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1,1'-Azobis-1,2,3-triazole: A High-Nitrogen Compound with Stable N₈ Structure and Photochromism

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Abstract: Treatment of 1-amino-1,2,3-triazole with sodium dichloroisocyanurate led to isolation of 1,1'-azobis-1,2,3-triazole, which was well characterized. Its structure was determined by X-ray crystallographic analysis, and its thermal stability and photochromic properties were investigated.

Nitrogen-rich compounds based on C/N heteroaromatic rings with high nitrogen content are at the forefront of high-energy materials research.^{1–4} Recently, the combination of an azo group with high-nitrogen heteroaromatic rings has been extensively studied because the azo linkage not only desensitizes but also dramatically increases the heats of formation of high-nitrogen compounds such as DAAT (1) and TAAT (2), where the azo group is bonded to carbon (Figure 1).^{5,6} Such azo compounds (e.g., azobenzene-based compounds 3)⁷ are well known as diazoic dyes and thermally reversible photochromic materials⁸ and are now being used in the fields of optical recording memory, photorefractive materials, photooptical switches, and molecular machines.^{9,10} However, if the azo group were attached to the nitrogens of heteroaromatic rings to create a rather long chain of catenated nitrogens, such a structure could result in unique properties.^{11,12} Moreover, in contrast to the toxicity of many azobenzene-based compounds, these high-nitrogen azo compounds are nontoxic and harmless.

In our previous study,^{11,12} 4,4'-azo-1,2,4-triazole (4)¹¹ and 2,5,2'-triazido-1,1'-azo-1,3,4-triazole^{12a} were obtained via N–NH₂ coupling in 4-amino-1,2,4-triazole. Herein, we report the effective synthesis and properties of 1,1'-azobis-1,2,3-triazole (6, Scheme 1), containing eight directly linked nitrogen atoms (N₈ structure).

The larger the number of directly linked nitrogen atoms, the more difficult the compound is to synthesize. The difficulties in synthesizing and handling polynitrogen compounds are a direct consequence of their high endothermicities; a further complication is the almost complete absence of methodology for preparing such compounds. Treatment of an acetonitrile solution of 1-amino-1,2,3-triazole (5) with sodium dichloroisocyanurate (SDCI) at low temperature for 30 min led to isolation of 6 in 78% yield as a yellow solid that was well characterized.

Some acyclic–cyclic compounds with four-nitrogen chains,^{13,14} six-nitrogen chains, and seven-nitrogen chains,¹⁵ and especially 7,^{14b} 8,¹⁶ and 9¹⁷ (Figure 2), which have eight-nitrogen chains (N₈ structure), have been well documented, but in most of these compounds the nitrogen chains were linked with bulky organic species such as phenyl groups. In contrast, 6 has a simpler structure and much higher nitrogen content (over 68%). Although Bottaro reported the preparation of 1,1'-azobis-1,2,4-triazole and 1,1'-azobis(3-nitro-1,2,4,5-tetrazole) with a low yield in a patent,¹⁸ no physical properties or proofs of structures were given for the compounds.

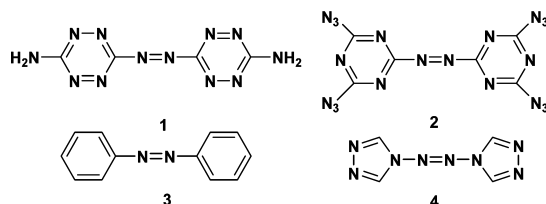
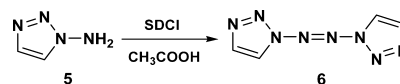


Figure 1. Different types of azo compounds.

Scheme 1. Synthesis of 1,1'-Azobis-1,2,3-triazole



We obtained crystals of 6 suitable for X-ray crystallographic analysis by crystallization from acetone. The crystal structure of 6 adopts a planar molecular structure (*C_i* symmetry) with two almost planar triazoles, a planar N₄ chain, and an *E* configuration about the azo bond (Figure 3). Moreover, as in 1,4-bis(1-methyltetrazol-5-yl)-1,4-dimethyl-2-tetrazene,¹³ there are significant differences between 6 and N₄H₄ (2-tetrazene)¹⁹ with respect to their bond lengths. The bond length between the N atoms of the azo group increases considerably from 1.205 Å in N₄H₄ to 1.2502(17) Å (N4–N4A) in 6. On the other hand, the bond lengths of the formal N–N single bonds decrease from 1.429 Å (N₄H₄) to 1.3795(13) Å (N1–N4) in 6 and 1.379(5) Å in 7 (N1–N4),^{14b} which indicates a stronger delocalization of the azo π bond along the N₄ moiety within 6.

Since the generation of N₂ as an end product of propulsion or explosion is highly desired, compounds containing a backbone of directly linked nitrogen atoms are of great interest.¹³ Therefore, many molecules that are mostly nitrogen but incorporate heteroa-

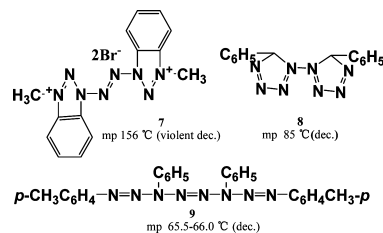


Figure 2. Compounds with eight-nitrogen chains (N₈ structure).

