A C-C bonded 5,6-fused bicyclic energetic molecule: exploring an advanced energetic compound with improved performance

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A C-C bonded 5,6-fused bicyclic energetic molecule: exploring an advanced energetic compound with improved performance

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A C-C bonded amino-nitro pyrazole (7) and its ring-expansion product (9) have been synthesized and characterized. The synthetic route to 9 proceeds in several steps from the commercial substrate diethyl oxalate and acetone. The process was found to be straightforward, practical and easily scalable. Both of these structures were confirmed by single crystal X-ray diffraction. Compound 9 with a high density (1.85 g cm^{-3}) at room temperature, excellent thermal stability (T_d: 315 ^oC), good detonation performance and low sensitivity to impact and friction has potential as a high-temperature energetic material.

Given the growing demand for high energy density compounds (HEDMs) in applications as propellants, explosives and pyrotechnics, compounds with high performance, insensitivity, high thermal stability and decomposition gases which are environmentally friendly are ideal candidates. With the goal of developing HEDMs with utopian characteristics, chemists and materials scientists worldwide are engaged in the search for a variety of strategies to achieve this target via the generation of nitrogen-rich compounds,[1] cage strain molecules,[2] cocrystals,[3] and metal-organic frameworks,[4] among others. Nitrogen-rich compounds are subjects of much interest since they have high positive heats of formation, high energy and many N-N bonds in the ring which result in dinitrogen as a prominent decomposition product.[5] Although a variety of different nitrogen-rich energetic compounds have been enthusiastically developed, the design and synthesis of an ideal high energy density compound having a majority of the desired properties remain challenging.

From the molecular level, it may be difficult to solve the fundamental contradiction between energy and sensitivity. However, generation of new molecules has provided a unique platform to investigate structure-performance relationships in an effort to understand the inherent properties and to develop effective methods for balancing these two competing entities. Many studies have shown that adjacent amino and nitro groups in a molecule not only results in the retention of good detonation performance but also reduces mechanical sensitivities due to intra-/inter-molecular hydrogen bonds as well as ''push–pull'' electronic delocalization.[6] Typical examples are 2,4,6-triamino-1,3,5-trinitrobenzene (TATB),[7] 1,1-diamino-2,2-dinitroethene (FOX-7)[8] and 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105).[9]

Recently, the reaction of a diazonium salt with sodium nitroacetionitrile was demonstrated to be an efficient route to access fused compounds with adjacent amino-/nitro-groups[10] with higher thermal stability and lower sensitivity compared to the parent molecules. Based on a literature search, all fused compounds are prepared based on single rings, but C-C bonded fused bicyclic compounds have not been reported. It may be that such a structure could exhibit unique characteristics and integrate all of the desired properties. In this study, the synthesis of a C-C bonded amino-/nitro-pyrazole (**7**), which consists of two 3-amino-4-nitropyrazole rings is reported. Its ring-expansion product (**9**) with two 5,6-fused systems with promising properties was prepared and as a result it may find applications as an energetic material especially as a heat-resistant explosive due to its superior thermal stability.

The synthetic route to **9** is shown in Scheme 1. The intermediate **4** was prepared according to the literature.[11] It was treated with thionyl chloride in methanol at reflux to give **5**. Treatment of **5** with aqueous ammonia at room temperature resulted in the amide **6** which formed amine **7** via the Hoffman reaction (liquid bromine was added to the suspension of **6** in aqueous NaOH solution).[12] When a suspension of **7** was treated with 2.2 equiv of sodium nitrite in dilute sulfuric acid at 5 °C, followed by addition of sodium nitroacetonitrile, **8** was isolated in high yield (70%). Finally, compound **9** was prepared by cyclization of **8** in a mixture of methanol and water at reflux.

