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Energetic Tricyclic Polynitropyrazole and Its Salts: Proton-Locking Effect of Guanidium Cations

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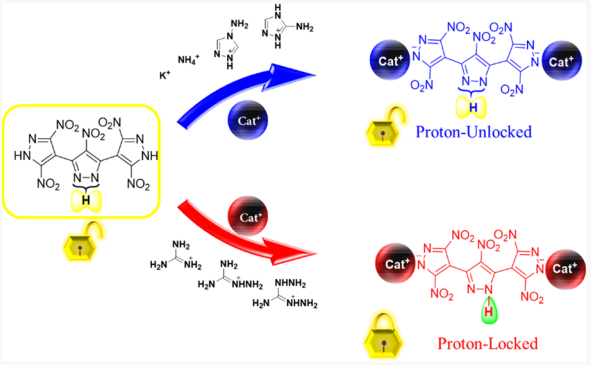
ABSTRACT: An axisymmetric polynitro-pyrazole molecule, 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole (**5**), and its salts (**6**–**12**) were prepared and fully characterized. These compounds not only show promising energetic properties but also show a unique tautomeric switch via combining different cations with the axisymmetric compound (**5**). Its salts (**6**–**9**) remain axisymmetric when the cations are potassium, ammonium, or amino-1,2,4-triazolium. However, when the cations are guanidiums, the salts (**10**–**12**) dramatically become asymmetric owing to the fixed proton. The introduction of guanidium cations breaks the tautomeric equilibrium by blocking the prototropic transformations and results in the switch-off effect to tautomerism. The structural constraints of ^{1}H NMR and ^{13}C NMR spectra provide strong evidence for the unusual structural constraint phenomenon. These stabilized asymmetric tautomers are very important from the point of molecular recognition, and this research may promote further developments in synthetic and isolation methodologies for novel bioactive pyrazole-based compounds.



INTRODUCTION

Tautomeric equilibria are very important to molecules, especially to heterocycles. It is impossible to interpret correctly the detailed mechanisms of reactions of tautomeric heterocycles without knowing the dominant tautomeric structure.[1,2] Furthermore, correctly representing the potentially tautomeric heterocycles would help to interpret and explore their biological activity and function.[3] The chemical reactivity and the bioactivity of heterocyclic compounds are highly influenced by their isomeric and tautomeric behaviors.[4] Prototropic tautomerism exists when the two tautomers differ only by the position of a proton. Different from all other types (metallotropy, acylotropy and elementotropy, methylotropy), prototropic tautomerism is quite special because of the small proton, which is insensitive to steric effects but which can also form hydrogen bonds.[5] Thus, to verify and control prototropic tautomerism is very important to basic structural chemistry and biochemistry.

Pyrazole is a five-membered heterocycle which contains two adjacent nitrogen atoms, where the proton can move freely from one to another. Its derivatives have attracted great attention due to their usefulness in the field of drug discovery, agricultural research, and energetic materials.[6−8] They are of considerable pharmacological relevance because of their antibacterial,[9] fungicidal,[10] antimicrobial,[11] herbicidal,[12] insecticidal,[13] anti-inflammatory,[14] and anticancer activities.[15] Some *NH*-pyrazole-containing compounds and their derivatives have been proved with diverse medical and biological effects.[8,10,14,16] 3,4-Diphenyl-1*H*-pyrazole-1-propanamine, a derivative of 3,4-diphenyl NH-pyrazole, exhibits marked antidepressant activity.[16] However, its isomer 4,5-diphenyl-1*H*-pyrazole-1-propanamine is completely inactive in preliminary antidepressant screens. Therefore, confirming the structures of *NH*-pyrazole compounds is of great importance and significance, since the position of the proton decides the properties of the molecule and directly influences the chemical reactivities and biological activities of both the molecule and its derivatives.

However, owing to the prototropic transformations of *NH*-pyrazoles, it is hard to observe the free proton in the ^{1}H nuclear magnetic resonance (NMR) spectra of *NH*-pyrazole derivatives.[17,18] The problem of "tautomeric blindness" has adversely affected many hierarchies of structural sciences from crystal structures to biological functions.[19] In this work, a series of energetic salts (**6**–**12**) based on 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole (**5**) were prepared. Interestingly, a structural constraint behavior based on the axisymmetric *NH*-

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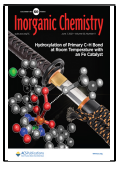