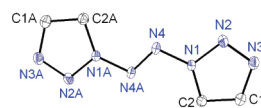


Figure 3. Molecular structure of 6 at 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

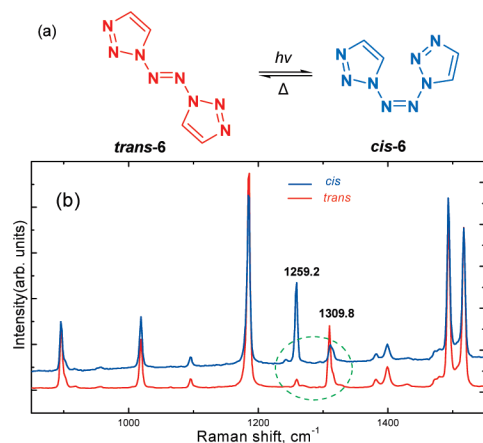


Figure 4. *Trans*–*cis* isomers of **6** (a) and their Raman spectra (b). The peaks at 1259.2 and 1309.8 cm^{-1} correspond to $\text{N}=\text{N}$ stretching vibration.

toms into the structure to provide additional stability were studied. The thermal stability of **6** was also investigated using differential scanning calorimetry (DSC; see Supporting Information, Figure S4a), which showed **6** to be surprisingly stable. **6** has N_8 structure ($\text{N}_3\text{--N}_2\text{--N}_1\text{--N}_4\text{--N}_4\text{A--N}_1\text{A--N}_2\text{A--N}_3\text{A}$), and it undergoes thermal decomposition at 193.8 $^{\circ}\text{C}$, which would be, to the best of our knowledge, the highest decomposition temperature reported for compounds with eight-nitrogen chains (Figure 2).^{13b,14b,16,17} Its decomposition temperature is also much higher than those of hexazene (N_6) ligand (140 $^{\circ}\text{C}$) and N_5^+ (70 $^{\circ}\text{C}$),^{15b,20} demonstrating the importance of combining acyclic and cyclic moieties¹³ in stabilizing the catenated nitrogen atoms. The presence of the delocalized π -system probably also accounts for the remarkable stability of this type of compounds.

The crystal density of **6** was determined to be 1.640 g/cm^3 and was calculated to be 1.620 g/cm^3 . The heat of formation of **6** was predicted to be +962 kJ/mol (+5869 kJ/kg) by well-established methods (Supporting Information, Table S3). **6** has higher density and heat of formation than **4** due to its longer nitrogen chain. The value of H_{50} of **6** is 16.6 cm [less sensitive than TAAT (6.2 cm) and PETN (11 cm), but slightly more sensitive than RDX (28 cm)] (Supporting Information, Table S5).²¹

Surprisingly, **6** is a photochromic molecule that undergoes a reversible color change when subjected to irradiation, so it could be a prospective “green” photochromic material. In the natural state **6** is light yellow, and it becomes blue upon irradiation by sunlight or xenon light (Supporting Information, Figures S9 and S10). This unique photochromic feature of **6** is due to its *trans*–*cis* photoisomerization (Figure 4a), which was confirmed by Raman spectroscopy (Figure 4b and Supporting Information, Figure S12). The difference between the characteristic Raman bands of *trans*-**6** and *cis*-**6** is about 51 cm^{-1} ; this blue-shift is distinctly larger than those for other types of azo compounds.²²

Figure 5a shows the UV–vis spectral changes of **6** in the solid state upon irradiation at room temperature in the 200–800 nm region. The characteristic absorption peak of **6** is located at 594.5 nm. The absorption peaks located at 234 and 346 nm are assignable to the $\pi\rightarrow\pi^*$ electronic transition of the heterocycle and the $n\rightarrow\pi^*$ electronic transition of the azo group, respectively, suggesting that many conjugated double bonds exist in **6** which cause red-shifts compared with azobenzene-based compounds. Moreover, the photochromism of **6** is in accordance with the first-order kinetics (Supporting Information, Figure S11), and the photochromism rate constant is about $3.8 \times 10^{-3} \text{ s}^{-1}$.²³

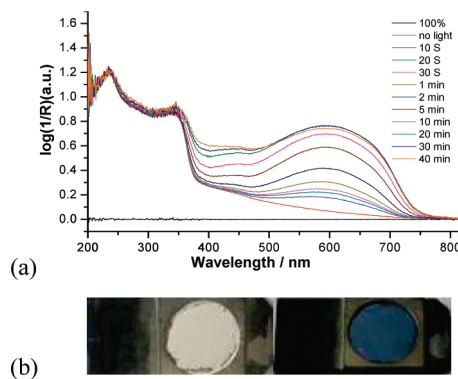


Figure 5. UV–vis spectral changes (a) and color change (b) of **6** in the solid state upon irradiation at room temperature.

In conclusion, 1,1'-azobis-1,2,3-triazole, a novel high-nitrogen compound having the highest decomposition temperature reported for compounds with eight-nitrogen chains, was designed and synthesized, and its photochromism was investigated. Further efforts to this end are underway and will be reported in due course.

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Supporting Information Available: Experimental procedures, compound characterization data, crystallographic data (CIF), computational details, and supplemental figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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