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Polynitropyrazole derivatives of pentanitroisowurtzitane

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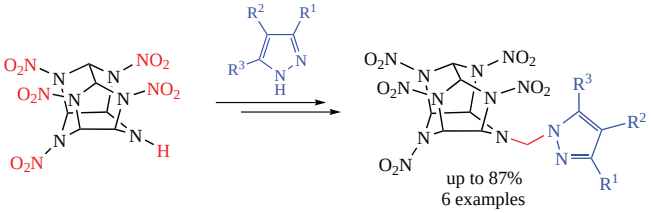
High energetic compounds of pentanitroisowurtzitane series containing various polynitropyrazolyl substituents attached to the frame through a methylene linker were synthesized in two steps from the corresponding *NH* precursors and paraformaldehyde. The structures of the compounds obtained were characterized by spectral methods, and their energy characteristics were estimated.



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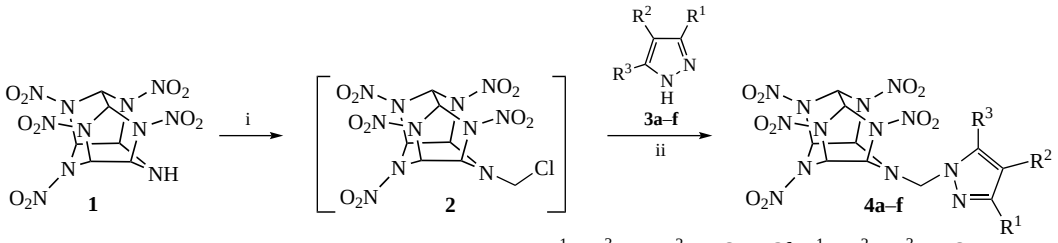
To create high energetic materials with characteristics above the currently existing standards, the broad range of potential structures has to be explored. 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) is among the promising representatives of polycyclic nitrogen rich frameworks. To date, CL-20 is the standard among high density and high energetic materials. Despite its high enthalpy of formation, high density, favorable oxygen balance and high thermal stability, CL-20 also has a number of drawbacks such as high sensitivity to mechanical stimuli, polymorphism and poor adhesion of crystals. On the other hand, functionalization of its frame may provide compounds superior in a number of parameters. The synthesis of CL-20 analogs and derivatives was actively developed in recent years,[1–8] which was reviewed in detail.[9] At the same time, nearly no attempts to introduce high-enthalpy heterocycles into CL-20 molecule were made. The only work[10] reports a synthesis of polynitrohexaazaisowurtzitane derivatives containing 5-substituted tetrazole moieties, however no energetic performance of these compounds were given.

One of the modern directions in the search for new high energetic compounds involves the use of the pyrazole molecule as a structural core for incorporating explophoric groups.[11–16] Pyrazole has a rather high enthalpy of formation (105.4 kJ mol^{-1}) and is readily nitrated with a sulfuric acid–nitrous acid mixture, while its polynitro derivatives easily undergo additional functionalization by *cine*- and *ipso*-substitution reactions on treatment with nucleophiles.[12,17,18] Data on the properties of nitropyrazoles obtained over the last 15 years have shown that compounds of this family are characterized by a beneficial combination of sufficiently high energetic performance, high thermostability and low sensitivity to external stimuli, which makes them prospective for creating energy-rich materials.[19–21]

This work deals with the synthesis and study of the properties of hybrid compounds consisting of polynitropyrazoles and 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane **1** bound by a methylene linker. The method is based on alkylation of various nitropyrazoles with 2,4,6,8,12-pentanitro-10-chloromethyl-2,4,6,8,10,12-hexaazaizowurtzitane **2** in the presence of bases (Scheme 1). The starting isowurtzitane derivative **1** was obtained by the Bellamy procedure.[22]

