of the 1,2,4-oxadiazole ring provides the products **269**–**271** (Scheme 56). These compounds have good

Table 36. Physicochemical properties of compounds **254**, **256**, **261** and **262** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
254a	186	1.73	430.7	27.0	7892	7	254	108
254b	213	1.70	286.6	24.3	7529	22	324	108
254c	166	1.72	345.1	26.8	7889	10	216	108
256a	203	1.66	505.0	30.5	8493	14	160	108
256b	190	1.68	174.3	25.4	7721	18	192	108
256c	165	1.81	291.9	33.6	8682	6	120	108
261	200	1.88	325.7	28.6	8484	28	280	109
261a	209	1.77	261.9	25.8	8324	28	>360	109
261b	243	1.78	407.9	28.6	8715	24	324	109
261c	218	1.84	317.3	30.5	8787	18	324	109
261d	268	1.72	227.1	22.6	7953	>40	>360	109
261e	249	1.70	326.1	23.6	8136	>40	>360	109
261f	250	1.69	441.5	24.5	8298	>40	>360	109
261g	223	1.68	566.2	26.0	8498	>40	>360	109
261h	253	1.74	467.2	22.5	7880	>40	>360	109
261i	250	1.74	607.2	23.8	8032	>40	>360	109
261j	254	1.73	542.8	23.4	8032	>40	>360	109
261k	242	1.73	430.6	22.6	7936	>40	>360	109
261l	264	1.76	684.0	26.8	8471	>40	>360	109
261m	279	1.72	366.5	19.8	7428	>40	>360	109
261n	248	1.72	474.3	20.7	7548	>40	>360	109
262	150	1.92	435.5	35.9	9087	20	252	109
262a	200	1.77	108.3	27.0	8433	24	>360	109
262b	232	1.78	429.1	31.5	9018	20	324	109
262c	191	1.87	235.7	35.3	9135	16	288	109
262d	274	1.71	126.0	23.3	8050	>40	>360	109
262e	231	1.70	348.0	25.0	8342	>40	>360	109
262g	216	1.68	868.6	28.3	8835	>40	>360	109
262h	222	1.76	634.5	24.2	8052	>40	>360	109
262i	174	1.75	915.4	25.9	8257	>40	>360	109
262k	247	1.75	581.3	23.9	8100	>40	>360	109
262l	176	1.79	1083.1	30.0	8822	>40	>360	109
262m	214	1.72	417.0	19.7	7344	>40	>360	109
262n	180	1.71	633.9	20.9	7516	>40	>360	109
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

thermal stabilities ($T_{\mathrm{dec}} > 240$ °C) and detonation properties ($D = 7271-7909$ m s^{-1}, $P = 20.9-24.8$ GPa), which exceed those of trinitrotoluene (Table 37).

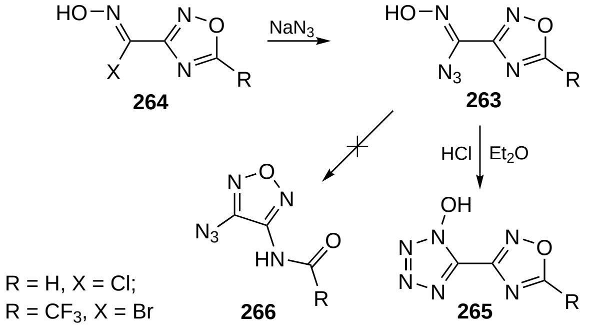
In 2017, a method was developed to prepare energetic derivatives of 1,2,4-oxadiazole containing a directly linked hydroxytetrazole ring.[71] 3,3′-Bis(5-cyano-1,2,4-oxadiazole) (**272**) was obtained from bis(1,2,4-oxadiazole) **240** in two steps. Further addition of hydroxylamine and diazotization of the product in hydrochloric acid gives bis(chloroxime) **273**. The final step of the process involves the replacement of the chlorine atom by an azide group followed by cyclization with hydrochloric acid in dioxane to give 3,3′-bis[5-(1-hydroxy-1H-tetrazol-5-yl)-1,2,4-oxadiazole] (**274**), which is converted to the salts **274a–e** (Scheme 57). Similarly, di(cyano)oxadiazole **276** is obtained from ethyl cyanoformate *via* the intermediate diethyl 1,2,4-oxadiazole-3,5-dicarboxylate **275**. The product (**277**) of the addition of hydroxylamine to the compound **276** in alcohol is further subjected to diazotization with subsequent replacement of the chlorine atom by an azide group and formation of diazidoxime **278**. Cyclization of the latter using hydrochloric acid in dioxane gives 3,5-bis(1-hydroxy-1*H*-tetrazol-5-yl)-1,2,4-oxadiazole (**279**), which is converted to the ammonium salt **279a**. Heterocycles **274**, **274a**, **279a** are insensitive to impact, friction and electrostatic discharge, and the decomposition temperature of all these compounds, according to differential scanning calorimetry data, exceeds the similar parameter of hexogen.[71]

