

# Design and Synthesis of Bistetrazole-Based Energetic Salts Bearing the Nitrogen-Rich Fused Ring

Wen-Hao Cui, Qi Liu, Zhiwen Ye, and Ying He\*



Cite This: <https://doi.org/10.1021/acs.orglett.3c02131>



Read Online

ACCESS |



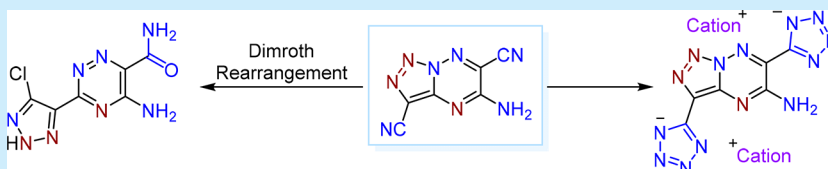
Metrics & More



Article Recommendations



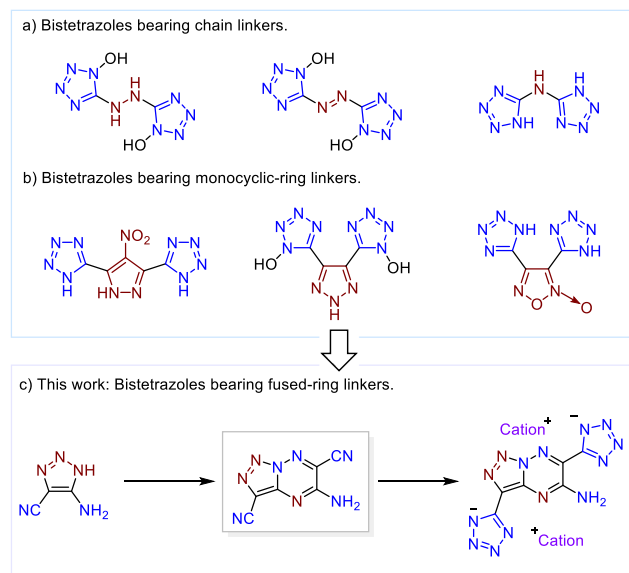
Supporting Information



**ABSTRACT:** A series of bistetrazole-based energetic salts bearing a nitrogen-rich fused ring were designed and synthesized. Among them, compounds 4–10 showed good detonation properties and excellent thermostability. By treating nitrogen-rich fused ring 3 with concentrated hydrochloric acid, a new type of Dimroth rearrangement was observed that afforded compound 12 efficiently. This new transformation herein constitutes a valuable addition to the Dimroth rearrangement.

The tetrazole scaffolds have been of great interest and are widely used in the fields of pharmaceutical science,<sup>1</sup> organic chemistry,<sup>2</sup> and material science.<sup>3</sup> On the other hand, tetrazole moieties as energetic backbones have drawn much attention in recent decades because of their distinguished characteristics, including easy synthetic feasibility, high nitrogen content, relatively low sensitivity, and good stability. Therefore, much efforts have been paid on the development of high-energy-density materials (HEDMs) bearing tetrazole derivatives.<sup>4</sup> In this context, many linked or bridged tetrazoles have been synthesized via the combination of tetrazoles and linkers, thus affording different kinds of bis-, tris-, and tetra-tetrazole energetic materials.<sup>5</sup> Although most of the linkers are energetic moieties, a variety of them are limited to the chain linkers (e.g.,  $-N=N-$ ,  $-N-N-$ , and  $-N-$ ) and monocyclic ring linkers (e.g., furazan, triazole, and pyrazole) (panels a and b of Figure 1). The diversity of bistetrazole-based energetic materials still needs to be expanded to meet the requirement of HEDMs.

Introducing the fused ring into energetic compounds, which are named after fused cyclic energetic materials, has been identified as competitive candidates for HEDMs. Fused heterocyclic-ring-based energetic materials bearing a coplanar polycyclic structure possess considerably higher heats of formation and ring strain energy stored in the molecules, thus exhibiting excellent characteristics of good energetic performance, enhanced thermal stability, and low sensitivities.<sup>6</sup> Inspired by this fact, we envisioned that incorporating tetrazoles and an energetic fused ring may generate novel nitrogen-rich energetic materials (Figure 1c). Moreover, considering that the acidic proton exited in the tetrazole ring, further transformation to ionic compounds would be possible to further increase the nitrogen content and decrease the sensitivity. We anticipate that a series of new fused ring



**Figure 1.** State of the art for the synthesis of bistetrazole-based energetic compounds.

energetic ionic materials bearing bistetrazoles would be synthesized efficiently.

