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1,1′-Azobis(tetrazole): A Highly Energetic Nitrogen-Rich Compound with a N_{10} Chain

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Supporting Information

ABSTRACT: The reaction of 1-aminotetrazole with acidic sodium dichloroisocyanurate allowed isolation of 1,1′-azobis(tetrazole). The rare chain of 10 nitrogen atoms in this compound was confirmed by X-ray crystallography, and the physical and explosive properties of the azo compound were characterized. The title compound possesses both exceedingly high explosive performance and sensitivity.

Energetic materials research encompassing all propellants, explosives, and pyrotechnics has long attracted intense work in the chemical sciences, with participating scientists including Liebig, Berzelius, and Gay-Lussac.[1,2] This tradition has led to many chemical advances. For example, work with silver fulminate, which has the same composition as silver cyanate, led to the concept of isomerism.[3] Studies of unstable compounds on the borderline of existence and nonexistence allow elucidation of the fundamental properties affecting chemical stability and bonding.[4−6]

The unique stability of the dinitrogen molecule arising from its strong, short triple bond means that decomposition of compounds containing nitrogen with the formation of nitrogen gas is highly favored energetically.[7] This is especially true for singly and doubly bonded nitrogen systems where compounds with N−N bonds have even higher positive heats of formation than their counterparts with noncontiguous nitrogen atoms.[8] For example, comparison of the azotriazoles 1,1′-azobis(1,2,3-triazole) (**1**) and 1,1′-azobis(1,3,4-triazole) (**2**) (Figure 1) reveals that the former possesses a higher, more positive heat of formation than the latter, resulting from the increased number of N−N bonds.[8]

Unfortunately, despite their potential significance[9,10] to both theory and technology, compounds containing extended chains of nitrogen atoms are not well-known; this arises from both the endothermicities and associated stability problems and the relative scarcity of N−N bond-forming reactions known in the literature (especially when compared with carbon!). For example, the recent publication of **1**[8] marked the discovery of a surprisingly stable compound containing a chain of eight nitrogen atoms, one of the few[8,11−13] compounds with such a long nitrogen chain, whereas comparable and longer carbon compounds are plentiful, well-known, and stable.

Azo coupling reactions have been used to prepare useful azo-based energetic materials such as azotetrazoles,[14] triazoles,[15] and furazans[16] and have even allowed the preparation of eight-linked nitrogen compound **1**.[8] The azo homocoupling of 1-aminotetrazole (**3**) gave the first fully characterized compound containing 10 linked nitrogen atoms. A search of the literature indicated only one mention[17] of compounds with 10 connected nitrogen atoms, formed from the reaction of 5-Ar-1-dichloroaminotetrazole (Ar = Ph, 1-ClPh, 4-MePh) with potassium iodide. However, only the melting points and a single elemental analysis were reported, and comments on the highly explosive nature of the reaction products were provided, albeit with no proof of the structure.[17]

From the treatment of **3** in acetonitrile at 0 °C with an aqueous acidic solution of sodium dichloroisocyanurate, we obtained a precipitate of colorless 1,1′-azobis(tetrazole) (**4**; Figure 2) after dilution with a dilute bicarbonate solution and filtration (Scheme 1). Sodium dichloroisocyanurate was chosen as the azo coupling reagent because it was used successfully for **1**,[8] and attempted coupling using *t*-BuOCl led only to decomposition. The precipitated N_{10} compound **4** was not dried in the funnel because attempts to manipulate the dry solid inevitably led to extremely loud explosions and the destruction of labware. Instead, the wet solid was transferred to the desired analytical instrument, the water was allowed to evaporate, and the measurement taken (e.g., loading a Raman tube). Attempts to store the sensitive product in solution led to the slow release of nitrogen gas and decomposition.

We obtained colorless crystals of **4** sufficient for X-ray crystallographic analysis by the overnight evaporation of an acetone solution of **4**. The N_{10} compound crystallizes in the orthorhombic space group *Pbca* with four formula units in the unit cell and a density of 1.774 g cm^{-3}. The structure of **4** about the azo double bond is trans, and the azo double bond is 1.178 Å long, shorter than that in the N_8 compound **1** at 1.250 Å.[8] The tetrazole rings have bond lengths and angles comparable to those of other 1-substituted tetrazoles.[18]

The N_{10} compound **4** has a calculated solid-state heat of formation of +1030.0 kJ mol^{-1}, 68 kJ mol^{-1} higher than that of the N_8 compound **1**, as a result of the higher nitrogen content, and only 71 kJ mol^{-1} lower than that of diazidotetrazine,[5] which has been claimed (in 2005, we were unable to find a higher published material) to have the highest heat of formation for a binary CN compound. The performance properties of **4** were calculated using the experimental density and the *EXPLO5.04* (5.03) code. **4** has a very high explosive performance of 9185 (9371) m s^{-1}, which is slightly higher than that of HMX, one of the most powerful explosives in common military use with a detonation velocity of 9058 (9215) m s^{-1}. It is interesting to note

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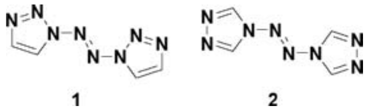


Figure 1. Azotriazoles.

