Ring Closure of Polynitroazoles via an N,N'-Alkylene Bridge: Towards High Thermally Stable Energetic Compounds

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High thermal stability is one of the important factors in the design of high-performance insensitive energetic compounds. A straightforward synthesis of tricyclic energetic molecules (**2**, **3**, **5** and **6**) has been developed through bridging ethylene-/propylene- moieties featuring two polynitroazoles. Remarkably, such ring closure reactions lead to higher thermal stability. In addition, the influence of 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (**1**) and 5,5'-dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (**4**) with or in the absence of an N,N'-alkylene bridge on the structural and electrostatic potentials (ESP) was established theoretically. The high thermal stability and good detonation properties may make these materials useful as replacements for trinitrotoluene (TNT).

Introduction

The synthesis of novel energetic molecules and particularly in nitrogen-rich heterocyclic chemistry has gained increasing attention over the past few years.[1] Although traditional explosives face environmental pollution problems because they are prepared mainly based on a benzene backbone, such as trinitrotoluene (TNT), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), such molecules are still in use nowadays. The toxic issues continue to require solution. Nitrogen-rich energetic compounds are very attractive since the presence of C-N and N-N bonds in five- or six-membered rings may result in environmentally friendly decomposition products, high positive heats of formation and hydrogen bond networks that can potentially enhance stability and reduce sensitivity.[2]

Current molecular design for promising candidates for application in energetic materials focuses on the modification of functional groups based on the nitrogen-rich backbone. Many types of nitrogen-rich energetic molecules have been prepared in recent years and investigated for their unique structures and properties. The ultimate aim is to synthesize an ideal energetic molecule with good detonation performance and low sensitivity. In addition, high thermal stability is also important since it can enhance safety in manufacturing, storage and handling.[3]

In order to fine tune energetic properties, many bridged energetic biheterocyclic compounds including symmetric N,N'-ethylene bridged bis-azoles (bis-aminotetrazoles, bis(nitroamino-1,2,4-triazolates), bis(nitropyrazoles),[4] asymmetric N,N'-ethylene bridged 5-aminotetrazole and 3,4,5-trinitropyrazole moieties,[4a, 5] asymmetric N-methylene-C linked tetrazole-based compounds,[6] N-diazo-bridged nitroazoles[7] and oxy-bridged tetrazoles[8]) have been investigated. Now a skillful approach for fine tuning the properties of energetic compounds through ring closure of polynitroazoles with an N,N'-ethylene bridge (**2** and **5**) or an N,N'-propylene bridge (**3** and **6**) was developed. All the compounds have been fully characterized by multinuclear NMR (^{1}H, ^{13}C and ^{15}N), and infrared spectra, elemental analyses, and DSC as well as single crystal X-ray diffraction. The results demonstrate that a ring closure strategy via N,N'-alkylene bridges can improve thermal stability.

Results and discussion

Synthesis

In Scheme 1, the synthetic routes for the preparation of the ring closure products (**2**, **3**, **5** and **6**) appear. The starting materials, 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (**1**)[9] and 5,5'-dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (**4**),[10] were synthesized according to the literature. The syntheses of ethylene/propylene bridged compounds were realized using the corresponding sodium salts, which were prepared by treatment of sodium bicarbonate with **1** or sodium carbonate with **2**. Then reaction of the sodium salts with stoichiometric amounts of 1,2-dibromoethane or 1,3-dibromopropane in DMF at 80 °C resulted in the desired ring closure products. The products were obtained by filtration after pouring the reaction mixture into ice water. In addition, due to the moderate solubility of the ethylene/propylene bridged nitro-bi-1,2,4-

