View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Q. Ma, H. Gu, J. Huang, F. Nie, G. Fan, L. Liao and W. Yang, *New J. Chem.*, 2018, DOI: 10.1039/C7NJ03939E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

Journal Name

LETTER



Formation of trinitromethyl functionalized 1,2,4-triazole-based energetic ionic salts and a zwitterionic salt directed by a intermolecular and intramolecular metathesis strategy

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

Qing Ma,^{‡a} Hao Gu,^{‡b} Jinglun Huang, ^a Fude Nie, ^a Guijuan Fan^{*a}, Longyu Liao^{*a} and Wei Yang^{*c}

www.rsc.org/

Published on 18 January 2018. Downloaded by University of Reading on 18/01/2018 02:49:42

lonic salts of 5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole and an unexpected energetic zwitterion 5-diazonium-3-trinitromethyl-1,2,4-triazolate were synthesized by a intermolecular and intramolecular metathesis strategy. Compared with its ammonium (6), hydrazinium (7) and hydroxylammonium (8) salts, 5,5'bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (5) exhibits lower sensitivities (*IS*: 22.5 J, *FS*:252 N). It is worth noting that energetic salt 8 exhibits 1.97 g cm⁻³ and an excellent calculated detonation velocity of 9468 m s⁻¹ as well as energetic zwitterion 5-diazonium-3-trinitromethyl-1,2,4-triazolate (14) exhibits a high density of 1.893 g cm⁻³ and an excellent calculated detonation velocity of 9317 m s⁻¹, which are both superior to that of HMX (9254 m s⁻¹).

Trinitromethyl (TNM) group is a very powerful explosophore, which can increase the oxygen balance in molecules and make its derivatives attractive candidates for environmentally friendly high energy and density material (HEDM) applications.1 A typical protocol for the synthesis of Ntrinitromethylazoles involves N-alkylation of the corresponding NH azoles with methyl vinyl ketone or bromoacetone in the presence of a base, followed by nitration of the resulting intermediates with nitric acid or a mixture thereof with sulfuric acid.² In contrast to N-trinitromethyl compounds, the generation of C-trinitromethyl moieties were more difficult due to the lack of suitable intermediates and corresponding chemical activity. Recently, azo-1,2,4-triazole, bis-1,2,4oxadiazole and tetrazole featuring TNM moiety have been released,³ but these researches were still not adequate for deeply building the relationship between oxidizers bearing TNM moiety and other significant physicochemical characteristics such as density, sensitivity and detonation property.

Very recently, there is a growing interest in the development of energetic zwitterions such as primary energetic materials for laser-induced explosives and explosion.4b,4c In the previous work, the strategy for incorporating zwitterion into energetic frameworks falls into two categories: a) oxygen atom in hydroxyl group as an anion and diazolium in neighbouring carbon as a cation;⁴ b) nitrogen atom in azole ring as an anion and diazolium in neighbouring carbon as a cation.⁵ It is worth noting that the property and application of above-mentioned energetic zwitterions have not been fully considered during the synthesis except for high nitrogen content of diazo-group. Meanwhile, researches on highly energetic zwitterions will be also challenging. Therefore, the combination of TNM group and zwitterion in one molecule should lead to interesting structures and different energetic Herein, we report a series properties. of 5.5'bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole ionic salts as well as a zwitterion 5-diazonium-3-trinitromethyl-1,2,4-triazolate via a intermolecular and intramolecular metathesis strategy. Their interesting chemical reactions, electronic and thermal stabilities. physicochemical properties and energetic properties were further investigated in detail.

The starting materials, oxamidrazone (2) and 2-(5-amino-1H-1,2,4-triazol-3-yl) acetic acid (12) were synthesized according to the literatures.⁶ As shown in Scheme 1, a mixture of oxamidrazone (2) with ethyl-3-ethoxy-3-iminopropionate hydrochloride was cyclized in acetic acid at 105-110°C and 5,5'-bis(acetic acid ethyl ester)-3,3'-bi-1H-1,2,4-triazole (3) was obtained by neutralizing the above-mentioned mixture at 5–10 °C. Alkalization of 3 with 0.5M NaOH solution at 10°C and then acidification of the above solution with 2M HNO₃ at 0°C led to 5,5'-bis(acetic acid)-3,3'-bi-1H-1,2,4-triazole (4). The desired 5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (5) was produced from the nitration of 4 with concentrated sulphuric acid and 96% nitric acid. Further treatment of 5 with ammonia solution (7N), hydrazine monohydrate and 50% aqueous

^{a.} Institute of Chemical Materials, China Academy of Engineering Physics, P.O.Box 919-311, Mianyang 621999, China. E-mail: fanguijuan@caep.cn; longyuliao@caep.cn.

