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One-step synthesis to an insensitive explosive: *N*,*N*′-bis((1*H*-tetrazol-5-yl) methyl)nitramide (BTMNA)

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ABSTRACT

RDX is used widely as a practical secondary explosive for civilian and military applications because of its high chemical stability and explosive power. However, a major shortcoming of RDX is its high sensitivity which leads to numerous accidents by accidental initiation. One of the major challenges in worldwide energetic materials research is the design and synthesis of insensitive high performing explosives. In this work, *N*,*N*′-bis((1*H*-tetrazol-5-yl)methyl)nitramide (BTMNA) (Mitchell et al., 2017) is obtained by a one-step reaction in >90 yield. The structure of BTMNA was confirmed by elemental analysis and X-ray single crystal diffraction. As a result of hydrogen bonding, the crystal density of BTMNA is 1.822 g/cm^3 at 100 K. The thermal decomposition temperature is 198 °C, and the impact and friction sensitivities are remarkable at 30 J, and 360 N. BTMNA, in its role as an insensitive RDX alternative, has a detonation velocity and pressure of 8732 m/s and 29.4 GPa, respectfully, thus making it a practical replacement for RDX.

During the last decade, new high-energy-density materials (HEDMs) have attracted considerable interest worldwide for civilian and military applications, and many compounds with high detonation performance have been synthesized [1]. However, it is extremely difficult to combine high detonation performance and low sensitivity into a single compound [2]. The cost of chemical syntheses of new HEDMs is a very important factor to be considered. Trinitrotoluene (TNT) was prepared in 1863 by German chemist Julius Wilbrand and was originally used as a yellow dye [3]. TNT is valued because of its insensitivity to shock and friction with a reduced risk of accidental detonation compared to more sensitive explosives such as nitroglycerin [4]. In industry, TNT is produced in a three-step process: 1) toluene is nitrated with a mixture of sulfuric and nitric acid to produce mononitrotoluene (MNT); 2) MNT is separated and then renitrated to dinitrotoluene (DNT); and finally 3) DNT is nitrated to trinitrotoluene (TNT) with an anhydrous mixture of nitric acid and oleum [5]. But the detonation performance of TNT is not good enough for modern explosive industry. So far, RDX is currently the most important explosive for military applications because its outstanding properties are based on its high chemical stability and high explosive power that considerably surpass that of TNT [6]. It is obtained by treating hexamethylenetetramine with white fuming nitric acid. But RDX has a high sensitivity value which results in accidental initiation. 1,1-Diamino-2,2-dinitroethene (FOX-7) was first synthesized 23 years ago [7]. Recently, this compound has emerged as a potential candidate for use as an insensitive HEDM, attracting substantial interest because of its high performance as an explosive is comparable to RDX with a markedly lower sensitivity to impact and friction which thus avoids accidental initiation [8]. The production of FOX-7 is based on a commercial starting material and the synthesis is straightforward. FOX-7 is attractive because of its straightforward synthesis at lower production costs and high detonation properties. The low sensitivity of this HEDM reduces dramatically the risk of serious and fatal accidents during its handling and application [9]. ATB (2,4,6-triamino-1,3,5-trinitrobenzene) is an insensitive high explosive (IHEs) and is useful where extreme safety is required. However, relative to RDX, TATB has a low detonation performance [10]. Although HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazoctane), TKX-50 (dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate) and Cl-20 (hexanitrohexaazaisowurtzitane) have higher detonation performances, due to their high sensitivity and complicated synthetic processes, their wide use in the explosive industry is modest [11]. As a result, one of the biggest challenges in worldwide energetic materials research is to synthesize a compound that balances sensitivity

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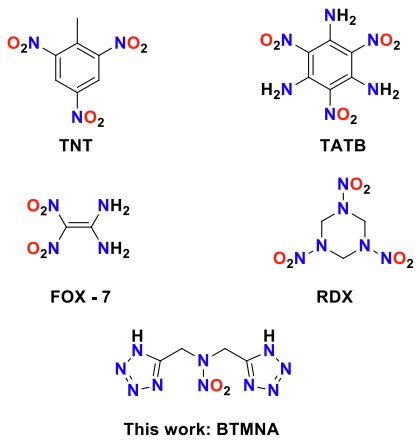


Fig. 1. Some reported applicable energetic materials and this work.

