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Supporting Information

Achieving Balanced Energetics Through Cocrystallization

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SI 1. Experimental

Caution: Although no unplanned detonations were encountered during this work, ammonium dinitramide is an energetic oxidizing agent. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, impact, or flame. Be aware that the potential for severe injury exists if these materials are handled improperly. Liquid assisted grinding experiments were conducted while wearing steel-woven Kevlar gloves, a protective face shield, and while standing behind a blast shield.

Ammonium dinitramide (ADN) was received from ARDEC at Picatinny Arsenal. Dichloromethane (DCM) and ethanol (EtOH) were obtained from Fisher Scientific and Decon Laboratories, respectively. Acetonitrile (MeCN) and diethyl ether (ether) were obtained from Fisher Scientific, passed through an activated alumina column, and stored over 4Å molecular sieves prior to use. Pyrazine, 99+%, was obtained from Acros Organics. Oxone, monopersulfate compound, was obtained from Sigma Aldrich. Pyrazine-1,4-dioxide (PDO) was prepared by the published method.[1]

Synthesis

***ADN-PDO** by liquid assisted grinding (LAG)*
PDO (5.50 mg, 0.0450 mmol) and ADN (11.3 mg, 0.0900 mmol) were combined in a mortar and ground for 20 minutes with 4-5 drops of MeCN added via syringe over the course of grinding.

***ADN-PDO** by fusion*
PDO (2.75 mg, 0.0225 mmol) and ADN (5.64 mg, 0.0450 mmol) were combined on a glass cover slip (24mm × 60mm) and heated to 117 °C with a 2 minute hold at this temperature. The melt was cooled to room temperature yielding a mixture containing **ADN-PDO**.

***ADN-PDO** from solution*
PDO (6.28 mg, 0.0560 mmol) was placed in a 4 mL vial with 3 mL MeCN, this was brought to a boil and then allowed to cool over 6 hours while on an orbital shaker generating a saturated solution. ADN (93.3 mg, 0.752 mmol) was placed in a 4 mL vial. The PDO solution (2 mL) was syringe filtered (0.45 μm pore size) into the 4 mL vial containing ADN. This vial was shielded from light and placed on an orbital shaker. At 24 hours **ADN:PDO** crystals were visible and continued to grow up to 48 hours. Crystals were recovered by filtration and (quickly) rinsed with ether (3 × 3 mL).

Characterization

Single-Crystal X-Ray Structure Determination

Single-crystal X-ray diffraction data were collected using a Rigaku XtaLAB Synergy-S X-ray diffractometer with an α kappa goniometer geometry configuration; an Oxford Cryostream 800 low temperature device is also equipped. The X-ray source is a PhotonJet-S microfocus Cu source (λ = 1.54187 Å) set at an approximate divergence of 9.5 and operated at 50 kV and 1 mA. X-ray intensities were measured with a HyPix-6000HE detector held 34.00 mm from the sample. The data were processed using CrysAlisPro v38.46 (Rigaku Oxford Diffraction) and were absorption corrected. The structures were determined using OLEX2[2] as well as SHELXT[3] and refined with SHELXL.[4] All non-hydrogen atoms were refined anisotropically with hydrogen atoms idealized positions.

Powder X-Ray Diffraction

All powder pattern data were collected using a Panalytical Empyrean system utilizing Cu-Kα radiation (λ = 1.54187 Å) and operating at 45 kV and 40 mA. The system uses a Bragg-Brentano HD X-ray optic and an X'Celerator Scientific detector operating in a continuous 1D scan mode. Scans were conducted according to the following parameters: 2θ = 5° to 50°, step size = 0.008°, and step speed = 100 seconds. The data were worked up using Excel 2010.

