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Nitrogen-Rich 4,4'-Azobis(1,2,4-triazolone) Salts—Synthesis and Promising Properties of a New Family of High-Density Insensitive Materials

Jiaping Zhu,[a] Shaohua Jin,[a] Li Wan,[a] Chunyuan Zhang,[a] Lijie Li,[a] Shusen Chen,[a] and Qinghai Shu,[a,*]

4,4′-azo-bis(1,2,4-triazolone) (ZTO) based salts from alkaline (Li⁺, K⁺, Na⁺, Cs⁺), alkaline earth metal salts (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) and hydrazinium salt were synthesized in a simple, straightforward manner and were characterized by IR, NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction of seven salts (Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, N₂H₅⁺) were also given. The X-ray structures show that in the title compounds, the metal atoms are bonded to the nitrogen and oxygen in the bistetrazole ring to form the sandwich structure. In addition, thermal stabilities of all title compounds were determined with thermogravimetric-differential thermal Analysis (TG-DTA). All these new materials exhibit excellent thermal stabilities, high density, acceptable detonation properties, and excellent insensitivity to impact (h_{50} > 60 cm). Especially, the barium, caesium and strontium salts are of great interest as potential high-density insensitive materials.

Introduction

High nitrogen content compounds (HNCs) have a large number of N–N and C–N bonds, and possess large positive heats of formation on them. The low percentage of hydrogen and carbon in these compounds are easy to achieve a good oxygen balance and produces more number of moles of gaseous products per gram.[1–5] Desirable characteristics for HNCs such as high heats of combustion, high specific impulse, high propulsive power, as well as smokeless combustion make them very useful as explosives, propellants, and pyrotechnics.[6–10] Along with the development of ionic liquids and their applications in energetic fields, nitrogen-rich heterocyclic halide-free energetic salts have gradually become a hot topic, as these salts are environmentally friendly high-energy-density materials (HEDMs), and they have attracted considerable interest due to the lower vapor pressures, higher heats of formation, enhanced thermal

stabilities, and readily modified properties compared with their atomically similar non-ionic analogues.[11] This provides a powerful methodology for the design and synthesis of HEDMs for specific purposes.

In a continuous effort to seek more powerful, less sensitive, eco-friendly energetic materials, we are interested in heterocyclic compounds that contain a high percentage of both oxygen and nitrogen and lower amounts of carbon and hydrogen, which would be endothermic and have high heats of formation. Generally, the incorporation of a triazole sketch is a known strategy for increasing thermal stability and improving energetic performances. Energetic triazolone derivatives such as 4-Amine-1,2,4-triazol-5-one (ATO), 4,4'-azo-bis(1,2,4-triazolone) (ZTO) and 3-Nitro-1,2,4-triazol-5-one (NTO) are of keen interest, especially owing to their excellent insensitivity and thermal stability.[12-15]
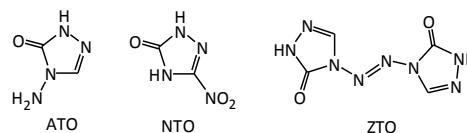
Scheme 1 The structure of ATO, NTO, and ZTO

Herein, we report the preparation and full characterization including the crystal structures of various salts of ZTO, including the alkali metals lithium, sodium, potassium, caesium, alkali earth metals magnesium, calcium, strontium, barium, and hydrazinium. The prepared salts were investigated in term of thermal stability and mechanical sensitivity performances, suggesting that they could be used as high energy with low sensitivity materials.

Results and Discussion

Synthesis

ZTO was synthesized according to scheme 2 from ATO by one-pot method by our optimized procedure from C. Ma and J. G. Zhang.[16,18] It bears two protons which are readily available in aqueous solution and can be deprotonated by reaction with the respective alkali metal hydroxides or carbonates. The alkali

metal salts with lithium (**1**), sodium (**2**), potassium (**3**), caesium (**4**), and hydrazinium salt (**5**) as well as the alkali earth metal salts magnesium (**6**), calcium (**7**), strontium (**8**) and barium (**9**) were prepared according to scheme 3. The solubility of ZTO is fairly good in hot water, but poor in cold water. The reactions therefore were carried out under high temperature in water, ensure that the starting material is fully dissolved. The choice of the metal source has to depend on the solubility of the respective materials. The lithium (**1**), sodium (**2**), potassium (**3**), caesium (**4**), hydrazine (**5**), magnesium (**6**), calcium (**7**), strontium (**8**) and barium (**9**) salt was prepared using the hydroxides since their solubility in water is higher than the respective carbonates.
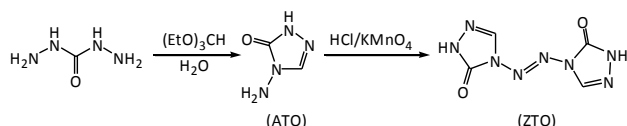
Scheme 2 Synthesis of 4,4′-azo-bis(1,2,4-triazolone) (ZTO).
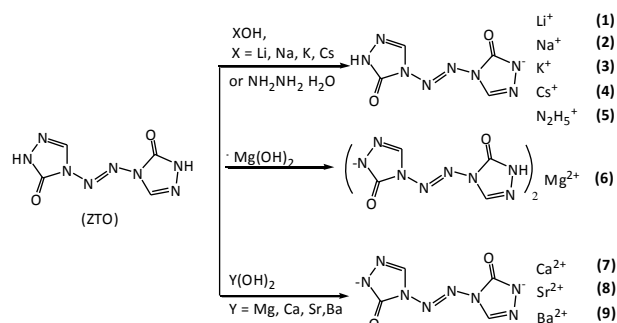
Scheme 3 Synthesis of ZTO salts **1-9**.

