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$C_6N_{10}O_4$: Thermally Stable Nitrogen-Rich Inner Bis(diazonium) Zwitterions

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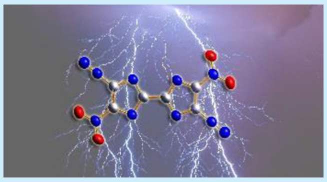
Supporting Information

ABSTRACT: Two nitrogen-rich inner bis(diazonium) salts, the 4,4′-dinitro-5,5′-diazo-2,2′-bisimidazole (**2**) and the 4,4′-dinitro-5,5′-diazo-3,3′-bispyrazole (**4**) zwitterions, are described. Compound **2** was synthesized unexpectedly from the nitration of 4,4′-dinitro-5,5′-diamino-1*H*,1′*H*-2,2′-bisimidazole (**1**) in a mixture of trifluoroacetic anhydride and 100% nitric acid. Both **2** and **4** show good thermal stability, especially **2** has a decomposition temperature of 199 °C, which is the highest one in any of the reported hydrogen-free nitrogen-rich diazonium salts.



Diazonium compounds have been investigated extensively since the first one was reported in 1858.[1] They can be used as valuable building blocks or intermediates in a wide range of organic syntheses.[2] In general, the synthesis of a diazonium salt is initiated by the diazotization of an aromatic amine with sodium nitrite and a mineral acid or in an organic solvent using an alkyl nitrite reagent.[3−6] Some of them are prepared by the nitration in a mixed acid.[7−9] With the development of isolation technology and characterization methods, many more diazonium salts have been isolated and confirmed by their solid state structures. Nevertheless, the diazonium salts are most generally used *in situ* without isolation due to their extremely dangerous nature rising from low thermal stability and chemical instability.

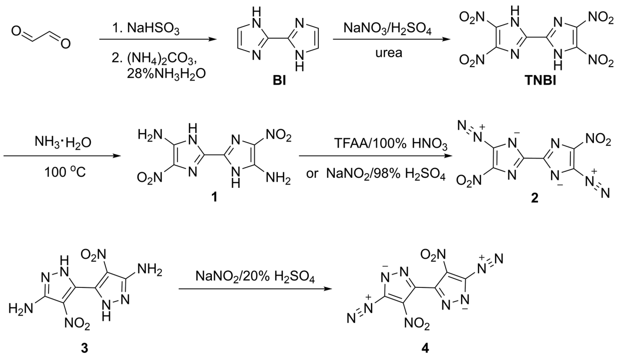
Diazonium moieties are easily initiated by shock and impact, and therefore, they have been well studied as lead-free primary explosives. A typical example is 2-diazo-4,6-dinitrophenol (DDNP), which is now commercially available in many countries and has extensive application in percussion caps and in detonators. However, DDNP has several drawbacks including high sensitivity to mechanical stimuli, photosensitivity, and high toxicity as well as low detonation performance (detonation velocity, 6900 m s^{-1}; detonation pressure, 24.2 GPa),[10] which encouraged us to search for environmentally friendly and highly energetic candidates. Although some other nitrogen-rich diazonium salts, such as the 4-diazo-3,5-dinitropyrazole zwitterion (DDNPz)[11] and zwitterionic diazonium tetrazolyl-1,2,3-triazolate,[7] show promising performance as potential green primary explosives, due to their low thermal stability (<160 °C), the most important criterion for a primary explosive, i.e., stability to least to 180 °C,[12] is not realized.

In addition, only one hydrogen-free nitrogen-rich inner bis(diazonium) salt (inner salt 5,5′-bis(3-diazo-1,2,4-triazole)) has been reported.[13,14] However, its decomposition temperature is only 120 °C, which limits its practical application. Additionally, due to its elemental composition (only C and N), it has a low density of 1.73 g cm^{-3} and a very modest detonation performance (νD, 7780 m s^{-1}; *P*, 26.7 GPa).

Now two new ternary CNO-inner bis(diazonium) salts, 4,4′-dinitro-5,5′-diazo-2,2′-bisimidazole zwitterion (**2**) and 4,4′-dinitro-5,5′-diazo-3,3′-bispyrazole zwitterion (**4**) and their X-ray crystal structures are described. Both compounds have good thermal stability and excellent detonation performance, which make them good candidates for the next generation of green lead-free primary explosives.

