

Full-nitro-nitroamino Cooperative Action: Climbing the Energy Peak of Benzenes with Enhanced Chemical Stability

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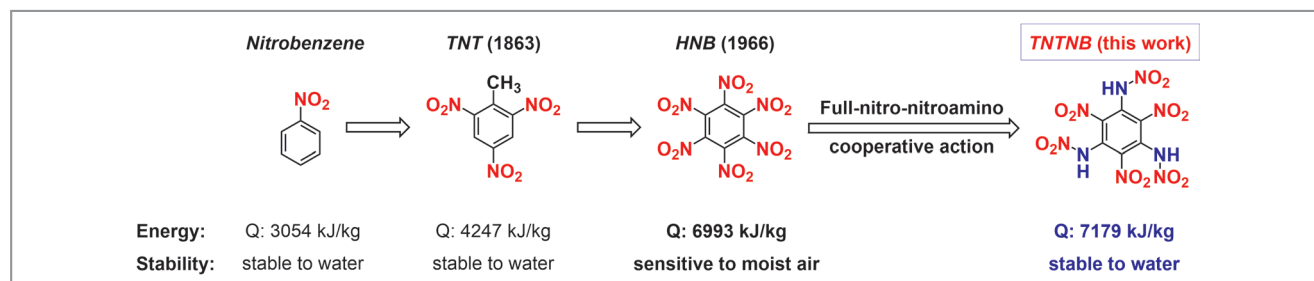
Explosive organic materials – such as nitroglycerine, HMX or nitrocellulose – are extremely important for a number of civil and commercial applications, besides those related to military use, for example in mining or in engineering. Polynitrobenzenes are well-known high-energy-density materials (HEDMs) (Scheme 1), which contain oxidizers (nitro groups) and fuel components (benzene ring) within a single molecule, and generate energy rapidly through self-redox reactions. The most representative energetic polynitrobenzenes are 2,4,6-trinitrotoluene (TNT, 1863, the most famous explosive) and hexanitrobenzene (HNB, 1966, the only fully nitrated benzene). Generally, the energy of these materials progressively increases with an increasing number of nitro groups, but their stability follows the opposite trend (Scheme 1). Particularly, hexanitrobenzene (HNB), which has a fully nitrated structure, exhibits the highest energy (detonation heat, $Q = 6993 \text{ kJ kg}^{-1}$) among the organic explosives so far, but has poor chemical stability and decomposes rapidly in moist air. To date, striking a balance between energy and chemical stability, as well as further increasing the energy while simultaneously improving the stability of polynitrobenzenes, is a significant challenge in the area of novel HEDMs.

To overcome this challenge, the group of Professor Siping Pang at the Beijing Institute of Technology (P. R. of China) recently proposed an interval full-nitro-nitroamino cooperative strategy to design an unprecedented type of fully nitrated benzene, 1,3,5-trinitro-2,4,6-trinitroaminobenzene (TNTNB, Scheme 1), by replacing three interval nitro groups of HNB with three nitroamino groups. “After we designed the target molecule, the synthesis of TNTNB was then explored,” ex-

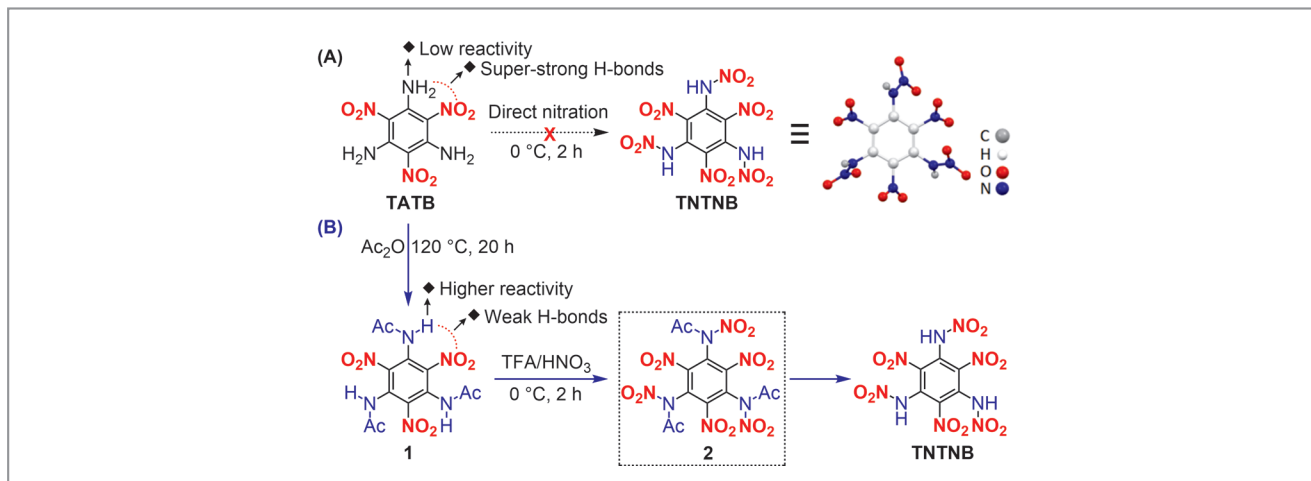
plained Professor Pang. He continued: “However, the most direct method, that is the one-step nitration of amino groups in 1,3,5-trinitro-2,4,6-triaminobenzene (TATB), failed to give TNTNB. This is mainly due to the strong intramolecular H-bonds which passivate the amino groups of TATB, resulting in low reactivities.”