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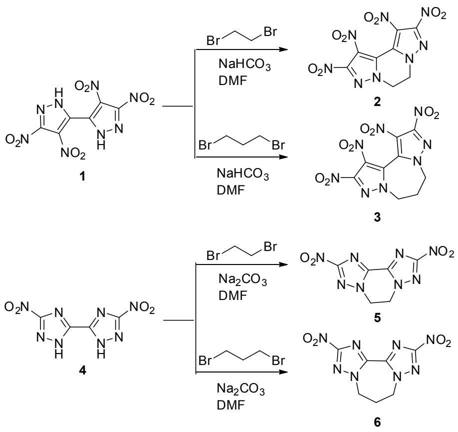
Electronic Supplementary Information (ESI) available: Includes theoretical calculation, crystallographic data (CCDC: 1818128-1818130 and 1818132) and NMR spectra.. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthesis of ring closure materials **2**, **3**, **5** and **6**

triazole in a mixture of DMF and water, additional amounts of the products (**5** or **6**) were extracted with ethyl acetate. Attempts to introduce methylene ($-CH_2-$) or methylnitroaminomethyl ($-CH_2NNO_2CH_2-$) bridges did not give the expected cyclic products.

NMR spectra

Due to the symmetric structures of **2** and **5**, in the ^1H NMR spectra, the hydrogen signals in the ethylene bridges were observed as a singlet. In **3** and **6**, the hydrogen signals were found as a triplet and a quintet for the two different $–CH_2$ groups in the propylene bridge. The coupling constant of ^3J (H,H) is 7.0 Hz for both the triplet and quintet in **3**; in **6**, the coupling constant is 5.1 Hz for ^3J (H,H). The ^{15}N NMR spectra are shown in Fig. 1. Compounds **2** and **3** were recorded in CD_3CN, while **5** and **6** were obtained in d_6-DMSO. The assignments are based on reported compounds[9-11] and ^1H-^{15}N HMBC spectra (Supporting Information). There are four signals for **2** and **3** because of their symmetric structure. However, due to the effect of the different bridges, the signals (N1 and N2) are shifted to lower fields. In **5** and **6**, there are also four signals. The trends are similar to those in **2** and **3**. The introduction of a propylene bridge causes the nitrogen signals (N1, N3 and N2) to shift a little to lower field.

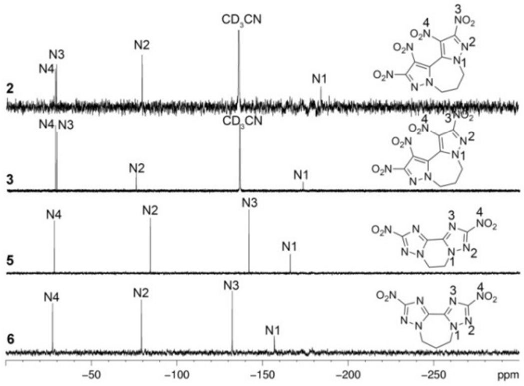


Fig. 1 The ^{15}N NMR spectra of **2**, **3**, **5** and **6**

Single crystal X-ray diffraction studies

Single-crystals suitable for X-ray diffraction studies were obtained by slow room temperature evaporation of a solution in acetonitrile (**2**, **3**) or ethyl acetate (**5**, **6**). The detailed crystallographic refinement parameters and structural data for compounds **2**, **3**, **5** and **6** are given in the Supporting Information. Compound **2** crystallizes in the trigonal space group $P3_221$ with six molecules in the unit cell. A solvent molecule of acetonitrile is also found in the unit cell. The structure is shown in Fig. 2. All the nitro groups are twisted out of the planes of the pyrazole rings. The center six-membered ring is distorted and the torsion angle of N(10)-C(11)-C(12)-N(13) is 51.0(4)^o.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The calculated crystal density is 1.667 g cm^{-3} at 20 ^oC. The molecular structure is shown in Fig. 3. Due to the introduction of a propylene bridge, the center seven-membered ring is also distorted. The torsion angles of N(10)-C(11)-C(12)-C(13) and C(11)-C(12)-C(13)-N(14) are 37.0(3)^o and 40.2(3)^o, respectively. In addition, the bond lengths of N10-C11 (1.475 Å) and C11-C12 (1.516 Å) in **3** are slightly longer than those in **2** (N10-C11: 1.470 Å; C11-C12: 1.510 Å).