Nitrogen-rich salts derived from compound **274** have been used to study the effect of the counter-ion on the density of the structure and crystal packing.[119] The density of such salts varies

Table 37. Physicochemical properties of compounds **269**–**271** in comparison with similar parameters of trinitrotoluene.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
269	241.1	1.76	344.9	24.8	7909	>40	>360	118
270	256.6	1.66	275.8	20.9	7451	>40	>360	118
271	261.6	1.87	−328.8	23.7	7271	>40	>360	118
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

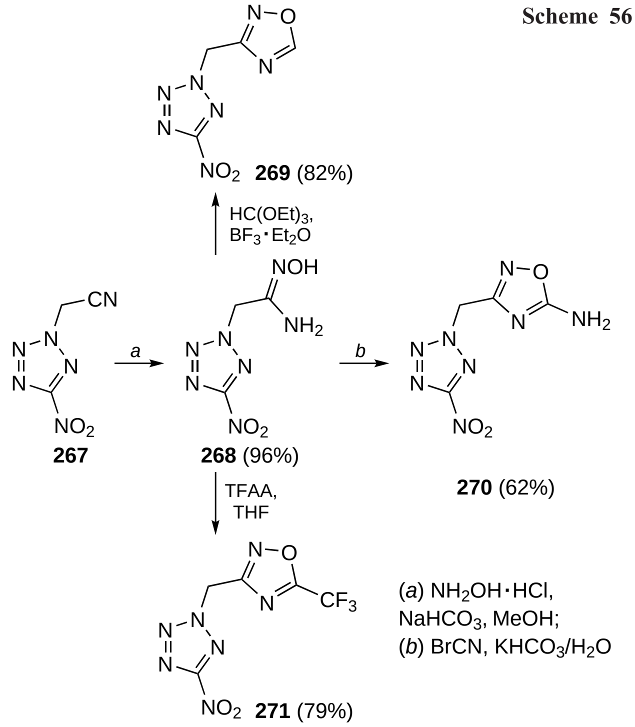
Scheme 55



from 1.54 to 1.87 g cm^{-3}, but their detonation properties have not been investigated (yields are also not given).

This synthetic methodology was developed in a study,[43] where a series of high-energy compounds based on 1,2,4-oxadiazole containing various energetic substituents, including the 1-hydroxytetrazole moiety, were obtained. The interaction of chloroxime **20** with sodium azide gives azidoxime **280** and its subsequent cyclization in acidic medium leads to the target 5-(1,2,4-oxadiazol-3-yl)-1-hydroxytetrazole **281** (Scheme 58). Reaction with bases in alcohol gives a series of energetic salts **281a**–**c**.

