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Energetic Materials

Synthesis and Characterization of a Stable, Catenated N_{11} Energetic Salt**

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Nitrogen-rich compounds are the most promising candidates for high energy density materials (HEDM), as they are environmentally benign and possess a high energy density.[1] In recent years, nitrogen-rich compounds containing long catenated nitrogen atom chains, have attracted considerable interest in research areas such as propellants, explosives, and pyrotechnics. This attraction is due to the high positive heat of formation and unique features of energetic compounds containing catenated N–N bonds. Some energetic azo compounds containing eight-nitrogen and ten-nitrogen chains have been prepared and characterized (Figure 1).[2]

However, the larger the number of directly linked nitrogen atoms in the compound, the more difficult it is to synthesize it.[3] The difficulty in the synthesis of these nitrogen-rich compounds arises from their high endothermic and thermodynamic instability. In comparison with carbon analogues, the short triple bonds in these molecules are formed from continuous N–N single or double bonds accompanied by a large release of energy. Therefore, continuous N–N bonds tend to be more easily broken than the corresponding carbon chains.[4]

An efficient approach to generate a rather long catenated nitrogen atom chain is the oxidative azo coupling of the N–NH_2 moiety of the heteroaromatic ring to form a tetrazene structure (N–N=N–N).[5] Recently, 1,1′-azobis-1,2,3-triazole (**1**)[2b] and 2,2′-azobis(5-nitrotetrazole) (**2**),[2a] both with an N_8 structure, and 1,1′-azobistetrazole (**3**)[2c] with an N_{10} structure were synthesized sequentially using sodium dichloroisocyanurate (SDIC) as an azo coupling reagent. Unfortunately, **2** and **3** are thermally unstable, decomposing at low temperatures, and are even unstable in solution. Recently, our group synthesized 1,1′-azobis(5-methyltetrazole)[2e] (**4**), which contains a relatively stable N_{10} structure, by employing one of the three azo coupling reagents, including trichloroisocyanuric acid (TCICA), sodium dichloroisocyanurate (SDIC) and *tert*-butyl hypochlorite (*t*BuOCl). In particular, TCICA was used for the first time to oxidize N–NH_2 into tetrazene derivatives. However, studies on the synthesis of nitrogen-rich compounds with continuous nitrogen atom chains generated by the new formation of N–N bonds are relatively scarce. Herein, we report the synthesis and characterization of the chloride salt of 1,1′-(triaz-1-ene-1,3-diyl)bis(1*H*-tetrazol-5-amine) (**6**), which contains an N_{11} structural adduct with 5-aminotetrazole (ATA; Cl**6**·2 ATA). To the best of our knowledge, the continuous N_{11} chain in the title compound is the longest nitrogen sequence reported thus far.

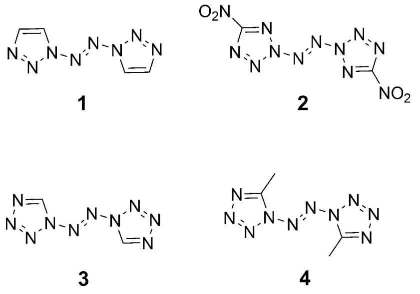
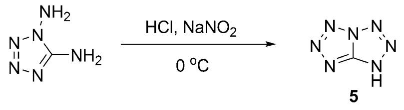


Figure 1. Energetic compounds with catenated nitrogen atoms.

We originally intended to prepare 3*H*-tetrazolo[1,5-*d*]tetrazole (**5**) according to a known procedure by treatment of 1,5-diaminotetrazole (DAT) with sodium nitrite in concentrated HCl solution (Scheme 1).[6] However, compound **5** was not obtained from the reaction. Rather, after evaporating the reaction solvent under vacuum and treating the residue with ethanol, a high yield of the chloride salt of **6** and 5-aminotetrazole (ATA) was recovered. The formation of **6** is probably due to an azo coupling between the diazonium salt of DAT and undiazotized DAT in acid solution. The formation of a new nitrogen–nitrogen bond is the result of a reaction between relatively electron-poor and electron-rich nitrogen atoms. The amino group attached to the nitrogen atom of DAT is easier to transform into a diazonium ion than C–NH_2 under strongly acidic conditions. Electrophilic attack of the amino group of DAT by a diazonium salt gives rise to the corresponding product. Azo reaction between the diazonium salt of C–NH_2 and an amine derivative has been well investigated, whereas that of a diazonium salt of N–NH_2 has been scarcely reported, owing to its instability.[7] The adduct of ATA was formed following a diazotization-deamination sequence in which the diazonium group of the



Scheme 1. Synthesis of 3*H*-tetrazolo[1,5-*d*]tetrazole.