The efficiency of such reactions often depends both on the solvent and on the nature of the base. Polynitropyrazoles **3a–f** readily form the relative anions on treatment with bases. When we were selecting the alkylation conditions, we found that the reaction was most efficient in MeCN with a small excess of



a $R^1 = R^3 = H$, $R^2 = NO_2$ **3f** $R^1 = R^2 = R^3 = NO_2$
b $R^1 = R^2 = NO_2$, $R^3 = H$ **4f** $R^1 = R^2 = NO_2$, $R^3 = Cl$
c $R^1 = R^3 = NO_2$, $R^2 = H$
d $R^1 = R^2 = NO_2$, $R^3 = NH_2$
e $R^1 = R^3 = NO_2$, $R^2 = NH_2$

Scheme 1 *Reagents and conditions*: i, $(CH_2O)_x$, $SOCl_2$, room temperature, 24 h; ii, base (KOH, Et_3N, Na_2CO_3, K_2CO_3), MeCN, room temperature, 0.25–24 h.

K_2CO_3 or Na_2CO_3 as the base, and in cases of substrates **3a**–**e** it proceeded well at room temperature to give the target compounds **4a**–**e** in good yields. Moreover, the reaction time and yield of the target compounds are also affected by the structure of the started compounds. The 4-nitropyrazole derivative **4a** is formed after 24 h in 69% yield. The dinitropyrazole compounds **4b**,**c** are formed within 3.5 h in optimum yields. For aminodinitropyrazolisowurtzitanes **4d**,**e**, the maximum yields are reached in 15 min, while further exposure decreases the yields. This process is affected by the position of the substituents in the pyrazole ring; in the case of 5-amino-3,4-dinitropyrazole **3d**, the maximum yield of the target compound **4d** is 49%, while in the case of 4-amino-3,5-dinitropyrazole **3e**, the maximum yield of **4e** reaches 87%. Similarly to the previously reported results,[23–26] alkylation of 3,4,5-trinitropyrazole **3f**, regardless of the base, proceeded with the replacement of the 5-positioned NO_2 group by the chloride ion released in the course of reaction, which led to 3,4-dinitro-5-chloropyrazol-1-yl derivative **4f**. Alkylation of unsymmetrically substituted nitropyrazoles **3b**,**d** resulted in individual regioisomeric products **4b**,**d**. The alkylation direction of the anions of these nitropyrazoles containing no other electron-acceptor groups is determined by the nitro group: an isomer with the N-substituent most distant from the nitro group is formed.[27–32]

Compounds **4a**–**f** were characterized by IR spectroscopy, multinuclear NMR and high-resolution mass spectrometry. The structures of **4a**,**d** were ultimately confirmed by X-ray diffraction analysis (Figure 1).† They crystallize as solvates to form a triclinic crystal system (**4a**) with space group $P\bar{1}$ and monoclinic crystal system (**4d**) with space group $P2/c$. The nitro groups in compound **4d** are arranged in different planes relative to each other due to spatial hindrance, the torsion angle N(1)–C(1)–C(2)–N(2) is 17.4(2)°, while the torsion angles

