Nitrogen-Rich Energetic Salts: Both Cations and Anions Contain Tetrazole Rings

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Nitrogen-rich compounds are a kind of new type of energetic material and have good application prospects. They generally have high densities, high positive heats of formation, good thermal stability, and a series of excellent properties. Nitro-rich energetic salts in which cations and anions contain tetrazole rings possess more N=N and C-N bonds. These can help the salts achieve better performance. Their distinct advantages make them attractive for applications in gas generators and high-energy-density materials and as propellant additives.

Keywords: anion, cation, nitrogen-rich energetic salts, tetrazole ring

INTRODUCTION

The synthesis of nitrogen-rich heterocyclic compounds has received increasing interest in recent years. The presence of N=N and C-N bonds in nitrogen-rich compounds confers high positive heats of formation and form a large amount of hydrogen bonds, which help them to gain low sensitivities, good thermal stabilities, and relatively high densities. These distinct advantages of nitrogen-rich compounds compared to traditional carbon-based energetic materials (e.g., 2,4,6-Trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)) give them attractive application prospects in gas generators, high-energy-density materials, and propellant additives.

5-Aminotetrazole (5-AT; Thiele 1893, 1898; Thiele and Marais 1893), which was first prepared by Thiele in 1893, has a nitrogen content of almost 82.3%. 1,5-Diaminotetrazole (DAT; Stollé and Gaertner 1931; Raap 1969; Caponik and Karavai 1984; Gálvez-Ruiz et al. 2005; Joo et al. 2008) has a higher nitrogen content of 84%. These two compounds exhibit relatively high thermal stabilities due to their aromatic structure. Both can be used as starting materials for preparing tetrazole-based compounds. The cations or anions that contain tetrazole rings have been extensively studied as energetic moiety of energetic salts because of their high nitrogen contents and good properties (Figures 1 and 2). All of these ions can be prepared from 5-AT or DAT.

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5-AT and DAT both can react with strong acids to form corresponding tetrazolium cations. The methyl group can be readily brought in by quaternization using iodomethane to generate methyl tetrazolium cations. The nitrotetrazolate (Klapötke et al. 2008a) and 1-methyl-5-nitriminotetrazolate (Klapötke, Stierstorfer, and Wallek 2008) cations have relative stabilities contrasting to their neutral molecules, which is beneficial to improving the densities and oxygen balances of energetic salts. Tetrazolium salts can be used as the starting material for the synthesis of energetic salts by metathesis reactions.

The most research interest in energetic salts that have the structure of bistetrazole in anions lies in 5,5'-1 H-bistetrazole (BHT; Ye et al. 2005; Guo et al. 2010), bis(tetrazoyl-5-yl)-amines (BTA; Ye et al. 2005; Klapötke et al. 2008b; Guo et al. 2010), 5,5'-azotetrazole (ZT; Thiele 1898; Hiskey, Goldman, and Stine 1998; Hammerl et al. 2001, 2002, 2005; Ye et al. 2005; Klapötke and Sabaté 2008, 2009; Y. H. Wang et al. 2008;), and 5,5'-hydrazine-1,2-diylbis (tetrazole) (HBT; Klapötke and Sabaté 2007, 2008; Eberspächer, Klapötke, and Sabaté 2009a; 2009b; Karaghiosoff, Klapötke, and Sabaté 2009). Disodium 5,5'-azo-tetrazolate pentahydrate (1) was first synthesized by Thiele in 1898 through an oxidizing reaction of 5-AT with potassium permanganate under basic conditions (Scheme 1). 5,5'-Azotetrazolate anion (ZT$^{2-}$) has a nitrogen content of 85.4%. 1 is an important intermediate compound for synthesis of metal (Hammerl et al. 2002) and nonmetal azotetrazolate salts (Hammerl et al. 2005). These salts usually have high nitrogen contents and are expected to possess reasonable sensitivities. Therefore, ZT$^{2-}$ has gained a lot interest from researchers. Recently, the preparation of HBT was reported (Klapötke and Sabaté 2007). This compound possesses good thermal stability and high detonation velocity in contrast to 5,5-azotetrazole, which is stable at temperatures below −30°C in methanol solution (Klapötke and Sabaté 2008). The corresponding metal salts can be obtained by reactions of HBT with metal hydroxide in a nitrogen atmosphere (Karaghiosoff, Klapötke, and Sabaté 2009). HBT$^{2-}$ salts with ammonium, hydrazinium, and guanidinium are found to have high detonation parameters and insensitive properties (Eberspächer, Klapötke, and Sabaté 2009b).