Compound **5** crystallizes in the monoclinic space group C2/c with four molecules in the unit cell. The calculated crystal density is 1.733 g cm^{-3} at 20 ^oC. The molecular structure is shown in Fig. 4a. The nitro groups are nearly coplanar with the triazole rings and the torsion angle of O(2)-N(3)-C(4)-N(5) is 2.8(2)^o. The ethylene bridge makes the middle ring a little

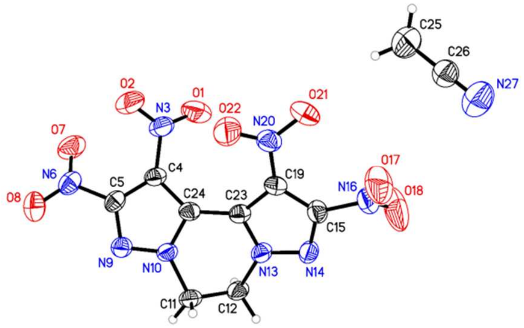


Fig. 2 Molecular structure of **2**

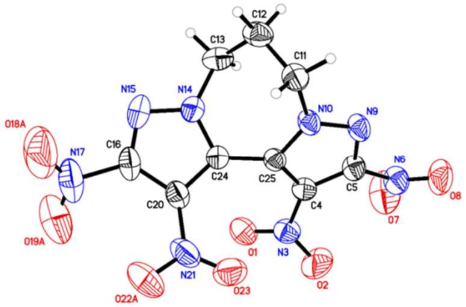
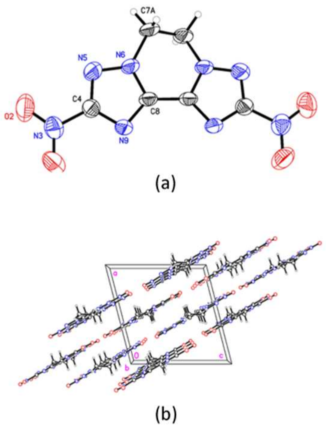


Fig. 3 Molecular structure of **3**



(a)

(b)

Fig. 4 (a) Molecular structure of **5**. (b) The packing diagram of **5.**

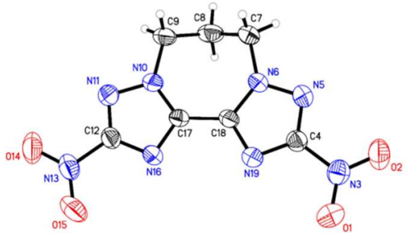


Fig. 5 Molecular structure of **6**

distorted with a torsion angle of C(8)-N(6)-C(7A)-C(7A = 41.9(8)°, however, the packing diagram was build up with staggered paralleled units viewed along from *b* axis (Fig. 4b). The layers are stabilized by short contacts with O1…C8 (3.109 Å) and N6…O2 (3.060 Å).

Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The calculated crystal density is 1.634 g cm^{-3} at 20 °C. The molecular structure is shown in Fig. 5. In contrast to **5**, the atoms of the nitro bis-1,2,4-triazole are essentially in the same plane with a torsion angle of N(10)-C(17)-C(18)-N(19) = 178.30(14)°. However, the relatively long propylene bridge is twisted out of the plane of the nitro-bis-1,2,4-triazole ring. Then the mixed disordered molecules and lack of hydrogen bonds could be the main reason for the low density.

Physical and detonation properties

The thermal behavior of the title compounds **2**, **3**, **5** and **6** was analyzed by differential scanning calorimetry (DSC) with a heating rate of 5 °C min^{-1}. These materials show remarkably high thermal stabilities with decomposition temperatures of more than 260 °C (Table 1). In comparison, the closed ring products display higher thermal stability than their non-bridged parent molecules (**1**: 243 °C and **4**: 251 °C). The decomposition temperature by introduction of a propylene bridge is almost 20 °C higher than that of its ethylene bridged analog.