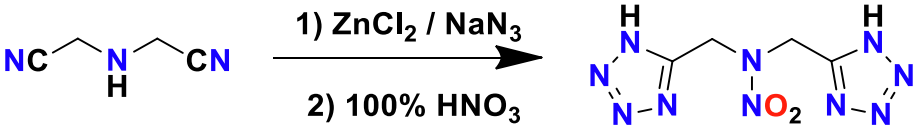
and high performance. At the same time, the synthesis of the compound must be simple, short, in high yield, and easy to carry out (Fig. 1) [6,12].

Now we report the synthesis of an insensitive RDX alternative: *N*,*N*′-bis((1*H*-tetrazol-5-yl)methyl)nitramide (BTMNA), which balances detonation performance, sensitivity and thermal stability. BTMNA can be synthesized in a one-step reaction after 12 h in high yield (Scheme 1). Commercially available iminodiacetonitrile is the starting material which is reacted with sodium azide in the presence of zinc chloride in aqueous solution at 100 °C for 8 h. A white zinc tetrazole complex is formed by a click reaction and collected by filtration [13]. Then the white solid was added to 100% nitric acid with stirring for 12 h. The mixture was poured onto ice. The white needle crystals, BTMNA, were obtained in >90% yield. Normally click reactions require HCl to remove the Zn salts, but in this process nitric acid was used to remove the zinc salts and introduce the nitro group in high yield.

Slow evaporation of a methanol solution of BTMNA gives crystals suitable for X-ray diffraction analysis, where it crystallized in the monoclinic $P2_1$ space group with a good crystal density of 1.822 g/cm^3 at 100 K as a tetrazole derivative. The oxygen atom (O1) on the nitramino moiety forms an intramolecular hydrogen bond with the proton of NH (N3–H3) of tetrazole (Fig. 2a), with a relatively short hydrogen acceptor length, N–H···O (2.415 Å). The intramolecular hydrogen-bonding interaction tends to result in stronger covalent bonds, which is seen from the comparative bond lengths in this geometrically symmetric structure [C1–N1 (1.445 Å) versus C3–N1 (1.455 Å), C1–C2 (1.497 Å) versus C3–C4 (1.515 Å)]. As an oxygen-rich building block, the nitroamino group plays the role of linker connecting two nitrogen-rich tetrazoles (Fig. 2b) (Table 1).

In addition to the intramolecular hydrogen-bonding interaction, the intermolecular interaction indicates that the tetrazole units play a dual role as both an H-bond donor and an H-bond acceptor. Hydrogen-bond interactions were found between the neighboring tetrazole rings, thereby leading to H-bond induced assembly in the crystal packing (Fig. 2c and d). The unit cell of BTMNA along the *a* axis (Fig. 2c) shows the different nitrogen atoms (N5, N6, N9 and N10) of the tetrazole ring participating as H-bond acceptors (Fig. 2a and d).

In order to gain additional insight into the relationship between physical properties and structure, Hirshfeld surface plots and two-dimensional finger print spectra of BTMNA were analyzed systematically using CrystalExplorer17.5 software [14]. Based on the analysis of the images of the Hirshfeld surfaces, the red spots represent high contact



Scheme 1. One-step synthesis of *N*,*N*′-bis((1*H*-tetrazol-5-yl)methyl)nitramide (BTMNA).

