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Azo-bridged triazoles: Green energetic materials

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Abstract

In this short review, excerpts from the literature of azo-bridged triazoles (mainly 1,2,4-triazoles), some of their derivatives (chloromethyl, dinitro and trinitro pyrazole substituted ones, etc.) and some of their salts, have been presented focusing on the most recent investigations. These classes of compounds, known as high nitrogen compounds, are generally high energy density materials. Therefore, if available some of their ballistic properties were included.

Keywords: Azo-bridged; Triazoles; Energetic materials; High nitrogen compounds

1. Nitrogen-rich compounds

A novel approach in the field of energetic materials is to replace some conventional explosives with high-nitrogen compounds. These materials possess a higher proportion of nitrogen by mass, as compared to conventional explosives, so that they derive their energy output from this factor, in contrast to the redox reactions of fuel elements (carbon, hydrogen) as in the case of classical ones. When overall properties are considered, insensitivity toward destructive stimuli is also an important criterion for energetic materials. However, most azido-functionalized compounds which generally possess high destructive power are sensitive to heat, impact, and friction. Hence, they are difficult to handle safely which is a great restriction for their further applications. Thus, the conflict between high energy and inherent instability of nitrogen-rich compounds requires a deeper understanding of the factors involved structurally and thermodynamically and consequently makes this research area challenging. After many decades of effort in the development of high-energy materials, the key concerns in weapon systems remain to be higher performance and lower sensitivity. Nowadays, the most desirable characteristics for new energetic materials include high positive heat of formation, high density, pressure and high detonation velocity, but high thermal stability and low sensitivity toward external forces such as mainly impact, shock, and friction. High-nitrogen compounds (e.g., azoles) in combination with energetic substituents such as nitro ($—NO_2$), nitrato ($—ONO_2$), nitramine ($—NHNO_2$), and nitroimine ($=NNO_2$) functionalities are of particular interest because these compounds additionally have satisfactory oxygen content. In high-nitrogen compounds, nitrogen gas (N_2) is the major product of explosion; they burn more cleanly than other organic explosives, meanwhile producing less carbon monoxide, soot and other incompletely oxidized toxic explosive residues (e.g., CO, NO, etc.). However, the requirements of insensitivity and high energy along with positive oxygen balance are most of the time contradictory to each other; hence, the development of new high energy density materials (HEDMs) is an interesting and challenging problem but difficult due to some synthetic handicaps.

Highly energetic compounds characterized by the presence of polynitro groups are one of the important classes of useful energetic materials. The involvement of nitro groups in structures generally tends to decrease the heat of formation but contributes markedly to the overall energetic performance. Also, the nitro group contributes to enhance the oxygen balance and density of the material, which are important in order to improve the detonation performance (pressure and velocity) [1–6]. Traditional polynitro compounds produce energy primarily from the combustion of the carbon backbone while consuming the oxygen provided by the nitro groups (inter or intramolecular redox reactions) (Fig. 1). Several well known explosives are triaminotrinitro benzene (TATB), 1,3,5,-trinitrotriazacyclohexane (RDX), 1,3,5,7-tetranitrotetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro

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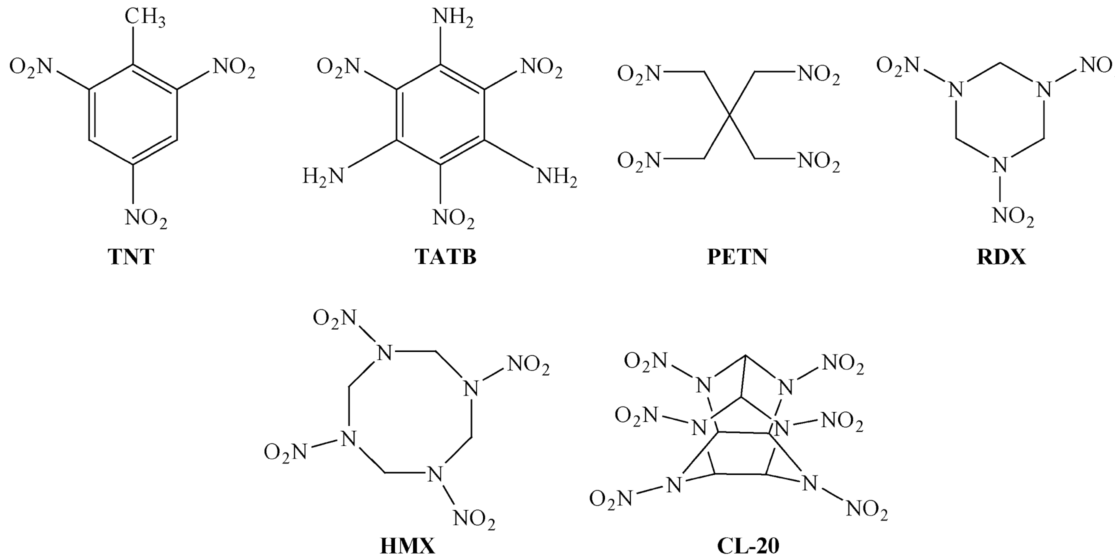