Accordingly, the group believed that the key to accomplishing the nitration of TATB was to enhance the activity of the inert amino groups. Thus, an acylation–activation–nitration method was proposed. Professor Pang said: “In this method, a highly reactive acetylation reagent – acetic anhydride – was employed to activate and acetylate TATB to produce acetamide **1** (Scheme 2). X-ray data indicated that the large acetyl groups successfully destroy the strong H-bonds in TATB and improve the reactivity of the amino groups. Acetamide **1** was then treated with TFA/HNO₃ to successfully give TNTNB, which was structurally confirmed by single-crystal X-ray diffraction. It should be noted that TNTNB is only the second known hexanitro-containing benzene derivative. Moreover,” continued Professor Pang, “TNTNB was successfully synthesized through an amino–acylation–nitration method, effectively addressing the longstanding problem of the unsuccessful nitration of inert TATB since it was first prepared in 1888. It also confirms that the acylation–activation–nitration method can be an effective tool to activate and nitrate inert amino compounds and prepare more high-performing energetic materials in the future.”

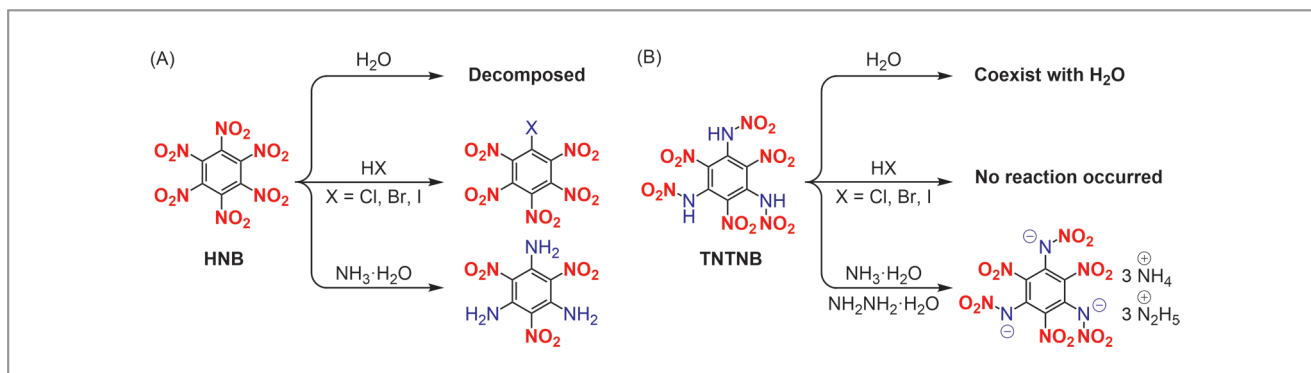
In addition, the authors emphasized that TNTNB exhibits very promising energetic performance. “Especially, its high heat of detonation ($Q = 7179 \text{ kJ kg}^{-1}$), which is even higher



Scheme 1 The state-of-the-art of nitrobenzenes and the design of TNTNB using a full-nitro-nitroamino cooperative strategy.



Scheme 2 (A) Failed synthesis of TNTNB. (B) Successful synthesis of TNTNB using the acylation–activation–nitration method.



Scheme 3 Chemical stability of HNB and TNTNB with water, acids, and bases, respectively.

than those of the state-of-the-art explosives HNB ($Q = 6993 \text{ kJ kg}^{-1}$) and CL-20 ($Q = 6534 \text{ kJ kg}^{-1}$), renders TNTNB a new energy peak for organic explosives. TNTNB also exhibits better water, acid, and base stability than HNB (Scheme 3),” said Professor Pang, who concluded: “Moreover, its acidic characteristics facilitate the formation of energetic salts, effectively improving the thermal stability of TNTNB. This will allow the preparation of diverse energetic derivatives.”

Mattias Fomok

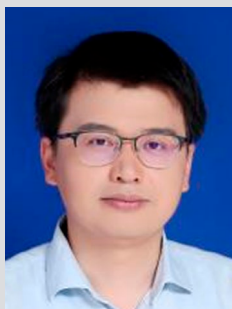
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