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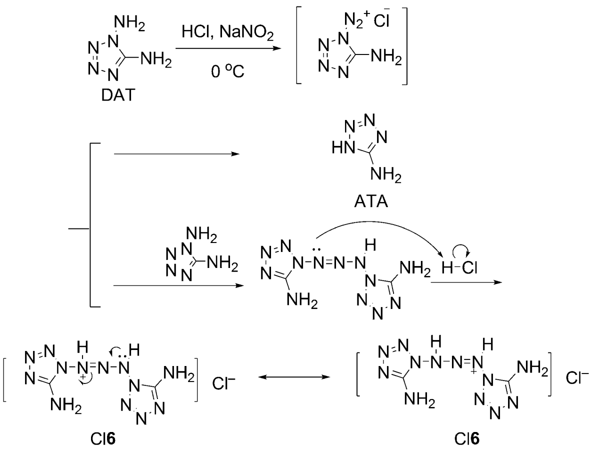
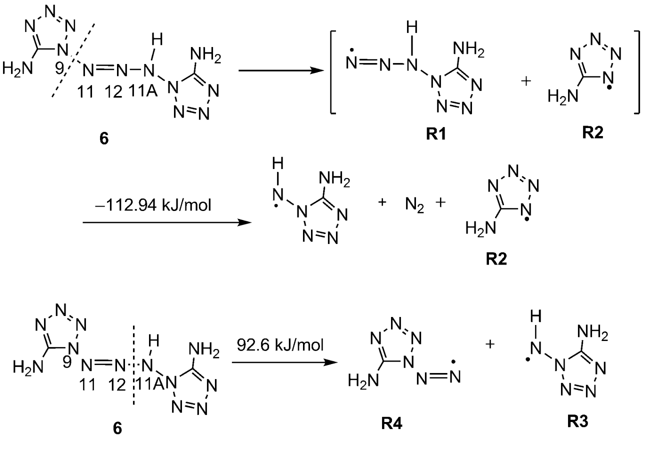
unreacted diazonium salt of DAT was replaced by a hydrogen atom through treatment with ethanol (Scheme 2).[8–10] We attempted to isolate compound **6** from solution by neutralization with $NaHCO_3$. Unfortunately, Cl**6**·2 ATA decomposed immediately into DAT and ATA, along with the release of N_2 gas. To investigate the stability of **6**, we computed the bond dissociation energies (BDEs) for the two weakest bonds with the smallest bonding populations (Scheme 3). The rupture of the N9–N11 bond (resulting in radicals **R1** and **R2**) leads to the formation of N_2 gas, because radical **R1** collapses into N_2 and an ATA radical. Consequently, the rupture of this N–N bond releases 112.94 kJ mol^{-1} of energy. The BDE value for the N12–N11A bond (resulting in radicals **R3** and **R4**) is as low as 92.60 kJ mol^{-1}. This value is much lower than that of the N–NO_2 bond found in commonly used explosives. For example, the BDE for the N–NO_2 bond in RDX is 160.24 kJ mol^{-1} at the same computational level. Therefore, the theoretical calculations indicate that **6**, which possesses an acyclic/cyclic N_{11} chain is unstable, which is in good agreement with the experiment.



Scheme 2. Possible reaction pathway for the formation of Cl**6**·2 ATA.

Single crystals of Cl**6**·2 ATA suitable for X-ray diffraction measurements were obtained by recrystallization from ethanol. The ORTEP diagram of Cl**6**·2 ATA is shown in Figure 2, and structural details are given in the Supporting Information. There are two equivalent ATA molecules and one symmetrical chloride salt of **6** in the crystal unit. The compound crystallizes in the *P*21/*c* monoclinic space group with a cell volume of 887.6 Å^3. The bond distances and angles of the ATA moieties are in accordance with the literature values of the ATA adduct of 5-amino-1*H*-tetrazolium nitrate.[11] For chloride salt **6**, the N9–N11 (1.430 Å) and N11–N12 (1.378 Å) bond distances lie between an N–N single bond (1.460 Å) and double bond (1.250 Å), which can be explained by the hyperconjugation effect. The tetrazole ring is practically planar, with a deviation of no more than 0.0071 Å from the plane. The bond angle of N11-N12-N11A (180°) and N9-N11-N12 (145°) indicates an almost linear configuration for the five continuous nitrogen atoms. The torsion angles N11-N9-C2-N6 (−176.1°) and N8-N9-N11-N12 (−173.4°) show that an acyclic planar N_3 chain (N11-N12-N11A) is slightly twisted out of the tetrazole plane. This is a small deviation from planarity that does not detract significantly from the planarity of the molecule (mean deviation 0.0309 Å), which accounts for the good delocalization of π electron density over the entire molecule. The supercell consisting of layers of molecules of **6** are arranged in a wavelike layer structure along the *b* axis. The layers are formed by three flight stands along the *a* axis, which is depicted in Figure 3.