Crystal structures

Single-crystal X-ray measurements were accomplished for ZTO salts 2–9 and are all discussed in details. All compounds could be recrystallized from water resulting in the formation of hydrate as crystalline species, and only caesium salt **4** was obtained water free, which has high density as 2.378 g cm^{-3}.

By detailed examination of the crystal structure of compound 2–9, no significant changes were found in the bis-triazolone ring in comparison to mother compound ZTO. As expected, the metal ions coordinate with N, O atoms of bis-triazolone rings and water molecules in the assembly, displaying hexa-coordinate of K$^+$, Cs$^+$ and Ba^{2+}, while penta-coordinate in the case of Na$^+$. As a result, a slight twist of bis-triazolone ring is only found in case of caesium salt **4**, while others show a completely planar assembly. Table S1 lists the results of the crystal structure solution and refinement for complexes 2–9. The selected bond lengths, bond angles, torsion angles and hydrogen bond lengths are listed in Table S2–5 for compounds 2–9, respectively.

As seen in Fig. 1, **ZTO** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell and a density of 1.804 g cm^{-3}, which is higher than the previously reported[16b] 1.688 g cm^{-3} due to the different crystal system and absence of water molecules in unit cell. The crystal structure of ZTO adopted a planar molecular structure [torsion angle: C(1)–N(3)–N(4)–N(4$^{\#1}$) = −1.1°; C(2)–N(3)–N(4)–N(4$^{\#1}$) = 178.7°; and N(3)–N(4)–N(4$^{\#1}$)–N(3$^{\#1}$) = 180.0°] with two almost planar triazolones, a planar N$_4$ chain, and an *E*

configuration about the azo bond. The bond lengths of N(3)–N(4), N(4)–N(4$^{\#1}$) are 1.371 Å, 1.253 Å between the isolated N–N (1.450 Å) and isolated N=N (1.250 Å), which indicate a stronger delocalization of the azo π bond along the N$_4$ moiety within ZTO.[19] The intermolecular hydrogen bonds are formed between the –NH group and O, N atoms belong to ZTO molecule (Fig. S1), where N(2) atom acts as donor, and N(1) and O(1) atoms as acceptors with hydrogen distances of 2.080–2.530 Å and angles of 129.0–149.0°. These extensive intermolecular hydrogen bonds make an important role to the stability of ZTO.
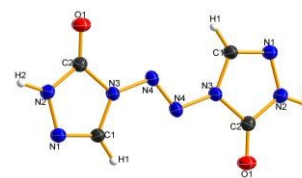

Fig. 1 Crystal structure of ZTO.

Complex **2**[20] is the sodium salt of ZTO as yellow plates with crystallized water. As seen in Fig. 2, **2** crystallizes in the monoclinic space group *C*2/*c* with eight molecules in the unit cell and a density of 1.738 g cm^{-3}, and the symmetric unit is made up of Na$^+$ inon, ZTO$^-$ anion and two coordinated water. In comparison to neutral ZTO, there are no significant changes regarding the bond lengths and the torsion angles of bistriazolone rings. The five membered 6π electron aromatic triazole rings are almost planar for **2** as well as for its mother compound ZTO. In addition to contacts with the Na$^+$ cations, intensive hydrogen bond was found between bistriazolone rings and water molecules.

Fig.2 Crystal structure of sodium 4,4′-azo-bis(1,2,4-triazolone) (**2**).

Compared with complex **2**, the potassium derivative **3** crystallizes in the monoclinic space group $P2_1/c$ (Fig. 3), with four molecules in each unit cell, resulting slightly higher density of 1.807 g cm^{-3} than that of **2**, and a unit cell volume of 1854.7 Å^3 (Table S1), which has higher density than reported[16a] due to the different crystal system and lacking of water molecules in cell. The crystallographic studies reveal that the symmetric unit is made up of K$^+$ inon, ZTO$^-$ anion and coordinated water. The structure of two types K coordination respectively forms the lightly distorted 6-coordinated octahedral through O and N is shown in Fig. 3. In crystal structure, each potassium center is coordinated by five adjacent ZTO$^-$ anions through three K–O and one water molecule through K–O. The bond length of K–O is 2.664–2.806 Å, between 2.240 and 3.300 Å, which is called partial coordination bond by Hathaway et al..[21]
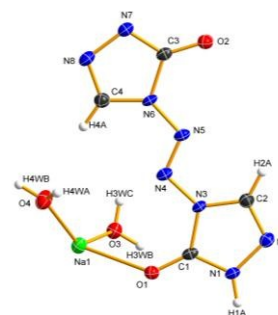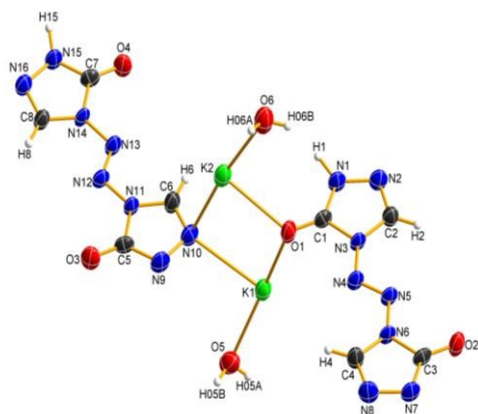
Fig. 3 Crystal structure of potassium 4,4′-azo-bis(1,2,4-triazolone) (**3**).