Raman Spectroscopy

Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope and the following configurations: 1) a 633nm laser, 1800 lines/mm gratings, 50 µm slit size, and a RenCam CCD detector; where spectra were collected in extended scan mode with a range of 3600 - 2800 cm^{-1}. 2) a 785 nm laser, 1200 lines/mm gratings, 65 µm slit size, and a RenCam CCD detector; where spectra were collected in extended scan mode with a range of 3600 - 400 cm^{-1}. 3) a 532 nm laser, 1800 lines/mm gratings, 50 µm slit size, and a RenCam CCD detector; where spectra were collected in static scan mode centered on 3050 cm^{-1}. All spectra were analyzed using the WiRE 3.4 software package (Renishaw). Calibration was performed using silicon standards.

Dynamic Vapor Sorption (DVS)

Dynamic vapor sorption (DVS) experiments were performed using a Q5000 SA Dynamic Vapor Sorption Analyzer. Sample mass was monitored from 0-96% RH at steps of 2% RH allowing 1200 minutes for equilibration and starting from initial masses of 8-15 mg.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded on a TA Instruments Q10 DSC. All experiments were carried out at a heating rate of 10 °C/min, covering a temperature range of 30 °C to 350 °C. Samples of ADN were analyzed in a Tzero™ DSC High Pressure Capsule Kit, all other samples were analyzed in Tzero™ hermetic aluminum DSC pans. The instrument was calibrated using an indium standard and all DSC thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) thermograms for each sample were recorded on a TA Instruments Q50 TGA. All experiments were conducted on platinum TGA sample pans under a nitrogen purge of 50 mL/min with a heating rate of 10 °C/min, covering a temperature range of 27 °C to 400 °C. The instrument was calibrated using the Curie points of alumel and nickel standards and all TGA thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5.

SI 2. Crystallographic Data

Table 1. Room temp. and 100 K crystal structure data

	ADN-PDO	**ADN-PDO**	ADN
Stoichiometry	2:1	2:1	—
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Temperature (K)	293(2)	100.0(1)	298.(1)
a (Å)	11.5920(4)	11.5631(4)	6.90644(17)
b (Å)	8.1878(4)	8.1527(3)	11.9004(3)
c (Å)	7.2273(3)	7.0435(3)	5.63722(13)
α (°)	90	90	90
β (°)	101.236(4)	100.541(4)	100.264(2)
γ (°)	90	90	90
Volume (Å^3)	672.817	652.789	455.905
ρ_{calc} (g cm^{-3})	1.778	1.833	1.808
R_1/wR_2	3.58/10.26	3.03/8.21	2.89/8.07
GOF	1.076	1.064	1.090