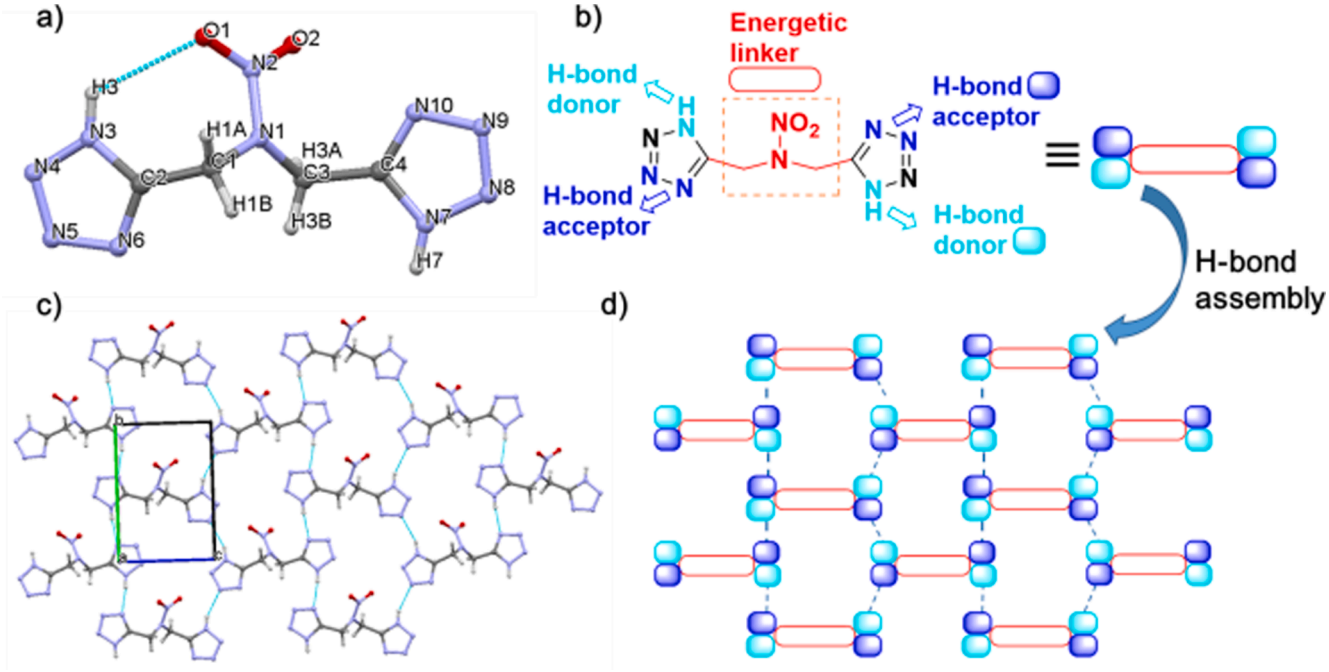


Fig. 2. (a) X-ray crystal structure of BTMNA. (b) Molecular structure and model of BTMNA. (c) Unit cell view of BTMNA along *a* axis. (d) H-bond assembly model of BTMNA.

Table 1
Physical and energetic properties of **BTMNA** compared with other applicable energetic materials.

	ρ[a] (g·cm^{-3})	Dv[b] (m/s)	P[c] (GPa)	ΔH_f[d] [(kJ/mol)/(kJ/g)]	T_{dec}[e] (°C)	IS[f] (J)	FS[g] (N)	OB[h] (%)
BTMNA	1.79	8732	29.4	573.4/2.53	198	30	360	−63.72
TNT	1.65	6881	19.5	−31.7/−0.14	295	15	353	−73.97
FOX-7[i]	1.89	8930	34.0	−53.1/−0.36	274	60	>350	−21.62
TATB[i]	1.93	7606	31.0	75.0/0.29	350	>50	350	−55.78
PETN[i]	1.78	8564	31.4	−502.8/−1.59	160	3	60	−10.12
HMX[i]	1.90	9320	39.5	104.8/0.36	280	7	120	−21.61
RDX[i]	1.80	8795	34.9	92.6/0.36	204	7	120	−21.61

[a] Density measured – gas pycnometer at 25 °C.
[b] Calculated detonation velocity.
[c] Calculated detonation pressure.
[d] Heat of formation.
[e] Decomposition temperature (onset).
[f] Impact sensitivity.
[g] Friction sensitivity.
[h] OB = oxygen balance (%); for $C_aH_bO_cN_d$: 1600(c-2a-b/2)/Mw; Mw = molecular weight of compound.
[i] Ref. [6,19].