Heats of formation were computed by using the Gaussian 03 program[12] with isodesmic reactions (Supporting Information). As can be seen, owing to the nitrogen rich backbone, compounds **2**, **3**, **5** and **6** show positive heats of formation, while TNT and TATB have negative values. Detonation performance values were obtained with EXPLO5 v6.01.[13] The detonation velocities lie between 7336 to 8135 m s^{-1}, exceeding that of TNT. The highest one (8135 m s^{-1}) approaches the value of TATB (8179 m s^{-1}). All the compounds also exhibit higher detonation pressures than TNT.

Sensitivities toward impact and friction were determined by standard BAM technology. While all of them exhibit insensitive friction sensitivities (> 360 N), the impact sensitivities of **2** and **5** are 15 and 22 J, respectively. In contrast to the ethylene bridged compounds (**2** and **5**), the presence of a propylene bridge (**3** and **6**) lowers the impact sensitivities to 28 and 30 J, respectively. The trend is also in accordance with the theory of Pollitzer and Murray.[14] The calculated electrostatic potentials (ESP) of the surfaces of the molecules are related to impact sensitivities. In energetic compounds, more extensive areas with larger and stronger positive potentials usually result in increased impact sensitivities.[14] The ESP-mapped vdW surfaces[15] of those molecules are shown in Fig. 6. Significant surface local minima and maxima of ESP are represented

Table 1. Physicochemical and energetic properties of **2**, **3**, **5** and **6**

Compds	ρ[a] ($g{\cdot}cm^{-3}$)	Dv[b] ($m\ s^{-1}$)	P[c] (GPa)	ΔH_f[d] ($kJ\ mol^{-1}/kJ\ g^{-1}$)	T_m[e] (°C)	T_{dec}[f] (°C)	IS[g] (J)	FS[h] (N)
2	1.762	8135	28.1	326.6/0.96	233	261	15	>360
3	1.677	7700	24.1	280.1/079	278	280	28	>360
5	1.733	7838	24.1	345.3/1.37	304	307	22	>360
6	1.634	7336	19.7	307.2/1.15	325	328	30	>360
TNT	1.654	6881	19.5	-59.3/-0.26	81	300	15	353
TATB	1.930	8179	30.5	-139.7/-0.54	-	350	50	>360

[a] Density (measured with a gas pycnometer at 25 °C.) [b] Detonation velocity calculated with EXPLO5 v6.01. [c] Detonation pressure calculated with EXPLO5 v6.01. [d] Heat of formation. [e] Melting point. [f] Decomposition temperature (onset temperature at a heating rate of 5 °C min^{-1}). [g] Impact sensitivity. [h] Friction sensitivity.

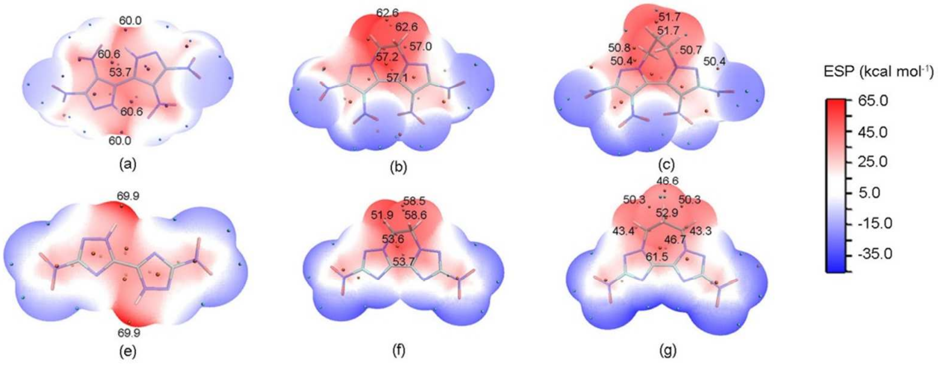


Fig. 6 ESP-mapped molecular vdW surface of **1**-**6** (a:**1**, b:**2**, c:**3**, d:**4**, e:**5**, f:**6**). Surface local minima and maxima of ESP are represented as cyan and orange spheres, respectively. Only the strong positive ESPs are labeled.

as cyan and orange spheres.

