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Electronic Supplementary Information

Curious Cases of 3,6-Dinitropyrazolo[4,3-c]pyrazole-based Energetic Cocrystals with High Nitrogen-content: An Alternative to Salt Formation

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Crystal Data

X-ray Crystallography. The X-ray intensity data were measured on a Bruker Apex 2 CCD system equipped with a graphite monochromator and a Mo-Kα fine focus tube (0.71073 Å). An Oxford Cobra low temperature device was used to maintain the temperature at 150K. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm and data were corrected for absorption effects using the multi-scan method (SADABS)[1]. The structures were solved and refined using the Bruker SHELXTL Software Package[2].

Crystallographic data for **3**: $C_8H_{10}N_{14}O_4$, FW = 366.30, monoclinic, space group P21/c, a = 6.2903(3), b = 7.2315(3), c = 15.5555(7), β = 92.037(2), V = 707.15(5), Z = 2, T = 150 K, μ(MoKα) = 0.142 mm^{-1}, ρ_{calcd} = 1.720 g cm^{-3}, $2\Theta_{max}$= 56.546, 25675 reflections collected, 1742 unique (Rint = 0.0313) R1 = 0.0335 (I > 2σ(I)), wR2 = 0.0897 (all data), CCDC 1048548; Crystallographic data for **4**: $C_8H_{10}N_{14}O_4$, FW = 366.30, triclinic, space group P-1, a = 5.4207(1), b = 6.797(2), c = 10.530(3), β = 77.868(3), V = 358.62(2), Z = 1, T = 150 K, μ(MoKα) = 0.140 mm^{-1}, ρ_{calcd} = 1.696 g cm^{-3}, $2\Theta_{max}$= 56.546, 3234 reflections collected, 1460 unique (Rint = 0.0142) R1 = 0.0319 (I > 2σ(I)), wR2 = 0.0822 (all data), CCDC 983225.

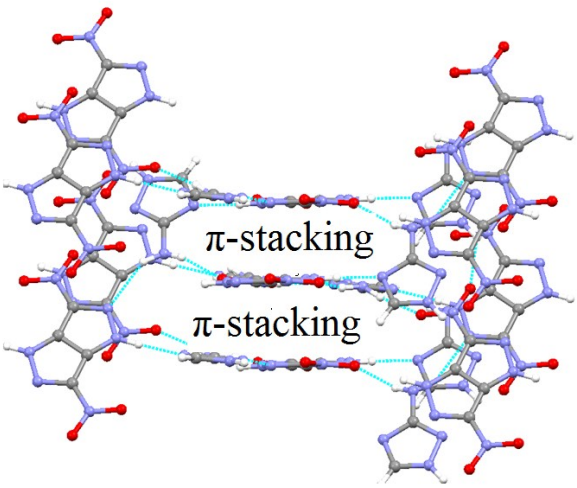


Figure S1. The π-stacking interactions for **3**.

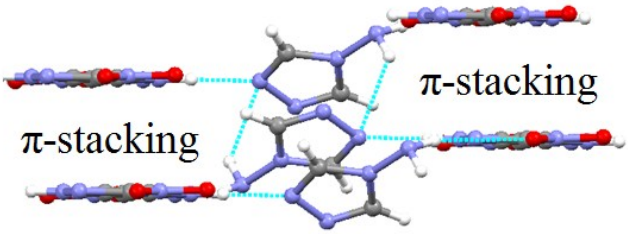


Figure S2. The π-stacking interactions for **4.**

Experimental Section

Safety Precautions. While we have experienced no difficulties in the syntheses and characterization of these materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a **a**safety shield. Face shield and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials.

General Methods. Commercial analytical grade reagents were purchased from Aldrich and Acros Organics and used without further purification. ^{1}H and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively. A 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz was used to obtain ^{15}N spectras. Chemical shifts in the ^{1}H, and ^{13}C spectra are reported relative to Me_4Si and ^{15}N NMR to $MeNO_2$. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C min^{-1}. Densities were measured at room temperature using a Micromeritics AccuPyc 1330 gas pycnometer. IR spectra were recorded using KBr pellets for solids on a Bio-Rad model 3000 FTS spectrometer. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fallhammer and a BAM friction tester.

3,6-Dinitropyrazolo[4,3-c]pyrazole/3-amino-1,2,4-triazole (1:2) cocrystal (**3**): 3,6-Dinitropyrazolo[4,3-c]pyrazole[3] (0.20 g, 1 mmol) was suspended in 10 mL methanol and 0.5 mL water. To this solution were added 3-amino-1,2,4-triazole (0.168 g, 2 mmol). The reaction mixtures were stirred with heating (50 °C) for 6h then cooled to room temperature. The resulting precipitate was collected by filtration and washed with methanol to yield **3** (0.34 g, 93%). Light yellow solid; IR (KBr): 3462, 3366, 3247, 1630, 1566, 1523, 1491, 1388, 1348, 1236, 1040, 1007, 820 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.50 (s, 4H, NH, CH), 5.89 (br, 4H, NH_2) ppm; ^{13}C NMR (DMSO-d_6): δ157.27, 146.87, 138.22, 136.70 ppm; elemental analysis, calcd (%) for $C_8H_{10}N_{14}O_4$ (366.10): C: 26.23; H: 2.75; N: 53.54; Found, C: 26.24; H: 2.78; N: 53.21.