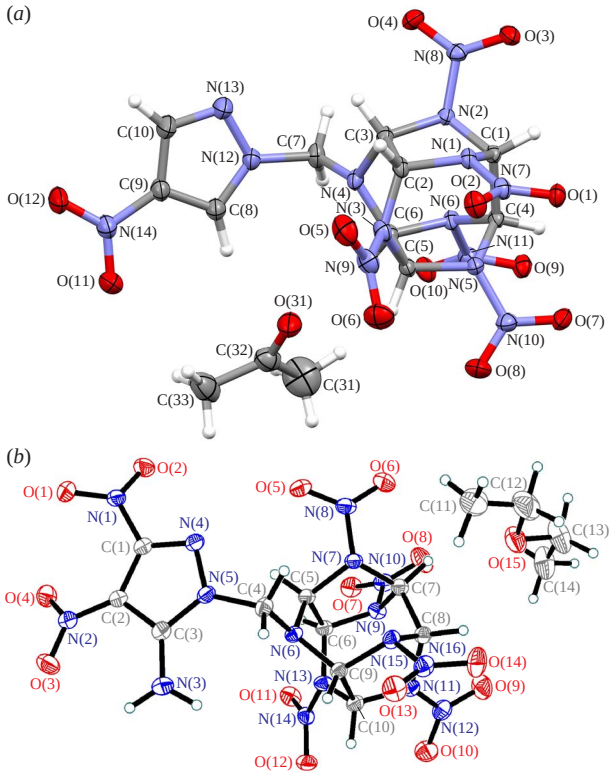


Figure 1 Single-crystal X-ray diffraction data of (*a*) compound **4a** and (*b*) compound **4d** with atoms shown as thermal ellipsoids at 50% probability level.

N(5)–N(4)–N(4)–C(1)–N(1), N(4)–N(5)–C(3)–C(2) and N(4)–N(5)–C(3)–N(3) are 174.58(12)°, –2.07(15)° and 176.49(13)°, respectively. However, the pyrazole cycle in general retains a planar structure.

The following parameters of compounds **4a**–**e** were determined by experimental and computational methods: thermal stability (T_m and T_d), density (d), impact and friction sensitivities (IS and FS), detonation velocity (v_{oD}), and relative metal acceleration ability (η). The data obtained are summarized in Table 1 and Figure 2.

Figure 2 shows thermogravimetric and differential scanning calorimetry (DSC) curves obtained upon linear heating of compounds **4a**–**e**.

All the compounds studied have no melting points, while their decomposition temperatures lie in a rather wide range, 162–214 °C. Compounds **4a** and **4e** showed the best thermal stability. Compounds with the 3,4-dinitropyrazole substituents (**4b** and **4d**) have the lowest temperature of the start of intense

Table 1 Physicochemical and special properties of compounds **4a**–**e**.[a]

Entry	Sample	T_d/°C[b]	IS/J[c]	FS/N[c]	d[d]/ g cm^{-3}	$\Delta_f H$[e]/ kJ mol^{-1}	v_{oD}[f]/ km s^{-1}	η[g]
1	**4a**	214	3.8 ± 0.9	185 ± 20	1.757	554	8.2	0.89
2	**4b**	172	5 ± 3	210 ± 30	1.841	594	8.6	0.94
3	**4c**	204	4.1 ± 0.4	150 ± 20	1.834	575	8.6	0.94
4	**4d**	162	5.5 ± 1.2	150 ± 25	1.787	565	8.6	0.91
5	**4e**	209	3.9 ± 0.4	140 ± 25	1.823	567	8.6	0.93
6	CL-20	235	4.2 ± 0.5	80 ± 10	2.044	435 (377 ± 13)	9.7 (9.7)	1.08 (1.09)

[a] Melting points could not be determined. [b] Onset decomposition temperature. [c] Sensitivities to shock and friction determined by the BAM method using STANAG standards (refs. 33, 34). [d] Gas density determined by a pycnometer at 25 °C. [e] Calculated enthalpy of formation of condensed phase; experimental data are given in parentheses. [f] Calculated detonation velocity; experimental data are given in parentheses. [g] Calculated metal acceleration ability with respect to HMX.

† *Crystal data for* **4a**. Crystals of $C_{13}H_{16}N_{14}O_{13}$ (M = 576.40) are triclinic, space group $P\bar{1}$, at 100 K, a = 8.4288(2), b = 9.5788(2) and c = 14.1442(3) Å, α = 88.255(2)°, β = 77.164(2)°, γ = 77.275(2)°, V = 1085.88(4) Å^3, Z = 2, d_{calc} = 1.763 g cm^{-3}, μ(CuK$_\alpha$) = 1.391 mm^{-1}, F(000) = 592, 28748 reflection were measured and 4692 independent reflections (R_{int} = 0.0273) were used in the further refinement. The refinement converged to wR_2 = 0.1115 and GOF = 1.086 for all independent reflections [R_1 = 0.0391 was calculated against F for 4443 observed reflections with $I > 2\sigma(I)$].