Similar with complex **3**, the caesium derivative **4** crystallizes in the orthorhombic space group *Pnna* with four molecules in each unit cell (Fig. 4), leading to a extremely high density of 2.378 g cm^{-3}, and a unit cell volume is 966.6 Å^3. The crystallographic studies reveal that caesium center coordinates with one oxygen atom of water molecule [Cs(1)–O(2) = 3.417 Å], two oxygen atom of ZTO$^-$ anion [Cs(1)–O(1) = 3.221 Å and Cs(1)–O(1$^{\#1}$) = 3.091 Å] and three nitrogen atoms of ZTO$^-$ anion [Cs(1)–N(1$^{\#5}$) = 3.283 Å, Cs(1)–N(1$^{\#6}$) = 3.283 Å, and Cs(1)–N(4$^{\#1}$) = 3.521 Å], respectively. As seen from Fig. 4 and Table S3, in the ZTO$^-$, the dihedral angles of C(1)–N(3)–N(4)–N(4$^{\#9}$) (20.6 °) and C(2)–N(3)–N(4)–N(4$^{\#9}$) (–167.3 °) indicate that the two triazole rings are not in one plane.
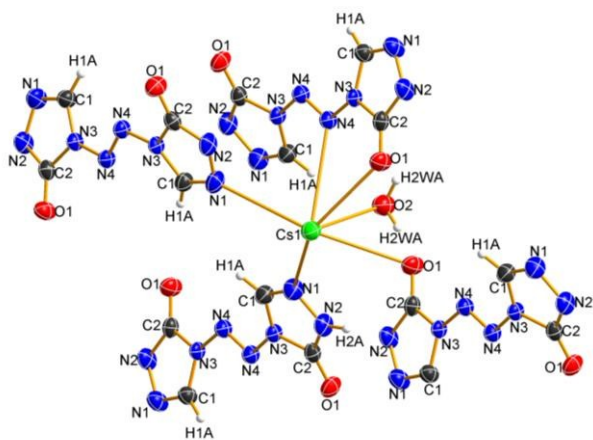

Fig. 4 Crystal structure of caesium 4,4′-azo-bis(1,2,4-triazolone) (**4**).

In contrast to the potassium salt and caesium salt, the hydrazinium derivative **5** contains no crystal water in the structure (Fig. 5). **5** crystallizes in the triclinic space group *P*–1 with two molecules in each unit cell, resulting a relative low density as 1.679 g cm^{-3}, and a unit cell volume is 451.47(5) Å^3. As seen from Fig. 5, the hydrogen atom has been transferred from N(1) in the ring of ZTO to N(10) in the hydrazine (N$_2$H$_4$) owing to the acid base neutralization reaction between the ZTO and N$_2$H$_4$·H$_2$O. Thanks to many N–H, C–O, and N–N bond existed in the structure of **5**, the ionic bond of N$_2$H$_5^+$ and ZTO$^-$ is strengthened by a lot of N–H…O and N–H…N hydrogen bond interactions from Table S3. These hydrogen bond interactions form a 3D framework of **5** as shown in Figure S2, which could be a key factor for good thermal stability of **5**.
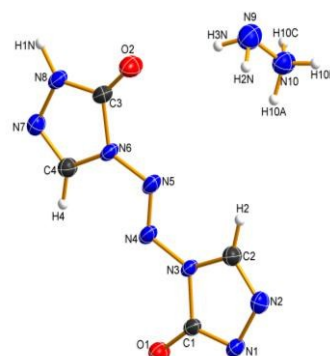
Fig. 5 Crystal structure of hydrazine 4,4′-azo-bis(1,2,4-triazolone) (**5**).