As can be seen in Fig. 6a-6c, the positive ESP region of **1** is nearly homodispersed over the entire molecule, while that of **2** is located on one side. The percentage of the overall surface (most positive ESP region between 55 and 66 kcal mol^{-1}) is 1.13%, which is less than that of **2** (3.36%), indicating that **1** is less sensitive than **2**. In comparing **2** with **3**, the former exhibits a larger and stronger electropositive area than **3** (0%). This evidence indicates that **3** is less sensitive than **2**, which also agrees with the experimental results. For **5** and **6**, the percentage of **5** (0.91%) is larger than that of **6** (0.25%), supporting the observation that **5** with an ethylene bridge is more sensitive than **6** with propylene bridge. However, the percentage of **4** is 2.56%, which is much higher than that of **5**; The maximum ESP for **4** is almost 69.9 kcal mol^{-1}, which is also very much larger than that (58.6 kcal mol^{-1}) in **5**. This supports the experimental observation that the impact sensitivity should be larger, in this case 10 J.[10b]

Conclusions

In conclusion, an efficient synthesis of ring closure of polynitroazoles with N,N'-ethylene/propylene bridges is demonstrated. All the compounds were fully characterized with multinuclear NMR and infrared spectra, elemental analysis as well as with single crystal X-ray diffraction. The incorporation of N,N'-ethylene/propylene bridges into polynitroazoles improves thermal stability. The new compounds have excellent thermal stability with **6** having the highest decomposition temperature at 328 °C. These compounds exhibit better detonation performance than TNT and **2** is comparable to TATB. The sensitivities toward impact and friction are also better than TNT. The remarkable high thermal stability and good detonation performance as well as the "green" nitrogen rich backbone make them potential candidates in the field of energetic materials. Such ring closure strategy could open the route to the design of highly thermally stable energetic compounds.

Experimental section

Caution! The compounds in this study are potentially energetic materials. Although we did not encounter explosions during preparation and handling, mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Manipulations must be carried out by using appropriate standard safety precautions.

General methods

All reagents were purchased from AKSci or Alfa Aesar in analytical grade and were used as received. ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported relative to $(CH_3)_4Si$ and ^{15}N NMR to nitromethane. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of 5 °C min^{-1}. Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

Computational Methods

Gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1, SI). Enthalpies of reaction were obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. Solid state heats of formation were calculated with Trouton's rule according to equation (1) (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[16]

$$\Delta H_{sub} = 188 / Jmol^{-1}K^{-1} \times T \quad (1)$$

X-Ray crystallography data

Clear colorless plate crystals of dimensions 0.124 × 0.122 × 0.026 mm^3 (**2**), 0.231 × 0.180 × 0.020 mm^3 (**3**), 0.260 × 0.159 × 0.033 mm^3 (**5**), and a clear colorless block crystal of dimensions 0.249 × 0.143 × 0.041 mm^3 (**6**) were mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Data were collected at room temperature (20°C). Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[17] Data reduction was performed using *SAINT* [v8.34A][18] and *XPREP* [v2014/2].[19].Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/5.][20] The structure was solved and refined with the aid of the program SHELXL-2014/7.[21] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model. In **2**, nitro groups attached to C16 and C20 display two-component disorder. The ratio of major:minor components has been refined with a free variable to a final ratio of 78:22. In **5**, the ethylene bridge displayed two-component disorder with 77:23 ratio between the major:minor components. Bonds to the minor component have been restrained to the equivalent bond lengths in the major component.