The synthetic route to **2** is given in Scheme 1. 4,4′,5,5′-Tetranitro-2,2′-bisimidazole (TNBI) was prepared from commercially available glyoxal and sodium bisulfite.[15] TNBI was heated at 100 °C for 12 h in aqueous ammonia in a sealed tube, which resulted in the formation of 4,4′-dinitro-5,5′-diamino-1*H*,1′*H*-2,2′-bisimidazole (**1**). When **1** was treated with a mixture of trifluoroacetic anhydride (TFAA) and 100% nitric acid at 0 °C, the 4,4′-dinitro-5,5′-diazo-2,2′-bisimidazole zwitterion (**2**) was isolated and confirmed by single crystal X-

Scheme 1. Synthesis of Inner Bis(diazonium) Salts 2 and 4



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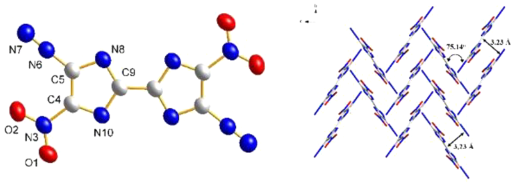
ray diffraction. Since the yield of **2** is low (37%), alternative synthetic attempts were tried. When **1** was treated with a mixture of sodium nitrite and dilute sulfuric acid (20%), only a trace of **2** was isolated, which may be a result of the very low solubility of **1** in such dilute sulfuric acid. When concentrated sulfuric acid was used, the yield of **1** was improved to 80%.

The inner bis(diazonium) salt (**4**) was observed as an intermediate in our previous study,[17] but it was not isolated. 4,4′-Dinitro-5,5′-diamino-2*H*,2′*H*-(3,3′-bipyrazole) (**3**, Scheme 1) was treated with sodium nitrite in 20% H_2SO_4 at 0 °C for 30 min. The product was collected by filtration and washed with water. It is not necessary to add a base to bind the acid as previous studies have suggested.[16] Compound **4** was also fully characterized by IR, ^{13}C and ^{15}N NMR, and single crystal X-ray diffraction analysis.

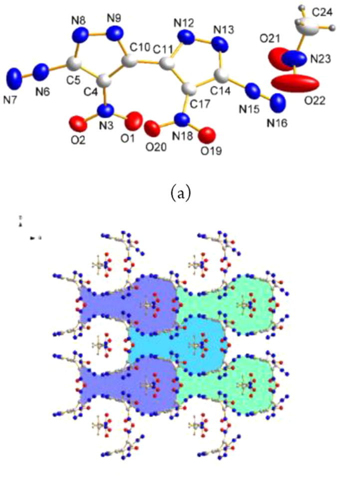
Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell and with a crystal density of 1.834 g cm^{-3} at 296 K. The molecular structure is given in Figure 1a. The atoms N7, N6, and C5 lie in the same plane with a bond angle of N(7)−N(6)−C(5) = 179.3(2)°. The bond length of N6−N7 is 1.100(2) Å, which is a typical N−N triple bond and is comparable to those reported for inner diazonium salts.[7,11] The bond length of C(5)−N(6) is 1.360(2) Å, which is between the bond length of the C=N double bond (1.28 Å) and the C−N single bond (1.47 Å). All of the atoms are nearly coplanar. The torsion angles of O(1)−N(3)−C(4)-N(10) and C(5)−N(8)−C(9)-C(9)#1 are −1.1(3)° and −179.2(2)°, respectively. The packing diagram shows a zigzag shape and is given in Figure 1b. The molecules are stacked along the *b* axis with a distance of 3.23 Å between layers and at an angle of 75.14°.



(a) (b)

Figure 1. (a) Molecular structure of **2**. (b) Packing diagram of **2** along *a* axis.