Most tetrazole energetic salts are received from the reaction of two different compounds. One case is that the cations are tetrazolium-based and anions are inorganic like nitrate, dinitramide, perchlorate, and azido groups. The other case is that anions are tetrazolate-based and cations are multi-amino compounds such as ammonium, guanidium, aminoguanidium, diamino- or triaminoguanidium, etc. These energetic salts exhibit novel properties of high density, high positive heats of formation, and high thermal stability. Many of them are potential candidates for high-energy-density materials. However, little literature exists on the energetic salts consisting of tetrazolium cations and tetrazolate anions.

In this context, we intended to synthesize the energetic salts whose cations and anions both contain tetrazole rings. These salts may have some distinct properties including high nitrogen

\[
\begin{align*}
\text{NaOH, H}_2\text{O} & \quad \text{KMnO}_4 & \quad \text{Na}^+ \\
\text{5H}_2\text{O} & \quad \text{Na}^+ \\
\end{align*}
\]

**SCHEME 1** Synthesis of disodium azotetrazole.
content, high nitrogen atom numbers, high positive heats of formation, thermal stability, and environmental friendliness. Tetrazole energetic salts reported in the literature were commonly alternatively prepared through metathesis reactions of their silver salts with halogenide salts or barium salts with sulfate salts. However, silver tetrazolate salts always have poor stability and high sensitivity for stimulation, which might not be safe as the starting materials (Gao et al. 2007). Barium tetrazolate salts possess relatively good stability and low sensitivity. However, water molecules exist in these compounds. With all this in mind, we firstly prepared the tetrazole-based sulfate and barium tetrazole-based intermediates. Then metathesis reactions were used to attempt to prepare the expected energetic salts.

RESULTS AND DISCUSSION

DAT was synthesized according to the method reported by Gálvez-Ruiz et al. (2005). Both 5-AT and DAT were readily protonated by concentrated HCl to form 5-aminotetrazolium hydrochloride (2) and 1,5-diaminotetrazolium hydrochloride (3). 4-Methly-1,5-diaminotetrazolium cation could be obtained through a quaternization reaction of DAT with iodomethane. Compounds 4–6 were prepared in high yields by reaction of silver sulfate with corresponding tetrazolium halogenic salts (Scheme 2). A new method to prepare sodium 5,5ʹ-azotetrazolate pentahydrate (1) using bromine instead of potassium permanganate as the oxidizer was found by our research group (H. S. Wang 2005). This method avoided generating manganese dioxide and afforded a consideration of preparing azolate salts through a “one-pot” method. Barium 5,5ʹ-azotetrazolate pentahydrate (7) could be synthesized following the literature (Hammerl et al. 2002). The reflux reaction of 7 and magnesium powder in aqueous solution under a stream of nitrogen could generate barium.
5,5’-hydrazine-1,2-diylbis (tetrazolate) pentahydrate (8) (Scheme 2). An attempt was made to prepare energetic salts of 9–14 by metathesis reactions of the obtained barium compounds with corresponding sulfate as shown in Scheme 3. All of the salts relating to HBT$^{2-}$ should be prepared under the protection of nitrogen.

During the process of preparing energetic salts of 9 and 10, a gas release was observed. 5-AT or DAT was found in the product after working up the reaction. When attempting to prepare 12 and 13, 5-AT or DAT with HBT were found in the final products. These might be caused by the weak acidity and basicity of cations or anions. The expected energetic salts were unstable and easily decomposed to the starting materials (Scheme 3). Energetic salts 11 and 14 were prepared by using 6 reacting with one molar equivalent of 7 and 8 in aqueous solution in a short time.

Compound 5 crystallizes in the monoclinic space group $P2_1/c$. The unit cell consists of two tetrazolium cations and one sulfate anion. The crystallographic data and structure refinement parameters are listed in Table 1. The bond angles and distances together with structure and packing diagram figures for 5 can be found in the Supporting Information. The bond lengths and angles in tetrazolium cation are very similar to other tetrazolium salts (Karaghiosoff et al. 2008).