Magnesium derivative **6** crystallizes in the monoclinic space group *C2/c* with two ZTO moieties and one magnesium center in each unit cell (Fig. 6), leading to a lowest density as 1.644 g cm^{-3}, and a unit cell volume is 2402.4(11) Å^3. The presence of large amount of water molecules in the cell also contributed to the low density of **6**.
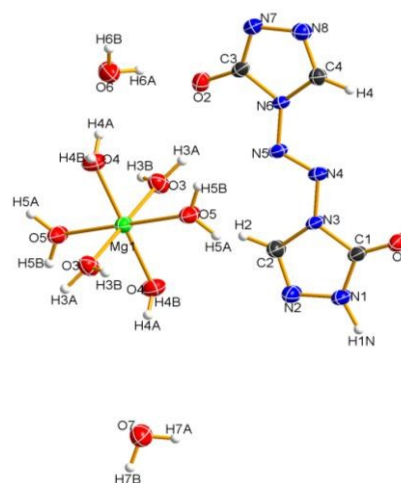
Fig. 6 Crystal structure of magnesium 4,4′-azobistriazolone (**6**).

Calcium derivative **7** crystallizes in the monoclinic space group *P*–1 with one molecule in each unit cell (Fig. 7), and eight water molecules present in the symmetric cell, leading to a relative low density as 1.867 g cm^{-3}, and a unit cell volume is 544.7(4) Å^3.

Fig. 7 Crystal structure of calcium 4,4′-azobistriazolone (**7**).

Strontium derivative **8** crystallizes in the triclinic space group *P*–1 with two molecules in each unit cell (Fig. 8), leading to a relative high density as 2.077 g cm^{-3}, and a unit cell volume is 565.8(3) Å^3.

In complex **8**, Sr(1) is coordinated by two adjacent ZTO²⁻ anion through one Sr–O [Sr(1)–O(1) = 2.540(4) Å], one Sr–N [Sr(1)–N(1) = 2.747(5) Å] and four water molecules through four Sr–O [Sr(1)–O(3) = 2.661(4) Å, Sr(1)–O(4) = 2.671(4) Å, Sr(1)–O(5) = 2.578(4) Å and Sr(1)–O(6) = 2.607(5) Å].
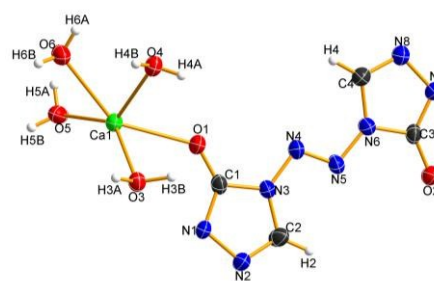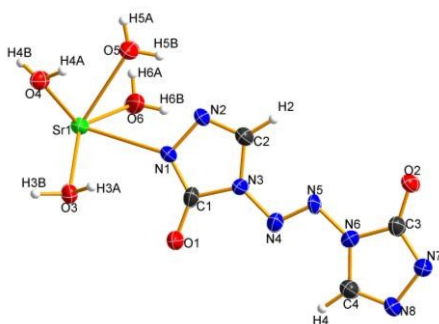

Fig. 8 Crystal structure of strontium 4,4′-azobistriazolone (**8**).

Barium derivative **9** crystallizes in the triclinic space group *P*–1 with two molecules in each unit cell (Fig. 9), leading to a relative high density as 2.261 g cm⁻³, and a unit cell volume is 592.8(2) Å³. As seen from Table S3, the strong intermolecular hydrogen bonding presents in the structure of **9**, where O(3), O(4), O(5) and O(6) atoms act as donors while O(1), O(2), N(1), N(2) and N(7) atoms as acceptors with hydrogen distances of 1.830–2.190 Å and angles of 135.0–169.0 °, anticipating the good stability of [BaZTO 4H₂O]∞.
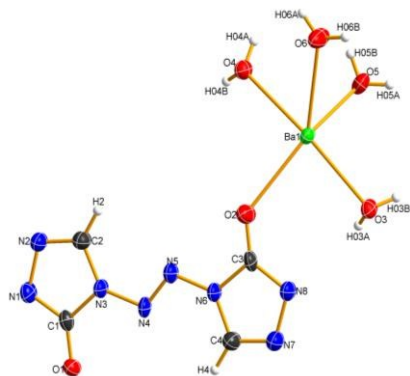

Fig. 9 Crystal structure of barium 4,4′-azo-bis(1,2,4-triazolone) (**9**).

Thermal behaviour

Due to the high nitrogen content of ZTO⁻ and ZTO²⁻ anion, the studied ZTO salts are potentially energetic compounds. Therefore, it is useful to assess their physical and thermal properties and compare them with those of commonly used explosives like TNT, RDX and HMX, TATB and ε-CL-20.

The thermal stability of the alkali metals and alkali earth metals salt of ZTO were determined using TG/DTA at a heating rate of 5 ℃ min⁻¹, and the data are given in Fig. S38-49, Table S6-7. ZTO is thermally stable to 260.0 ℃, and an exothermic peak is observed at 288.8 ℃, higher than those of other reported azo linked TAAT (200 ℃), DAAT (252 ℃), [22,23] and traditional energetic RDX (230 ℃) and is comparable to that of TNT (300 ℃).[24] The presence of the delocalized π-system probably was also accounted for the

remarkable stability of this type of compounds.[5] All of the title ZTO salts show decomposition temperatures lower than neutral ZTO but higher than 200 ℃, even higher than 270 ℃ in the case of **3**, **5** and **8**. The TG curves showed that the thermal decomposition of most of the studied ZTO salts can be divided into three principal stages except **3**, **4**, and **5** which have only two stages. The first stage occurs in the range of 80–150 ℃ with the loss of different water molecules, corresponding. The exothermic decomposition was recorded in the second stage in the temperature range of 210–400 ℃. The title compounds **4** and **7** with higher density even than ε-CL-20, but display much better thermal stability than RDX and ε-CL-20.