^{b.}School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, China.

^{c.} Department of chemistry and chemical biology, Harvard University, Cambridge, Massachusetts, 02138, USA. E-mail: wei_yang@fas.harvard.edu

⁺ Electronic Supplementary Information (ESI) available: Experimental details, NMR, DSC, computational details. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

[‡] These authors contributed equally to this work.

and -154.75 (N5) ppm.

hydroxylamine resulted in the formation of salts **6–8**. The dipotassium 5,5'-bis(trinitromethyl)- 3,3'-bi-1,2,4-triazolate (**9**)



Scheme 1 Synthesis of 5 and its energetic salts.

was obtained by treatment of **5** with an alkaline solution of hydroxylamine with potassium hydroxide in anhydrous ethanol at 0° C.



Scheme 2 Synthesis of energetic zwitterion 14

Published on 18 January 2018. Downloaded by University of Reading on 18/01/2018 02:49:42

Synthesis of 5, 5-diazonium-3-trinitromethyl-1,2,4-triazolate (14) was obtained with the same nitration methodology by first cyclization of 10 and 11, followed by the nitration of 12 with concentrated sulphuric acid and 96% nitric acid (Scheme 2). It is found that nitration of 12 with concentrated sulphuric acid and 100% nitric acid could lead to another compound 13 which was revealed by T. Hermann et al.⁷ Unexpectedly, a novel energetic zwitterion 14 was achieved by using 96% nitric acid. Diazotization of the primary amine followed by tri-nitration at the α -postion of carboxylic group make the 2-H of triazole more acidic and led to the zwitterionic inner salt 14 after deprotonation (Scheme 3). Such a reaction has rarely been reported and may provide a new method for preparing high energy zwitterionic compounds.



Scheme 3 Proposed mechanism for synthesizing 13 and 14 from 12.

The ¹⁵N spectra of **5**, **8** and **14** are shown in Fig. 1, which are determined based on the literatures.^{3a,5} Compound **5** and **14** were recorded in acetone-d₆, and compound **8** was recorded in DMSO-d₆. For compound **5**, there are four well resolved signals at δ =–33.33 (N4), –71.94 (N3), –125.95 (N1) and –146.80 (N2) ppm. For compound **8**, five well resolved signals at δ =–22.47 (N4), –51.70 (N3), –133.66 (N1), –181.42 (N2) and –286.64 (N5) ppm are



detected. For compound 14, there are six well resolved signals at line

 δ =-11.00 (N2), -12.28 (N1), -32.59 (N6), -55.13 (N4), 39193,07 (N3)

Fig.1 Selected ¹⁵N NMR spectra of 5, 8 and 14.

Single crystals of 5-2H₂O suitable for single-crystal X-ray diffraction were obtained by slow evaporation from a solution of methanol and water in 3:1 volume ratio, whereas 14 crystallizes from dichloromethane. Compound 5.2H₂O crystallizes as a colorless plate crystal in the monoclinic C2/c space group with four molecules per unit cell and has a calculated density of 1.828 g cm⁻³ at 130(2) K. It is illustrated from Fig. 2a that 5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole co-crystallized with two water molecules as well as 4·2H₂O. The C1-N1-C2-C3 torsion angle of -175.89(10)° and C2-N1-C1-C1A torsion angle of -179.40(14) ° indicate that the two triazole rings are almost coplanar. The N2–N3 bond length of 1.3458(14)Å is close to the N1– N2 bond length of 1.364(2) in 4·2H₂O (see ESI⁺), which are all shorter than the normal N–N bond length of 1.47 Å. The packing diagram shows that 4.2H₂O packs in "V-shaped" packing in Fig. 2b, whereas 5·2H₂O has a parallel-layer packing. Though the single crystal of 5 contained two water molecules, ¹H NMR (see ESI[†]) of 5 confirmed there was no water in the target product.