3,6-Dinitropyrazolo[4,3-c]pyrazole/4-amino-1,2,4-triazole (1:2) cocrystal (**4**): 3,6-Dinitropyrazolo[4,3-c]pyrazole[3] (0.20 g, 1 mmol) was suspended in 10 mL methanol

and 0.5 mL water. To this solution were added 4-amino-1,2,4-triazole (0.168 g, 2 mmol). The reaction mixtures were stirred with heating (50 °C) for 6h then cooled to room temperature. The resulting precipitate was collected by filtration and washed with methanol to yield **3** (0.35 g, 95%). Light yellow solid; IR (KBr): 3341, 3081, 1524, 1373, 134, 1221, 1069, 1013, 983, 816 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 8.39 (s, 4H, NH, CH), 6.21 (br, 4H, NH_2) ppm; ^{13}C NMR (DMSO-d_6): δ144.06, 137.91, 131.66 ppm; elemental analysis, calcd (%) for $C_8H_8N_{14}O_4$ (316.24): C: 26.23; H: 2.75; N: 53.54; Found, C: 26.11; H: 2.73; N: 53.23.

Theoretical Section

The structures of **3**, **4** and possible salt isomers were optimized at BLYP-D3/def2-QZVPP method[4] and the relative energies were calculated using QRCA 3.0[5]. The single point energies for **3**, **4** and their possible salts are -1378.31, -1378.19, -1378.26, -1378.16 hartree, respectively. The relative energies results are also presented in Figure S3.

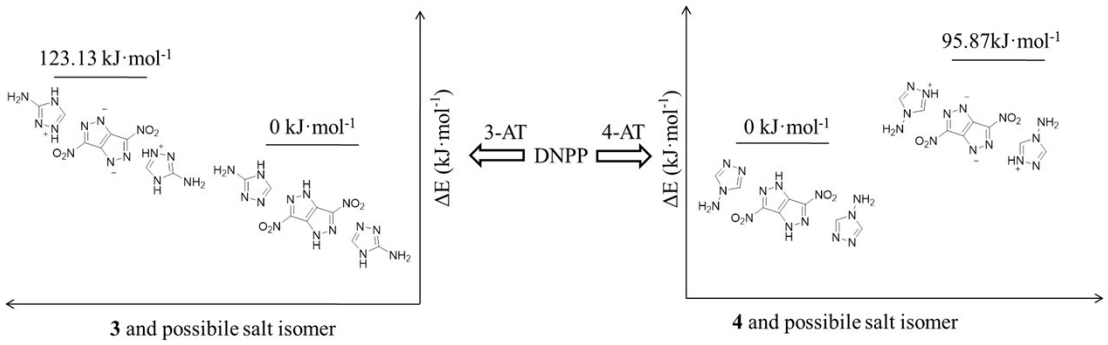
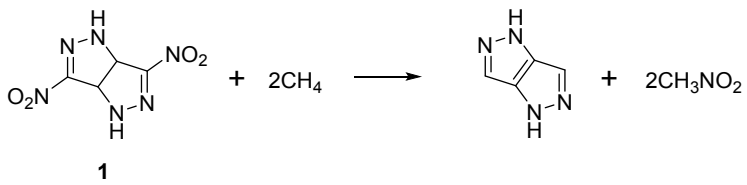


Figure S3. Relative Energies of **3**, **4** and their possible salts.

Heat of formation

All enthalpy calculations were performed with the Gaussian 03 (Revision D.01) suite of programs[6]. The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using B3LYP functional with 6-31+G** basis set[7]. Single-point energies were calculated at the MP2/6-311++G** level.[8] Atomization energies for DNPP, 3-AT and 4-AT were obtained by employing the G2 ab initio method.[9] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

As mention in the manuscript, the heat of formation for **1** was determined using isodesmic reaction (**Scheme S1**). The heats of formation of other compounds in Scheme S1 were determined from NIST WebBook[10].



Scheme S1. Isodesmic reactions for calculating heats of formation for DNPP (**1**).

Table S1. G2 ab initio method results.

	H^{298}/a. u.
pyrazolo[4,3-c]pyrazole	-373.163711
3-AT	-297.144818
4-AT	-297.079876
C	-37.78432
H	-0.5
O	-74.98203
N	-54.51798

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