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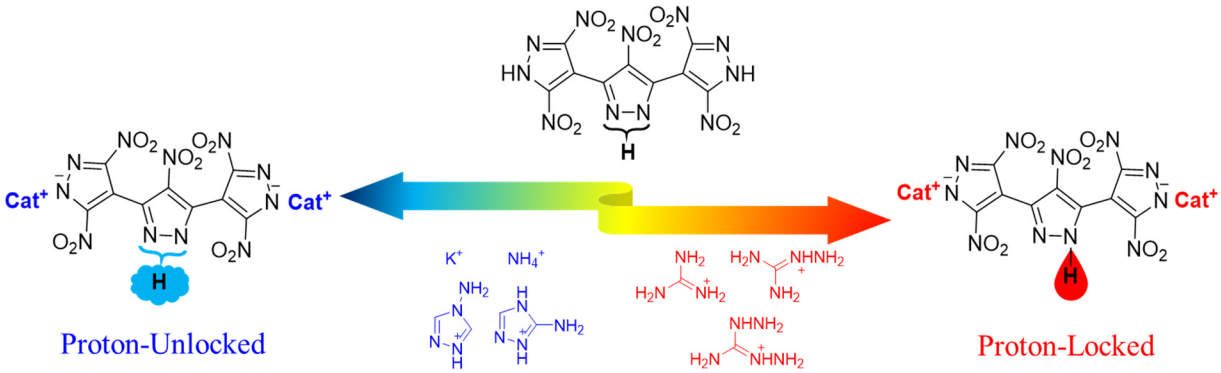
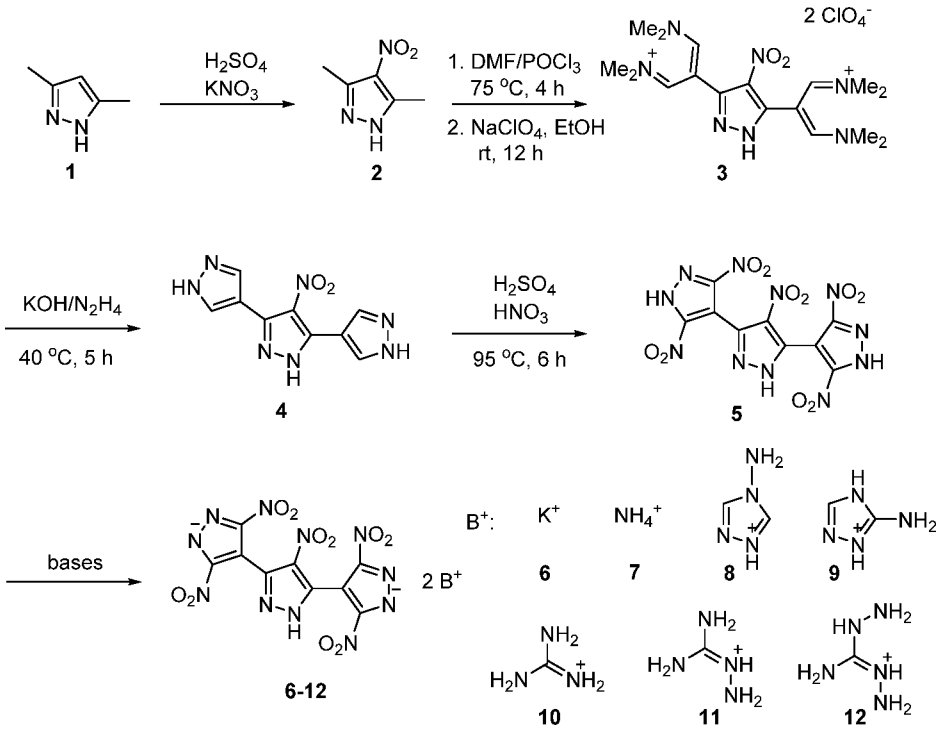


Figure 1. Tautomeric switches to 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole-based salts.

Scheme 1. Synthetic Routes to 5 and Its Salts 6−12



pyrazole derivative (**5**) is observed where the free proton on the NH is manipulated by the reacting cations. The proton can remain in a free state for one kind of cation, or locked to one nitrogen and result in a structural constraint as is the case when bonded to guanidinium cations (Figure 1). Cations function as tautomeric switches to 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole-based salts. In addition, these salts have been investigated as energetic materials because of their poly-nitro moieties and high nitrogen content.

RESULTS AND DISCUSSION

Synthesis. The synthetic route is shown in Scheme 1. 3,5-Dimethyl-1*H*-pyrazole (**1**) was nitrated with a mixture of KNO_3/H_2SO_4 to form 3,5-dimethyl-4-nitro-1*H*-pyrazole (**2**). The conversion of the methyl group to the 1,5-diazapentadienium moiety was initiated by treating **2** with phosphorus oxychloride ($POCl_3$) and *N*,*N*-dimethylformamide (DMF) at 75 °C for 4 h. The resulting reaction mixture was diluted with ethanol and followed by the addition of aqueous sodium perchlorate, which resulted in the formation of the perchlorate salt (**3**). The cyclization product (**4**) was achieved by reacting **3** with hydrazine monohydrate in an aqueous potassium hydroxide solution. Further nitration of **4** with a mixture of H_2SO_4/HNO_3 at 95 °C led to the formation of 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole (**5**). The energetic salts (**6**−**12**) were prepared easily through neutralization by the reactions of **5** with corresponding bases.[20] All the compounds were fully characterized by ^{1}H and ^{13}C NMR and elemental analysis. Among them, the ammonium (**7**), 4-amino-1,2,4-triazolium (**8**), aminoguanidium (**11**), and diaminoguanidium (**12**) salts were further confirmed by single crystal X-ray diffraction analysis.