Scheme 3. Two possible ruptures of the weak bonds in **6**.

The ^1H NMR spectrum of Cl**6**·2 ATA shows only one signal at 7.88 ppm in [D$_6$]DMSO, which is attributed to the fast exchange of protons among the three amino groups of **6** and ATA. There are three signals in the ^{13}C NMR spectrum: two signals for the tetrazole carbon in molecule **6** were observed at 152.5 and 150.1 ppm, whereas the signal at 153.8 ppm was assigned to the carbon atom of ATA. This is higher field than the analogous signal in ATA itself (156.1 ppm), because of intermolecular hydrogen bonding between ATA and the chloride salt Cl**6** (Supporting Information, Figure S5).

The thermal stability of Cl**6**·2 ATA was also investigated using differential scanning calorimetry (DSC) and thermogravimetry (TG; Figure 4), which showed a total weight loss of 76 %, which corresponds to a thermal decomposition of the entire molecule in two steps. Strong endothermicity occurs at a temperature range of 119.4–166.5 °C, which shows that the

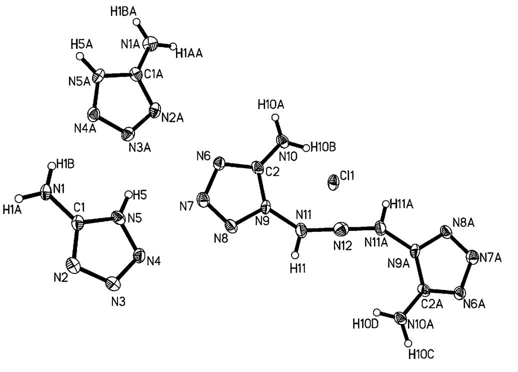


Figure 2. Molecular structure of Cl**6**·2 ATA. Ellipsoids set at 50 % probability.

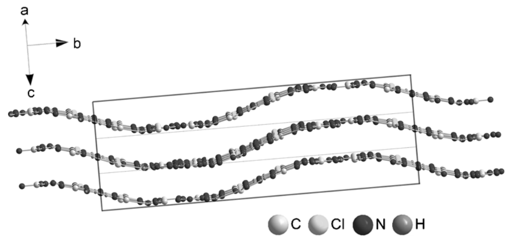


Figure 3. Views along the *a* and *c* axes in the structure of Cl**6**·2 ATA.

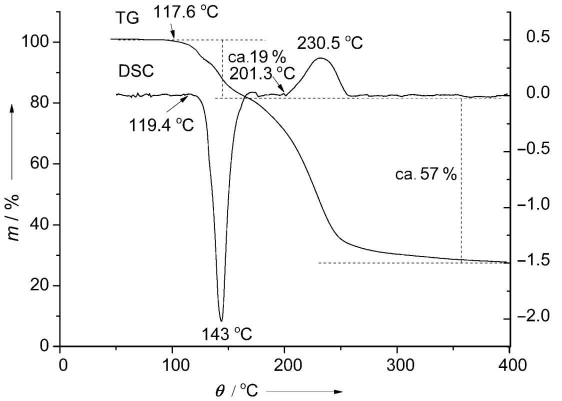


Figure 4. TG and DSC spectra of Cl**6**·2 ATA.

compound melts with concomitant decomposition, corresponding to a mass loss of 19%. The second stage occurs at a temperature range of 201.3–257.2 °C , which is followed by exothermal degradation at 230.5 °C. DSC and TG reveal relatively high thermal stability for Cl6·2 ATA.

The energetic performance of both Cl**6**·2 ATA and **6** was calculated using the Gaussian 03 suite of programs. The crystal density of Cl**6**·2 ATA is 1.563 g cm^{-3}, which is similar to that of **6** (calculated density = 1.60 g cm^{-3}). Cl**6**·2 ATA has a calculated heat of formation of 1499.01 kJ mol^{-1}, which is higher than the reported values for both the N_8 compounds **1** and **2** and the N_{10} compounds **3** and **4**, and is 311.2 kJ mol^{-1} higher than that of **6**. The detonation velocity was predicted to be 7220 m s^{-1}, which is comparable to that of TNT,[12] and 1090 m s^{-1} lower than **6**, because of the relatively low energy of chloride ions (Supporting Information, Table S9). Impact and friction sensitivity measurements were made using the standard BAM method.[13] With regards to impact and friction values (10 J, 160 N), Cl**6**·2 ATA is less sensitive than RDX.

In conclusion, Cl**6**·2 ATA, a novel nitrogen-rich energetic salt containing the longest reported nitrogen chain (N_{11}), was obtained by an azo coupling reaction from 1,5-diaminotetrazole. The formation of **6** arises from the first example of an azo reaction between the diazonium salt of N–NH_2 and an amine derivative. This type of nitrogen-nitrogen bond-forming reaction provides a new means for the discovery of novel nitrogen-rich energetic compounds.