Kinetic parameters

Based on the multiple non-isothermal heat flow curves obtained at four different heating rates of 2, 5, 10 and 20 ℃ min⁻¹, the values of the extrapolated onset temperature (T_e), the peak temperature (T_p) are obtained by heat flow curves of the exothermic decomposition process (Table 1). The values of the apparent activation energy (E_K and E_O) (where subscript K: Kissinger's method; subscript O: Ozawa–Doyle's method), the pre-exponential factor (A) and linear correlation coefficient (r_K and r_O) of the second process are determined by Kissinger's method[25] and Ozawa–Doyle's method[26], respectively.

As seen from Table 2, the apparent activation energies (E_a) obtained by Kissing method agree well with that obtained by Ozawa method. They are in the normal range of kinetic parameters for the thermal decomposition reaction of the solid materials.[27]

$$T_{ei} = T_{e0} + n\beta_i + m\beta_i^2 \qquad (1)$$

where n and m are coefficients, $i = 1$–4.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_o R T_{e0}}}{2R} \qquad (2)$$

where E_o is the value of the apparent activation energy obtained by Ozawa's method.

The values of T_{e0} for ZTO and its complexes in the exothermic decomposition stage corresponding to $\beta \rightarrow 0$ obtained by Eq. (1) are 266.31, 238.26, 202.05, 242.01, 207.58, 268.43, 250.62, and 234.17 ℃, respectively. The critical temperatures of thermal explosion (T_b) obtained by Eq. (2) are 268.62, 243.49, 204.27, 243.93, 209.84, 270.67, 253.62, and 237.18 ℃, respectively.[28] The result indicates that the thermodynamically stable sequence is Mg(ZTO)₂ 8H₂O < CaZTO 4H₂O < NaZTO 2H₂O < CsZTO H₂O < BaZTO 4H₂O < LiZTO < KZTO H₂O < SrZTO H₂O < ZTO < N₂H₅ZTO.

Sensitivities

By applying the China National Military Standard, the impact and friction sensitivities of **1-9** were determined.[29] The impact sensitivities of the studied salts were determined with a fall hammer apparatus. At the time of the test, the room temperature was 23 ℃ and relative humidity was 65%.

The results are tabulated in Table 1 together with other physical-chemical properties of interest and compared with those of commonly used energetic materials. According to our tests, none of the compounds turned out to sensitive either to impact ($h_{50} > 60$cm) or to friction (> 0%) and are thus safe for transport or using. As indicated in Table 2, no explosion was observed when submitting the title salts **1–9** to the impact

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sensitivity test. In comparison with commonly used energetic compounds TNT, RDX, HMX, ε-CL-20, the compounds described here are less sensitive to both impact and friction.

Table 1 Physico-chemical properties of the studied ZTO salts.

	ZTO	1	2	3	4	5	6
Formula	$C_4H_4N_8O_2$	$C_4H_3N_8O_2Li$	$C_4H_7N_8NaO_4$	$C_8H_{10}N_{16}K_2O_6$	$C_4H_5CsN_8O_3$	$C_4H_8N_{10}O_2$	$C_8H_{26}MgN_{16}O_{14}$
M_r [g/mol]	196.15	202.06	254.17	504.52	344.05	228.20	594.76
Is [h_{50}][a]	65.0	71.8	75	64.5	82.6	69.3	67.4
$p\%$ [b]	20	0	0	0	0	0	0
Fs [%][c]	12	0	0	0	0	0	0
N [%][d]	57.10	55.43	44.06	44.40	32.55	61.35	37.66
Endo. (℃)[e]	–	252.18	96.76 (−H_2O) 132.1 (−2H_2O)	145.30 (−H_2O)	210.02	153.41	134.38 (−H_2O)
Dec. (℃)[f]	288.75	268.97	216.88	278.09	234.00	285.97	207.06
Density [g cm^{-3}][g]	1.804, 153K	–	1.738, 293 K	1.807, 153 K	2.378, 296 K	1.679, 296 K	1.644, 153 K
	7	**8**	**9**	**TNT**	**RDX**	**HMX**	**ε-CL-20**
Formula	$C_8H_{20}Ca_2N_{16}O_{12}$	$C_4H_4N_8O_3Sr$	$C_8H_{20}N_{16}O_{12}Ba_2$	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$
M_r [g/mol]	612.56	299.95	807.08	227.13	222.12	296.16	438.19
Is [h_{50}][a]	67.8	67.3	66.8	157 ±0.3 [30]	23.3 ±0.3[30]	26.1 ±0.3[33]	21[37]
$p\%$[b]	0	0	0	0	80±8	100	100
Fs[c]	0	0	0	0[31]	76[32]	100[33]	100
N[%][d]	36.67	37.34	27.75	18.49	37.84	38.84	38.35
Endo.(℃)[e]	138.04 (−H_2O)	152.80	99.88 (−4H_2O)	81	–	–	–
Dec. (℃)[f]	226.15	287.01	248.77	290	205	279	249
Density [g cm^{-3}][g]	1.867, 153 K	2.077, 153 K	2.261, 153 K	1.648, 298 K[34]	1.806, 298 K[35]	1.904, 298 K[36]	2.044 298 K[37]