NMR Spectroscopy. Substitution, solvent, concentration, and temperature are the four main factors that affect the positions of the tautomeric equilibrium.[21] In this research, ^{1}H and ^{13}C NMR spectra of the molecules are measured in d_6-DMSO at 25 °C. Therefore, the only variable factor for the salts is the cation.

According to the literature, the structure of **5** was reported by Shevelev's group in 1993.[22] In the ^{1}H NMR spectrum, three

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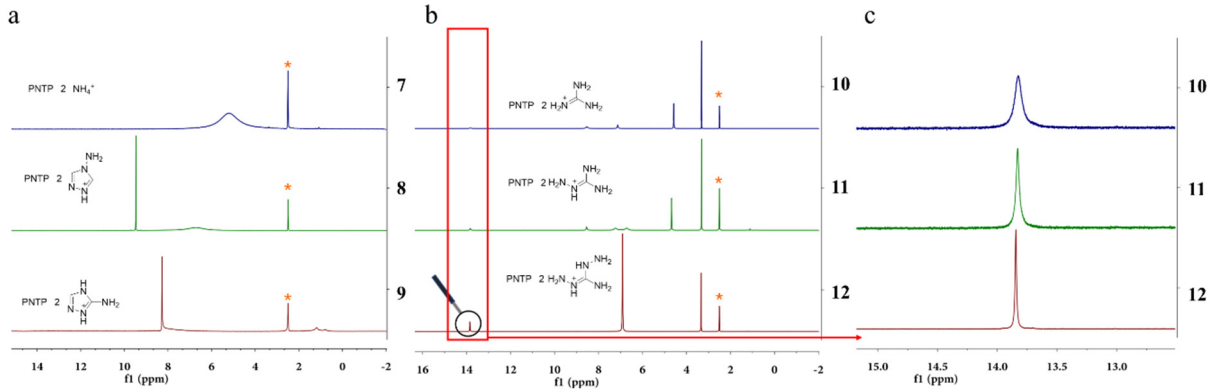

Figure 2. (a) ^{1}H NMR spectra of **7**−**9**. (b) ^{1}H NMR spectra of **10**−**12**. (c) Zoom-in ^{1}H NMR spectra (12−15 ppm) of **10**−**12**.