SI 3. ORTEP Diagrams

ADN-PDO

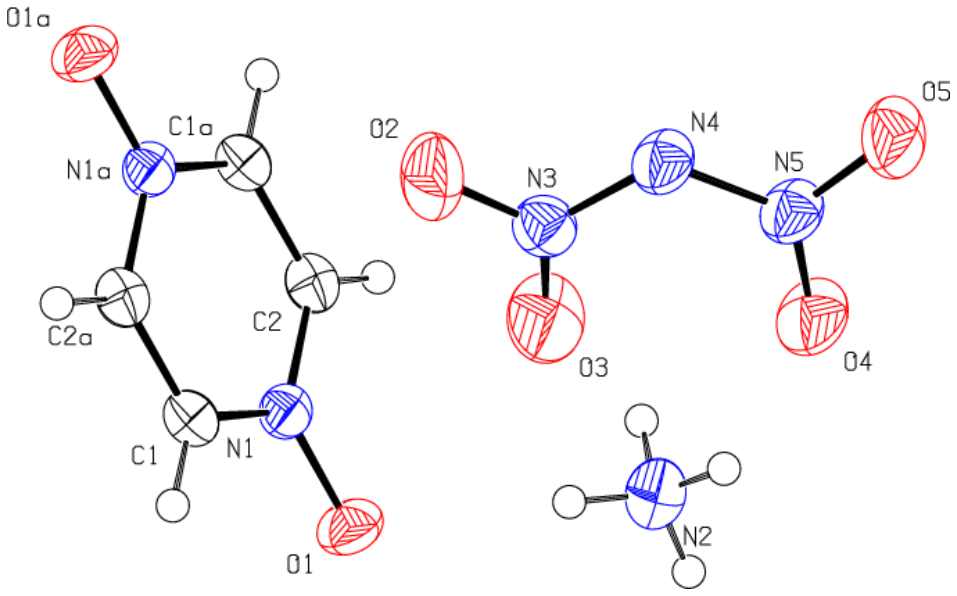

Figure S1. ORTEP diagram of **ADN-PDO** at 100.0(1) K

ADN

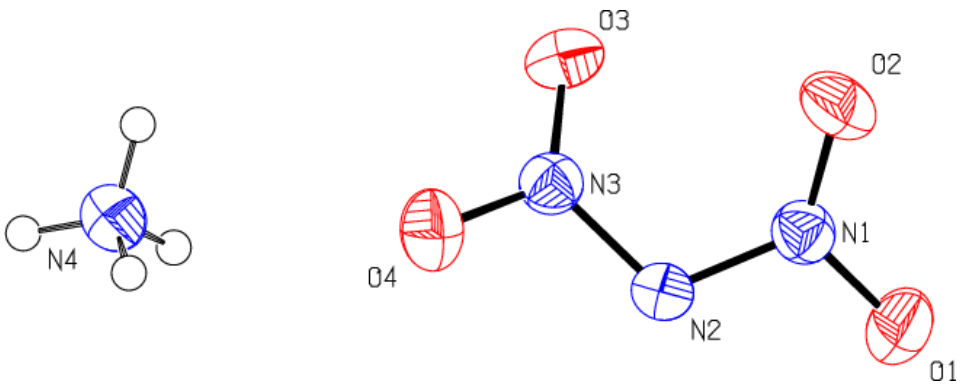

Figure S2. ORETEP diagram of ADN at 298(1) K

SI 4. Raman Spectra for ADN, PDO, and ADN-PDO

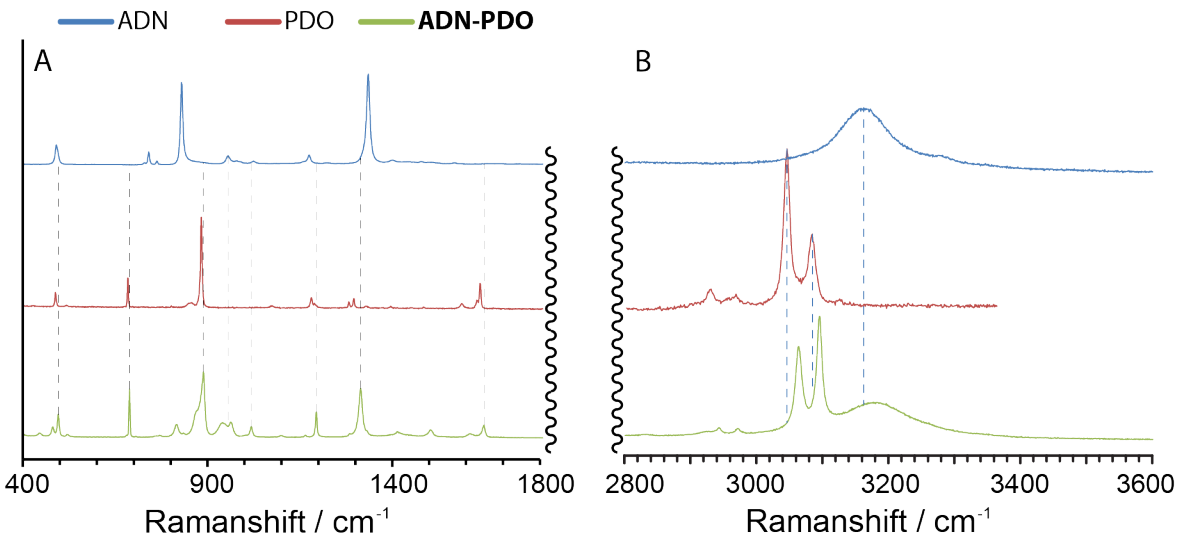

Figure S3. Raman spectra of ADN, PDO, and **ADN-PDO**. A) Collected using an excitation wavelength of 785 nm. B) ADN, and **ADN-PDO** collected using an excitation wavelength of = 633 nm; PDO collected at λ = 532 nm.