Fig.2 (a) Thermal ellipsoid plot (50%) and labelling scheme of **5·2H₂O**. (b) Ball-and-stick packing diagram of **5·2H₂O** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

Compound **14** crystallizes as an orange prism crystal in the orthorhombic space group $P2_12_1$ with four molecules per unit cell, and a high calculated density of 1.934 g cm⁻³ at 130 K. It can be seen from Fig. 3a that the triazole ring and the carbon atom from trinitromethyl are nearly coplanar, which are

Published on 18 January 2018. Downloaded by University of Reading on 18/01/2018 02:49:42

Journal Name

further revealed by the N3–N2–C2–C3 torsion angle of 179.63(18)° and the C1–N1–C2–C3 torsion angle of 179.92(18)°. Additionally, the triazole ring and the diazo group are considered to be approximately in the plane, which can be illustrated from the N2–N3–C1–N4 torsion angle of -177.40(18) ° and the C2–N1–C1–N4 torsion angle of 177.19(19)°. The diazonium bond N4–N5 bond length of 1.095(2) Å in the range of N=N triple bond is almost equal to those of other previously reported diazonium inner salts (1.088(2) Å,^{11a} 1.096(3) Å,^{11b} 1.111(2) Å ^{11c} and 1.112(2) Å ^{11d}). The packing diagram of **14** from Fig. 3b shows an irregular packing due to its absent hydrogen bonding interaction. Fig. 3c gives the physical map of large prism-like yellow crystals at the ambient temperature.



Fig.3 (a) Thermal ellipsoid plot (50%) and labelling scheme of **14**. (b) Ball-and-stick packing diagram of **14** viewed down the *a* axis. (c) Prism-like yellow crystals of **14** grew from dichloromethane at the ambient temperature.

To investigate the electronic structures of these new compounds, the ultraviolet and visible spectra (UV-vis) of 5-9 and 14 were collected in anhydrous methanol solution (Fig.4). All compounds are in the B band of the UV from 250 nm to 400 nm, which mainly corresponds to $n \rightarrow \pi^*$ electronic transition. Concretely speaking, it is obvious that 6-9 display absorbances around 354 nm owing to the electrostatic interaction after the formation of energetic salts, where neutral compound 5 shows no absorbance. Different from salts 5–9, ziwitterion 14 displays an alternative absorbance at 273 nm. Interestingly, dihydroxylammonium salt 8 exhibits an intense absorbance at 354 nm when compared with other salts bearing the same frameworks. In addition, the characteristic absorbance of salt 8 has a bathochromic shift at 237 nm relative to other compounds which basically show the consistent absorbances from 205 to 210 nm. This may be explained by different intra- or intermolecular interactions because the hydrogen bonding interaction induced by dihydroxylammonium cation is usually stronger than those from other cations.⁸ Because no hydrogen bonding interaction exists in 14, it is rational that no characteristic absorbance appears at 354 nm.

As shown in Table 1, the thermal behavior of all the title compounds was investigated by DSC-TG. They show thermal stability from 127–218 °C at the heating rate of 5 °C min⁻¹. It is worth noting that **6–9** possess higher thermal decomposition temperature than **5** after the formation of salts, especially **7**