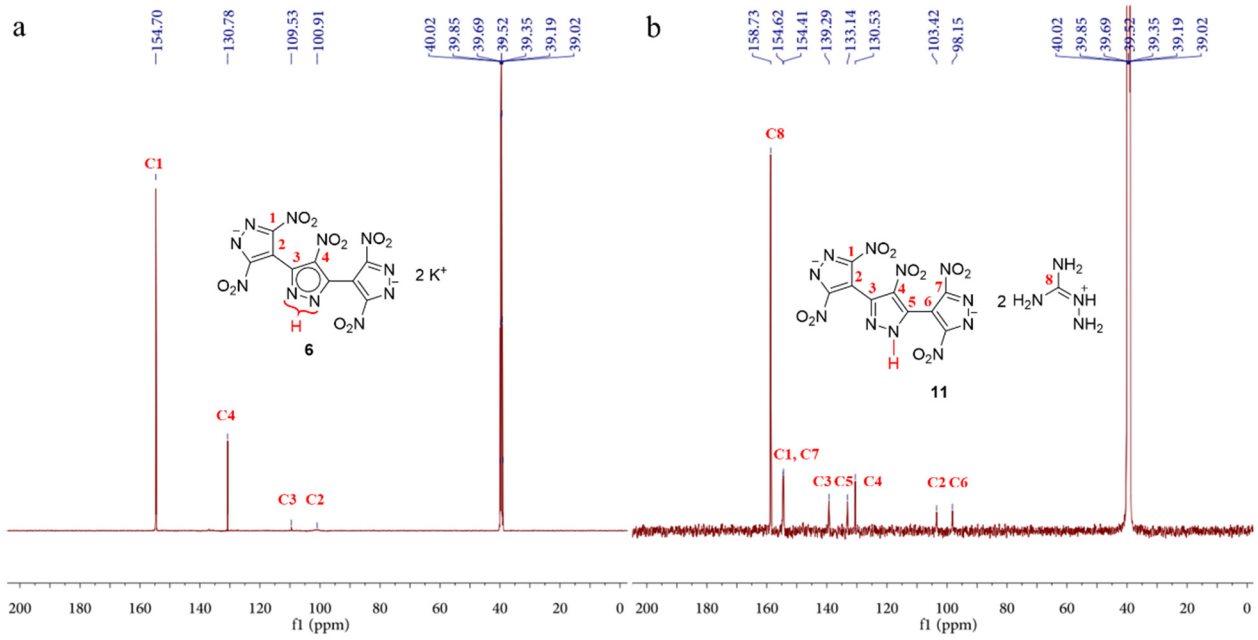

Figure 3. ^{13}C NMR spectra of (a) **6** and (b) **11**. All the spectra are recorded in d_6-DMSO. The *x*-axis represents the chemical shift δ in ppm. The red stars represent the peak of d_6-DMSO at 2.5 ppm.

peaks were reported at 13.86, 9.16, and 8.25 ppm. For the ^{13}C NMR spectrum, five peaks were recorded at 140.7, 136.3, 129.1, 126.2, and 113.5 ppm. In our NMR measurements, this is the case for **5** where only one characteristic peak at 7.20 ppm is seen in the ^{1}H NMR spectrum (Figure S3), and four peaks at 150.7, 133.5, 131.3, and 101.4 ppm appear in the ^{13}C NMR spectrum (Figure S4). Although all measurements were made in d_6-DMSO as the solvent, their results are quite different from ours. The results arouse our interests to study more details on the NMR spectra, especially those energetic salts.

^{1}H NMR Spectra of Salts. The ^{1}H NMR spectra for **7**−**12** are shown in Figure 2. The broad peak around 5.22 ppm is the NH signal of the ammonium group in **7** (Figure 2a). The ^{1}H NMR spectrum of **8** has peaks at 6.67 and 9.44 ppm, which represent the NH of the amino group (−NH_2) and −N−CH−N− of the triazole ring, respectively. The characteristic peak at 8.28 ppm in the spectrum of **9** arises from the CH of triazole ring. In all three cases, only the protons from the cations are seen. The Roving proton of the anion 4,4′-(4-nitro-1*H*-pyrazole-3,5-diyl)-3,3′,5,5′-tetranitrobipyrazolate (NPTP) is invisible owing to rapid prototropic tautomerism. By contrast, the NMR spectra of **10**−**12** are quite intriguing (Figure 2b). Except for the characteristic peaks for the three guanidium cations, there are fewer obvious peaks around 13.8 ppm (zoomed in as Figure 2c). On the basis of the same anion, these peaks (around 13.8 ppm) in **10**−**12** can be assigned to the fixed proton of the NH in the central pyrazole. It is quite unsual to observe this particular proton in pyrazole. By the formation of the NPTP guanidium salts, the Roving proton is successfully stabilized and the structure is locked. The locked effect solves the problem of "tautomeric blindness" in the pyrazole ring, which would play a very positive role in promoting many hierarchies of structural sciences from molecule crystal structures to biological functions.

^{13}C NMR Spectra of Salts. The ^{13}C NMR spectra of all compounds are given in the Supporting Information. The assignments of the signals are based on theoretical calculations using Gaussian 09. The ^{13}C NMR spectra of the potassium salt (**6**) and the aminoguanidium salt (**11**) are fully analyzed here. As shown in Figure 3a, the four peaks represent four kinds of carbon in different chemical environments in **6**. All the carbons originate from the NPTP anion, which indicates the nine

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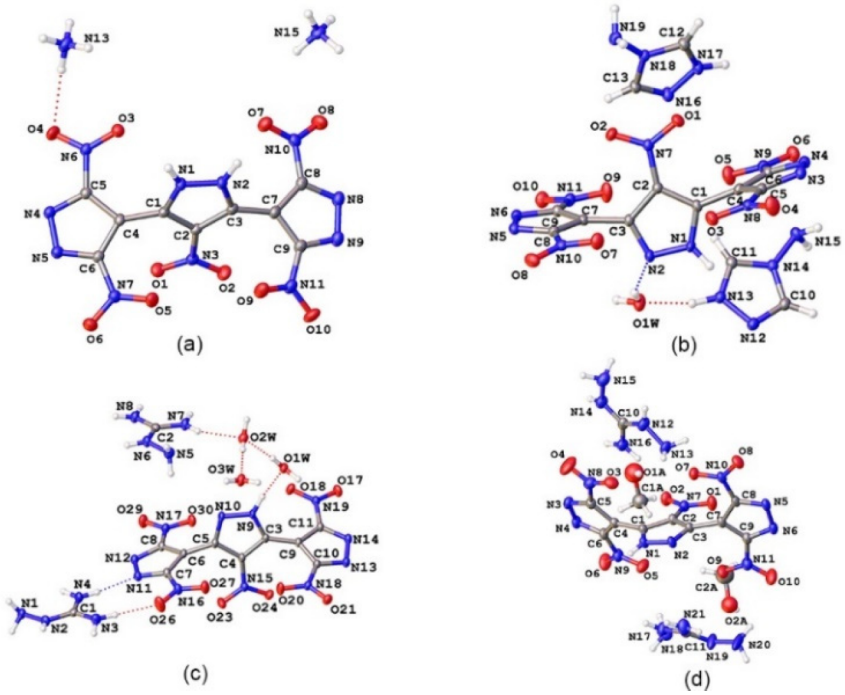