SI 5. PXRD diffraction patterns for relevant materials

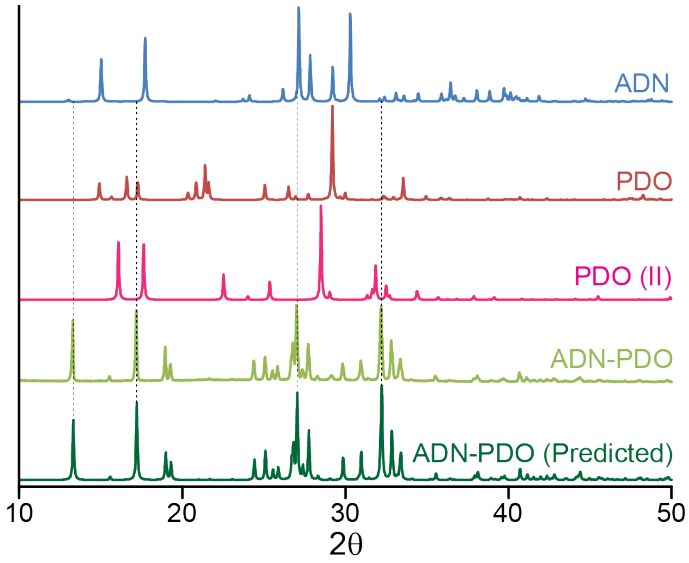

Figure S4. PXRD data for ADN, PDO, PDO (II), **ADN-PDO**, and a powder pattern predicted using the room temp. single crystal structure for **ADN-PDO**. PDO has a polymorph, denoted here as PDO(II).