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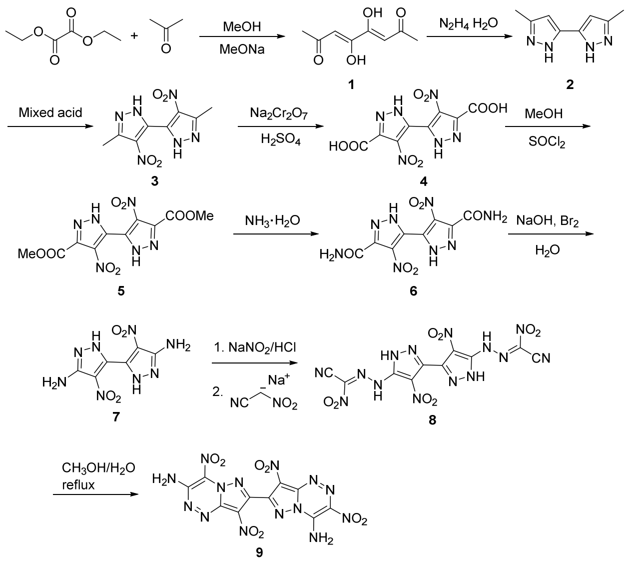
Electronic Supplementary Information (ESI) available: Includes theoretical calculation, crystallographic data (CCDC: 1948968, 1848975, 1848976) and DSC plot. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthesis of **9**

Two crystal structures of **7** obtained from crystallization from different solvents were found from hot water and acetonitrile, respectively. The molecular structure of **7**•CH_3CN is given in Fig. 1a. In **7**•CH_3CN, there are two unsymmetrical molecules in the unit cell. In comparing **7**•$2H_2O$ (Fig. 2a) with **7**•CH_3CN, no influence on the bond lengths is found although different molecules of crystallization are found in the molecular structures.

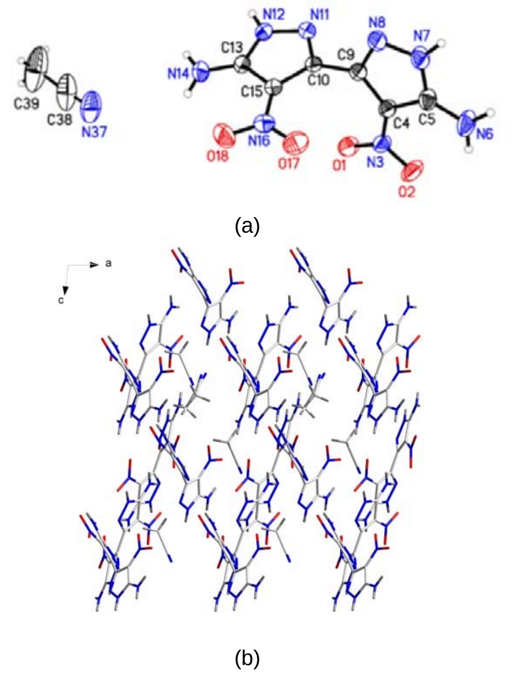


Fig. 1 (a) Molecular structure of **7**•CH_3CN solvate by thermal displacements ellipsoids with 50% probability. Another molecule is omitted for clarity. (b) A view of the packing diagram along the *b* axis.

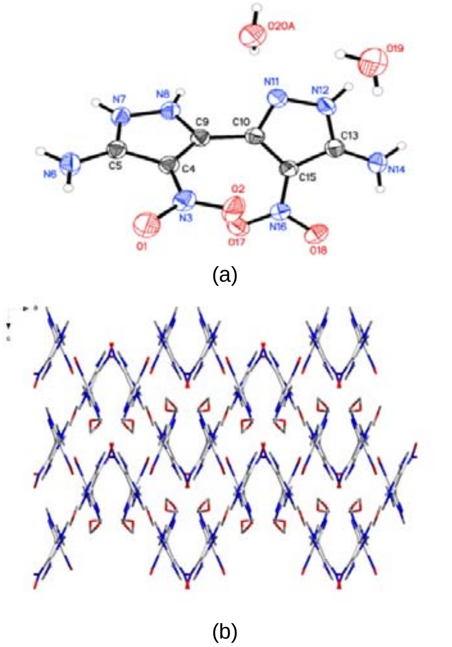


Fig. 2. (a) Molecular structure of **7**•$2H_2O$ solvates by thermal displacements ellipsoids with 50% probability. (b) A view of the packing diagram along the *b* axis