Figure 4. Molecular structures of (a) 7·8.5H_2O, (b) 8·H_2O, (c) 11·3H_2O, and (d) 12·2CH_3OH. For clarity, the water molecules are omitted in 7·8.5H_2O.

Table 1. Energetic Properties and Detonation Parameters

comp	ρ,[a] g·cm^{-3}	Dv,[b] m s^{-1}	P,[c] GPa	ΔH_f[d] kJ mol^{-1}/(kJ g^{-1})	Q,[e] kJ kg^{-1}	T_{dec},[f] °C	IS,[g] J	FS,[h] N
5	1.85	8345	29.7	387.4/0.91	−5073.9	300	30	>360
6	1.92	7372	22.9	33.1/0.07	−4666.1	358	25	>360
7	1.68	7713	23.5	303.5/0.66	−4713.8	302	40	>360
8·H_2O	1.72	7767	23.9	1019.6/1.72	−4985.3	235	40	>360
9	1.75	7724	23.4	749.1/1.26	−4330.8	290	>40	>360
10·H_2O	1.73	7683	22.8	252.0/0.46	−4319.3	326	>40	>360
11	1.76	8027	24.8	466.2/0.82	−4276.7	241	40	>360
12	1.78	8323	27.0	683.81/1.13	−4505	217	36	>360
TNT[i]	1.654	6824	19.4	−59.3/-0.26	−4426.8	295	15	>353
TATB[i]	1.94	8201	28.1	−154/-0.54	−3858.4	350	50	>360

[a]Density measured by a gas pycnometer at 25 °C. [b]Calculated detonation velocity from EXPLO5_V6.05.02. [c]Calculated detonation pressure from EXPLO5_V6.05.02. [d]Calculated molar enthalpy of formation in the solid state. [e]Calculated heat of detonation. [f]Temperature of decomposition (onset). [g]Impact sensitivity. [h]Friction sensitivity. [i]Data are from EXPLO5 database.

carbons only give four signals. The phenomenon could be attributed to the axial symmetric structure of **6**. The axisymmetric property comes from the unstoppable prototropic tautomerism, free rotation of lateral pyrazole around the central pyrazole, and symmetrical lateral 3,5-dinitropyrazole group. This phenomenon also exists in the ^{13}C NMR spectra of the neutral compounds **4** and **5** and NPTP salts **7**−**9**.

However, in the case of the NPTP guanidium salts **10**−**12**, there are seven characteristic peaks corresponding to seven kinds of carbon in the NPTP anion. Taking **11** as an example, eight peaks are found in Figure 3b. Seven peaks (C1−C7: 98.2−153.6 ppm) are derived from the carbon atoms from the NPTP anion, and the peak C8 at 158.7 ppm is assigned to the carbon in the guanidium cation. The introduction of guanidium cations destroys the axial symmetry structure of **11**. The proton on the NH of the central pyrazole is retained on one nitrogen atom and is no longer roving. The combination of guanidium cations with an NPTP anion causes an unusual lock effect for the prototropic tautomerism of the pyrazole group, which is rarely reported.

Both the ^1H NMR and ^{13}C NMR spectra of the NPTP guanidium salts reveal an unusual phenomenon as a result of blocking the prototropic transformations. In this work, the prototropic tautomerism was controlled precisely and clearly verified. The fixed asymmetric tautomers are very important from the point of molecular recognition. A clear and exact molecular recognition helps to investigate the biological activity and function of the tautomers. Thus, this proton-locking strategy by the guanidium cations of NH-pyrazole molecules could promote the development of heterocyclic chemistry, structural chemistry, and biochemistry.