Scheme 56



Scheme 57

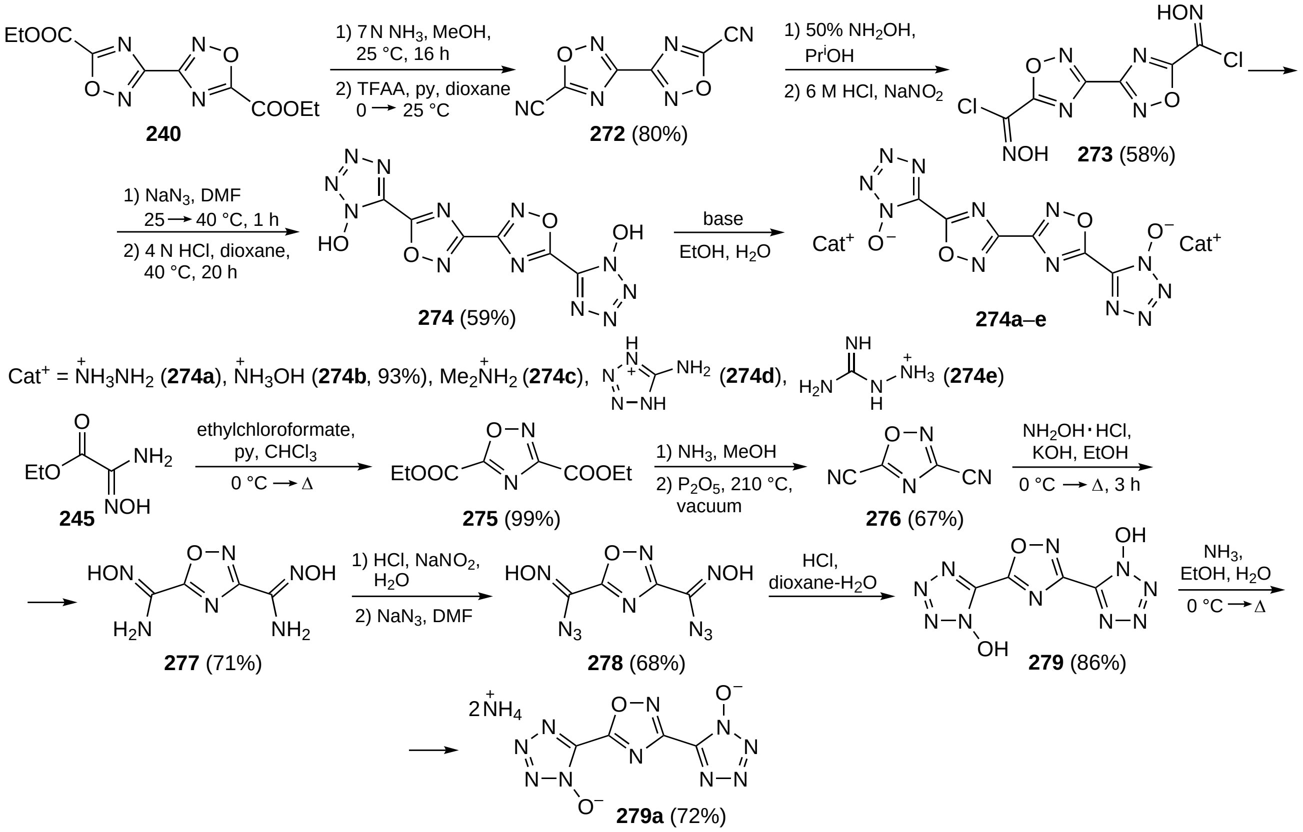
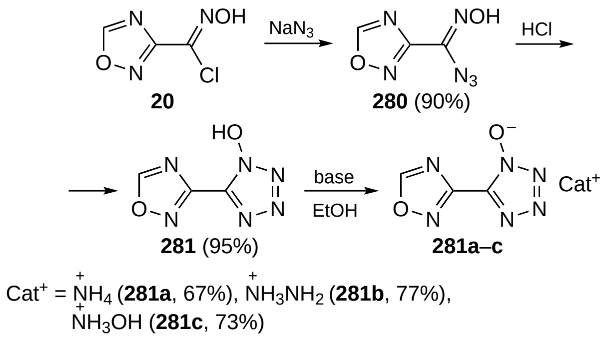


Table 38. Physicochemical properties of compounds **281** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
281	143	1.69	363.0	25.0	8037	6	72	43
281a	174	1.72	322.0	28.0	8576	10	120	43
281b	152	1.71	478.0	30.4	8929	8	108	43
281c	141	1.79	372.0	32.7	8913	8	96	43
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 58



Compound **281** melts at 133 °C and decomposes at 143 °C, while its salts decompose without melting between 141 and 174 °C. The salts also show a detonation performance ($D = 8576-8929$ m s^{-1}, $P = 28.0-32.7$ GPa) higher than that of hexogen, which allows to propose them as potential explosives. It should be noted that the neutral compound **281** is the most impact sensitive in this series (IS = 6 J, FS = 72 N) (see Table 38).