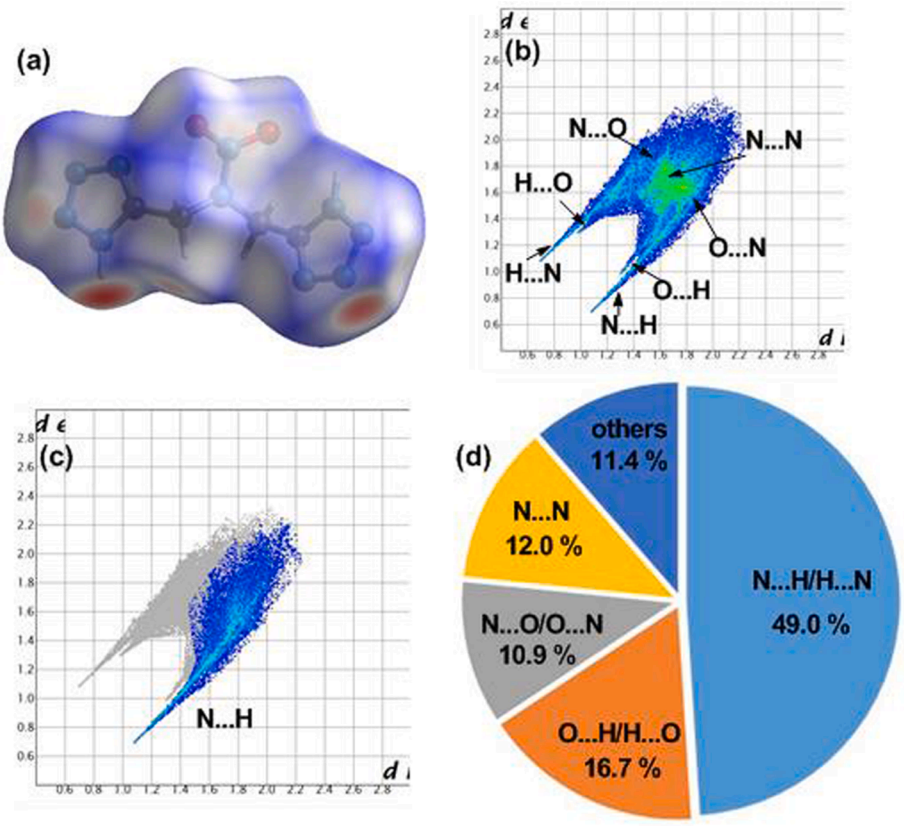


Fig. 3. Hirshfeld surface calculations of BTMNA as well as two-dimensional fingerprint plots in the crystal structures. (a) The Hirshfeld surface that uses color coding to represent the proximity of close contacts around the BTMNA molecule (white, d = van der Waals (vdW) distance; blue, d > vdW distance; red, d < vdW distance). (b) The fingerprint plots in crystal stacking found in BTMNA. (c) The N···H atomic contacts percentage contribution to the Hirshfeld surface for BTMNA. (d) The percentage contributions of the individual atomic contacts to the Hirshfeld surface.

populations, while blue and white spots are for low contact populations. This indicates that the negative (red) or positive value (blue and white) of d_{norm} depends on the intermolecular contacts being shorter (red) or longer (blue and white) than the van der Waals separations. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) was determined by the equation [$d_{norm} = (d_i - d_i^{vdW})/r_i^{vdW} + (d_e - d_e^{vdW})/r_e^{vdW}$] in which d_i is measured from the surface to the nearest atom interior to the surface interior, while d_e is measured from the surface to the nearest atom exterior to the surface interior, where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms [15]. As shown in Fig. 3a, BTMNA appears as T-shaped blocks with red dots dispersed in many orientations. Red dots indicate intermolecular strong (N···H and H···N) interactions. Intermolecular strong hydrogen bonds can also be confirmed by regular 2D fingerprint plots. As is shown in Fig. 3b, two pairs of striking spikes on the bottom left indicating N···H/H···N interactions (exterior spikes) and H···O/O···H interactions (interior spikes) can be seen, suggesting that there are two kinds of strong intermolecular interactions (hydrogen bonds) between N and H atoms or O and H atoms.

While in Fig. 3c, a pair of remarkable spikes on the bottom left which indicates N···H and H···N interactions dominated the weak interactions compared to H···O and O···H in the 2D fingerprint plots of crystals of BTMNA. In Fig. 3d, the individual atomic contacts percentage contributions also were consistent with the conclusion, in which N···H and H···N interactions possess 49.0% of total weak interactions for BTMNA, while H···O and O···H interactions possesses 16.7% of total weak interactions. The percentage of hydrogen bond interactions for BTMNA is 65.7%, which indicates that BTMNA will be denser relative to tetrazole derivatives and less sensitive than some energetic materials since the

hydrogen bonds can improve the impact and friction sensitivities [16].