The crystal structure of compound 11 has been analyzed according to Klapötke’s research (Klapötke and Sabaté 2008). 11 crystallizes in a triclinic system and space group $P$ with $Z = 1$. All of the atoms of ZT anions are coplanar. After the azo bond in 11 was converted to a hydrazino group to form 14 (Han et al. 2014), obvious changes were observed from the crystal structure. Being different from 11, salt 14 crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Tables 2 and 3 show the selected bond lengths and angles in cations and anions for 11 and 14. The N-N distances for salts 11 and 14 are between 1.270(3) and 1.449(3) Å (N-N distance in HN = NH and H$_2$N-NH$_2$ are 1.252 and 1.449 Å, respectively). C-N distances are between 1.305(2) and 1.454(3) (C-N distances in H$_2$C = NH and CH$_3$-NH$_2$ are 1.273 and 1.471 Å, respectively). The bond lengths and angles of 14 are similar to those of 11 with the exception of the link bridge distance to two tetrazole rings of anions, which are 1.250(3) and 1.412 (2) Å. Angle variations ranging from 2.65° (N10-C2-N6) to 6.35° (N4-C1-N5) were observed in the anion. As we know from the literature, all atoms in ZT$^{2-}$ anions are approximately coplanar; when the azo bond of ZT$^{2-}$ was converted to the hydrazino group to form HBT$^{2-}$, two tetrazole ring planes of HBT$^{2-}$ are proved to form two approximately perpendicular planes (89.72°). A structure and packing diagram of 14 is shown in Figures 1 and 2. The greatest difference from the geometric structure of 11 is that the two MeDAT$^{+}$ cation rings in 14 are nearly parallel to

![Scheme 3](image-url)
the two tetrazole planes of HBT\(^2\)\(^-\) (the dihedral angles are 10.43\(^\circ\) and 2.64\(^\circ\), respectively). This indicates the existence of \(\pi-\pi\) stacking interactions, which help to stabilize the structure.

The existence of a large number of C-N and N-N bonds help to form a large number of hydrogen bonds. Table 4 shows the hydrogen bond geometry of 11 and 14. Salt 11 usually contains two water molecules, which is beneficial for forming hydrogen bonds and layer structures. The absence of crystal water results in nonlayered structures and a decreasing number of hydrogen bonds. Salt 14 does not have crystal water but forms more hydrogen bonds in contrast to 11. All atoms in HBT\(^2\)\(^-\) anions except two C atom have been shown to form hydrogen bonds, which is different from the condition of the ZT\(^2\)\(^-\) anion in 11.

The stabilities and melting points of salts 2–8, 11, and 14 were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis, respectively. All of the salts show good stability.
Compounds 11 and 14 both give rapid decomposition without melting at around 177 and 192°C. Their weight losses are 76.92 and 95.29% from the TG curves. 14 shows higher stability than 11, because more atoms form hydrogen bonds in HBT$^-$ anions from the crystal structures.

The heat of formation is an important characteristic for energetic salts. All ab initio calculations were carried out using Gaussian 98 (Sheldrick 1997). Geometric optimization of the structures and frequency analyses were performed using the B3LYP with the 6-31G** basis set and single-point energies were calculated at the MP2(full)/6−311++G** level. Heats of formation of the simple cations or anions such as tetrazole cations or anions were determined using atomization

| Bond | 11° | 14° | Angle | 11° | 14° |
|------|-----|-----|-------|-----|-----|
| N1-C1 | 1.336(3) | 1.330(2) | C1-N1-N2 | 103.6(2) | 103.17(13) |
| N1-N2 | 1.333(3) | 1.356(2) | N3-N2-N1 | 109.9(2) | 110.55(14) |
| N2-N3 | 1.322(3) | 1.309(2) | N2-N3-N4 | 109.7(2) | 109.10(14) |
| N3-N4 | 1.336(3) | 1.355(2) | C1-N4-N3 | 104.0(2) | 103.85(14) |
| N4-C1 | 1.339(3) | 1.337(2) | N4-C1-N5 | 129.8(2) | 123.45(16) |
| N5-C1 | 1.415(3) | 1.397(2) | N1-C1-N5 | 112.8(2) | 113.32(16) |
| N5-N6 | 1.250(3) | 1.412(2) | N1-C1-N5 | 117.4(2) | 123.13(16) |
| N6-C2 | 1.399(3) | 1.381(2) | C1-N5-N6 | 112.4(2) | 112.97(14) |
| N7-C2 | 1.332(3) | 1.335(2) | C2-N6-N5 | 113.3(2) | 118.58(15) |
| N7-N8 | 1.336(3) | 1.360(2) | N7-C2-N6 | 127.3(2) | 123.50(16) |
| N8-N9 | 1.324(3) | 1.307(2) | C2-N7-N8 | 104.4(2) | 103.44(14) |
| N9-N10 | 1.337(3) | 1.353(2) | N9-N8-N7 | 109.6(2) | 109.58(14) |
| N10-C2 | 1.344(3) | 1.332(2) | N8-N9-N10 | 109.7(2) | 110.10(14) |