SI 6. Thermal analysis of ADN-PDO obtained from LAG and Solution methods

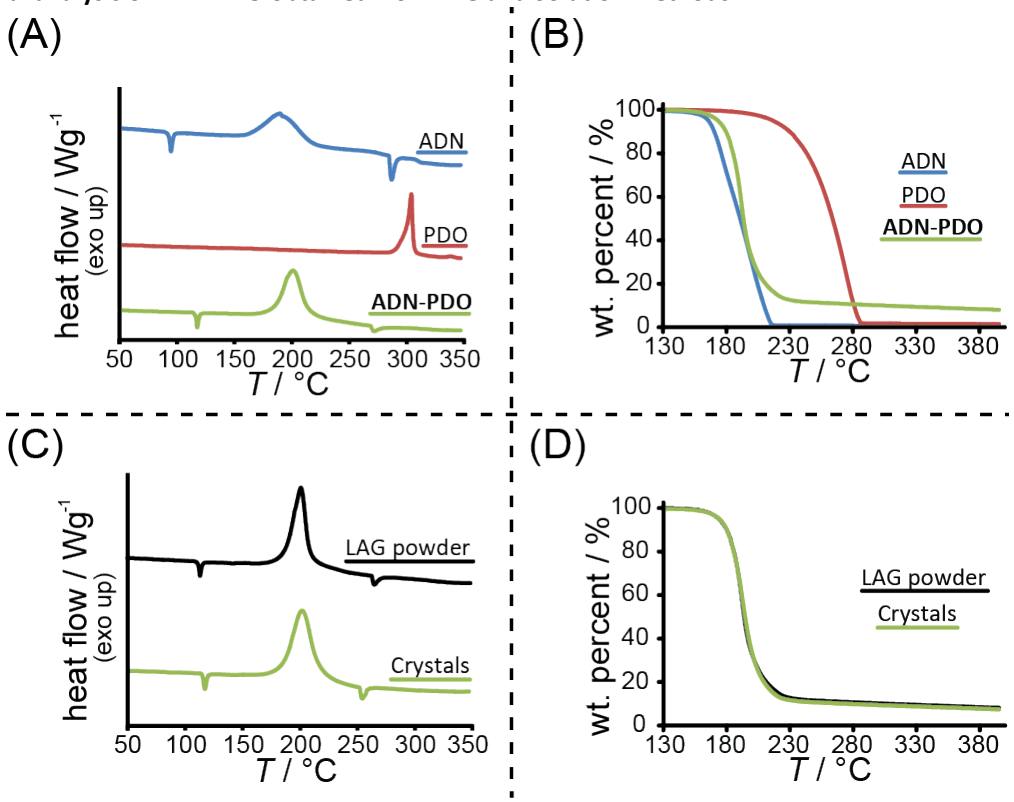

Figure S4. DSC thermograms and TGA traces, **(A)** and **(B)** respectively, for ADN (blue), PDO (red), and **ADN-PDO** (green), as well as DSC thermograms and TGA traces, **(C)** and **(D)** respectively, for **ADN-PDO** obtained from solution crystallization (green) and LAG (black).

ADN-PDO$_{(powder)}$, obtained via LAG, is substantially the same as **ADN-PDO**$_{(crystals)}$, obtained via solution crystallization methods, by both Raman spectroscopy and PXRD. To ensure uniformity, however, thermal analyses of ADN, PDO, and **ADN-PDO** (crystals and powder), were conducted by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). By DSC, ADN melts at 91.4 °C (92 °C lit.) and begins decomposing at 160 °C.[5] PDO melts with concomitant decomposition beginning at 288 °C (290-300 °C lit.).[1] **ADN-PDO**$_{(crystals)}$ begins melting at 114 °C, 2 °C higher than **ADN-PDO**$_{(powder)}$ which melts at 112 °C. With continued heating the decomposition of **ADN-PDO**, both crystal and powder, commences at 176 °C. By TGA, ADN begins thermal decomposition at 157 °C whereas **ADN-PDO** obtained from either method, show mass loss beginning at 176 °C. PDO does not reach its melt/decomposition temperature under these conditions and instead undergoes sublimation.

SI 7. Dynamic Vaper Sorption

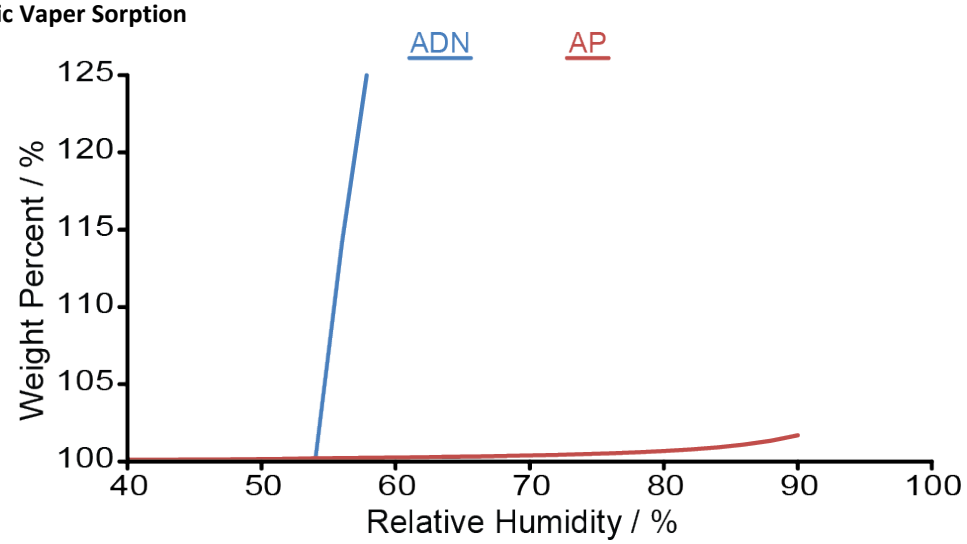

Figure S5. Dynamic vaper sorption traces for ADN (blue) and ammonium perchlorate (red).