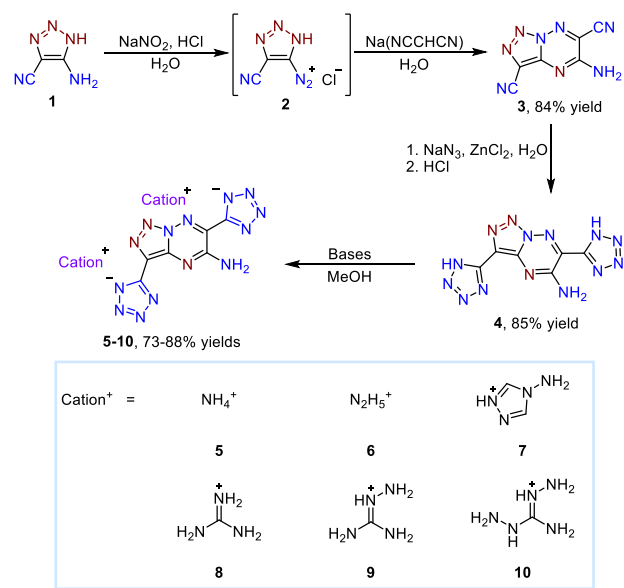
**Received:** June 30, 2023

Herein, we report a practical synthesis of a new nitrogen-rich fused ring linker that could be used for the construction of tetrazole-based energetic materials. In this regard, a series of new family bistetrazole-based energetic ionic compounds were synthesized, and their energetic properties, including thermal stabilities, sensitivities, and calculated detonation performances were performed.

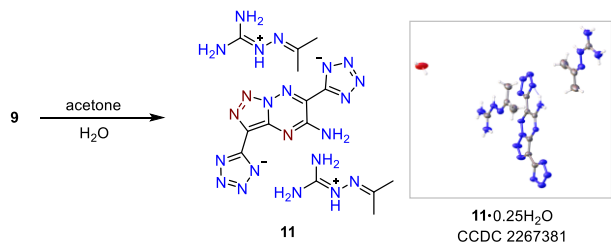
We initially carried out the diazotization of 5-amino-1*H*-1,2,3-triazole-4-carbonitrile (**1**),<sup>7</sup> which produced the diazonium intermediate **2** (Scheme 1a). Without the isolation of

### Scheme 1. Synthesis of Fused-Ring-Based Bistetrazole **4** and Its Energetic Salts

a) Synthesis of bistetrazole-based ionic salts.

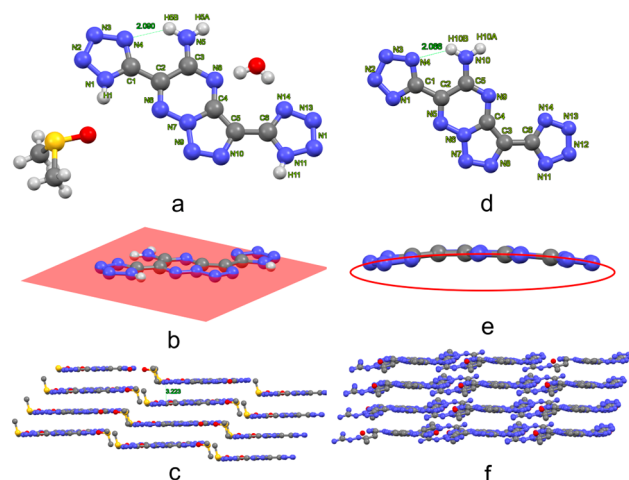


b) Transformation of **9** to **11**.



compound **2**, subsequent addition of sodium malononitrile led to the fused ring compound **3** in 84% yield. With the double  $-\text{CN}$  groups in compound **3**, the zinc-chloride-promoted reaction of compound **3** with sodium azide proceeded smoothly to afford bistetrazole **4** in 85% yield. As a result of the acidic proton existing in compound **4**, the incorporation of nitrogen-rich energetic bases to compound **4** generated a series of bistetrazole-based energetic salts **5–10** in 73–88% yields (Scheme 1a). Interestingly, when we subjected energetic salt **9** to the mixed solvent of acetone and water, the condensation reaction between the cation of compound **9** and acetone would occur, affording a new energetic salt **11**. The structure of compound **11** was confirmed by single-crystal X-ray analysis (Scheme 1b).