The heat of formation was calculated using the Gaussian 03 (Revision E.01) suite of programs. Because of the presence of the tetrazole groups, BTMNA has a very high positive heat of formation (ΔH_f) 2.53 kJ/g, in comparison with TNT, PETN, FOX, TATB, RDX and HMX. BTMNA is a nitrogen-rich compound with about 61.93% of nitrogen mass. Its oxygen percentage is about 14.15% of mass only. It is much lower than that of about 43.22% for RDX. BTMNA has a lower oxygen balance (−63.72%) which is just higher than the oxygen balance (−73.97%) TNT, but much lower than that of RDX (−21.61%). The low oxygen balance of BTMNA can cause the incomplete combustion which will influence its detonation performance. Detonation velocities and pressures were calculated based on traditional Chapman–Jouget thermodynamic detonation theory by using the Explo5 program (version 6.01) [17]. The detonation pressure (P) of BTMNA is 29.4 GPa, and the detonation velocity (D_v) is 8732 m/s. BTMNA exhibits excellent detonation properties compared to TATB (P: 31.0 GPa, D_v: 7606 m/s), RDX (P: 34.9 GPa, D_v: 8795 m/s), and PETN (P: 31.4 GPa, D_v: 8564 m/s). BTMNA has moderate density (1.822 g/cm^3 at 100 K, and 1.79 g/cm^3 at room temperature) and excellent thermal stability (T_d = 198 °C). While the detonation properties of BTMNA are similar, it exhibits better values for impact and friction sensitivities (IS: = 30 J, FS: = 360 N), which exceed the values of PETN (IS: = 3 J, FS: = 60 N), RDX (IS: = 7 J, FS: = 120 N) and HMX (IS: = 7 J, FS: = 120 N). This suggests that BTMNA may be a practical replacement for RDX in the explosive industry.

In order to evaluate the efficacy of this material for HEDM applications, compatibility tests were carried out for compound BTMNA with four energetic components, viz., RDX, FOX-7 (1,1-diamino-2,2-dinitroethene), TNBI (4,4′,5,5′-tetranitro-2,2′-bisimidazole), and TNP (3, 4, 5-trinitropyrazole) using a literature method [18]. DSC measurements (SI) show that BTMNA has good compatibility with RDX and FOX-7 and had slightly sensitized or moderate compatibility with TNBI, while it has poor compatibility with TNP.

In summary, *N*,*N*′-bis((1*H*-tetrazol-5-yl)methyl)nitramide (BTMNA) was synthesized in one step from commercially available iminodiacetonitrile and was fully characterized using various spectroscopic techniques, elemental analyses and crystal structure. BTMNA was obtained in >90% yield suggesting that it can be prepared on a large scale. Based on X-ray structure, BTMNA has a higher calculated crystal density of 1.822 g cm^{-3} at 100 K comparable with other tetrazole derivatives. Finally, to evaluate the effectiveness of this material for HEDM applications, the detonation properties were calculated and sensitivities to impact, friction, and compatibility were experimentally determined. BTMNA was found to be a promising HEDM candidate with an outstanding performance that slightly exceeds that of RDX, and impact and friction sensitivities which are much lower than those of RDX and comparable to those of TATB.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.128697.