| Bond | 11° | 14° | Angle | 11° | 14° |
|------|-----|-----|-------|-----|-----|
| N11-C3 | 1.343(3) | 1.341(2) | C3-N11-N12 | 109.5(2) | 109.96(14) |
| N11-N12 | 1.366(3) | 1.366(2) | C3-N11-C4 | 128.4(2) | 127.67(14) |
| N11-C4 | 1.454(3) | 1.455(2) | N12-N11-C4 | 122.0(2) | 122.11(14) |
| N12-N13 | 1.270(3) | 1.270(2) | N13-N12-N11 | 108.0(2) | 108.24(14) |
| N13-N14 | 1.361(3) | 1.361(2) | N12-N13-N14 | 108.2(2) | 107.95(14) |
| N14-C3 | 1.343(3) | 1.350(2) | C3-N14-N13 | 109.5(2) | 110.10(14) |
| N14-N15 | 1.449(3) | 1.387(2) | C3-N14-N15 | 128.4(2) | 129.86(15) |
| N16-C3 | 1.312(3) | 1.305(2) | N13-N14-N15 | 122.1(2) | 119.93(14) |

| Bond | 11° | 14° | Angle | 11° | 14° |
|------|-----|-----|-------|-----|-----|
| N11-C3 | 1.343(3) | 1.341(2) | C3-N11-N12 | 109.5(2) | 109.96(14) |
| N11-N12 | 1.366(3) | 1.366(2) | C3-N11-C4 | 128.4(2) | 127.67(14) |
| N11-C4 | 1.454(3) | 1.455(2) | N12-N11-C4 | 122.0(2) | 122.11(14) |
| N12-N13 | 1.270(3) | 1.270(2) | N13-N12-N11 | 108.0(2) | 108.24(14) |
| N13-N14 | 1.361(3) | 1.361(2) | N12-N13-N14 | 108.2(2) | 107.95(14) |
| N14-C3 | 1.343(3) | 1.350(2) | C3-N14-N13 | 109.5(2) | 110.10(14) |
| N14-N15 | 1.449(3) | 1.387(2) | C3-N14-N15 | 128.4(2) | 129.86(15) |
| N16-C3 | 1.312(3) | 1.305(2) | N13-N14-N15 | 122.1(2) | 119.93(14) |

*Data from Klapötke and Sabaté (2008).
energies at the G2 level. The whole optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Isodesmic reactions were designed to obtain the heats of formation of cations and anions (Schmidt, Gordon, and Boatz 2005). The enthalpy of isodesmic reaction ($\Delta H_{298}^\circ$) was obtained by combining the MP2/6–311+ +G** energy difference for the reaction, the scaled zero-point (B3LYP/6-31 + G**), and other thermal factors (See Supporting Information).

FIGURE 1 Tetrazole-based cations and anions (Cat = cation; An = anion).

FIGURE 2 (a) Molecular structure of 14 (thermal displacement at 50% probability). Hydrogen atoms are shown. (b) Packing diagram of 14 (viewed down the a axis). Dashed lines indicate hydrogen bonding.
The heats of formation for salts \(2\)–\(6\), \(11\), and \(14\) were calculated by Born-Haber energy cycles (Figure 3). Heats of formation of salts could be obtained through the formula (1):

\[
\Delta H^0_f(\text{inoic salt, } 298K) = \Delta H^0_f(\text{cation, } 298K) + \Delta H^0_f(\text{anion, } 298K) - \Delta H_L.
\]