Fig.4 UV-vis spectroscopy of **5-9** and **14** in anhydrous methanol solution

5-8 and 14 exhibit positive heat of formation that are superior to those of pentaerythritol tetranitrate (PETN), 1,3,5trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7tetranitro-1,3,5,7-tetrazocine (HMX). The experimental densities of these compounds are in the range of 1.82-1.95 g cm⁻³ which equal or exceed those of common oxidizers and explosives. For dipotassium salt 9, its theoretical density is up to 2.15 g cm⁻³, which is normally high as well as some reported dinitromethyl dipotassium salts.9 Impact and friction sensitivity (IS and FS) are tested using the standard BAM methods. The diazolium triazolate 14 is a typical hydrogen-free compound of only C, N and O atoms. It's very sensitive as well as previously hydrogen-free explosives such as benzotrifuroxan (BTF) (IS<3J)¹⁰ and trinitrotris(triazolo)benzene (TNTTB) (IS=3J).¹¹ It is worth noting that 6-8 showed high impact sensitivities comparable to that of 14, expect 9 which is relatively lower. The phenomenon can be rationalized in terms of extensive O···O contact interaction between bis(trinitromethyl) groups and its obvious decreasing in gem-dinitromethyl groups. The IS and FS of 14 show that it is more sensitive than PETN. The electrostatic discharge device (ESD) measurements show that only 7 and 9 are less sensitive towards electrostatic discharge (7=0.33J, 9=0.39 J) than RDX and HMX (RDX=HMX=0.20 J). Other compounds show that they are easy to be initiated (5=0.11 J; 6=0.15 J; 8=0.12 J; 14=0.09 J).

Density was measured with helium gas pycnometer at 25 °C except compound **14** was determined by X-ray diffraction at 298 K. The experimental densities of compounds **5–14** are in the range of 1.86–2.15 g cm⁻³. The calculated detonation pressures (*P*) and detonation velocities (*D*) were estimated based on traditional Chapman-Jouget thermodynamic detonation theory using EXPLO5 program (v6.02).¹² The detonation pressures of the present compounds lie in the range of 33.7 to 39.9GPa and detonation velocities lie between 8800 m s⁻¹ and 9468 m s⁻¹. Specific impulses (*I*_{sp}) of the referenced compounds were also calculated by using EXPLO5 code. Among them, the resulting *I*_{sp} values of **5** (260.2 s), **8** (262.5 s) and **14** (268.4 s) is comparable to those of RDX (267.7 s), HMX (267.5 s) and PETN (270.1 s), but much higher than that of common oxidants such as ADN (202 s).¹⁵

LETTER

COMMUNICATION

Page 4 of 6

Journa	l Name
--------	--------

Table 1. Energetic properties and detonation parameters of the title compounds							View Article Online DOI: 10.1039/C7NJ03939E					
Comp.	N (%) ^[a]	Ω _{CO2} (%) ^[b]	Ω _{CO} (%) ^[c]	$T_d^{[d]}$	<i>IS</i> (J) ^[e]	FS(N) ^[f]	ESD(J) ^[g]	d (g cm ⁻³) ^[h]	∆ _f H (kJ mol⁻¹) ^[j]	<i>P</i> (GPa) ^[k]	D (m s ⁻¹) ^[I]	I _{sp} (s) ^[m]
5	53.84	-3.69	18.43	148	22.5	252	0.11	1.89	331.9	36.2	9073	260.2
6	53.84	-13.67	6.83	188	1	6	0.15	1.86	-45.1	33.7	8800	250.2
7	53.84	-16.06	3.21	218	3	16	0.33	1.94	250.9	34.9	8933	258.6
8	64.29	-6.40	12.79	191	5	144	0.12	1.97	44.9	39.9	9468	262.5
9	33.32	-19.03	3.81	161	8	288	0.39	2.15	-258.2	36.0	9280	194.5
14	59.14	0	19.67	127	<1	5	0.09	1.89 ⁱ	521.7	37.6	9317	268.4
PETN ¹³	17.72	-10.12	15.18	150	3	60	0.10	1.77	-407	31.4	8564	270.1
RDX ¹⁴	37.84	-21.61	0	210	7.5	120	0.20	1.81	80.0	34.7	8872	267.7
HMX ¹⁴	37.84	-21.61	0	279	7	120	0.20	1.90	104.8	39.2	9254	267.5

[a] Nitrogen content. [b] Oxygen balance assuming the formation of CO₂. [c] Oxygen balance assuming the formation of CO. [d] Decomposition point from DSC at the heating rate of 5 °C min⁻¹. [e] Impact sensitivity measured by drop-hammer test according to standard BAM methods. [f] Friction sensitivity measured by a friction tester according to standard BAM methods. [g] Electrostatic discharge device. [h] Density measured by gas pycnometer at 25 °C. [i] Density recalculated from low-temperature X-ray density, $\rho_{298K}=\rho_T/(1+\alpha_v(298-T_0))$ $\alpha_v=1.5\times10^{-4}$, T₀ is the crystal testing temperature. [j] Calculated solid heat of formation by Gaussian 09 package at M06-2X/6-311++G(d,p) level.¹⁶ [k] Detonation pressure. [l] Detonation velocity. [m] Specific impulse (neat compound).