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[1] a) Y. Q. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2012**, *18*, 987 – 994; b) J. J. Sabatini, J. M. Raab, R. K. Hann, Jr., R. Damavarapu, T. M. Klapötke, *Chem. Asian J.* **2012**, *7*, 1657 – 1663; c) J. J. Sabatini, A. V. Nagori, G. Chen, P. Chu, R. Damavarapu, T. M. Klapötke, *Chem. Eur. J.* **2012**, *18*, 628 – 631; d) G. H. Tao, D. A. Parrish, J. M. Shreeve, *Inorg. Chem.* **2012**, *51*, 5305 – 5312; e) G. Steinhauser, G. Giester, C. Wagner, P. Weinberger, B. Zachhuber, G. Ramer, M. Villa, B. Lendl, *Inorg. Chem.* **2012**, *51*, 6739 – 6745; f) Y. H. Joo, H. X. Gao, D. A. Parrish, S. G. Cho, E. M. Goh, J. M. Shreeve, *J. Mater. Chem.* **2012**, *22*, 6123 – 6130; g) Z. Fu, R. Su, Y. Wang, Y. F. Wang, W. Zeng, N. Xiao, Y. K. Wu, Z. M. Zhou, J. Chen, F. X. Chen, *Chem. Eur. J.* **2012**, *18*, 1886 – 1889; h) N. Fischer, D. Izsák, T. M. Klapötke, S. Rappenglück, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 4051 – 4062.
[2] a) T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Dalton Trans.* **2012**, *41*, 9451 – 9459; b) Y. C. Li, S. H. Li, C. Qi, H. J. Zhang, M. Y. Zhu, S. P. Pang, *Acta Chim. Sin.* **2011**, *18*, 2159 – 2165; c) T. M. Klapötke, D. G. Piercey, *Inorg. Chem.* **2011**, *50*, 2732 – 2734; d) Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, *J. Am. Chem. Soc.* **2010**, *132*, 12172 – 12173; e) Y. X. Tang, H. W. Yang, J. H. Shen, B. Wu, X. H. Ju, C. X. Lu, G. B. Cheng, *New J. Chem.* **2012**, *36*, 2447 – 2450.
[3] a) K. O. Christe, *Propellants Explos. Pyrotech.* **2007**, *32*, 194 – 204; b) M. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5032 – 5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924 – 4928; c) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112 – 2118; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004 – 2009.
[4] F. R. Benson, *The High Nitrogen Compounds*, Wiley, New York, **1984**, pp. 1 – 10.
[5] a) C. Qi, S. H. Li, Y. C. Li, Y. Yuan, X. K. Chen, S. P. Pang, *J. Mater. Chem.* **2011**, *21*, 3221 – 3225; b) S. H. Li, S. P. Pang, X. T. Li, Y. Z. Yu, X. Q. Zhao, *Chin. Chem. Lett.* **2007**, *18*, 1176 – 1178; c) S. H. Li, H. G. Shi, C. H. Sun, X. T. Li, S. P. Pang, Y. Z. Yu, X. Q. Zhao, *J. Chem. Crystallogr.* **2009**, *39*, 13 – 16; d) J. Heppekausen, T. M. Klapötke, S. M. Sproll, *J. Org. Chem.* **2009**, *74*, 2460 – 2466; e) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *Propellants Explos. Pyrotech.* **2004**, *29*, 325 – 332.
[6] M. A. M. Taha, *J. Indian Chem. Soc.* **2005**, *82*, 172 – 174.
[7] H. Zollinger, *Diazo Chemistry I: Aromatic and Heteroaromatic Compounds*, VCH, Weinheim, **1994**, pp. 11 – 24.
[8] C. W. Rees, A. A. Sale, *J. Chem. Soc. Perkin Trans. 1* **1973**, 545 – 550.
[9] S. Hauptmann, H. Wilde, K. Moser, *J. Prakt. Chem.* **1971**, *313*, 882 – 888.
[10] C. W. Rees, R. C. Storr, *J. Chem. Soc. C* **1969**, 756 – 760.
[11] T. M. Klapötke, C. M. Sabaté, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1867 – 1874.
[12] H. H. Klause in *Energetic Materials* (Ed.: U. Teipel), VCH, Weinheim, **2005**, pp. 1 – 25.
[13] a) Tests were conducted according to the *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 4th rev. ed., United Nations Publication, New York, **2003**; b) 13.4.2 Test 3 (a)(ii) BAM Fallhammer, pp. 75–82; c) 13.5.1 Test 3 (b)(i): BAM friction apparatus, pp. 104–107.