Table 4

| D-H···A   | D-H | H···A | D···A | D-H···A |
|-----------|-----|-------|-------|--------|
| 14        |     |       |       |        |
| N5-H5 N···N7\(^i\) | 0.88(2) | 2.26(2) | 3.134(2) | 169.2(19) |
| N6-H6 N···N3\(^\text{ii}\) | 0.92(2) | 2.10(2) | 2.966(2) | 157.4(18) |
| N15-H15A···N1\(^\text{iii}\) | 0.89(2) | 2.48(2) | 3.190(2) | 136.9(18) |
| N15-H15B···N3 | 0.91(2) | 2.56(2) | 3.300(2) | 140.6(18) |
| N16-H16A···N2\(^\text{ii}\) | 0.92(2) | 1.94(2) | 2.837(2) | 166.1(19) |
| N16-H16B···N4\(^\text{iv}\) | 0.93(2) | 1.89(2) | 2.817(2) | 172(2) |
| N21-H21A···N15\(^\text{ii}\) | 0.88(2) | 2.34(2) | 3.197(2) | 164.4(19) |
| N21-H21B···N10\(^\text{ii}\) | 0.86(2) | 2.54(2) | 3.040(2) | 117.5(17) |
| N22-H22A···N9\(^\text{ii}\) | 0.94(2) | 1.91(2) | 2.843(2) | 173(2) |
| N22-H22B···N8\(^\text{v}\) | 0.90(2) | 1.99(2) | 2.878(2) | 167(2) |
| C4-H4B···N7\(^\text{vi}\) | 0.98 | 2.50 | 3.446(2) | 162 |
| C4-H4 C···N2\(^\text{vii}\) | 0.98 | 2.56 | 3.209(2) | 124 |
| 11\(^\text{a}\) |     |       |       |        |
| N16-H16A···N3\(^\text{viii}\) | 0.80(2) | 2.13(2) | 2.929(2) | 170(2) |
| N22-H6 N···N3\(^\text{viii}\) | 0.84(2) | 2.04(2) | 2.863(2) | 165(3) |
| N14-H14A···N1\(^\text{viii}\) | 0.95(3) | 1.95(3) | 2.884(3) | 167(2) |
| N14-H14A···N20\(^\text{viii}\) | 0.83(2) | 2.03(2) | 2.852(3) | 168(3) |

\(^a\)Data from Klapötke and Sabaté (2008).

Symmetry codes: (i) \(x-1, y, z\); (ii) \(-x+1, y-1/2, -z+3/2\); (iii) \(x+1, y, z\); (iv) \(-x+2, y+1/2, -z+3/2\); (v) \(x-1, -y-3/2, z-5/2\); (vi) \(x, y+1, z\); (vii) \(-x+1, y+1/2, -z+3/2\); (viii) \(1-x, 1-y, 1-z\).

The heats of formation for salts \(2\)–\(6\), \(11\), and \(14\) were calculated by Born-Haber energy cycles (Figure 3). Heats of formation of salts could be obtained through the formula (1):

\[
\Delta H^0_f(\text{inoic salt, } 298K) = \Delta H^0_f(\text{cation, } 298K) + \Delta H^0_f(\text{anion, } 298K) - \Delta H_L.
\]

\[
\text{Cat}^+ \text{An}^- \quad \text{Cat}^+ \quad \text{An}^- \quad \text{Cat}^+(\text{gas}) + \text{An}^-(\text{gas}) \quad \text{Cat}^+(\text{gas}) + \text{An}^-(\text{gas})
\]

\[
\Delta H^0_f(\text{Cat}^+) = \Delta H^0_f(\text{Cat}^+)(\text{gas}) + \text{mC(s)} + \text{nH}_2(\text{g}) + \text{oN}_2(\text{g}) + \text{pO}_2(\text{g}) + \text{qS(s)}
\]

\[
\Delta H_L
\]

\[
\Delta H^0_f(\text{An}^-) = \Delta H^0_f(\text{An}^-)(\text{gas})
\]

\[
\text{FIGURE 3 Born-Haber energy cycle for the formation of energetic salts (Cat = cation; An = anion).}
\]
The lattice energy of ionic salt \( \Delta H_L \) could be predicted by Jenkins, Tudela, and Glasser’s (2002) method (formula (2)), where \( U_{\text{POT}} \) is the lattice potential energy. \( n_M \) and \( n_X \) depend on the nature of the ions \( M^p_+ \) and \( X^q_- \), respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

\[
\Delta H_L = U_{\text{POT}} + \left[ p\left(n_M/2 - 2\right) + q\left(n_X/2 - 2\right) \right]RT.
\]

The lattice potential energy, \( U_{\text{POT}} \), can be calculated using Eq. (3):

\[
U_{\text{POT}}(\text{kJ mol}^{-1}) = \gamma(\rho_m/M_m)^{1/3} + \delta,
\]

where \( \rho_m \) is the density (g cm\(^{-3}\)), \( M_m \) is the chemical formula mass of the ionic material (g), and the coefficients \( \gamma \) (kJ mol\(^{-1}\) cm) and \( \delta \) (kJ mol\(^{-1}\)) are assigned literature values. The densities of salts 2, 4, and 6 were calculated according to the literature (Jenkins et al. 1999; Ye and Shreeve 2007).