SI 8. Performance data

Table 2. Tabulated calculated (Cheetah.7.0) performance values

Energetic material	I_{sp} / s	P_{cj} / GPa	D_v / kms^{-1}	$OB(CO_2)$
AP	157	17.7	6.43	+34%
ADN	202	28.9	8.17	+26%
ADN-PDO	259	33.3	8.94	-18%
M1[6]	208	17.8	6.93	-53%
EX-99[6]	237	25.5	7.89	-42%
ADN-PDO/Al/GAP*	270	26.4	7.82	-44%
Ariane-5[6]	261	21.1	6.70	-38%
Space shuttle[6]	260	23.1	7.00	-21%
TATB	200	34.6	8.46	-56%
RDX	266	35.8	8.84	-58%

*70:15:15 ratio by weight. Calculated at a chamber pressure of 68.046 atm, exhaust pressure of 1 atm, and all compositions at TMD. The heat of formation for **ADN-PDO** is obtained by considering the material as a physical mixture of the constituents and Cheetah 7.0 calculations were performed using the Sandia JCZS product library revision 32. The heat of formation for pyrazine-1,4-dioxide was taken from the literature.[7]

*Determination of the heat of reaction of **ADN-PDO***

Differential scanning calorimetry (DSC) thermograms were recorded on a TA Instruments Q10 DSC. All experiments were carried out at a heating rate of 10 °C/min, covering a temperature range of 30 °C to 250 °C. Samples were analyzed in a Tzero™ DSC High Pressure Capsule Kit. The instrument was calibrated using an indium standard and all DSC thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5. The data from 7 experiments were analyzed and the average heat of reaction found to be 4272 Jg^{-1} with a standard deviation of 276 (6.5%). Data from these experiments and a representative thermogram are provided in Figure S6.

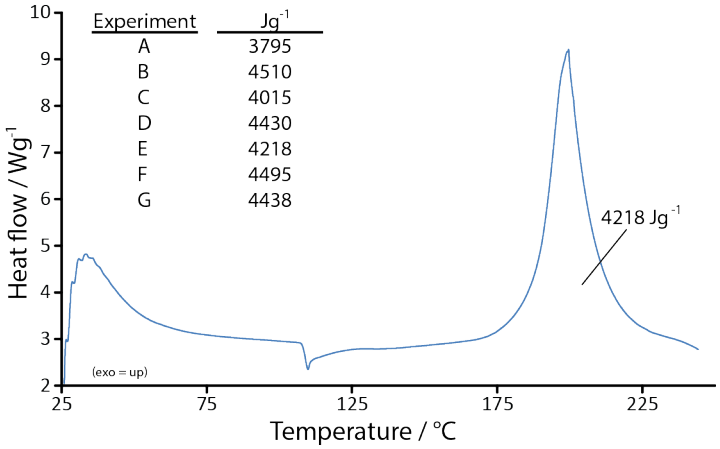

Figure S6. Data from the experimental determination of the heat of reaction of **ADN-PDO** and a representative thermogram.

SI 9. Sensitivity

Sensitivity to mechanical stimuli

The impact sensitivity of both ADN and **ADN-PDO** were determined using an in-house apparatus [8] whereby a 2.380 Kg stainless-steel impactor impinges samples of 2 mg ± 10% inside aluminum DSC pans resting on an anvil from varying heights. 20 samples of each material were tested with D_{h50} measured as the dropping height at which there was a 50% probability of detonation. The D_{h50} values were found to be 34 cm and 35 cm for **ADN-PDO** and ADN respectively. Literature values are used to compare ADN, TATB, RDX, and AP in Table 3.

Table 3. *Sensitivity to mechanical stimuli of some common energetic materials*

Energetic Material	Impact Sensitivity / Nm [9]
ADN	4
RDX	7.5
AP	15
TATB	50

SI 10. References

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