Suitable crystals for X-ray diffraction were obtained by crystallizing in a saturated solution of **4** dissolved in nitromethane. As a result, the obtained crystals are composed of a 1:1 molar ratio of **4** and nitromethane. Compound **4**·CH_3NO_2 crystallizes in the monoclinic space group *Cc* with four molecules per unit cell and with a crystal density of 1.721 g cm^{-3} at 296 K. The molecular structure is given in Figure 2a. Due to the presence of nitromethane, the crystal structure of **4** is unsymmetric. The parameters including bond lengths and bond angles show few differences between the two half pyrazole rings. The bond lengths of N6−N7 and N15−N16 are 1.095(4) and 1.090(3) Å, respectively. The bond length of C10−C11 is 1.460 Å, which is slightly shorter than that (1.466 Å) in the crystal structure of **3**.[16] The torsion angle of N(9)−C(10)−C(11)−C(17) is 120.5(3)°, while the nitro group (N3/O2/O1) and the diazonium group (N6/N7) are coplanar with their bonded half pyrazole ring. The torsion angles of N(6)−C(5)−N(8)−N(9) and O(2)−N(3)−C(4)−C(10) are −179.7(2)° and 177.7(3)°, respectively. The packing diagram is shown in Figure 2b. Although there are nitromethane molecules in the crystal structure, no hydrogen bonds are observed. Along the *c* axis, the nitromethane solvent is in the "vases" organized by the molecules of **4** through N16···O22 interactions (2.929 Å).



(a)

(b)

Figure 2. (a) Molecular structure of **4**·CH_3NO_2. (b) Packing diagram of **4**·CH_3NO_2 along *c* axis.

Although the solubility of **1** is low in d_6-DMSO, it is sufficient to obtain the ^1H and ^{13}C NMR spectra (Figures S1 and S2, Supporting Information). The ^{15}N NMR spectra of **2** and **4** are given in Figure 3. The assignments were based on comparison with theoretical calculations using Gaussian 09 (MPW1PW91/aug-cc-pVDZ)[18] and previously reported structures.[19,20] In the ^{15}N NMR spectrum of **2** (top, Figure 3), the signal for the nitro group was observed at −25.7 ppm. The chemical shifts for diazonium nitrogen atoms are at −38.7 and −146.0 ppm, respectively. In the ^{15}N NMR spectrum of **4** (bottom, Figure 3), all the resonances are also detected. The signals (N1 and N2) for the diazonium cation were found at −40.5 and −150.7 ppm. The nitrogen signals (N5 and N4) in the pyrazole ring were observed at −5.1 and −10.1 ppm, respectively. In the IR spectrum, the strong bands between 2300 and 2200 cm^{-1} are assigned to the diazonium groups (Figure S6 and Figure S7, Supporting Information).

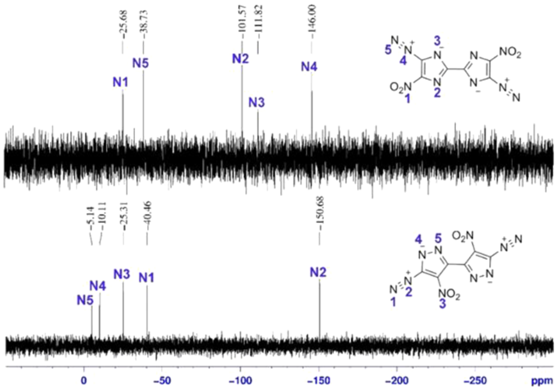


Figure 3. ^{15}N spectrum of **2** and **4**.

The molecular surface electrostatic potentials for **2** and **4** were calculated (Figure 4). The most positive part concentrates on the diazonium group indicating its electron-deficient nature. The negative region surrounds the nitro

Table 1. Physicochemical and Energetic Properties of 2 and 4 Compared with DDNPz, DDNP and Lead Azide

compd	2	4	DDNPz[k]	DDNP	$Pb(N_3)_2$
formula	$C_6N_{10}O_4$	$C_6N_{10}O_4$	$C_3N_6O_4$	$C_6H_2N_4O_5$	PbN_6
M [g mol^{-1}]	276.13	276.13	184.07	210.1	291.3
T_{dec} [°C][a]	199	150	154	157	315
Ω_{CO} [%][b]	−11.59	−11.59	8.69	−15.23	−11.0
N [%][c]	50.73	50.73	45.66	26.67	28.9
$N + O$ [%][d]	68.12	68.12	71.76	55.25	28.9
ρ [g cm^{-3}][e]	1.830	1.850	1.810	1.720	4.800
IS [J][f]	1	1	2.5	1	2.5−4
FS [N][g]	20−40	20	<5	24.7	0.1−1
ΔH_f [kJ mol^{-1}/ kJ g^{-1}][h]	819.7/2.97	987.2/3.58	407.8/2.22	321/1.52	450.1/1.55
νD [m s^{-1}][i]	8653	8943	9038	6900 (1.6 g cm^{-3})	5877
P [GPa][j]	31.1	34.0	35.0	24.2	33.4