Single-Crystal X-ray Structure Analysis. The structures of the molecules (**7**, **8**, **11**, and **12**) were further characterized by single crystal X-ray diffraction. Compound 7·8.5H_2O (Figure 4a) crystallizes in the triclinic space group $P\bar{1}$ with two formula moieties in the unit cell and a calculated crystal density of 1.643 g cm^{-3} at 100 K. The torsion angles of C(2)−

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C(1)−C(4)−C(6) and C(9)−C(7)−C(3)−C(2) are 52.8° and −55.6°, respectively. The structure is distorted, and both lateral pyrazoles are nonplanar with respect to the central one. Compound **8**·H_2O (Figure 4b) crystallizes in the monoclinic space group $P2_1/c$ with four formula moieties in the unit cell and a calculated crystal density of 1.764 g cm^{-3} at 100 K. The torsion angles of C(2)−C(1)−C(4)−C(6) and C(9)−C(7)−C(3)−C(2) are −91.6° and 87.0°, respectively. It demonstrates a more-distorted structure. Compound **11**·3H_2O crystallizes in the triclinic space group $P\bar{1}$ with two formula moieties in the unit cell and a calculated crystal density of 1.659 g cm^{-3} at 100 K. The molecular structure is given in Figure 4c. The torsion angles of C(8)−C(6)−C(5)−C(4) and C(4)−C(3)−C(9)−C(11) are −98.8° and 115.6°, respectively. Compound **12**·2CH_3OH (Figure 4d) crystallizes in the triclinic space group $P\bar{1}$ with two formula moieties in the unit cell and a calculated crystal density of 1.634 g cm^{-3} at 100 K. The torsion angles of C(9)−C(7)−C(3)−C(2) and C(6)−C(4)−C(1)−C(2) are −80.0° and 73.0°, respectively. The differences between the two twist angles in asymmetric **11**·3H_2O (16.8°) and **12**·2CH_3OH (7.0°) are larger than for the symmetric **7**·8.5H_2O (2.8°) and **8**·H_2O (4.6°).

Physicochemical and Energetic Properties. Considering the high nitrogen content and polynitro properties, these compounds have great potential as energetic materials.[23−25] To evaluate their performance, the energetic properties and thermal stabilities were compared with TNT and TATB and are listed in Table 1. The decomposition temperatures (onset) of the energetic salts range from 217 °C, comparable to that of TATB (1.94 g·cm^{-3}), to 358 °C. Compound **6** exhibits an ultrahigh thermostability. In addition, it has the highest density of 1.92 g·cm^{-3}, and the densities fall between 1.68 g·cm^{-3} and 1.92 g·cm^{-3}. All the new compounds have high positive solid-state heats of formation in the range from 33.1 kJ mol^{-1} to 1019.6 kJ mol^{-1}. All detonation performances surpass TNT (Dv > 7372 m s^{-1}, P > 22.8 GPa), and some of them are comparable to TATB. The detonation velocities of compounds range from 7372 m s^{-1} to 8345 m s^{-1}. The detonation pressures for compounds **5**−**12** are in the range from 22.8 to 29.7 GPa. On the basis of the same anion of NPTP, the detonation velocities and pressures of these salts are mainly influenced by the cations with different nitrogen contents. The potassium salt, without nitrogen content in the cation, shows the lowest detonation performance. The diaminoguanidium salt (**12**) with the highest nitrogen content has the highest detonation velocity (8323 m s^{-1}) of these salts. These new compounds have relatively low sensitivities to impact and friction, with impact sensitivities >25 J and friction sensitivities >360 N. Compound **5**, with good detonation properties (Dv, 8345 m s^{-1}; P, 29.7 GPa), high thermostability (T_{dec}, 300 °C), and low sensitivities (IS, 30 J; FS, >360 N), is a promising energetic material.

CONCLUSION

A series of energetic salts (**6**−**12**) based on 3,5-di(3,5-dinitropyrazol-4-yl)]-4-nitro-1*H*-pyrazole (**5**) were synthesized and fully characterized. They show high thermal stabilities and good detonation performances and insensitivities. In addition, owing to their high nitrogen content and polynitro properties, these compounds have potential application as energetic materials. On the other hand, we report intriguing tautomeric switches which have a turn-off effect to tautomeric equilibria. By manipulating the different cations, the free proton of the central *NH*-pyrazole in the NPTP anion can be locked on one certain nitrogen or unlocked to the free state. The research would be of benefit for the development of related heterocyclic chemistry, structural chemistry, and biochemistry.

EXPERIMENTAL SECTION

Caution! *The compounds in this work are potentially energetic materials that could explode under certain conditions (such as impact, friction, or electric discharge). Experiments should be performed on a small scale. Appropriate safety precautions, including the use of safety shields and personal protections (safety glasses, ear plugs, and gloves), are suggested all the time when handling these compounds.*

General. All reagents were purchased from SigmaAldrich in analytical grade and used without further purification. The NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer (Bruker AVANCE 300). IR spectra of the compounds were recorded using KBr pellets with a FT-IR Thermo Nicolet AVATAR 370 spectrometer. Density was measured with a Micromeritics AccuPyc II 1340 gas pycnometer at room temperature. Thermal decompositions were tested on a differential scanning calorimeter (TA Instruments Q2000) using a dry nitrogen gas purge with a heating rate of 5 °C min^{-1}. Elemental analyses (C, H, N) were conducted with a Vario Microcube Elementar Analyzer. Impact and friction sensitivity were measured using a standard BAM Fallhammer and a BAM friction tester.