Dong *et al.*[120] explored two different strategies for the synthesis of bis[5-(tetrazol-5-yl)-1,2,4-oxadiazole] **282** from available reactants and obtained its energetic nitrogen-containing salts **282a–e**. The method, based on the condensation of diaminoglyoxime with tetrazolylacetic acid **283** mediated by the intermediate acid chloride **284**, gave the target product in lower yields and has a longer reaction time compared to the [3+2] cycloaddition to di(cyano)oxadiazole **272** (Scheme 59). The resulting compounds are sufficiently thermostable ($T_{dec} > 216$ °C) and their detonation properties ($D = 7984-8112$ m s^{-1}, $P = 22.8-25.6$ GPa) are superior to those of trinitrotoluene (Table 39).

8. Compounds based on 1,2,4-oxadiazole and six-membered rings

The library of heterocycles used in the design of new-generation energetic materials is not limited to azoles. For example, studies[121,122] showed the possibility of obtaining hybrid structures containing tetrazine, a nitrogen-rich six-membered heterocycle, together with 1,2,4-oxadiazoles (Scheme 60). Starting from tetrazine **285** and azidooxadiazole **286**, a

Scheme 59

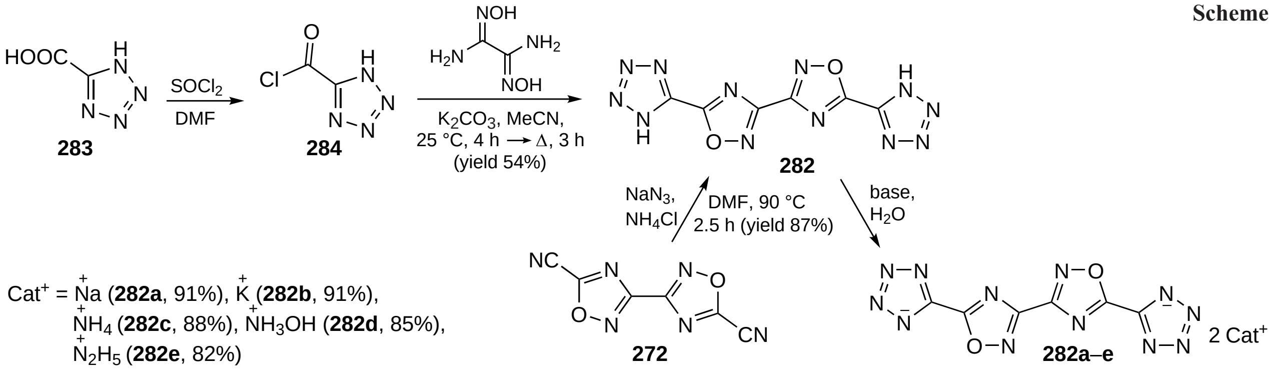


Table 39. Physicochemical properties of compounds **282** in comparison with similar parameters of known explosives.

Compound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	FS, N	Ref.
282	259.2	1.77	596.7	23.7	7984	20	360	120
282c	273.7	1.68	449.0	22.8	8043	>40	>360	120
282d	216.0	1.66	530.7	25.6	8100	>40	>40	120
282e	276.2	1.68	524.9	23.1	8112	>40	>360	120
CL-20	210	2.04	397.8	45.2	9706	4	94	39
HMX	280	1.91	74.8	39.2	9144	7	120	39
RDX	210	1.80	70.7	34.9	8795	7.4	120	39
TNT	295	1.65	−59.3	21.3	7303	36.6	353	39