However, the torsion angles are different: the torsion angle of C4-C9-C10-C15 is 52.6^o in **7**•$2H_2O$ while the torsion angles in **7**•CH_3CN are 64.7^o (C4-C9-C10-C15) and 46.1^o (C22-C27-C28-C33), (Electronic Supplementary Information), respectively. The water molecules in **7**•$2H_2O$ are disordered. Also, one hydrogen atom on the pyrazole ring displays two-component disorder and is alternately bound to N7 or N8. Hydrogen atom occupancies on both atoms have been fixed at 0.5. In **7**•CH_3CN, it is seen clearly that the hydrogen atoms are bonded to the nitrogen atoms (N7 and N12) close to C-amino groups. The details are given in the Supporting Information. Comparison of crystal packing diagrams along the *b* axis shows that the solvents (water and acetonitrile) play an important role in forming different kinds of hydrogen bonds. The packing diagram of **7**•$2H_2O$ shows V-shape interactions (Fig. 2b) while those of **7**•CH_3CN display irregular packing (Fig. 1b).

Suitable crystals of **9** for X-ray diffraction were obtained by slow evaporation from a mixture of methanol and nitromethane. It crystallizes as a **9**•CH_3OH•CH_3NO_2 complex in the Cc space group and the monoclinic crystal system. The molecular structure is shown in Fig. 3. The bond lengths of C-C bonds connecting the two pyrazole rings in **7** and **9** are comparable (in **7**•$2H_2O$: C9-C10 1.468 Å; in **7**•CH_3CN: C9-C10 1.466 Å in **9**•CH_3OH•CH_3NO_2: C14-C17 1.463 Å). However, the bond lengths of C-NO_2 bonds connected to the pyrazole rings have increased from 1.39 Å in **7** to 1.42 Å in **9**. In addition, the bond lengths of C-NO_2 bonds connected to the triazine rings are even longer (C3-N4: 1.457 Å and C25-N26: 1.442 Å). The torsion angle of C10-C14-C17-C18 is 66.9^o, but the amino

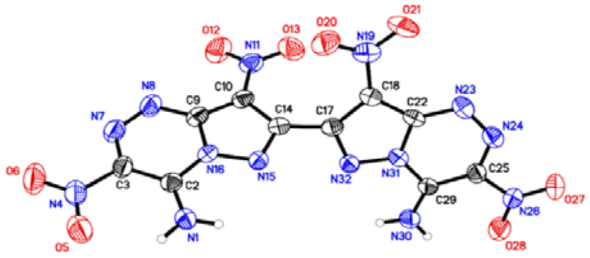


Fig. 3. (a) Molecular structure of **9**•CH_3OH•CH_3NO_2 by thermal displacement ellipsoids with 50% probability. The solvents methanol and nitromethane are omitted for clarity.

group (N1) and the nitro groups (N4 and N11) are coplanar with their bonded half fused ring.

The physical and calculated detonation performances are summarized in Table 1. Both **7** and **9** show high thermal stability, especially the onset decomposition temperature of **9** is 315 °C (Fig. S1), which is much higher than that of **7** (228 °C). The excellent thermal stability gives **9** a potential application in heat-resistant explosives. The densities were measured using a gas pycnometer at room temperature; compound **7** has a density of 1.72 g cm^{-3} while the density of **9** is 1.85 g cm^{-3}. The heats of formation were calculated by using Gaussion03 software.[13] As expected, both **7** and **9** show positive heats of formation with **9** much higher than **7** due to the incorporation of the fused ring. Using measured densities and calculated heats of formation, the detonation performance including detonation velocities and detonation pressures were evaluated using EXPLO5 v6.01.[14] Compound **7** has a detonation velocity (*vD*: 7779 m s^{-1}) and a detonation pressure (*P*: 23 GPa). The formation of the fused ring in **9** leads to better performance (*vD*: 8572 m s^{-1}; *P*: 31.4 GPa), which are also higher than those of TATB and comparable with those of LLM-105. The sensitivities to impact and friction are > 60 J and > 360 N, respectively, indicating that both can be classified as insensitive explosives.