The calculated heat of formation of \( \text{ZT}^2^- \) anions is 836.47 kJ mol\(^{-1}\) and that of \( \text{HBT}^2^- \) anions is 676.69 kJ mol\(^{-1}\). All of the tetrazole salts of 4, 5, 6, 11, and 14 exhibit positive heats of formation with respect to tetrazole molecule compounds. The calculated and experimental determined heats of formation of the tetrazole salts are presented in Table 5.

**TABLE 5**

Physical properties and thermochemical values of tetrazole-based salts

| Salts  | Cation | Anion     | \( T_m^a \) | \( T_d^b \) | \( d^c \) | N%\(^d\) | OB\(^e\) | \( \Delta H_{\text{cation}}^f \) | \( \Delta H_{\text{anion}}^g \) | \( \Delta H_{\text{L}}^h \) | \( \Delta H(298 \text{K})^i \) | Impact\(^j\) | Friction\(^j\) |
|--------|--------|-----------|-------------|-------------|---------|--------|--------|----------------|----------------|----------------|----------------|-----------|-----------|
| 2      | 5-AT\(^+\) | Cl\(^-\) | —           | —           | 1.577   | 57.6   | —      | 984.97        | -230.3          | 570.6          | 184.07          | —         | —         |
| 3      | DAT\(^+\) | Cl\(^-\) | 161.9       | 248.9       | 1.706   | 61.5   | -46.9  | 1042.56       | -230.3          | 564.74         | 247.52          | —         | —         |
| 4      | 5-AT\(^+\) | SO\(_4^{2-}\) | 167.0       | 1.761       | 52.2    | -69.7  | 984.97 | -585          | 1396.99         | -12.05         | —         | —         |
| 5      | DAT\(^+\) | SO\(_4^{2-}\) | 170.9       | 189.1       | 1.808   | 56.4   | -37.5  | 1042.56       | -585           | 1355.76        | 144.36          | —         | —         |
| 6      | MDAT\(^+\) | SO\(_4^{2-}\) | 144.3       | 196.5       | 1.667   | 51.5   | -63.8  | 998.74        | -585           | 1271.45        | 141.03          | —         | —         |
| 11     | MDAT\(^+\) | ZT\(_2^-\) | —           | 176.8       | 1.427   | 78.2   | -71.7  | 998.74        | 801.44           | 1144.77       | >30       | >360      |
| 14     | MDAT\(^+\) | HBT\(_2^-\) | 192.3       | 1.660       | 77.8    | -80.7  | 998.74 | 721.32         | 1178.65         | 1540.15       | >40       | >360      |

\(^a\)Melting point from measurement with \( \beta = 5^\circ \text{C min}^{-1} \) (°C).

\(^b\)Decomposition point (DSC onsets) from measurement with \( \beta = 5^\circ \text{C min}^{-1} \) (°C).

\(^c\)Density; salts 2, 4, 6 were calculated from empirical methods (Jenkins et al. 1999; Ye and Shreeve 2007) and others from X-ray.

\(^d\)Nitrogen content.

\(^e\)Oxygen balance.

\(^f\)Calculated molar enthalpy of formation of cations (kJ mol\(^{-1}\)).

\(^g\)Calculated molar enthalpy of formation of anions (kJ mol\(^{-1}\)).

\(^h\)Calculated molar lattice energy (kJ mol\(^{-1}\)).

\(^i\)Calculated molar enthalpy of formation of salts (kJ mol\(^{-1}\)).

\(^j\)Tests according to BAM (impact: J; friction: N).
EXPERIMENTAL SECTION

Caution

All of the nitrogen-rich compounds we used are energetic materials and tend to explode under certain conditions. Appropriate safety precautions should be taken when preparing.

General Methods

Infrared (IR) spectra were recorded with KBr plates using a Nicolet 6700 FTIR spectrometer (Madison, WI, USA). $^1$H-NMR spectra were recorded using a Bruker ARX400 spectrometer (Switzerland) at 400 Hz using $d_6$-DMSO as the solvent. Chemical shifts are reported in parts per million relative to tetramethylsilane (TMS). Element analyses were determined using a Vario EL elemental analyzer (Germany). DSC data were recorded by heating from 50 to 400°C at 5°C min$^{-1}$ using a differential scanning calorimeter (Q600SDT, TA Instruments Company, New Castle, DE, USA) in a dynamic nitrogen atmosphere (flow rate = 100 mL min$^{-1}$).