Computational Methods. The gas phase enthalpies of formation were calculated according to isodesmic reactions. The enthalpy of reaction is obtained by combining the MP2/6-311++G** energy difference for the reactions, the values of thermal correction (HT), the scaled zero point energies (ZPE), and other thermal factors. Detonation performances were calculated using EXPLO5 v6.05.02.[26] The solid-state heats of formation were based on Trouton's rule.

General Synthesis of Energetic Salts 4 and 5. *Synthesis of 3,5-Di(pyrazol-4-yl)-4-nitro-1H-pyrazole (4·H_2O).* Compound **2** was obtained according to the literature.[27] Compound **2** (2.82 g, 20.0 mmol) was added to a mixture of DMF (8 mL) and phosphorus oxychloride (5 mL) at room temperature. The reaction mixture was heated at 75 °C and stirred for 4 h. The mixture was cooled to 5−10 °C in an ice−water bath, and ethanol (8 mL) was added slowly. A solution of sodium perchlorate (4.90 g, 40.0 mmol) in water (15 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. The crude product (**3**) was collected by filtration, washed with isopropanol (20 mL), and dried in the air. Compound **3** was used without further purification. To a solution of **3** (3.08 g) in aqueous potassium hydroxide solution (1.54 g KOH in 30 mL water), hydrazine monohydrate (2.0 g, 40.0 mmol) was added dropwise. The reaction mixture was then heated at 40 °C and stirred for another 5 h. The precipitate (**4**) was collected by filtration and washed with water (20 mL), ethanol (15 mL), and diethyl ether (15 mL). Compound **4** was purified by recrystallization with water/methanol.

4·H_2O: White solid. T_m: 326 °C. $T_{d\ (onset)}$: 328 °C. ^{1}H NMR (d_6-DMSO): 13.16 (br), 8.12 ppm. ^{13}C NMR (d_6-DMSO): δ 139.3, 134.0, 127.0, 110.3 ppm. IR (KBr): $\tilde{\nu}$ = 3124, 2987, 1545, 1432, 1328, 1299, 1175, 1085, 864, 765, 741, 702, 668, 622 cm^{-1}. Elemental analysis calcd for $C_9H_9N_7O_3$ (263.21): C 41.07, H 3.45, N 37.25%. Found: C 41.63, H 2.97, N 37.73%.

Synthesis of 3,5-Di(3,5-dinitropyrazol-4-yl)]-4-nitro-1H-pyrazole (5). Compound **4** (1.47 g, 6.00 mmol) was added to a mixture of sulfuric acid (10 mL) and nitric acid (8 mL) at 0 °C. The reaction mixture was heated at 95 °C and stirred for 6 h. The solution was poured into ice water (120 g), and a white solid was collected by filtration and washed with water (20 mL) to leave **5**, which can be purified by recrystallization with hot water.

5: White solid. $T_{d\ (onset)}$: 300 °C. ^{1}H NMR (d_6-DMSO): 7.20 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 150.7, 133.5, 131.3, 101.3 ppm. IR (KBr): $\tilde{\nu}$ = 3461, 1537, 1467, 1420, 1372, 1323, 1212, 1168, 1008, 967, 841, 820, 812, 770, 731, 715, 664, 615 cm^{-1}. Elemental analysis calcd for $C_9H_3N_{11}O_{10}$ (425.19): C 25.42, H 0.71, N 36.24%. Found: C 25.39, H 0.47, N 36.71%.

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General Procedure for Synthesis of Energetic Salts (6−12). An energetic base (4.0 mmol of potassium bicarbonate, aqueous ammonia, 4-amino-1,2,4-triazole, 3-amino-1,2,4-triazole, guanidine carbonate, aminoguanidine bicarbonate, or 1,3-diaminoguanidine hydrochloride) was added to a suspension of **5** (0.51 g, 2.0 mmol) in water (50 mL). The reaction mixture was heated to 50 °C and stirred for 30 min. The precipitate was collected by filtration to give the product, which was purified further by recrystallization with water/methanol.

6: Light-yellow solid. $T_{d\ (onset)}$: 358 °C. ^{13}C NMR (d_6-DMSO): δ 154.7, 137.0 (br), 130.8, 100.9 (br) ppm. IR (KBr): $\tilde{\nu}$ = 3574, 1647, 1616, 1508, 1448, 1395, 1345, 1207, 1159, 1107, 1018, 958, 850, 817, 770, 726, 707, 664, 646 cm^{-1}. Elemental analysis calcd for $C_9HK_2N_{11}O_{10}$ (501.37): C 21.56, H 0.20, N 30.73%. Found: C 21.56, H 0.42, N 30.78%.