Scheme 60

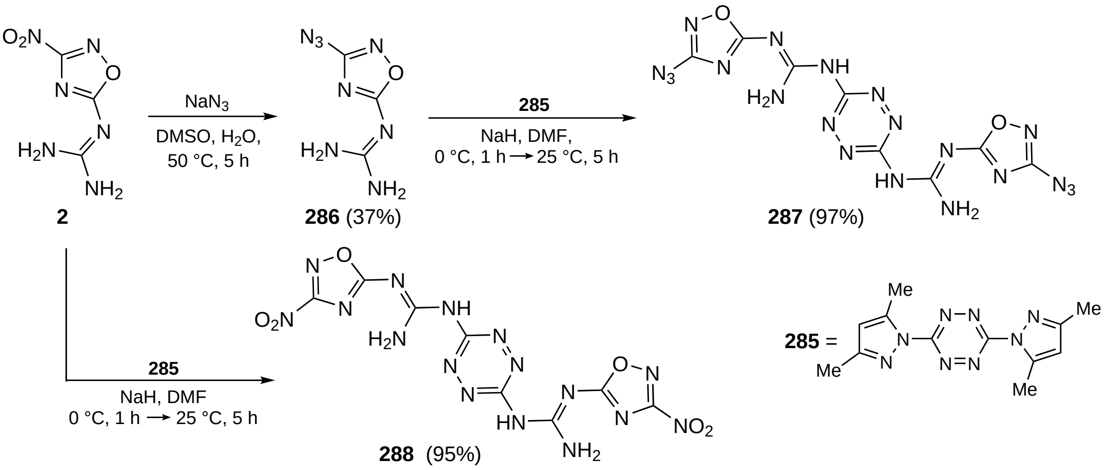


Table 40. Physicochemical properties of compounds **286**–**288** in comparison with similar parameters of known explosives.

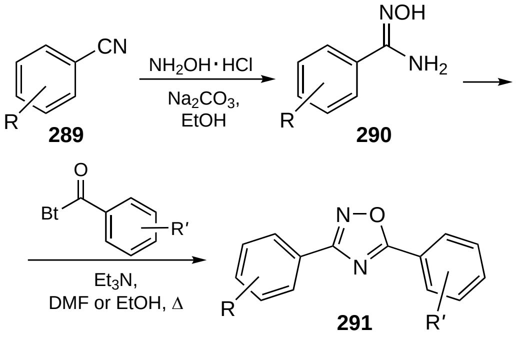
Com-pound	T_{dec}, °C	ρ, g cm^{-3}	ΔH_f^o, kJ mol^{-1}	P, GPa	D, m s^{-1}	IS, J	Ref.
286	196	1.69	535.0	24.9	7630	20	121
287	210	1.73	1564.0	25.0	7592	30	121
288	328	1.81	957.0	28.5	8002	>70	122
CL-20	210	2.04	397.8	45.2	9706	4	39
HMX	280	1.91	74.8	39.2	9144	7	39
RDX	210	1.80	70.7	34.9	8795	7.4	39
TNT	295	1.65	–59.3	21.3	7303	36.6	39

diazidooxadiazole derivative **287** was obtained and reaction with compound **2** gave the product **288**.

Product **288** has an outstanding thermal stability (T_{dec} = 328 °C) and low impact sensitivity (IS = 70 J), and its detonation velocity and pressure (D = 8002 m s^{-1}, P = 28.5 GPa) exceed similar parameters of trinitrotoluene and are only slightly lower than those of hexogen (Table 40).

Examples of the preparation of a variety of polynitro-3,5-diaryl-1,2,4-oxadiazoles are described and the influence of nitro groups in the aromatic ring on the energy parameters of a number of such compounds is estimated (Scheme 61).[123] The reaction of mono- or dinitro-substituted aryl cyanides **289** with hydroxylamine hydrochloride in aqueous ethanol gives the corresponding amidoximes **290**, then the mixture of the corresponding amidoxime and *N*-acylbenzotriazole in boiling dimethyl formamide or ethanol in the presence of triethylamine affords polynitro-3,5-diaryl-1,2,4-oxadiazoles **291**. It was found that the density of the resulting structures correlated directly with the number of nitro groups and it was suggested that 3,5-bis(2,4,6-trinitrophenyl)-1,2,4-oxadiazole will have density and detonation characteristics similar to those of hexogen. However, the properties of the above structures have not been investigated.