X-ray Crystallography

A colorless crystal of 14, 0.37 mm × 0.20 × 0.10 mm in size, was obtained for the X-ray diffraction study. Data were collected by a Rigaku diffractometer equipped with a Saturn 70 CCD using graphite monochromatic Mo Kα radiation ($\lambda = 0.071073$ nm) at 103(2) K in the $\varphi$ and $\omega$ scan modes.

Unit cell parameters were measured by least-squares methods in the range of $3.0^\circ < \theta < 27.5^\circ$. The structure was solved by the direct methods using SHELXS-97 and refined by means of full-matrix least-squares procedures on $F^2$ with the SHELXL-97 program. The H atoms bonded to N were located in difference Fourier maps and the H atoms bonded to C were placed in calculated positions, with C-H = 0.98 Å; all hydrogen atoms were included using a riding model.

CCDC 779222 (14) and 779223 (5) contain the supplementary crystallographic data for this article; these can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.cam.ac.uk/data_request/cif.

Sodium Azotetrazole Pentahydrate (1)

A mixture of NaOH (20.04 g, 0.5 mol) and 5-aminotetrazole monohydrate (10.32 g, 0.1 mol) was stirred and dissolved in H$_2$O (120 mL) at 60°C and then bromine (0.22 mol) was slowly added to the mixture. The obtained solution was stirred for 30 min at 60°C and then anhydrous sodium sulfite was added until the color of the solution became glassy yellow. After evaporating most of the water, the mixture was cooled to room temperature and transferred to a refrigerator for crystallization. The product was obtained by filtration and washed thoroughly with cold water (12.48 g, 83.2%).
General Procedure for 2–5

5-Aminotetrazolium hydrochloride (2) and 1,5-diaminotetrazolium hydrochloride (3) were prepared according to Denffer, Klapötke, and Sabaté (2008). 5-AT or DAT was suspended in methanol and reacted with an excess of (37%) hydrochloric acid. The reaction mixture was heated to reflux. 5-Aminotetrazolium sulfate (4) and 1,5-diaminotetrazolium sulfate (5) were obtained by metathesis reactions of silver sulfate with 2 or 3, respectively.

**DATC (3)**

Yield 81.15%; white solid; M.p.: 161.9°C; elemental analysis calcd. (%) for CH$_5$N$_6$Cl (136.5): C 17.73 (17.71), H 3.58 (3.69), N 61.86 (61.99); MS (EI, 70Ev): m/z = 100.0 [DATC]$^+$, m/z = 36.0 [HCl$^+$]; IR (KBr): ν = 3313, 3277, 3251, 3163, 3068, 1724, 1620, 1578 cm$^{-1}$; $^1$H-NMR (400 MHz, [D6] DMSO): δ = 7.84 ppm (br. s, 1 H; NH).

**5-ATS (4)**

Yield 95.51%; M.p.: 167.07°C; MS (EI, 70Ev): m/z = 269.0 [M + H]$^+$; IR (KBr): ν = 3373, 3296, 3256, 1697, 1647 cm$^{-1}$; $^1$H NMR (400 MHz, [D6] DMSO): δ = 9.87 ppm (br. s, 1 H; NH).

**DATS (5)**

Yield 96.59%; M.p.: 170.9°C; white solid; elemental analysis calcd. (%) for C$_2$H$_{10}$N$_{12}$SO$_4$ (298.0): C 8.12 (8.05), H 3.23 (3.26), N 56.39 (56.38); MS (EI, 70Ev): m/z = 100.0 [DATS]$^+$, m/z = 64.0 [SO$_2^+$], m/z = 48.0 [SO$^+$]; IR (KBr): ν = 3338, 3294, 3273, 3194, 3085, 1720, 1619 cm$^{-1}$; $^1$H-NMR (400 MHz, [D6] DMSO): δ = 6.98 ppm (br. s, 1 H; NH).