The single crystal of compound **4** was obtained by slow evaporation from dimethyl sulfoxide (DMSO). As shown in Figure 2a, the crystallization of compound **4** contains one molecular DMSO and  $\text{H}_2\text{O}$ , which is in the triclinic space



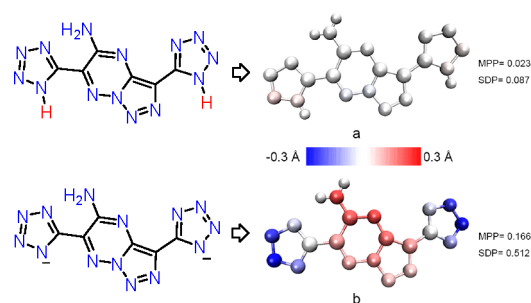
**Figure 2.** (a) Single-crystal structure of compound **4**·DMSO· $\text{H}_2\text{O}$  (CCDC 2267384). (b) Planarity of compound **4**. (c) Crystal packing diagram of compound **4**. (d) Crystal structure of the anion of compound **11**. (e) Planarity of the anion of compound **11**. (f) Crystal packing diagram of compound **11**.

group  $P\bar{1}$ , with two molecules in the unit cell ( $Z = 2$ ). The short bond length of 2.090 Å between N4 and the proton on N5 indicated a strong intramolecular hydrogen bond effect. In addition, all atoms of compound **4** are in the same plane (Figure 2b), which is confirmed by the torsion angles of N1–C1–C2–N6 [ $2.7(2)^\circ$ ], N5–C1–C2–C3 [ $-1.4(2)^\circ$ ], C4–C5–C6–N14 [ $-1.2(3)^\circ$ ], and N6–N7–N9–N10 [ $-179.15(14)^\circ$ ]. Moreover, the crystal packing of compound **4** exhibits an intense face-to-face stacking with an interlayer distance of 3.223 Å, which is shorter than the typical geometrical parameters of aromatic  $\pi$ – $\pi$  interactions (3.65–4.00 Å).<sup>8</sup> All of these results suggest that this bistetrazole-based fused energetic compound **4** may have relatively low sensitivity.

On the other hand, compound **11** crystallizes in the triclinic space group  $P\bar{1}$ , possessing two molecules in the unit cell ( $Z = 2$ ) with 0.25 molecular  $\text{H}_2\text{O}$  of crystallization. As for the anion moiety, the intramolecular hydrogen bond could also be seen from the short bond length (2.066 Å) between N4 and the proton on N10 (Figure 2d). However, different from the molecule of compound **4**, in this regard, the atoms in the anion are in an arc-like plane (Figure 2e). In addition, the crystal packing of compound **11** exhibits a cage-like structure (Figure 2f).

To further verify their planar properties, the analysis of molecular planarity parameters (MPPs) and span of deviation from the plane (SDP) was carried out.<sup>9</sup> As shown in Figure 3a, all atoms in compound **4** are almost white, which proves that the planarity of compound **4** is excellent. In contrast, the big deviation to the fitting plane of the anion of compound **11** is observed, with the red and blue color atoms shown in Figure 3b. Nevertheless, in both cases, the maximum span perpendicular to the fitting plane is less than 0.3 Å, which is beneficial for the conjugation of  $\pi$  electrons.

The physicochemical and detonation properties of these energetic compounds were then investigated (Table 1). The thermal stabilities were carried out using differential scanning calorimetry (DSC) at a scan rate of  $5^\circ\text{C min}^{-1}$ . As a result, all compounds **4–11** possess excellent thermal stabilities. The decompose temperatures ranged from 207 to 266  $^\circ\text{C}$ , which