Scheme 61



R, R′ = 2-NO_2, 3-NO_2, 4-NO_2, 2,4-$(NO_2)_2$, 3,5-$(NO_2)_2$;
Bt is benzotriazol-1-yl

9. Conclusion

To summarize, the analysis of literature data reveals a diversity of types of 1,2,4-oxadiazole-based energetic structures. In recent years, a large number of high-energy compounds have been obtained containing one or two 1,2,4-oxadiazole rings in combination with conventional explosophoric groups (nitro, azido, azo groups, *etc*.). It should be noted, however, that the variety of such structural combinations is very limited, leading researchers to look for other ways to create an 'ideal' energetic material. In this context, it is obvious that a promising trend is the combination of the 1,2,4-oxadiazole core with other known explosophoric heterocycles (pyrazole, triazole, tetrazole as well as isomeric oxadiazoles) in a molecule. Implementing such a synthetic strategy is largely combinatorial and usable for the preparation of energetic materials, not only based on 1,2,4-oxadiazole, leading to an avalanche-like increase in the number of publications on this subject and a simultaneous growth of competition in the scientific community for the priority obtaining of the most promising materials. A certain diversification of the 1,2,4-oxadiazole-based energetic bi- and polyheterocyclic structures synthesized so far should be noted: for example, combinations of the 1,2,4-oxadiazole ring with pyrazole or 1,2,5-oxadiazole cores are widely represented in the literature, whereas similar structures based on the combination of the 1,2,4-oxadiazole ring with triazole or 1,3,4-oxadiazole cores are very few in number. Obviously, this can be due to the inaccessibility of functional derivatives of 1,2,4-(or 1,3,4)-oxadiazole and 1,2,3-(or 1,2,4)-triazole, which will require the development of new synthetic methods to carry out such studies in the coming years.

One of the strategies of obtaining heterocyclic combinations based on 1,2,4-oxadiazole can also be considered as the synthesis of energetic salts derived therefrom, which are usually characterized by higher stabilities in comparison with neutral precursors. Despite the fact that the 1,2,4-oxadiazole ring is not capable of salt formation, the introduction of NH-azoles or functional groups with high acidity (*e.g*. dinitromethyl group) as substituents into such a molecule helps to obtain a wide range of energetic salts. Varying the cationic part in ionic structures allows to control the physicochemical properties of target high-energy materials, although it should be noted that they may have increased hygroscopicity.

In conclusion, it is important to point out that the literature sources systematized in this review have been published over the last 15 years, since earlier publications on the above subject are practically non-existent. This is due, first of all, to the fact that the 1,2,4-oxadiazole heterocycle has not been considered as an energetic group throughout the XX century, being surpassed by more potent derivatives based on tetrazole, 1,2,5-oxadiazole and tetrazine. However, modern trends in the development of energetic materials science dictate requirements for the balance of physicochemical properties of high-energy materials, *i.e.* the search for a less potent but more thermally stable and less sensitive compound. These criteria are largely met by the 1,2,4-oxadiazole-based systems, which already represent quite a promising class of energetic components. We have no doubt that the study of synthetic approaches for the design of energy-rich 1,2,4-oxadiazoles will be intensively developed in the coming years and will lead to the creation of new promising materials based thereon.

10. List of abbreviations and designations

Bt — benzotriazol-1-yl,
Cat — cation,
CL-20 — 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane,
D — detonation velocity,
DBU — 1,8-diazabicyclo[5.4.0]undec-7-ene,
DFT — density functional theory,
ESD — electrostatic discharge sensitivity,
FS — friction sensitivity,
$\Delta H^{\mathrm{f}}_{\mathrm{o}}$ — standard enthalpy of formation,
HMX — octogen (cyclotetramethylenetrinitramine),
IS — impact sensitivity,
Oxone® — potassium peroxymonosulfate,
P — detonation pressure,
PETN — pentaerythritol tetranitrate,
PIDA — di(acetoxy)iodobenzene,
py — pyridine,
r — density,
RDX — hexogen (cyclotrimethylenetrinitramine),
SDIC — sodium dichloroisocyanurate,
Selectfluor® — 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate),
T_{dec} — decomposition temperature,
TCA — trichloroacetic acid,
TCAA — trichloroacetic anhydride,
TEA — triethylamine,
TFA — trifluoroacetic acid,
TFAA — trifluoroacetic anhydride,
TfO — trifluoromethanesulfonate (triflate),
TNT — trinitrotoluene,
Ts — *p*-toluenesulfonyl (tosyl).

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