7: White solid. $T_{d\ (onset)}$: 299 °C. ^{1}H NMR (d_6-DMSO): 5.22 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 154.5, 136.3, 130.6, 100.9 ppm. IR (KBr): $\tilde{\nu}$ = 3461, 1537, 1467, 1420, 1372, 1323, 1212, 1168, 1008, 967, 841, 820, 812, 770, 731, 715, 664, 615 cm^{-1}. Elemental analysis calcd for $C_9H_9N_{13}O_{10}$ (459.25): C 23.54, H 1.98, N 39.65%. Found: C 23.77, H 1.99, N 39.31%.

8·H_2O: White solid. T_m: 228 °C. $T_{d\ (onset)}$: 229 °C. ^{1}H NMR (d_6-DMSO): 9.48 (s, 4H), 6.70 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 152.3, 144.0, 134.7, 130.7, 100.9 (br) ppm. IR (KBr): $\tilde{\nu}$ = 3327, 3132, 1645, 1548, 1514, 1462, 1408, 1357, 1326, 1208, 1170, 1075, 1001, 968, 850, 813, 770, 720, 659, 629 cm^{-1}. Elemental analysis calcd for $C_{13}H_{13}N_{19}O_{11}$ (611.36): C 25.54, H 2.14, N 43.53%. Found: C 25.41, H 2.19, N 43.63%.

9: White solid. $T_{d\ (onset)}$: 290 °C. ^{1}H NMR (d_6-DMSO): 8.28 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 154.3, 151.0, 139.5, 136.2 (br), 130.6, 100.7 (br) ppm. IR (KBr): $\tilde{\nu}$ = 3433, 3352, 3242, 3161, 3071, 1680, 1559, 1532, 1512, 1449, 1401, 1348, 1314, 1252, 1211, 1172, 1038, 1022, 962, 943, 889, 850, 837, 814, 782, 768, 729, 697, 666, 621 cm^{-1}. Elemental analysis calcd for $C_{13}H_{11}N_{19}O_{10}$ (593.35): C 26.31, H 1.87, N 44.85%. Found: C 26.50, H 2.09, N 43.07%.

10·H_2O: White solid. $T_{d\ (onset)}$: 326 °C. ^{1}H NMR (d_6-DMSO): 13.84 (s, 1H), 6.91 (s, 12H) ppm. ^{13}C NMR (d_6-DMSO): δ 157.9, 154.6, 154.4, 139.3, 133.1, 130.6, 103.5, 98.2 ppm. IR (KBr): $\tilde{\nu}$ = 3469, 1663, 1548, 1491, 1450, 1395, 1347, 1309, 1211, 1161, 1018, 962, 849, 728, 703, 663 cm^{-1}. Elemental analysis calcd for $C_{11}H_{15}N_{17}O_{11}$ (561.35): C 23.54, H 2.69, N 42.42%. Found: C 23.54, H 2.71, N 42.10%.

11: White solid. T_m: 222 °C. $T_{d\ (onset)}$: 241 °C. ^{1}H NMR (d_6-DMSO): 13.83 (s, 1H), 8.54 (s, 2H), 7.24 (s, 4H), 6.71 (s, 4H), 4.68 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO): δ 158.7, 154.6, 154.4, 139.3, 133.1, 130.5, 103.4, 98.2 ppm. IR (KBr): $\tilde{\nu}$ = 3495, 3448, 3395, 3353, 1689, 1663, 1533, 1507, 1500, 1489, 1444, 1416, 1389, 1349, 1309, 1290, 1206, 1157, 1020, 1008, 958, 848, 836, 660, 619 cm^{-1}. Elemental analysis calcd for $C_{11}H_{15}N_{19}O_{10}$ (573.36): C 23.04, H 2.64, N 46.42%. Found: C 23.20, H 2.72, N 46.50%.

12: White solid. T_m: 213 °C. $T_{d\ (onset)}$: 217 °C. ^{1}H NMR (d_6-DMSO): 13.82 (s, 1H), 8.53 (s, 4H), 7.13 (s, 4H), 4.58 (s, 8H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.7, 154.5, 139.3 (br), 133.2 (br), 130.6, 103.4 (br), 98.1 (br) ppm. IR (KBr): $\tilde{\nu}$ = 3458, 1676, 1537, 1515, 1485, 1442, 1393, 1351, 1310, 1208, 1162, 1108, 1010, 961, 916, 848, 815, 698, 664, 600 cm^{-1}. Elemental analysis calcd for $C_{11}H_{17}N_{21}O_{10}$ (603.39): C 21.90, H 2.84, N 48.75%. Found: C 21.65, H 2.81, N 48.16%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01202.

The ^{1}H and ^{13}C NMR of all the compounds; crystal structure analysis of **7**, **8**, **11**, and **12**; and DSC plots of **5**−**12** (PDF)

Accession Codes

CCDC 2054157−2054160 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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