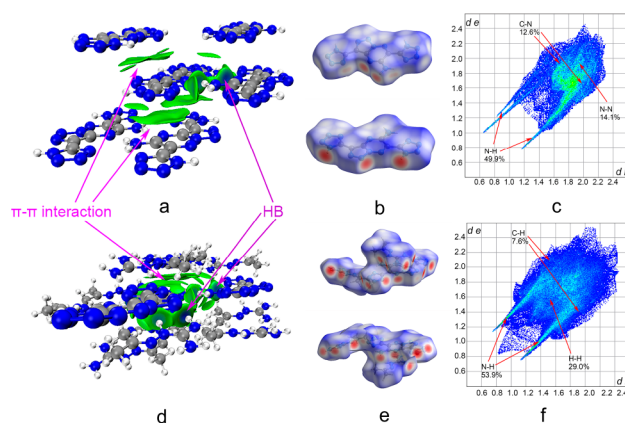


**Figure 3.** (a) MPP and SDP of compound 4. (b) MPP and SDP of the anion of compound 11.

are higher than that of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). A gas pycnometer was then used to measure the true densities of these compounds. The densities of compounds 4–11 are in the range of 1.462–1.856 g cm<sup>-3</sup>. It should be noted that compound 4, which possesses the highest density of 1.856 g cm<sup>-3</sup>, is even higher than that of RDX (1.80 g cm<sup>-3</sup>).

The heat of formation was calculated by the Gaussian 09 suite of programs.<sup>10</sup> All compounds have a relatively high heat of formation (764.5–1547.6 kJ mol<sup>-1</sup>). Detonation velocities ( $D_v$ ) and pressures ( $P$ ) were calculated by EXPLOS software.<sup>11</sup> The detonation velocities of compounds 4–10 lie in the range of 8024–8679 m s<sup>-1</sup> and are much higher than that of 2,4,6-trinitrotoluene (TNT) and close to that of RDX (8795 m s<sup>-1</sup>). The detonation pressures of compounds 4–10 lie in the range of 21.8–26.4 GPa, which are close to that of TNT (21.3 GPa). The impact sensitivities (IS) and friction sensitivities (FS) were measured by BAM sensitivity testers. As a result, compounds 4, 9, and 11 have relatively lower sensitivities (IS = 13 J and FS = 240 N, IS = 40 J and FS = 252 N, and IS = 40 J and FS = 252 N, respectively) than that of RDX (IS = 7.5 J and FS = 120 N).

An independent gradient model based on Hirshfeld partition (IGMH)<sup>14</sup> was then employed to investigate the sensitivity and weak interaction. The  $\pi$ - $\pi$  interaction (green) and hydrogen bond (HB, blue) of compounds 4 (Figure 4a) and 11 (Figure 4d) are beneficial to their sensitivities. Hirshfeld surface analysis and a two-dimensional (2D) fingerprint plot were employed to gain insight into the weak interaction in depth.<sup>15</sup> As shown in panels b and e of Figure 4, the red dots that appear on the edge of the surfaces indicate the high intimate contact, such as O...H and N...H interactions, whereas the blue regions indicate the low intimate contact,



**Figure 4.** (a–c) IGMH analysis, Hirshfeld surface, and 2D fingerprint plot of compound 4. (d–f) IGMH analysis, Hirshfeld surface, and 2D fingerprint plot of compound 11.

such as the interactions of the two groups, C...N and N...O interactions. The predominant interactions are exhibited in panels c and f of Figure 4. The percentages of N...H interactions in compounds 4 and 11 are 49.9 and 53.9%, respectively. The hydrogen-bond interaction N...H herein is supposed to be the main reason for their relatively lower mechanical sensitivities.

At last, we were pleased to find that the fused linker 3 could be easily transformed to compound 12 via a new type of Dimroth rearrangement<sup>16</sup> (Figure 5a). The structure of compound 12 was unambiguously confirmed by X-ray crystallographic analysis. The mechanism of the transformation is proposed, which is shown in Figure 5b. Hydrochloric acid first activates the N site of the fused ring, which promotes the ring-opening reaction via intermediate I to afford the intermediate II. Then, Cl<sup>-</sup> serves as the nucleophile to attack the -CN group, inducing the ring-closure reaction to give intermediate III. The aromatization then occurs via intramolecular isomerization to generate intermediate IV. Compound 12 would be obtained after the hydrolysis of -CN to the amide group.<sup>17</sup>

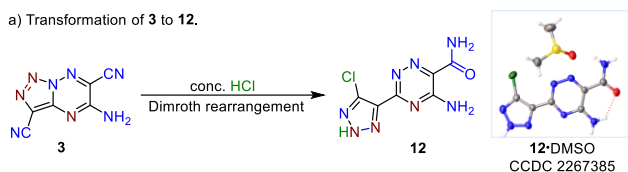
In conclusion, a new family of bistetrazole energetic compounds bearing a nitrogen-rich fused ring were designed and synthesized. The compounds 4–10 showed good detonation properties and excellent thermostability. The treatment of compound 3 with concentrated HCl induced a new type of Dimroth rearrangement, which provides a new

