

Growing Catenated Nitrogen Atom Chains**

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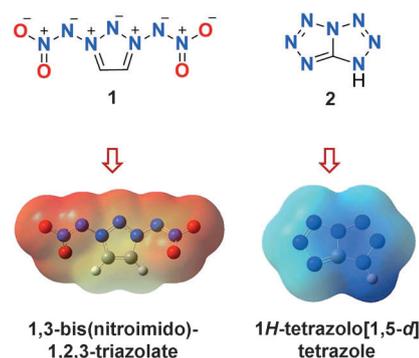
chain structures · energetic materials ·
 high-nitrogen compounds · nitrogen ·
 oxidative coupling

Within the field of materials science, high-nitrogen compounds represent an important class of energetic materials.^[1] As a result of the existence of a large number of inherently energetic N–N or N=N bonds within the molecules, high-nitrogen compounds possess very high positive heats of formation, thereby making them intrinsically high-energy materials. The energy of most compounds with high-nitrogen content mainly derives from the transformation of nitrogen-containing bonds. Such transformations are always accompanied by the release of enormous amounts of energy, which originates from the breaking and rearrangement of the highly energetic bonds, including N–N (160 kJ mol⁻¹), N=N (418 kJ mol⁻¹), and N≡N (954 kJ mol⁻¹) bonds, during the explosion.^[1d] In general, the higher nitrogen content means a higher heat of formation, which in turn leads to a higher energetic performance. From the viewpoint of organic chemistry, the design and synthesis of new high-nitrogen structures which can challenge or overcome the limit of the nitrogen content of existing compounds has unquestionably attracted significant interest from the academic community. With this background, continuing and dedicated efforts have been devoted to developing new strategies for high-nitrogen structures. However, in most cases, high nitrogen content and stability tend to be mutually exclusive, thereby making the synthesis and isolation of such highly energetic materials an interesting and enormous challenge.

In the early studies on high-nitrogen compounds, scientists mainly focused on the synthetic strategy of incorporating one or more azido groups into the nitrogen-rich molecular backbone,^[2] with the aim of achieving an ultrahigh nitrogen content. Since organic polyazido-substituted compounds have very high heats of formation, as one azido group adds approximately 87 kcal mol⁻¹ of endothermicity to the molecule, this class of high-nitrogen compounds has been at the forefront of high-energy research.^[3] By virtue of this strategy, a number of polyazido compounds with very high nitrogen content have been reported. Of these, tetraazidomethane is a well-known polyazido compound that was synthesized and isolated successfully with the highest nitrogen content

(93.33 % N).^[4] Indeed, most high-nitrogen polyazides possess very high positive heats of formation and, therefore, display excellent explosive performance. However, most of them are notorious for their extreme sensitivity toward external forces such as heat, shock, friction, and electrostatic discharge, which significantly limits their application potential for use on a large scale.

Recently, in pursuit of new high-nitrogen structures, a fascinating class of compounds containing long catenated nitrogen atom chains has been reported. Tartakovskii and co-workers^[5] as well as Klapötke et al.^[6] have successfully designed and synthesized a 1,3-bis-(nitroimido)-1,2,3-triazolate anion (**1**, Scheme 1), which has a chain of seven catenated



Scheme 1. High-nitrogen compounds containing seven catenated nitrogen atoms: Left: the alternating positively/negatively charged resonance form of the 1,3-bis(nitroimido)-1,2,3-triazolate anion; right: 1H-tetrazolo[1,5-d]tetrazole.

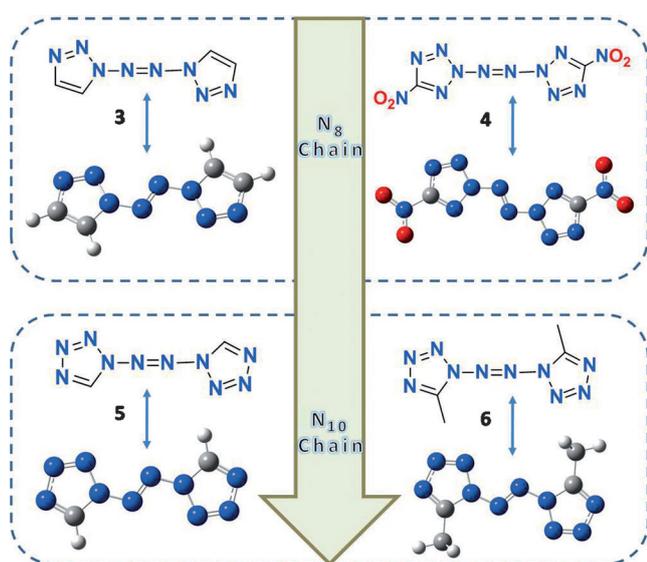
nitrogen atoms. Interestingly, when one resonance form is considered, an alternating positive/negative charge system is created that extends over nine atoms when the nitro group resonances are included.^[6] The hydroxylammonium salt based on the 1,3-bis-(nitroimido)-1,2,3-triazolate anion has a very high heat of formation (1038.2 kJ mol⁻¹) and, therefore, exhibits an excellent detonation velocity (9426 m s⁻¹). Moreover, a fused-ring structure containing a catenated N₇ chain has also been reported.^[7] By virtue of a smart cyclization strategy, 1,5-diaminotetrazole can be coupled with sodium nitrite in acidic solutions to give the 1H-tetrazolo[1,5-d]tetrazole (**2**, Scheme 1). This compound has a high nitrogen content of 88.28%; however, it appears that this compound is

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extremely unstable and its synthesis by the literature method is difficult to repeat.^[7]