In summary, 5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (5) and 5-diazonium-3-trinitromethyl-1,2,4-triazolate (14) were synthesized by a intermolecular and intramolecular metathesis strategy. Energetic salts (6–9) were synthesized based on 5. The chemical reaction mechanism of synthesizing unexpected energetic zwitterion 14 was proposed. Surprisingly, compound 8 shows high density (1.97 g cm⁻³) and good detonation performance (D: 9468 m s⁻¹, P:39.9 GPa), which indicates its potential application as a highly energetic material.

We are indebted to the NSAF Foundation of National Natural Science Foundation of China and China Academy of Engineering Physics (Grant No. U1530262), the National Natural Science Foundation of China (Grant No. 11402237) and the Science and Technology Development Foundation of China Academy of Engineering Physics (Grant No. 2015B0302055) for funding of this work. Prof. Qinghua Zhang was also gratefully acknowledged for providing gas pycnometer in the test of experimental densities.

Notes and references

- (a) A. V. Shastin, T. I. Godovikova and B. L. Korsunskii, Russ. Chem. Rev., 2003, 72, 279; (b) D. B. Lempert, I. L. Dalinger, Y.-J. Shu, A. I. Kazakov and A. B. Sheremetev, Chin. J. Explos. Propellants, 2016, 39, 16–21; (c) I. L. Dalinger, K. Yu. Suponitsky, A. N. Pivkina and A. B. Sheremetev, Propellants, Explos., Pyrotech., 2016, 41, 789–792; (d) A. B. Sheremetev, V. L. Korolev, A. A. Potemkin, N. S. Aleksandrova, N. V. Palysaeva, T. H. Hoang, V. P. Sinditskii and K. Yu. Suponitsky, Asian J. Org. Chem., 2016, 5, 1388–1397; (e) A. I. Kazakov, I. L. Dalinger, I. N. Zyuzin, D. B. Lempert, N. A. Plishkin and A. B. Sheremetev, Russ. Chem. Bull., 2016, 65, 2783–2788; (f) V. V. Bakharev, A. A. Gidaspov and V. E. Parfenov, Chem. Heterocyl. Comp., 2017, 53, 659–669; (g) V. V. Semenov, S. A. Shevelev, A. B. Bruskin, A. K. Shakhnes and V. S. Kuz'min, Chem. Heterocyl. Comp., 2017, 53, 728–732.
- (a) T. P. Kofman, G. Yu. Kartseva and E. Yu. Glazkova, Russ. J. Org. Chem., 2008, 44, 870–873; (b) T. P. Kofman, A. E. Trubitsin, I. V. Dmitrienko and E. Yu. Glazkova, Russ. J. Org.

Chem., 2008, **44**, 874–881; (c) I. L. Dalinger, I. A. Vatsadze, T. K. Shkineva, A. V. Kormanov, M. I. Struchkova, K. Yu. Suponitsky, A. A. Bragin, K. A. Monogarov, V. P. Sinditskii and A. B. Sheremetev, *Chem. Asian J.*, 2015, **10**, 1987–1996; (*d*) X. X. Zhao, S. H. Li, Y. Wang, Y. C. Li, F. Q. Zhao and S. P. Pang, *J. Mater. Chem. A*, 2016, **4**, 5495–5504; (*e*) S. Huang, J. Tian, X. Qi, K. Wang and Q. Zhang, *Chem. Eur. J.*, 2017, **23**, 1–9.