**Table 1. Physicochemical and Detonation Properties of Compounds 4–11 in Comparison to RDX and TNT**

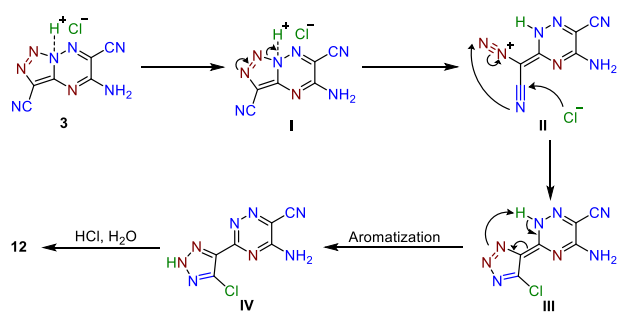
compound	$T_d^a$ (°C)	$\rho^b$ (g cm <sup>-3</sup> )	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> /kJ g <sup>-1</sup> )	$D_v^d$ (m s <sup>-1</sup> )	$P^e$ (GPa)	IS <sup>f</sup> (J)	FS <sup>g</sup> (N)
4	234	1.856	944.9/4.01	8196	24.2	13	240
5	207	1.663	863.5/2.82	8024	21.8	5	360
6	243	1.689	1149.6/3.42	8679	26.4	8	288
7	235	1.749	1547.6/3.51	8272	24.3	3	216
8	237	1.766	764.5/1.96	8289	23.3	1	160
9	238	1.651	1005.9/2.39	8089	22.1	40	252
10	213	1.664	1218.6/2.71	8479	24.4	4	180
11	266	1.462	1073.2/2.15	6924	14.6	40	252
RDX <sup>h</sup>	205	1.80	70.7/0.32	8795	34.9	7.5	120
TNT <sup>i</sup>	295	1.65	-59.3/-0.26	7303	21.3	15	353

<sup>a</sup>Thermal decomposition temperature (onset) under nitrogen gas (DSC at 5 °C min<sup>-1</sup>). <sup>b</sup>Measured densities, with a gas pycnometer at room temperature. <sup>c</sup>Calculated heat of formation. <sup>d</sup>Calculated detonation velocity. <sup>e</sup>Calculated detonation pressure. <sup>f</sup>Impact sensitivity. <sup>g</sup>Friction sensitivity. <sup>h</sup>From ref 12. <sup>i</sup>From ref 13.

a) Transformation of 3 to 12.



b) Proposed mechanism for the reaction.



**Figure 5.** State of the art for the transformation of compound 3 to compound 12.

strategy for molecular diversity. We expect that this methodology as well as the new energetic compounds have potential applications in both organic chemistry and energetic materials.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.3c02131>.

Experimental details, characterization data, computational details, and crystal data (PDF)

## Accession Codes

CCDC 2267381, 2267384, and 2267385 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

## ■ AUTHOR INFORMATION

### Corresponding Author

**Ying He** – School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, People's Republic of China; [orcid.org/0000-0001-9159-4606](https://orcid.org/0000-0001-9159-4606); Email: [yhe@njust.edu.cn](mailto:yhe@njust.edu.cn)

### Authors

**Wen-Hao Cui** – School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, People's Republic of China

**Qi Liu** – School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, People's Republic of China

**Zhiwen Ye** – School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, People's Republic of China

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.orglett.3c02131>

## Notes

The authors declare no competing financial interest.

**Caution:** Although there have been no explosions when dealing with these compounds, we strongly encourage to take strict precautions because of their relatively high energy and mechanical sensitivity.

## ■ ACKNOWLEDGMENTS

The authors thank Open Sharing Fund for the Large-Scale Instruments of Nanjing University of Science and Technology (NJUST) for the financial support.