References

[1] (a) L.A. Mitchell, G.H. Imler, D.A. Parrish, J.R. Deschamps, P.W. Leonard, D. E. Chavez, Acta Crystallogr. E 73 (2017) 1056–1061;
(b) J.P. Agrawal, High Energy Materials: Propellants, Explosives and Pyrotechnics, first ed., Wiley-VCH, Weinheim, 2010;
(c) H. Vogt, J. Balej, J.E. Bennett, P. Wintzer, S.A. Sheikh, P. Gallone, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, 2002;
(d) L. Hu, P. Yin, G. Zhao, C. He, G.H. Imler, D.A. Parrish, H. Gao, J.M. Shreeve, Conjugated energetic salts based on fused rings: insensitive and highly dense materials, J. Am. Chem. Soc. 140 (2018) 15001–15007.
[2] J.R. Deschamps, D.A. Parrish, R.J. Butcher, Polymorphism in Energetic Materials. 2008 NRL Review, USNRL, 2008, pp. 71–77.
[3] J Wilbrand, Notiz über Trinitrotoluol, Ann. Chem. Pharm. 128 (1863) 178–179.
[4] P.O.K. Krehl, History of Shock Waves, Explosions and Impact: A Chronological and Biographical Reference, Springer Science & Business Media, 2008, p. 404.
[5] T. Urbanski, Chemistry and Technology of Explosives. 1, Pergamon Press, 1964, pp. 389–391.
[6] A.F. Baxter, I. Martin, K.O. Christe, F. Haiges, Formamidinium nitroformate: an insensitive RDX alternative, J. Am. Chem. Soc. 140 (2018) 15089–15098.
[7] U. Bemm, H. Östmark, 1,1-Diamino-2,2-dinitroethylene: a novel energetic material with infinite layers in two dimensions, Acta Crystallogr. 54 (1998) 1997–1999.
[8] (a) A.J. Bellamy, in: Structure and Bonding, Springer, Berlin, 2007, pp. 1–33;
(b) H. Gao, J.M. Shreeve, The many faces of FOX-7: a precursor to high-performance energetic materials, Angew. Chem. Int. Ed. 127 (2015) 6433–6436.
[9] M. Anniyappan, M.B. Talawar, G.M. Gore, S. Venugopalan, B.R. Gandhe, Synthesis, characterization and thermolysis of 1,1-diamino-2,2-dinitroethylene (FOX-7) and its salts, J. Hazard. Mater. 137 (2006) 812–819.
[10] (a) P.W. Cooper, Explosives Engineering, Wiley-VCH, New York, 1996;
(b) D. David, Bull. At. Sci. (1994) 44.
[11] (a) H.W. Qiu, V. Stepanov, A.R. Di Stasio, T.M. Chou, W.Y. Lee, RDX-based nanocomposite microparticles for significantly reduced shock sensitivity, J. Hazard. Mater. 185 (2011) 489–493;
(b) Y. Bayat, M. Eghdamtalab, V. Zeynali, Control of the particle size of submicron HMX explosive by spraying in non-solvent, J. Energy Mater. 28 (2010) 273–284;
(c) N. Fischer, D. Fischer, T.M. Klapötke, D.G. Piercey, J. Stierstorfer, Pushing the limits of energetic materials – the synthesis and characterization of dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate, J. Mater Chem. 22 (2012) 20418–20422;
(d) G. Zhao, C. He, P. Yin, G.H. Imler, D.A. Parrish, J.M. Shreeve, Efficient construction of energetic materials via non-metallic catalytic carbon−carbon cleavage/oxime-release-coupling reactions, J. Am. Chem. Soc. 140 (2018) 3560–3563.
[12] M.B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A.K. Sikder, B. R. Gandhe, A.S. Rao, Environmentally compatible next generation green energetic materials (GEMs), J. Hazard. Mater. 161 (2009) 589–607.
[13] D.-Z. Wang, J.-Z. Fan, D. Jia, C.-C. Du, Zinc and cadmium complexes based on bis-(1H-tetrazol-5-ylmethyl/ylethyl)-amine ligands: structures and photoluminescence properties, CrystEngComm 18 (2016) 6708–6723.
[14] (a) M.A. Spackman, J.J. McKinnon, Fingerprinting intermolecular interactions in molecular crystals, CrystEngComm 4 (2002) 378–392;
(b) M.A. Spackman, D. Jayatilake, Hirshfeld surface analysis, CrystEngComm 11 (2009) 19–32.
[15] C. Zhang, X. Xue, Y. Cao, Y. Zhou, H. Li, J. Zhou, T. Gao, Intermolecular friction symbol derived from crystal information, CrystEngComm 15 (2013) 6837–6844.
[16] H. Gao, J.M. Shreeve, Azole-based energetic salts, Chem. Rev. 111 (2011) 7377–7436.
[17] M. Sućeska, EXPLO5, 6.01, Brodarski Institute, Zagreb, Croatia, 2013.
[18] Q.-L. Yan, X.-J. Li, L.-Y. Zhang, J.-Z. Li, H.-L. Li, Z.-R. Liu, Compatibility study of trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) with some energetic components and inert materials, J. Hazard. Mater. 160 (2008) 529–534.
[19] (a) J. Zhang, P. Yin, G.H. Imler, D.A. Parrish, J.M. Shreeve, N-functionalized nitroxy/azido fused-ring azoles as high-performance energetic materials, J. Mater. Chem. A. 4 (2016) 7430–7436;
(b) X. Zhang, J. Xiong, H. Yang, G. Cheng, Synthesis and detonation properties of 5-amino-2,4,6-trinitro-1,3-dihydroxy-benzene, ChemistryOpen 6 (2017) 447–451;
(c) G. Zhao, C. He, H. Gao, G.H. Imler, D.A. Parrish, J.M. Shreeve, Improving the density and properties of nitrogen-rich scaffolds by the introduction of a C-NO_2 group, New J. Chem. 42 (2018) 16162–16166.