No doubt designing longer nitrogen chains is a challenging task. One of the difficulties in synthesizing and handling such long nitrogen-chain structures is their poor stability, which is probably caused by their high endothermic character and thus their tendency to decompose with the elimination of N₂. Recently, Pang and co-workers^[8] successfully achieved the construction of a longer catenated nitrogen chain through oxidative azo coupling of the N–NH₂ moiety. In this strategy, the amino group attached to the triazole ring is first transformed into a diazonium ion under acidic conditions. A subsequent nucleophilic attack of the amino group of the 1-amino-1,2,3-triazole on this diazonium cation gives rise to the desired structure containing eight catenated nitrogen atoms (N₈ structure). The resulting N₈ compound, 1,1'-azobis-1,2,3-triazole (**3**, Scheme 2), has a nitrogen content of 68.27%. This



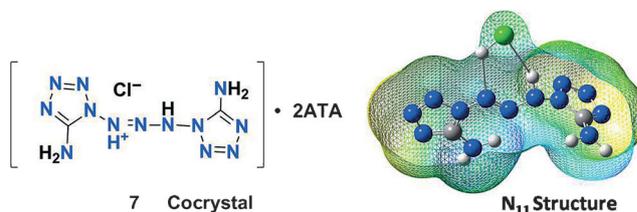
Scheme 2. Synthesis and the optimized structure of 1,1'-azobis-1,2,3-triazole (**3**) and 2,2'-azobis(5-nitrotetrazole) (**4**) with an N₈ chain, as well as 1,1'-azobis(tetrazole) (**5**) and 1,1'-azobis(5-methyltetrazole) (**6**) with an N₁₀ chain.

N₈ compound is thermally stable up to 193.8°C and has a relatively high heat of formation of 962 kJ mol⁻¹. Additionally, the azo group within the N₈ structure also endows the molecule with an interesting photochromic feature: it can undergo a reversible color change when subjected to irradiation.^[8] Similarly, azo coupling of 2-amino-5-nitrotetrazole can also lead to the formation of a highly energetic compound with a similar N₈ structure, 2,2'-azobis(5-nitrotetrazole (**4**, Scheme 2),^[9] which has a high heat of formation of 1092 kJ mol⁻¹ and an astounding sensitivity of $\ll 1\text{ J}$.

Structures containing ten catenated nitrogen atoms (N₁₀ structure) were synthesized very recently by employing the same strategy of azo coupling of N–NH₂ moieties.^[10,11] 1,1'-Azobis(tetrazole) (**5**, Scheme 2), which contains an N₁₀ structure, can be readily synthesized through an azo coupling reaction starting from 1-aminotetrazole. The nitrogen content

of **5** is 84.32%. Crystal-structure analysis revealed that **5** exists in the orthorhombic space group *Pbca* with four formula units in the unit cell. The calculated heat of formation and detonation velocity are 1030 kJ mol⁻¹ and 9185 ms⁻¹, respectively. Compound **5** is much more sensitive than the N₈ compound **3**, and its decomposition temperature is also much lower. Similarly, the azo homocoupling of 5-methyl-1-aminotetrazole gave the compound 1,1'-azobis(5-methyltetrazole) with an N₁₀ structure (**6**, Scheme 2). In comparison with 1,1'-azobis(tetrazole) (**5**), the introduction of a methyl group at the carbon atom of the tetrazole ring to give **6** resulted in a significantly decreased heat of formation (986 kJ mol⁻¹) and detonation velocity (7320 ms⁻¹); however, the thermal stability ($T_d = 127.2^\circ\text{C}$) of **6**, and its sensitivity toward impact were concomitantly improved.

The latest contribution addressed the synthesis of a stable N₁₁ chain structure.^[12] First, treatment of 1,5-diaminotetrazole (DAT) with sodium nitrite under strongly acidic conditions resulted in the facile formation of a diazonium ion, which subsequently underwent an azo coupling with the remaining DAT to give the desired catenated N₁₁ structure (**7**, Scheme 3), the longest nitrogen chain structure reported to



Scheme 3. Structure of a cocrystal containing an N₁₁ chain.

date. As a consequence of the instability of the ultralong catenated nitrogen atoms, this N₁₁ compound was isolated only in the form of a cocrystal—the corresponding chloride salt and bimolecular 5-aminotetrazole (ATA). Single-crystal analysis confirmed the structure of the catenated eleven nitrogen atoms in the chloride salt. Quantum chemical calculations show that the cocrystal has a heat of formation of 1499 kJ mol⁻¹. In contrast to other compounds with long nitrogen chains, this cocrystal containing an N₁₁ chain exhibits a relatively higher thermal stability ($T_d = \text{ca. } 120^\circ\text{C}$) and has a much lower sensitivity (IS = 10 J, FS = 160 N) than both the N₈ and N₁₀ compounds, which probably arises from the presence of the insensitive ATA moiety within the cocrystal. Although the pure neutral N₁₁ compound cannot be isolated because of its instability, this study also further demonstrates that the oxidative azo coupling of an N–NH₂ moiety is an efficient strategy for designing and synthesizing extended catenated nitrogen chains.

Overall, the construction of new high-nitrogen structures with highly catenated nitrogen chains has been achieved by several research groups through the azo coupling of N–NH₂ moieties. It is difficult to predict the exact number of nitrogen atoms that will finally be the limit to the catenated nitrogen atom chains, but we are convinced that the recent advances in the synthesis of such extended nitrogen chains will definitely

open new methods for the synthesis of new high-nitrogen materials in the foreseeable future. Additional work by theoreticians is required to guide the hands of synthetic chemists.

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