[a] Decomposition temperature (onset temperature at a heating rate of 5 °C min^{-1}). [b] Oxygen balance assuming the formation of CO. [c] Oxygen content. [d] Nitrogen and oxygen content. [e] Density, measured with a gas pycnometer (25 °C). [f] Impact sensitivity. [g] Friction sensitivity. [h] Heat of formation. [i] Detonation velocity calculated with EXPLO5 v6.01. [j] Detonation pressure calculated with EXPLO5 v6.01. [k] DDNPz: 4-diazo-3,5-dinitropyrazole zwitterion (ref 11).

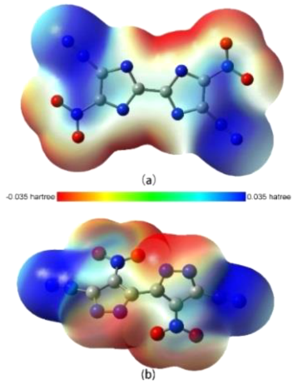


Figure 4. Molecular surface electrostatic potential (ESP) of (a) **2** and (b) **4** calculated at the B3LYP/6-31G(d,p) level at the 0.001 e/$bohr^3$ hypersurface. The legend for the color range is given in the middle, and the range is from −0.035 (red, electron-rich) to 0.035 (blue, electron-deficient) hartrees.

groups and the imidazole rings and the pyrazole rings. Unlike photosensitive DDNP, neither **2** nor **4** is sensitive to light even after exposure to ambient light for 4 weeks. Compound **4** has comparable decomposition temperature (150 °C) with traditional primary explosive DDNP (157 °C).[9] While compound **2** decomposes at 199 °C (Figure S8, Supporting Information), which is much higher than **4** and some other reported proton-free nitrogen-rich diazonium salts.[7,9,11] The heats of formation of **2** and **4** were calculated to be 819.7 and 987.2 kJ mol^{-1}, respectively, which is much higher than that of DDNPz. The measured density is 1.830 g cm^{-3} for **2** and 1.850 g cm^{-3} for **4**. With these values in hand, the detonation performances were calculated using EXPLO 5 v6.01software.[21] The results are shown in Table 1. The values for the detonation velocities (**2**, 8653 m s^{-1}; **4**, 8943 m s^{-1}) and the detonation pressures (**2**, 31.1 GPa; **4**, 34.0 GPa) are much higher than those of DDNP and lead azide. The sensitivities toward impact and friction were also determined. Compounds **2** and **4** show equal impact sensitivities of 1 J. The friction sensitivity of **2** is 20−40 N, while that of **4** is 20 N, which are comparable to DDNP and less sensitive than DDNPz.

In conclusion, two ternary (C/N/O) inner bis(diazonium) salts, the 4,4′-dinitro-5,5′-diazo-2,2′-bisimidazole (**2**) and 4,4′-dinitro-5,5′-diazo-3,3′-bispyrazole (**4**) zwitterions, are described. Compound **2** was prepared unexpectedly in a mixture of TFAA and 100% nitric acid. It was also obtained by using sodium nitrite and concentrated sulfuric acid in a yield of 80%. Both **2** and **4** were fully characterized, and their single crystal X-ray structures determined. They have good measured densities and high thermal stabilities, especially **2**, which has the highest decomposition temperature (199 °C) of any of the reported hydrogen-free nitrogen-rich diazonium salt. Considering their high detonation performance and sensitivities, they may be promising environmentally friendly primary explosive candidates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02875.

Synthesis, calculation detail, crystal refinements, NMR spectra, IR spectra, and DSC plots (PDF)

Accession Codes

CCDC 1915342 and 1936693 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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