[a] Impact sensitivity (BAM drophammer method). [b] Impact sensitivity (BAM drophammer method). [c] Friction sensitivity (BAM friction tester method). [d] Nitrogen content. [e] Endothermic peaks (i.e., melting or waster loss) from DTA at a heating rate of 5 ℃ min^{-1}. [f] Decomposition peaks (i.e., melting or waster loss) from DTA at a heating rate of 5 ℃ min^{-1}. [g] Density measured from X-ray diffraction.

Table 2 Thermal Kinetic parameters obtained by the data in Table 2.

	ZTO	1	2	3	4
E_K (kJ mol^{-1})	263.612	89.724	156.220	260.361	163.231
r_K	0.991	0.982	0.997	0.999	0.999
A (s^{-1})	1.552×10^{22}	1.793×10^{6}	1.546×10^{14}	2.667×10^{22}	3.288×10^{14}
E_O (kJ mol^{-1})	259.633	94.117	156.486	256.338	162.330
r_K	0.991	0.985	0.997	0.999	0.999
E_a (kJ mol^{-1})	261.622	91.921	156.353	258.349	163.266
T_{e0} (℃)	266.31 (269.14[16b])	238.26	202.05	242.01	207.58
T_b (℃)	268.62 (282.21[16b])	243.49	204.27	243.93	209.84
	5	**6**	**7**	**8**	**9**
E_K (kJ mol^{-1})	276.923	93.600	92.335	178.111	154.449
r_K	0.999	0.998	0.994	0.999	0.985
A (s^{-1})	3.863×10^{23}	9.150×10^{7}	2.648×10^{7}	2.303×10^{14}	1.493×10^{13}
E_O (kJ mol^{-1})	272.212	96.666	95.792	178.277	155.248
r_K	0.999	0.999	0.995	0.999	0.986
E_a (kJ mol^{-1})	274.567	95.132	94.064	178.194	154.849
T_{e0} (℃)	268.43	132.00	170.00	250.62	234.17
T_b (℃)	270.67	133.53	171.37	253.62	237.18

*E_K & E_O: the apparent activation energy calculated by Kissinger's method and Ozawa–Doyle's method, respectively; A: the pre-exponential factor; r_K & r_O: linear correlation coefficient determined by Kissinger's method and Ozawa–Doyle's method, respectively.

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Conclusions

Several salts of 4,4'-azo-bis(1,2,4-triazolone) (ZTO) with lithium(**1**), sodium(**2**), potassium (**3**), caesium (**4**), hydrazinium (**5**), calcium (**6**), calcium (**7**), strontium (**8**) and barium (**9**) were prepared and well characterized by IR, NMR, elemental analysis and TG-DTA analysis. Single-crystal x-ray measurements were accomplished for compounds **2–9**, delivering insights into structural characteristics as well as inter- and intra-molecular interactions. All these new materials exhibit excellent thermal stabilities, high density, acceptable detonation properties, and good insensitivity to impact ($h_{50} > 60$ cm). Especially, **4, 8** and **9** have high density of 2.261 (296 K), 2.077 (153 K), 2.378 (153 K) g/cm^3 and high thermal decomposition temperature of 248.77, 287.01 and 234.00 ℃, respectively, as well as low sensitivity to impact and friction, suggesting that they could be used as potential high-density insensitive materials.

Experiment section

Cautions!

ATO, ZTO and the studied ZTO salts are potentially energetic with increased sensitivities towards shock and friction. Therefore, proper safer precautions (safety glass, face shield, earthed equipment and shoes, gloves, and ear plugs) have to be applied when synthesizing and handling the described compounds.

Physical measurements and instrumentations

Infrared spectra were measured with a Bruker Spectrum One FTIR spectrometer as KBr. ^{1}H, ^{13}C NMR were recorded with a Bruker instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane. To measure elemental analyses, Vario EL III was employed. To determine the thermolysis performance of target compounds, and SHIMADZU DTG-60 (heating rate 2, 5, 10, 20 ℃ min^{-1}) were used. Further studies are listed in supporting information.