## ■ REFERENCES

- (1) (a) Myznikov, L. V.; Vorona, S. V.; Zevatskii, Y. E. Biologically active compounds and drugs in the tetrazole series. *Chem. Heterocycl. Compd.* **2021**, *57*, 224–233. (b) Wei, C.-X.; Bian, M.; Gong, G.-H. Tetrazolium compounds: Synthesis and applications in medicine. *Molecules* **2015**, *20*, 5528–5553. (c) Ostrovskii, V. A.; Trifonov, R. E.; Popova, E. A. Medicinal chemistry of tetrazoles. *Russ. Chem. Bull.* **2012**, *61*, 768–780. (d) Gao, C.; Chang, L.; Xu, Z.; Yan, X.-F.; Ding, C.; Zhao, F.; Wu, X.; Feng, L.-S. Recent advances of tetrazole derivatives as potential anti-tubercular and anti-malarial agents. *Eur. J. Med. Chem.* **2019**, *163*, 404–412. (e) Gao, F.; Xiao, J.; Huang, G. Current scenario of tetrazole hybrids for antibacterial activity. *Eur. J. Med. Chem.* **2019**, *184*, 111744. (f) Uppadhyay, R. K.; Kumar, A.; Teotia, J.; Singh, A. Multifaceted chemistry of tetrazole. Synthesis, uses, and pharmaceutical applications. *Russ. J. Org. Chem.* **2022**, *58*, 1801–1811. (g) Wang, S.-Q.; Wang, Y.-F.; Xu, Z. Tetrazole hybrids and their antifungal activities. *Eur. J. Med. Chem.* **2019**, *170*, 225–234.
- (2) (a) Neochoritis, C. G.; Zhao, T.; Dömling, A. Tetrazoles via multicomponent reactions. *Chem. Rev.* **2019**, *119*, 1970–2042. (b) Nasrollahzadeh, M.; Nezafat, Z.; Bidgoli, N. S. S.; Shafiei, N. Use of tetrazoles in catalysis and energetic applications: Recent developments. *Mol. Catal.* **2021**, *513*, 111788. (c) Aromí, G.; Barrios, L. A.; Roubeau, O.; Gamez, P. Triazoles and tetrazoles: Prime ligands to generate remarkable coordination mater. *Coord. Chem. Rev.* **2011**, *255*, 485–546. (d) He, Y.; Cai, C. Tetrazole functionalized polymer supported palladium complex: An efficient and reusable catalyst for the room-temperature Suzuki cross-coupling reaction. *Catal. Lett.* **2010**, *140*, 153–159. (e) He, Y.; Cai, C. Palladium tetrazole-supported complex as an efficient catalyst for the Heck reaction. *Transit. Met. Chem.* **2011**, *36*, 113–117.
- (3) (a) Kang, X.-M.; Tang, M.-H.; Yang, G.-L.; Zhao, B. Cluster/cage-based coordination polymers with tetrazole derivatives. *Coord. Chem. Rev.* **2020**, *422*, 213424. (b) Kizhnyaev, V. N.; Golobokova, T. V.; Pokatilov, F. A.; Vereshchagin, L. I.; Estrin, Y. I. Synthesis of energetic triazole- and tetrazole-containing oligomers and polymers. *Chem. Heterocycl. Compd.* **2017**, *53*, 682–692. (c) Pokatilov, F. A.; Kizhnyaev, V. N.; Akamova, E. V.; Edel'shtein, O. A. Effect of alkylation of tetrazole rings on the properties of carbochain and heterochain tetrazole-containing polymers. *Polym. Sci. Ser. B* **2020**, *62*, 190–195. (d) Kyarikwal, R.; Kundu, B. K.; Chakraborty, A.; Mukhopadhyay, S. A tris-tetrazole based nanostructured soft material: Studies on self-healing, AIEE, and rheological and fluorometric detection of 3-aminopyridine. *Mater. Chem. Front.* **2022**, *6*, 2835–2847.
- (4) (a) Manzoor, S.; Tariq, Q.-u.-n.; Yin, X.; Zhang, J.-G. Nitro-tetrazole based high performing explosives: Recent overview of synthesis and energetic properties. *Def. Technol.* **2021**, *17*, 1995–2010. (b) Kofen, M.; Lommel, M.; Wurzenberger, M. H. H.; Klapötke, T. M.; Stierstorfer, J. 1-(Azidomethyl)-5H-Tetrazole: A powerful new ligand for highly energetic coordination compounds. *Chem. - Eur. J.* **2022**, *28*, No. e202200492. (c) Kumar, P.; Ghule, V. D.; Dharavath, S. Facile synthesis of thermally stable tetrazolo[1,5-