1,2,9,10-Tetranitro-5,6-dihydrodipyrazolo[1,5-*a*:5',1'-*c*]pyrazine (**2**): Sodium bicarbonate (0.17 g, 2.0 mmol) was added to a solution of **1** (0.34 g, 1.0 mmol) in DMF (5 mL). The reaction mixture was stirred at room temperature for 15 minutes. Then 1,2-dibromoethane (0.19 g, 1.0 mmol) was added and the reaction mixture was heated at 90 °C with continued stirring for 12 h. After cooling to amibient temperature, the reaction mixture was poured into ice-water (100 mL), the precipitate was collected by filtration, and washed with ice-water (20 mL). The pure product (0.28 g, yield: 82%) was obtained by recrystallization from acetonitrile and water. Yellow solid. T_m: 233 °C. $T_{d\ (onset)}$: 261 °C. ^1H NMR (d_6-DMSO): 4.99 (s, 4H) ppm. ^{13}C NMR: δ 146.8, 126.2, 123.6, 48.0 ppm. IR (KBr): $\tilde{\nu}$ = 3024, 1629, 1571, 1544, 1524, 1476, 1405, 1375, 1359, 1338, 1321, 1237, 1117, 1070, 1056, 985, 934, 883, 870, 824, 808, 780, 761, 736, 728 cm^{-1}. $C_8H_4N_8O_8$ (340.17): Calcd C 28.25, H 1.19, N 32.94 %. Found: C 28.41, H 1.26, N 32.90 %.

1,2,10,11-Tetranitro-6,7-dihydro-5*H*-dipyrazolo[1,5-*a*:5',1'-*c*][1,4]diazepine (**3**): Sodium bicarbonate (0.17 g, 2.0 mmol) was added to a solution of **1** (0.34 g, 1.0 mmol) in DMF (5 mL) and the reaction mixture was stirred at room temperature for 15 minutes. Then 1,3-dibromopropane (0.20 g, 1.0 mmol) was added and the reaction mixture was heated at 90 °C with stirring for 12 h. After cooling to amibient temperature, the reaction mixture was poured into ice-water (100 mL), the precipitate was collected by filtration, and washed with ice-water (20 mL). The pure product (0.30 g, yield: 85%) was obtained by recrystallization from acetonitrile and water. Yellow solid. T_m: 278 °C. $T_{d\ (onset)}$: 280 °C. ^1H NMR (CD_3CN): 4.55 (t, *J* = 7.0 Hz, 4H), 2.73 (p, *J* = 7.0 Hz, 2H) ppm. ^{13}C NMR (CD_3CN): δ 148.9, 128.9, 127.4, 51.2, 31.3 ppm. IR (KBr): $\tilde{\nu}$ = 1618, 1561, 1542, 1514, 1471, 1405, 1343, 1331, 1305, 1261, 1226, 1181, 1118, 1085, 1056, 1007, 988, 906, 888, 868, 823, 807, 764, 754, 746, 713 cm^{-1}. Elemental analysis for $C_9H_6N_8O_8$ (354.19): Calcd C 30.52, H 1.71, N 31.64 %. Found: C 30.54, H 1.82, N 31.59 %.

2,9-Dinitro-5,6-dihydrobis([1,2,4]triazolo)[1,5-*a*:5',1'-*c*]pyrazine (**5**): Sodium carbonate (0.11 g, 1.0 mmol) was added to a solution of **4** (0.23 g, 1.0 mmol) in DMF (5 mL), and the reaction mixture was stirred at room temperature for 15 minutes. Then 1,2-dibromoethane (0.19 g, 1.0 mmol) was added, the reaction mixture was heated at 90 °C and stirred for 12 h. After cooling to amibient temperature, the reaction mixture was poured into ice-water (100 mL), the precipitate was collected by filtration and washed with ice-water (20 mL). More **5** (70%) were obtained by recrystallization from acetonitrile and water. White solids. T_m: 304 °C. $T_{d\ (onset)}$: 307 °C. ^1H NMR (d_6-DMSO): 5.04 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO): δ 161.9, 143.7, 46.0 ppm. IR (KBr): $\tilde{\nu}$ = 3010, 1637, 1550, 1466, 1443, 1424, 1399, 1343, 1307, 1233, 1203, 1150, 1086, 849, 835, 675, 648 cm^{-1}. Elemental analysis for $C_6H_4N_8O_4$ (252.15): Calcd C 28.58, H 1.60, N 44.44 %. Found: C 28.72, H 1.81, N 43.89 %.