**4-Methyl-1,5-Diaminotetrazolium Sulfate (6)**

1,5-Diaminotetrazolium iodide was obtained by quaternization reaction of DAT with MeI. 1,5-Diaminotetrazolium iodide (4.84 g, 20 mmol) was dissolved in 10 mL of H$_2$O at 80°C and Ag$_2$SO$_4$ (3.10 g, 10 mmol) was added and the mixture was stirred for 30 min in the dark. After removal of AgI, the solvents were evaporated in a rotary evaporator with a pressure of −0.1 MPa; the residue was washed with 3 × 5 mL EtOH and the product was obtained (3.07 g, 94.40%). White solid; M.p.: 144.3°C; MS (EI, 70Ev): m/z = 327.0 [M + H]$^+$; IR (KBr): ν = 3446, 3223, 3122, 3047, 2839, 1699, 1632, 1616, 1520 cm$^{-1}$; $^1$H-NMR (400 MHz, [D6] DMSO): δ = 8.1473 (br. s, 2 H; 5-NH$_2$), 6.5793 (br. s, 2 H; 1-NH$_2$), 6.5792 (br. s, 2 H; 1-NH$_2$), 3.8487, 3.6722, 5.6675, 3.6242, 3.6190, 3.4907 ppm (br. s, 3 H; 4-CH$_3$).
Barium 5,5’-Azotetrazolate Pentahydrate (7) and Barium 5,5’-Hydrazine-1,2-Diylibis (Tetrazolate) Pentahydrate (8)

7 was prepared following a literature synthesis. Compound 7 (6.04 g, 20 mmol) was suspended in 250 mL H₂O and reacted with magnesium powder (4.80 g 200 mmol) under a stream of nitrogen. The reaction mixture was refluxed for 3.5 h when the solution turned colorless. Then the hot mixture was filtered under the protection of nitrogen. This procedure should be very quick to prevent the filtrate from being oxidized by oxygen, and then the filtrate was precipitated in refrigerator under a nitrogen atmosphere for 3 h. Colorless crystals were collected and allowed to dry in nitrogen (5.87 g, 74.66%). White crystal; M.p.: 162–164°C (dec.); elemental analysis calcd. (%) for C₂H₁₂BaN₁₀O₅ (393): C 6.16 (6.09), H 3.02 (3.07), N 35.59 (35.54); MS (FAB−, xenon, 6 keV): m/z = 167.0 [C₂H₃N₁₀]−; IR (KBr): ν = 3394, 3253, 2260, 2150, 1637, 1533, 1450, 1350, 1236, 1219 cm⁻¹; ¹H-NMR (400 MHz, [D₆] DMSO): δ = 7.84 ppm (br. s, 1 H; NH).

Bis(4-Methyl-1,5-Diaminotetrazolium)-5,5’-Azo-Tetrazolate Dihydrate (11 · 2H₂O)

Compound 7 (3.93 g, 10 mmol) and compound 6 (3.26 g, 10 mmol) were stirred in 100 mL H₂O at 50°C for 5 min and barium sulfate was filtered off and then the filtrate was dried with air. Orange flaky crystals (4.20 g, 97.8%) were obtained. M.p.: 176.8°C (dec.); MS (EI, 70Ev): m/z = 395.0 [M + H]+; IR (KBr): ν = 3375, 3280, 3180, 3035, 2968, 1710, 1670 cm⁻¹; ¹H-NMR (400 MHz, [D₆] DMSO): δ = 8.99, 8.53 (br. s, 2 H; 5-NH₂), 6.94 (br. s, 1 H; 1-NH₂), 3.81 ppm (br. s, 3 H; 4-CH₃);

Bis(4-methyl-1,5-diaminotetrazolium)-5,5’-hydrazine-1,2-diylbis(tetrazolate) (14)

Compound 8 (0.79 g, 2 mmol) and compound 6 (0.66 g, 2 mmol) were added to a three-necked bottle and then 30 mL H₂O was added under a stream of nitrogen. The reaction mixture was stirred for 5 min at 50°C and barium sulfate was filtered off under a nitrogen atmosphere. The solvents were evaporated in vacuo. The product was washed with cold EtOH and dried in vacuo. White crystals (0.71 g, 89.9%) were obtained. M.p.: 192.3°C (dec.); MS (EI, 70Ev): m/z = 397.0 [M + H]+; IR (KBr): ν = 3307, 3244, 3174, 3030, 2843, 1709, 1657, 1616 cm⁻¹; ¹H-NMR (400 MHz, [D₆] DMSO): δ = 8.37 (br. s, 2 H; NH-NH), 6.57 (br. s, 4 H; 1-NH₂, 5-NH₂), 6.57 (br. s, 4 H; 1-NH₂, 5-NH₂), 3.66 ppm (br. s, 3 H; 4-CH₃).

SUPPLEMENTAL DATA

Supplemental data for this article can be accessed at www.tandfonline/uegm.

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