An irregular colourless crystal of dimensions 0.37×0.20×0.14 mm^3 (ZTO), a yellow crystal of dimensions 0.18×0.17×0.16 mm^3 (**2**), a yellow crystal of dimensions 0.37×0.16×0.15 mm^3 (**3**), a yellow crystal of dimensions 0.21×0.20×0.19 mm^3 (**4**), a yellow crystal of dimensions 0.21×0.20×0.18 mm^3 (**5**), a yellow crystal of dimensions 0.19×0.11×0.07 mm^3 (**6**), a yellow bright crystal of dimensions 0.13×0.09×0.05 (**7**), a yellow crystal of dimensions 0.09×0.06×0.03 mm^3 (**8**), and a yellow bright crystal of dimensions 0.22×0.12×0.08 mm^3 (**9**) were mounted on a Mite Gen Micro Mesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three–circle platform diffractometer equipped with a Bruker-AXS SMART APEX II CCD detector. The crystals were

irradiated using graphite monochromated MoKa radiation (λ=0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 153(2) and 293(2) K during data collection. The structure was solved by the direct methods (SHELXTL-97, DIAMOND 3.2) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[38–40] The hydrogen atoms were located theoretically and refined with riding model position parameters as well as fixed isotropic thermal parameters. The summaries of the structural determination and refinement for **1–6** are listed in Table 1. The selected bond distance and angles are listed in Supporting Information (Table S2–S4). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (the deposition CCDC numbers 1048057, 1063734, 1420716, 1420255, 1413030, 1435798, 1439859, 1440023, 1415595 for ZTO and **2–9**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data.

Synthesis

4-amine-1,2,4-triazole-5-one (ATO). m.p. 187–188 ℃ (186.3–188.1 ℃); ^{1}H NMR (d_6–DMSO) δ: 11.55 (s, 1H, NH), 7.82, 7.81 (s, 1H,CH), 5.28 (2H, NH$_2$) ppm; ^{13}C NMR (d_6–DMSO) δ: 155.47, 154.79 (CH), 139.78 (C=O) ppm; IR (KBr, cm^{-1}): ν = 3332 (–NH2), 3203 (–NH), 3133, 3073, 1708 (C=O), 1641 (C=N), 1616 (N=C–N), 1569 (N=N), 1456, 1247 (C–N), 1213, 941, 695.

4,4′-azo-bis(1,2,4-triazolone) (ZTO). m.p. 276–277 ℃; ^{1}H NMR (d_6–DMSO) δ: 12.36 (1H, NH), 8.64 (1H, CH) ppm; ^{13}C NMR (d_6–DMSO) δ: 149.81 (CH), 129.81 (C=O) ppm; IR (KBr, cm^{-1}): ν = 3221 (N–H), 3162 (C–H), 1723 (C=O), 1680 (N=N), 1545 (C=N), 1384 (C–N), 1339, 1261, 1189, 1043, 911, 845, 800, 762, 709, 569; MS (solid probe: EI) m/z (%): 85 (M$^+$, 100).

Lithium 4,4′-azo-bis(1,2,4-triazolone) (1). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of LiOH (0.20 g in 2 mL of water) was added dropwise. After reaction at room temperature for 30 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Yellow precipitate was obtained after filtration and dry under vacuum. Yield: 0.82 g (79.6%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.10 (1H, S, CH); IR (KBr, cm^{-1}): ν = 3184, 3115, 1612, 1507, 1345, 1203, 1033, 936, 854, 820; EA (found, calc. for C$_4$H$_3$N$_8$O$_2$Li, MW = 202.06): C (23.45 23.78), H (1.53, 2.1.50), N (55.52, 55.46); MS (ESI) m/z, observed: 84.01; C$_2$HN$_3$O [M]$^-$ requires: 84.02.

Sodium 4,4′-azo-bis(1,2,4-triazolone) (2). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of NaOH (0.80 g in 2 mL of water) was added drop wise. After reaction at room temperature for 30 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Bright

yellow needles crystallized from the solution overnight. Yield: 0.67 g (60.3%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.093 (1H, S, CH); IR (KBr, cm^{-1}): ν = 3398, 3141, 2306, 1662, 1607, 1517, 1341, 1255, 1196, 1017, 924, 812, 758, 714; EA (found, calc. for C$_4$H$_3$N$_8$O$_2$Na, MW = 254.17): C (18.82, 18.90), H (2.80, 2.78), N (44.07, 44.09); MS (ESI) m/z, observed: 195.04; C$_4$H$_3$N$_8$O$_2$ [M]$^-$ calculated: 194.95.

Potassium 4,4′-azo-bis(1,2,4-triazolone) (3). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of KOH (1.20 g in 2 mL of water) was added drop wise. After reaction at room temperature for 30 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Bright yellow needles crystallized from the solution overnight. Yield: 0.67 g (60.3%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.06 (1H, S, CH); IR (KBr, cm^{-1}): ν = 3223, 3121, 1619, 1500, 1334, 1253, 1203, 1017, 916, 823, 799, 748, 711; EA (found, calc. for C$_4$H$_3$N$_8$O$_2$K, MW=234.22): C (19.08, 19.12), H (1.63, 1.60), N (44.57, 44.60); MS (ESI) m/z, observed: 84.01; C$_2$HN$_3$O [M]$^-$ calculated: 84.02.