- b)[1,2,4]triazine substituted energetic materials: Synthesis and characterization. *Dalton Trans.* **2023**, 52, 747–753. (d) Benz, M.; Klapötke, T. M.; Stierstorfer, J. Krapcho decarboxylation of ethyl-carbazate: Synthetic approach toward 1,1'-diamino-5,5'-bistetrazole and its utilization as a high-performing metal-free initiator. *Org. Lett.* **2022**, 24, 1747–1751. (e) Klapötke, T. M.; Witkowski, T. G. Nitrogen-rich energetic 1,2,5-oxadiazole-tetrazole-based energetic materials. *Propellants Explos. Pyrotech.* **2015**, 40, 366–373. (f) Feng, S.; Yin, P.; He, C.; Pang, S.; Shreeve, J. M. Tunable Dimroth rearrangement of versatile 1,2,3-triazoles towards high-performance energetic materials. *J. Mater. Chem. A* **2021**, 9, 12291–12298.
- (5) (a) Qu, Y.; Babailov, S. P. Azo-linked high-nitrogen energetic materials. *J. Mater. Chem. A* **2018**, 6, 1915–1940. (b) Yadav, A. K.; Ghule, V. D.; Dharavath, S. Dianionic nitrogen-rich triazole and tetrazole-based energetic salts: Synthesis and detonation performance. *Mater. Chem. Front.* **2021**, 5, 8352–8360. (c) Dong, Z.; Ye, Z. Synthesis and properties of salts derived from  $C_4N_{18}^{2-}$ ,  $C_4N_{18}H_3^{3-}$  and  $C_4N_{18}H_3^{2-}$  anions. *J. Mater. Chem. A* **2020**, 8, 25035–25039. (d) Zhao, B.; Li, X.; Wang, P.; Ding, Y.; Zhou, Z. A novel facile transformation to 1,2-bis(3-nitro-1-(1H-tetrazol-5-yl))-1H-1,2,4-triazol-5-yl)hydrazinesalts. *New J. Chem.* **2018**, 42, 14087–14090. (e) Singh, J.; Staples, R. J.; Hooper, J. P.; Shreeve, J. M. Pyrazole bridges ensure highly stable and insensitive bistetrazoles. *Chem. Eng. J.* **2022**, 431, 133282. (f) Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J. M. Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5,5'-bis(tetrazolate). *Chem. Commun.* **2005**, 2750–2752. (g) Singh, J.; Staples, R. J.; Shreeve, J. M. Engineering bistetrazoles: (E)-5,5'-(Ethen-1,2-diyl)bis(1H-tetrazol-1-ol) as a new planar high-energy-density material. *Mater. Adv.* **2022**, 3, 6062–6068. (h) Hammerl, A.; Hiskey, M. A.; Holl, G.; Klapötke, T. M.; Polborn, K.; Stierstorfer, J.; Weigand, J. J. Azidoformamidinium and guanidinium 5,5'-azotetrazolate salts. *Chem. Mater.* **2005**, 17, 3784–3793. (i) Klapötke, T. M.; Mayer, P.; Stierstorfer, J.; Weigand, J. J. Bistetrazolylamines—synthesis and characterization. *J. Mater. Chem.* **2008**, 18, 5248–5258. (j) Huang, H.; Zhou, Z.; Liang, L.; Song, J.; Wang, K.; Cao, D.; Sun, W.; Bian, C.; Xue, M. Nitrogen-rich energetic monoanionic salts of 3,4-bis(1H-5-tetrazolyl)furoxan. *Chem. Asian J.* **2012**, 7, 707–714. (k) Guo, Y.; Gao, H.; Twamley, B.; Shreeve, J. M. Energetic Nitrogen rich salts of N,N-bis[1(2)H-tetrazol-5-yl]amine. *Adv. Mater.* **2007**, 19, 2884–2888. (l) Wang, S.; Li, C.; Lu, T.; Wang, G.; Yin, H.; Ma, Q.; Fan, G.; Chen, F.-X. Fused triazolotriazine bearing a gem-dinitro group: A promising high energy density material. *New J. Chem.* **2021**, 45, 9766–9769.