- 3 (a) V. Thottempudi, H. Gao and J. M. Shreeve, J. Am. Chem. Soc., 2011, 133, 6464–6471; (b) R. Haiges and K. O. Christe, Inorg. Chem., 2013, 52, 7249–7260; (c) M. A. Kettner and T. M. Klapötke, Chem. Commun., 2014, 50, 2268–2270; (d) M. A. Kettner, K. Karaghiosoff, T. M. Klapötke, M. Sućeska and S. Wunder, Chem. Eur. J., 2014, 20, 1–11.
- 4 (a) P. Yin, J. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.*, 2014, 20, 16529–16536; (b) D. Izsák, T. M. Klapötke, A. Preimesser and J. Stierstorfer, *Z. Anorg. Allg. Chem.*, 2016, 642, 48–55; (c) D. Fischer, J. L. Gottfried, T. M. Klapötke, K. Karaghiosoff, J. Stierstorfer and T. G. Witkowski, *Angew. Chem. Int. Ed.*, 2016, 55, 16132–16135.
- 5 (a) T. M. Klapötke, A. Nordheider and J. Stierstorfer, New J. Chem., 2012, 36, 1463–1468; (b) T. M. Klapötke, B. Krumm and C. Pflüger, J. Org. Chem., 2016, 81, 6123–6127; (c) Y. Du, J. Zhang, P. Peng, H. Su, S. Li and S. Pang, New J. Chem., 2017, 41, 9244–9249.
- (a) L. D. Popov, I. N. Shcherbakov, Yu. N. Tkachenko, S. A. Borodkin and V. A. Kogan, *Russ. J. Gen. Chem.*, 2006, **76**, 1219–1225; (b) V. M. Chernyshev, A. V. Chernysheva and V. A. Taranushich, *Russ. J. Appl. Chem.*, 2009, **82**, 276–281.
- 7 T. Hermann, T. M. Klapötke, B. Krumm and J. Stierstorfer, New Trends in Research of Energetic Materials, *Proceedings of the Seminar*, *19th*, Pardubice, Czech Republic, Apr. 20–22, 2016, 2016, 584–591.
- 8 (a) J. Zhang, Q. Zhang, T. T. Vo, D. A. Parrish and J. M. Shreeve, J. Am. Chem. Soc., 2015, 137, 1697–1704; (b) J. Zhang, L. A. Mitchell, D. A. Parrish, J. M. Shreeve, J. Am. Chem. Soc., 2015, 137, 10532–10535; (c) J. Zhang, S. Dharavath, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, J. Am. Chem. Soc., 2016, 138, 7500–7503.
- 9 (a) C. He and J. M. Shreeve, Angew. Chem. Int. Ed., 2016, 55, 772–775; (b) Y. Tang, C. He, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, Angew. Chem. Int. Ed., 2016, 55, 1–4; (c) L. Zhai, X. Qu, B. Wang, F. Bi, S. Chen, X. Fan, G. Xie, Q. Wei and S. Gao, ChemPlusChem, 2016, 81, 1–5.

Journal Name

- 10 N. Wang, B. Chen and Y. Ou, *Propellants Explos. Pyrotech.*, 1994, **19**, 145–148.
- 11 V. Thottempudi, F. Forohor, D. A. Parrish and J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2012, **51**, 9881–9885.
- 12 M. Sućeska, EXPLO5, version 6.02, 2013.
- 13 J. Zhang and J. M. Shreeve, J. Am. Chem. Soc., 2014, **136**, 4437–4445.
- 14 (a) T. M. Klapötke, M. Leroux, P. C. Schmid, J. Stierstorfer, *Chem. Asian J.*, 2016, **11**, 844–851; (b) T. M. Klapötke, M. Q. Kurz, R. Scharf, P. C. Schmid, J. Stierstorfer, M. Sućeska, *ChemPlusChem*, 2015, **80**, 97–106.
- 15 J. I. S. Oliveira, J. Aero. Technol. Manage., 2009, 1, 152–160.
- 16 Y. Zhao and D. G. Truhlar, *Theo. Chem. Acc.*, 2008, **120**, 215–241.

View Article Online DOI: 10.1039/C7NJ03939E

Published on 18 January 2018. Downloaded by University of Reading on 18/01/2018 02:49:42.

Table of content



Energetic trinitromethyl bistriazole and its ionic salts, as well as an unexpected energetic-zwitterion featuring trinitromethyl and diazonium moieties were synthesized by a intermolecular and intramolecular metathesis strategy.

New Journal of Chemistry Accepted Manuscript