Table 1. Physical and detonation properties of **7** and **9** in comparison with TATB and LLM-105.

Comds	T_d[a] [°C]	P[b] [g cm^{-3}]	$\Delta_f H$[c] [kJ mol^{-1}]	vD[d] [m s^{-1}]	P[e] [Gpa]	IS[f] [J]	FS[g] [N]
7	228	1.72	212	7779	23.0	>60	>360
9	315	1.85	899	8572	31.4	>60	>360
TATB	350	1.93	-139.7	8179	30.5	50	>360
LLM-105	342	1.92	11	8639	31.7	20	360

[a] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). [b] Measured densities - gas pycnometer at room temperature. [c] Calculated heat of formation. [d] Calculated detonation velocity. [e] Calculated detonation pressure. [f] Impact sensitivity. [g] Friction sensitivity.

Conclusions

In summary, a straightforward synthesis and full characterization of C-C bonded amino-nitro pyrazole (**7**) and C-C bonded 5,6-fused energetic molecule (**9**) are described. Both show high thermal stability especially the decomposition temperature of **9** at 315 °C. Given the good detonation performance and insensitivities, it has potential application in energetic materials, especially in heat-resistant explosives. In addition, the amino groups in **7** can be further functionalized to form some additional energetic functional pyrazole derivatives. Overall, this work not only provides a novel example for the design of C-C bonded amino-nitro fused systems but also provides new insights for the further development of thermally stable energetic compounds.

Experimental Section

Safety Precautions: Although we have encountered no difficulties during preparation and handling of these compounds, they are potentially explosive energetic materials; the diazotization reaction in Scheme 1 should be carried out at 0 –5 °C. The diazonium intermediate should not be isolated due to its potential sensitivity when dry. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Manipulations must be carried out by using appropriate standard safety precautions.

4,4'-Dinitro-2*H*,2'*H*-(3,3'-bipyrazole)-5,5'-dicarboxamide (**6**): A suspension of compound **4**[11] (4.68 g, 15.0 mmol) in methanol (60 mL) was cooled below 10 °C. Thionyl chloride (5.36 g, 45.0 mmol) was added slowly. The reaction mixture was refluxed for 3 h and then it was dried. Concentrated aqueous ammonia (60 mL) was added to the residue and the reaction mixture was stirred at room temperature for 24 h. After removing the excess aqueous ammonia, water (60 mL) was added. The suspension was acidified to pH = 1 by adding concentrated hydrochloric acid. The white precipitate was collected and washed with water (50 mL × 2) and dried in air (yield: 68%). White solid. T_m: 292 °C. $T_{d\ (onset)}$: 309 °C. ^1H NMR (d_6-DMSO): 8.39 (s, 2H), 8.10 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.9, 140.3, 1341, 130.5 ppm. IR (KBr): $\tilde{\nu}$ 3452, 3335, 3164, 1683, 1609, 1497, 1440, 1376, 1348, 1190, 1132, 1027, 926, 843, 762, 681 cm^{-1}. $C_8H_6N_8O_6$ (310.18): Calcd C 30.98, H 1.95, N 36.12 %. Found: C 30.72, H 2.20, N 36.09 %.