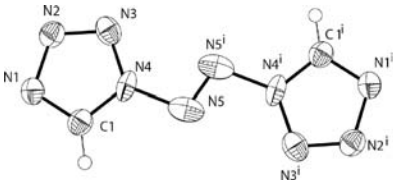
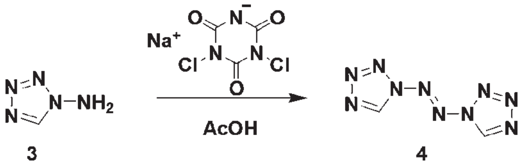


Figure 2. Molecular structure of **4** as it appears in the crystal structure. Non-hydrogen atomic displacement ellipsoids are 50% probability.

Scheme 1. Synthesis of 4



that the previously reported N$_8$ compound **1**[8] has a detonation velocity of 8029 (8323) m s^{-1}, making for a significant increase of almost 1000 m s^{-1}, as a result of the addition of two nitrogen atoms in place of CH groups (for complete calculation details of **4**, see the Supporting Information).

The most striking difference between the reported N$_8$ compound (**1**) and our N$_{10}$ compound (**4**) is the sensitivity; **1** is reported to be insensitive enough for handling, whereas with our N$_{10}$ compound **4**, we experienced several inadvertent explosions during handling such as allowing the dry powder to slide down the inside of a Raman tube or slowing down the rotation rate of a rotary evaporator as **4** crystallized. The material demands the utmost care in handling, and the sensitivities were well below the measurable limit ($\ll$5 N friction and $\ll$1 J impact) of our safety characterization equipment; the material violently explodes when impacted with a 150 g hammer at 2 cm (~0.03 J). It is among the most sensitive materials that we have handled. The decomposition temperature of **4** is far lower than that of compound **1**,[8] with an exothermic peak measured by differential scanning calorimetry of 80 °C (193.8 °C for **1**).

The ^{1}H and ^{13}C resonances for **4** occur at 9.33 and 143.2 ppm respectively in DMSO-d_6. In the ^{14}N spectra broad tetrazole resonances are visible at −5 and −99 ppm, and less broad resonances at −135, −140, −146, and −154 ppm, however due to the instability of **4** in solution, assignment of these peaks is unclear.

The reported[8] photochromicity of **1** provoked us to study the behavior of **4** under the influence of UV light. Exposure of a Raman tube of the sample to UV light from a commercial thin-layer chromatography plate visualization aid for 3 days led to the sample yellowing slightly and a new N═N stretching peak arising at 1260 cm^{-1} (Figure 3), similar to 1259 cm^{-1} as seen for *cis*-**1**. Quantitative conversion to the cis compound was not possible even with high-intensity UV light because only the surface of the material reacts. While such photochromic materials do have many applications, the high sensitivity of **4** would preclude application.[19,20]

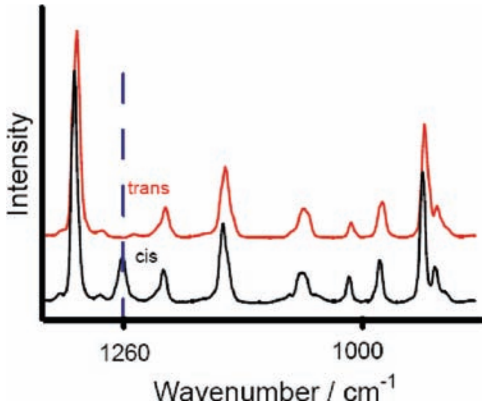


Figure 3. Raman spectrum: N═N stretch at 1260 cm^{-1} for *cis*-**4** arising from UV illumination.

In conclusion, we have demonstrated the ability of 1-amino-5*H*-tetrazole to azocouple, forming 1,1′-azobis(tetrazole), the first well-characterized compound with a chain of 10 nitrogen atoms, including crystallographic proof. This unique material possesses explosive performances comparable to those of the most powerful energetic materials in common use, with the source of this power being the very high heat of formation of this material. Unfortunately, this material is both thermally and physically unstable with a decomposition temperature of 80 °C and undergoes violent explosion when subjected to mild stimuli. Proof of the existence of this N$_{10}$ compound opens the possibility for the discovery of even longer chain nitrogen compounds, although the trend in increasing sensitivity from N$_8$ to N$_{10}$ compounds may present challenges for isolation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, characterization data, a CIF file, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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