Caesium 4,4′-azo-bis(1,2,4-triazolone) (4). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of CsOH (1.53 g in 5 mL of water) was added dropwise. After reaction at room temperature for 60 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 1.67 g (95.7%). ^{1}H NMR (400 MHz, d6–DMSO) δ: 8.48 (1H, S, CH); IR (KBr, cm^{-1}); ν = 3428, 3100, 1708, 1496, 1339, 1212, 852, 789, 739, 628, 577; EA (found, calc. for C$_4$H$_3$N$_8$O$_2$K, MW = 328.02): C (14.63, 14.65); H (0.94, 0.92); N (40.55, 40.52); MS (ESI) m/z, observed: 328.95; C$_4$H$_3$N$_8$O$_2$Cs [M]$^+$ calculated: 327.94.

Hydrazine 4,4′-azo-bis(1,2,4-triazolone) (5). ZTO (1.00 g, 5.10 mmol) was suspended in 5 ml of water and to it a solution of N$_2$H$_4$ H$_2$O (0.5 mL, 10.20 mmol) was added dropwise. After reaction at room temperature for 30 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 0.82 g (70.5%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.61 (CH); IR (KBr, cm^{-1}): ν = 3289, 3191, 3108, 2982, 2744, 2632,1724, 1621, 1526, 1480, 1341,1295, 1257, 1204, 1119, 1013, 951, 908, 875, 830; EA (found, calc. for C$_4$H$_8$N$_{10}$O$_2$, MW = 228.17): C (21.05, 21.06); H (3.51, 3.53); N (61.43, 61.39); MS (ESI) m/z, observed: 229.09; C$_4$H$_8$N$_{10}$O$_2$ [M]$^-$ calculated: 228.08.

Magnesium 4,4′-azo-bis(1,2,4-triazolone) (6). ZTO (1.00 g, 5.10 mmol) was suspended in 5 ml of water and to it a solution of Mg(OH)$_2$ (0.30 g in 20 mL of water) was added dropwise. After reaction at 100 ℃ for 30 min, the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 1.12 g (95.8%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.565 (CH); IR (KBr, cm^{-1}): ν = 3421, 3140, 1635, 1505, 1346, 1188, 1029, 937, 820, 790, 720, 626, 589; EA (found, calc. for C$_4$H$_2$N$_8$O$_2$Mg, MW = 218.42): C (22.12, 22.00); H (0.88, 0.92); N (51.44, 51.30); MS (ESI) m/z, observed: 414.06; C$_8$H$_6$N$_{16}$O$_4$ [2M]$^+$ calculated: 415.07.

Calcium 4,4′-azo-bis(1,2,4-triazolone) (7). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of Ca(OH)$_2$ (0.38 g in 20 mL of water) was added dropwise. After reaction at 100 ℃ for 30 min, the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 0.82 g (70.5%). ^{1}H NMR (400 MHz, d_6–

DMSO) δ: 8.275 (CH); IR (KBr, cm^{-1}): ν = 3418, 33137, 1627, 1520, 1503, 1344, 1262, 1192, 1023, 931, 804, 741, 716, 634, 597; EA (found, calc. for C$_4$H$_2$N$_8$O$_2$Ca, MW = 234.19): C (20.56, 20.51); H (0.91, 0.86); N (48.01, 47.85); MS (ESI) m/z, observed: 229.09; C$_4$H$_8$N$_{10}$O$_2$ [M]$^-$ calculated: 228.08.

Strontium 4,4′-azo-bis(1,2,4-triazolone) (8). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of Sr(OH)$_2$ H$_2$O (0.75 g in 10 mL of water) was added drop wise. After reaction at room temperature for 60 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 1.40 g (97.5%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.19 (1H, S, CH); IR (KBr, cm^{-1}) ν = 3440, 3165, 1721, 1648, 1546, 1384, 1343, 1262, 1188 1042, 1009, 908, 839, 796, 705; EA (found, calc. for C$_4$H$_4$N$_8$O$_3$Sr, MW = 299.95): C (15.96, 16.03); H (1.43, 1.35); N (37.25, 37.38); MS (ESI) m/z, observed: 84.01; C$_2$HN$_3$O [M]$^-$ calculated: 84.02.

Balcium 4,4′-azo-bis(1,2,4-triazolone) (9). ZTO (1.00 g, 5.10 mmol) was suspended in 5 mL of water and to it a solution of Ba(OH)$_2$ 8H$_2$O (1.61 g in 10 mL of water) was added dropwise. After reaction at room temperature for 60 min, 50 mL of methanol was added, and the resulting mixture was slowly cooled to room temperature. Yellow needles crystallized from the solution overnight. Yield: 1.61 g (94.7%). ^{1}H NMR (400 MHz, d_6–DMSO) δ: 8.14 (1H, S, CH); IR (KBr, cm^{-1}) ν = 3184, 3115, 1612, 1507, 1345, 1203, 1032, 936, 854, 820; EA (found, calc. for C$_4$H$_{10}$N$_8$O$_6$Ba, MW = 403.50): C (11.85, 11.91); H (2.52, 2.50); N (27.82, 27.77); MS (ESI) m/z, observed: 84.01; C$_2$HN$_3$O [M]$^-$ calculated: 84.02.

Acknowledgements

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