4,4'-Dinitro-5,5'-diamino-2*H*,2'*H*-(3,3'-bipyrazole) (**7**): Liquid bromine (0.26 ml, 5.0 mmol) was added dropwise to a solution of NaOH (0.96 g, 24.0 mmol) in water (20 mL) at 0–5°C. Amide **6** (0.65 g, 2.1 mmol) was added dropwise to the solution, and the reaction mixture was stirred for 30 min at 0–5°C. The temperature was increased to 55–60°C and maintained for 1 h. After cooling to 10 °C, the mixture was acidified with HCl to pH = 1. The precipitate was collected, washed with ice water and dried in air. Yield 0.43 g (80%).Orange solid. $T_{d\ (onset)}$: 228 °C. ^1H NMR (d_6-acetone): 6.88 (s, 4H) ppm. ^{13}C NMR (d_6-acetone): δ 147.7, 138.4, 117.3 ppm. IR (KBr): $\tilde{\nu}$ = 3450, 3344, 1646, 1486, 1458, 1399, 1372, 1199, 1133, 1063, 958, 830, 770, 738, 684 cm^{-1}. $C_6H_6N_8O_4$ (254.16): Calcd C 28.35, H 2.38, N 44.09 %. Found: C 28.15, H 2.63, N 43.54 %.

Synthesis of **8·H₂O**: Compound **7** (0.33 g, 1.29 mmol) was suspended in 20% H_2SO_4 (10 mL) and cooled in an ice-water bath. $NaNO_2$ (0.46 g, 3.56 mmol) dissolved in water (3 mL) was added dropwise to the cooled suspension and the mixture was stirred for 1 h to form the corresponding diazonium salt. The sodium salt of nitroacetonitrile was prepared by dissolving NaOH (0.2 g, 5 mmol) and nitroacetonitrile (0.42 g, 5 mmol) in ice water (5 mL) and the solution was added dropwise to the cooled reaction mixture. The reaction was stirred in the ice bath for 30 minutes and allowed to stir at room temperature for another 3 h. A yellow precipitate formed, was collected, washed with water, and air-dried to give **8** (0.42 g, 70% yield from **7**). Yellow solid. T_m: 99 °C. $T_{d\,(onset)}$: 204 °C. ^1H NMR (d_6-DMSO): 6.59 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 150.7, 138.7, 123.6, 123.5, 111.1 ppm. IR (KBr): $\tilde{\nu}$ 3368, 3222, 2234, 1619, 1551, 1465, 1371, 1306, 1263, 1221, 1164, 1106, 898, 838, 794, 768, 750 cm^{-1}. $C_{10}H_6N_{14}O_9$ (466.24): Calcd C 25.76, H 1.30, N 42.06 %. Found: C 25.85, H 1.43, N 42.03 %.

Synthesis of **9**: Compound **8** (0.42 g, 0.90 mmol) was suspended in methanol/water (1:1, 15 mL) and the mixture was heated to reflux and stirred at this temperature for 3 hours. After cooling to room temperature, the solvent was concentrated to approximately 5mL and the precipitate was filtered, washed with cold water (2 mL) and cold methanol (2 mL), and dried in air to yield **9**, as a yellow solid. Yield:0.35 g, 88%. Yellow solid. $T_{d\,(onset)}$: 315 °C. ^1H NMR (d_6-DMSO): 10.91 (s, 2H), 10.12 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 144.0, 143.8, 140.2, 138.7, 121.9 ppm. IR (KBr): $\tilde{\nu}$ 3632, 3429, 3403, 3294, 1666, 1604, 1561, 1532, 1518, 1503, 1431, 1407, 1376, 1341, 1294, 1204, 1181, 1103, 861, 831, 816, 770, 681 cm^{-1}. $C_{10}H_4N_{14}O_8$ (448.23): Calcd C 26.80, H 0.90, N 43.75 %. Found: C 26.74, H 1.20, N 42.48 %.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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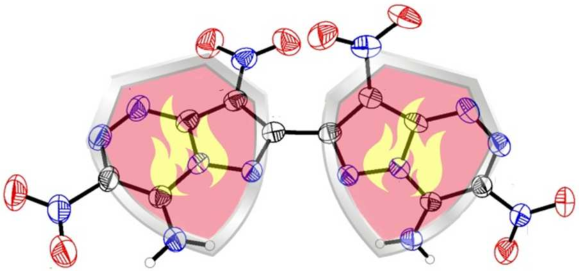

A C-C bonded 5,6-fused bicyclic energetic molecule is presented and shows promising properties as a heat-resistant explosive candidate.