Crystal data for **4d**. Crystals of $C_{14}H_{20}N_{16}O_{15}$ (M = 652.46) are monoclinic, space group $P2/c$, at 100 K, a = 20.9929(2), b = 8.16100(10) and c = 14.65210(10) Å, α = 90°, β = 90.0440(10)°, γ = 90°, V = 2510.24(4) Å^3, Z = 4, d_{calc} = 1.726 g cm^{-3}, μ(CuK$_\alpha$) = 1.370 mm^{-1}, F(000) = 1344. 31539 reflections were measured and 5444 independent reflections (R_{int} = 0.0330) were used in the further refinement. The refinement converged to wR_2 = 0.0997 and 0.1013 and GOF = 1.036 for all independent reflections [R_1 = 0.0375 and 0.0397 was calculated against F for 3 5069 observed reflections with $I > 2\sigma(I)$].

X-ray diffraction data were collected at 100 K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized CuK$_\alpha$-radiation. Intensity data were integrated and corrected for absorption and decay using the CrysAlisPro program. The structure was solved by direct methods using SHELXT and refined on F^2 using SHELXL-2018 in the OLEX2 program. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The locations of amino hydrogen atoms (H3A, H3B) were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All the other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters.

CCDC 2345726 and 2345730 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

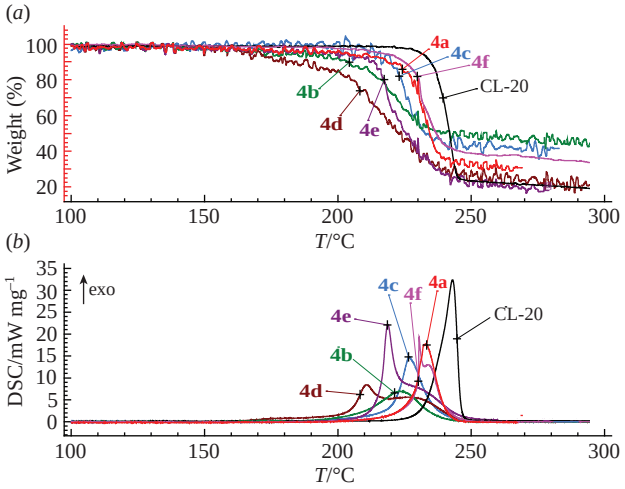


Figure 2 (*a*) Thermogravimetric and (*b*) differential scanning calorimetry analysis curves of compounds **4a–f**. Linear heating at a rate of 5 K min^{-1}.

decomposition. All the compounds obtained have higher enthalpy of formation and lower sensitivity than CL-20.

To determine the detonation parameters, the enthalpy of formation of the compounds was calculated. For this purpose, the gas-phase enthalpy of formation under standard conditions (pressure 0.1 MPa and temperature 298 K) was calculated using the AIQM1 semiempirical method[35] and supplemented with the modified Trouton equation[36] for the enthalpy of sublimation. Detonation parameters were then calculated using empirical equations implemented in the PILEM program.[37] As the experimental values of enthalpy of formation and detonation velocity are available for CL-20, one can estimate the errors of the chosen calculation methods. As it can be seen from Table 1, even a significant deviation of the thermochemical parameters from experimental ones does not lead to an error in the predicted detonation parameters.

In conclusion, we have synthesized new representatives of high energetic hybrid compounds of a series of polynitroisowurtzitane and polynitropyrazoles. The compounds obtained have high values of enthalpy of formation, 554–594 kJ mol^{-1}, are by 27–36% superior to CL-20 in this parameter, and have lower sensitivity than CL-20.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.025.

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