2,10-Dinitro-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[1,5-*a*:5',1'-*c*][1,4]diazepine (**6**): Sodium carbonate (0.11 g, 1.0 mmol) was added to a solution of **4** (0.23 g, 1.0 mmol) in DMF (5 mL), and the reaction mixture was stirred at room temperature for 15 minutes. Then 1,3-dibromopropane (0.20 g, 1.0 mmol) was added and the reaction mixture was heated at 90 °C for 12 h at this temperature. After cooling to amibient temperature, the reaction mixture was poured into ice-water (100 mL).The precipitate was collected by filtration and washed with ice-water (20 mL). The pure product (0.20 g, yield: 75%) was obtained by recrystallization from acetonitrile and water. white solids. T_m: 325 °C. $T_{d\ (onset)}$: 328 °C. ^1H NMR (CD_3CN): 4.79 (t, *J* = 5.1 Hz, 4H), 2.69 (p, *J* = 5.1 Hz, 2H) ppm. ^{13}C NMR (CD_3CN): δ 162.7, 145.4, 54.4, 23.8 ppm. IR (KBr): $\tilde{\nu}$ = 3016, 1563, 1555, 1500, 1473, 1421, 1370, 1340, 1317, 1243, 1178, 1087, 1043, 1024, 952, 897, 836, 726, 688, 651 cm^{-1}. Elemental analysis for $C_7H_6N_8O_4$ (266.17): Calcd C 31.59, H 2.27, N 42.10 %. Found: C 31.96, H 2.41, N 42.16 %.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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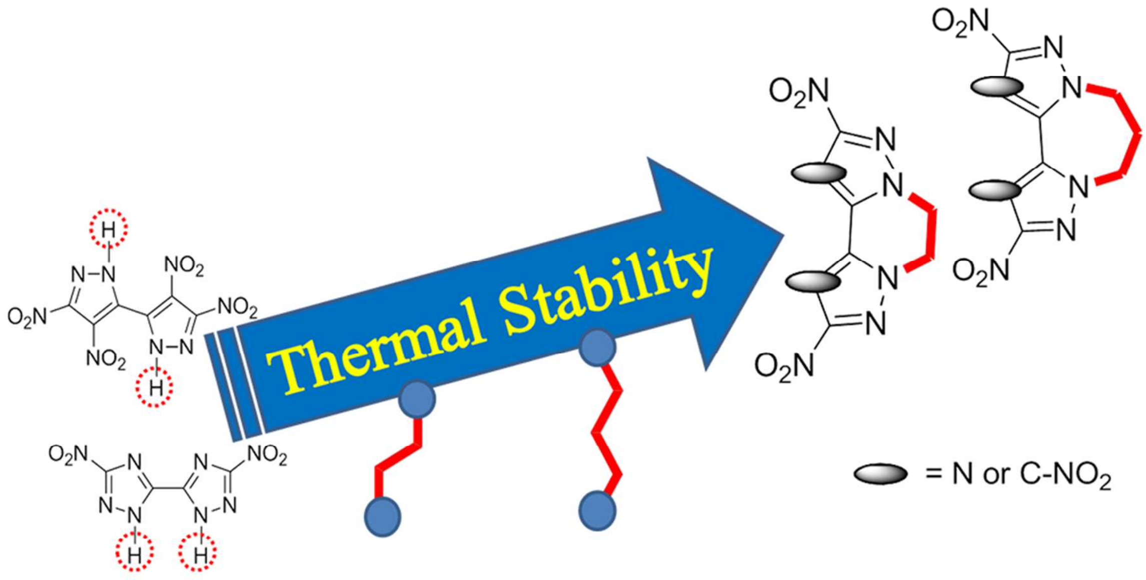

A straightforward ring closure reaction gave highly thermally stable tricylic N,N'-alkylene bridged polynitrobis-azoles.