- (6) For selected reviews and papers: (a) Feng, Y.; Deng, M.; Song, S.; Chen, S.; Zhang, Q.; Shreeve, J. M. Construction of an Unusual Two-Dimensional Layered Structure for Fused-Ring Energetic Materials with High Energy and Good Stability. *Engineering* **2020**, 6, 1006–1012. (b) Gao, H.; Zhang, Q.; Shreeve, J. M. Fused heterocycle-based energetic materials (2012–2019). *J. Mater. Chem. A* **2020**, 8, 4193–4216. (c) Cui, W.-H.; Zhou, W.-B.; Ye, Z.; He, Y. A practical synthesis of 3,4-diamino-6-azido-1H-pyrazolo[4,3-c]pyridin-5-ium energetic ionic compounds. *Org. Chem. Front.* **2023**, 10, 2642–2647. (d) Deng, M.; Feng, Y.; Zhang, W.; Qi, X.; Zhang, Q. A green metal-free fused-ring initiating substance. *Nat. Commun.* **2019**, 10, 1339. (e) Hu, L.; Yin, P.; Zhao, G.; He, C.; Imler, G. H.; Parrish, D. A.; Gao, H.; Shreeve, J. M. Conjugated energetic salts based on fused rings: Insensitive and highly dense materials. *J. Am. Chem. Soc.* **2018**, 140, 15001–15007.
- (7) Cao, W.; Qin, J.; Zhang, J.; Sinditskii, V. P. 4,5-Dicyano-1,2,3-triazole—A promising precursor for a new family of energetic compounds and its nitrogen-rich derivatives: Synthesis and crystal structures. *Molecules* **2021**, 26, 6735.
- (8) Jenkins, H. D. B.; Tudela, D.; Glasser, L. Lattice potential energy estimation for complex ionic salts from density measurements. *Inorg. Chem.* **2002**, 41, 2364–2367.
- (9) Lu, T. Simple, reliable, and universal metrics of molecular planarity. *J. Mol. Model.* **2021**, 27, 263.
- (10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
- (11) Súcska, M. *EXPLOS, Version 6.05.02*; Brodarski Institute: Zagreb, Croatia, 2019.
- (12) Tang, Y.; Kumar, D.; Shreeve, J. M. Balancing excellent performance and high thermal stability in a dinitropyrazole fused 1,2,3,4-tetrazine. *J. Am. Chem. Soc.* **2017**, 139, 13684–13687.
- (13) Chinnam, A. K.; Yu, Q.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Azo- and methylene-bridged mixed azoles for stable and insensitive energetic applications. *Dalton Trans.* **2020**, 49, 11498–11503.
- (14) (a) Lu, T.; Chen, Q. Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems. *J. Comput. Chem.* **2022**, 43, 539–555. (b) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, 33, 580–592. (c) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics.* **1996**, 14, 33–38.
- (15) Spackman, P. R.; Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Cryst.* **2021**, 54, 1006–1011.
- (16) (a) Wu, J.; Cheng, Y.; Lan, J.; Wu, D.; Qian, S.; Yan, L.; He, Z.; Li, X.; Wang, K.; Zou, B.; You, J. Molecular engineering of mechanochromic materials by programmed C–H arylation: Making a counterpoint in the chromism trend. *J. Am. Chem. Soc.* **2016**, 138, 12803–12812. (b) El Ashry, E. S. H.; Nadeem, S.; Shah, M. R.; Kilany, Y. E. Recent advances in the Dimroth rearrangement: A valuable tool for the synthesis of heterocycles. *Adv. Heterocycl. Chem.* **2010**, 101, 161–228. (c) Ganai, A. M.; Pathan, T. K.; Sayyad, N.; Kushwaha, B.; Kushwaha, N. D.; Tzakos, A. G.; Karpoomath, R. DBU mediated one-pot synthesis of triazolo triazines via Dimroth type rearrangement. *RSC Adv.* **2022**, 12, 2102–2106. (d) Li, Z.; Chen, J.; Wu, L.; Ren, A.; Lu, P.; Wang, Y. Preparation of 4-diazoisoquinolin-3-ones via Dimroth rearrangement and their extension to 4-aryltetrahydroisoquinolin-3-ones. *Org. Lett.* **2020**, 22, 26–30. (e) Nikolić, A. M.; Stanić, J.; Zlatar, M.; Gruden, M.; Anđelković, B.; Selaković, Ž.; Ajdačić, V.; Opsenica, I. M. Controlling Pd-catalyzed N-arylation and Dimroth rearrangement in the synthesis of N,1-diaryl-1H-tetrazol-5-amines. *J. Org. Chem.* **2021**, 86, 4794–4803.
- (17) It should be noted that the Dimroth rearrangement and hydrolysis of –CN to amide are relatively independent processes. The hydrolysis process could also occur before (or during) the Dimroth rearrangement.