Fig. 1. Traditional energetic polynitro compounds.

-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20) (Fig. 1). High-energy materials possessing several numbers of nitrogen atoms, so-called "high-nitrogen" compounds, have been shown to derive energy from the presence of many energetic N—N and C—N bonds.

Material scientists, interesting in energetic materials, are after high-energy density compounds with high detonation properties and low sensitivities [1–6]. Polynitropyrazole families, such as 3,4-dinitropyrazole, 3,5-dinitroprazole, 4-amino-3,5-dinitropyrazole, and 3,4,5-trinitropyazole, have been widely used in the development of energetic materials because they have good thermal stabilities, moderate detonation properties, and low friction and impact sensitivities [7–11]. Unfortunately, because of their acidity and water sensitivity, they have no use in the daily energetic world, unless the corresponding conjugate bases are used [12].

2. High-energy nitrogen-rich compounds

Certain classes of nitrogen-rich compounds are the most promising candidates for high energy density materials (HEDM), as they are environmentally benign and possess high energy density [9,13–24]. 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 mainly due to the high positive heat of formation which is the unique feature of energetic compounds containing catenated N—N bonds. Recently, some energetic azo compounds containing eight-nitrogen and ten-nitrogen chains have been prepared and characterized (Fig. 2) [25–28].

In the field of high-energy materials research, nitrogen-rich compounds based on C/N heteroaromatic rings with high-nitrogen content are at the forefront [21–28]. Recently, the combination of an azo group with high-nitrogen heteroaromatic rings has been extensively studied. The azo linkage not only desensitizes but also dramatically increases the heat of formation of high-nitrogen compounds such as DAAT (**5**) and TAAT (**6**) (Fig. 3), in which the azo group is bonded to carbon [29,30]. Such azo compounds (e.g., azobenzene-based compound **7**) [31] are well known as diazoic dyes and thermally reversible

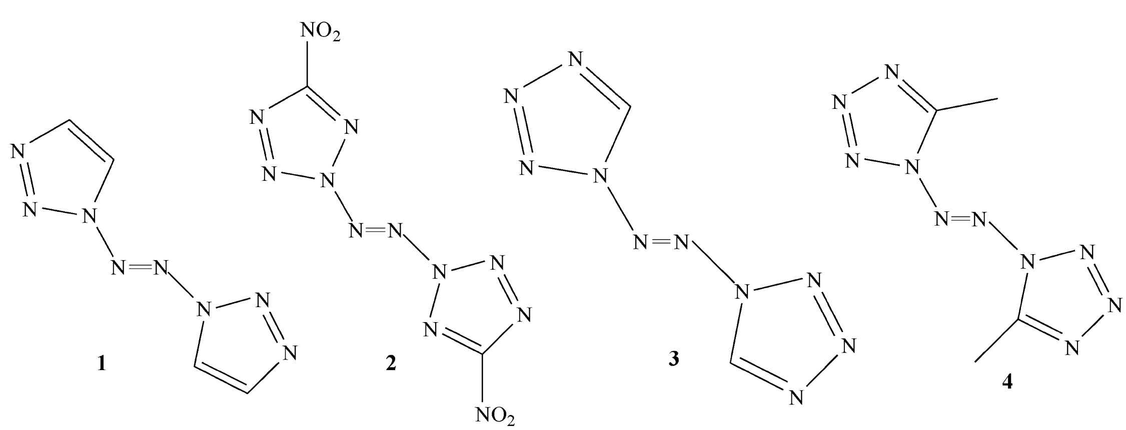

Fig. 2. Some energetic azo compounds.