Supplementary Information (SI) for CrystEngComm.

Supplementary Information

Balancing Energy and Safety in a Nitropyrazole-Based Melt-Cast Explosive Carrier: 1,4-Dimethyl-3,5-dinitropyrazole

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Content

1. General

X-ray single-crystal diffraction data were collected on Bruker SMART-1000 single crystal X-ray diffractometer. The Bruker Advance 400 NMR spectrometer was used at 400 MHz and 100 MHz, respectively, with methanol-d_4 as the solvent, the ^1H NMR and ^{13}C NMR spectra of the samples were tested. Japan Shimadzu-IR Tracer 100 was used, and potassium bromide was used to grind and press tablets at 4000-500 cm^{-1} range test. Thermal property measurements were conducted using a TGA/DSC Mettler Toledo calorimeter, which was equipped with an auto-cooling accessory. The samples were tested in a nitrogen atmosphere.

2. Spectral data of DMDNP

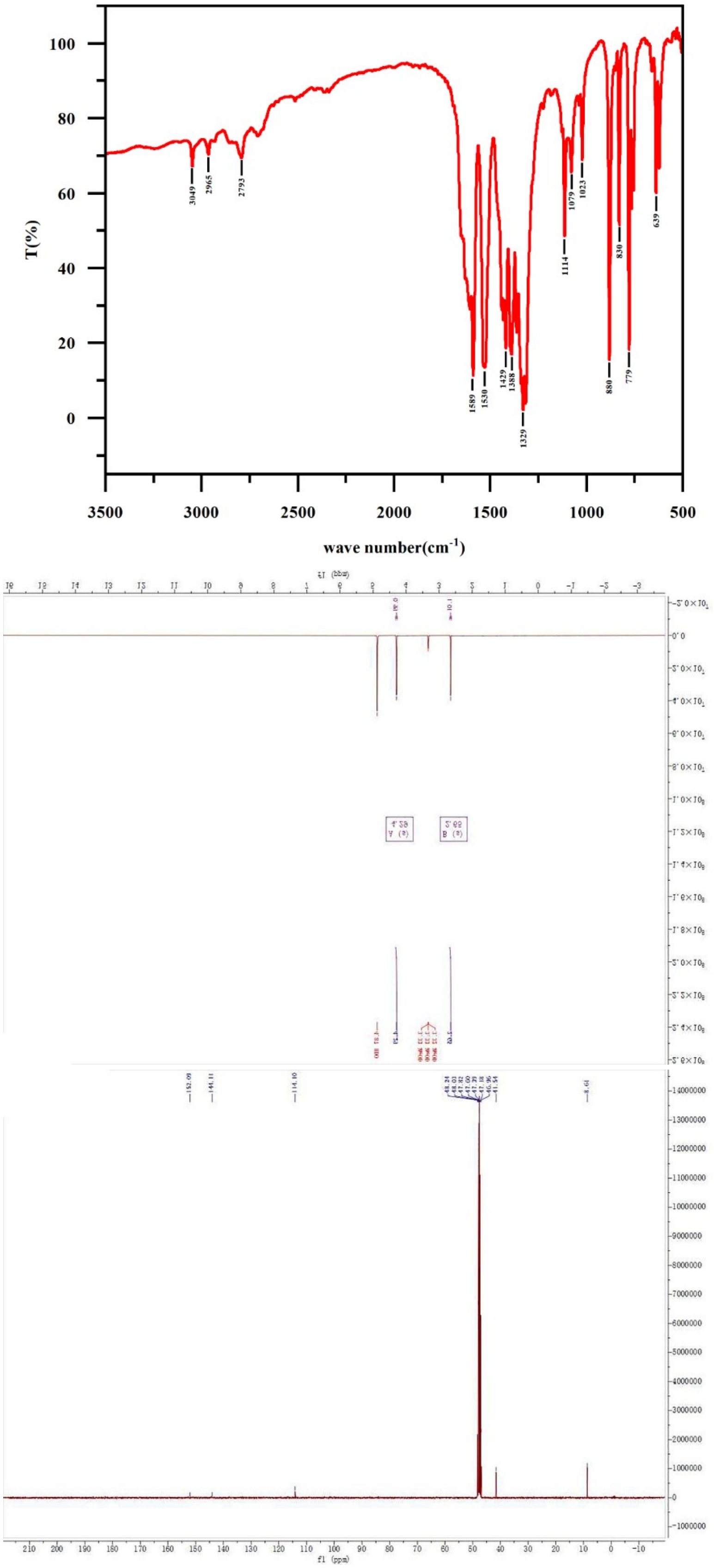


Fig. S1 Infrared spectrum, ^{1}H spectrum, and ^{13}C spectrum of DMDNP

3. Crystallographic data for DMDNP

Table S1. Crystallographic data for DMDNP.

Compound	DMDNP
Empirical formula	$C_5H_6N_4O_4$
Formula weight	186.14
Temperature / K	118.00(14)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å, b / Å, c / Å	13.3559(18), 6.2127(8), 9.4897(11)
α/°, β/°, γ/°	90.00, 106.536(12), 90.00
Volume / $Å^3$	754.85(16)
Z	4
ρ_{calc} / $mg \cdot mm^{-3}$	1.638
μ / mm^{-1}	0.143
F(000)	384
Crystal size / mm^3	0.31 × 0.25 × 0.17
2Θ range for data collection	7.3 to 52°
Index ranges	$-14 \le h \le 16$, $-5 \le k \le 7$, $-11 \le l \le 11$
Reflections collected	4507
Independent reflections	1464[R(int) = 0.0601 (inf-0.9Å)]
Data/restraints/parameters	1464/0/120
Goodness-of-fit on F^2	1.05
Final R indexes [$I>2\sigma(I)$ i.e. $F_o>4\sigma(F_o)$]	$R_1 = 0.0579$, $wR_2 = 0.1300$
Final R indexes [all data]	$R_1 = 0.0861$, $wR_2 = 0.1498$
Largest diff. peak/hole / e $Å^{-3}$	0.250/-0.276
Completeness	0.9926

4. Calculation method for enthalpy of solid phase formation

Due to the fact that most energetic compounds are solid condensed phases, calculating detonation performance necessitates the use of the solid enthalpy of formation ($\Delta H_{f,solid}$). According to Hess's law, the enthalpy of formation for the solid phase can be derived from the enthalpy of formation for the gas phase ($\Delta H_{f,gas}$) and the enthalpy of sublimation (ΔH_{sub}). The calculation formula is as follows:

$$\Delta H_{f,solid} = \Delta H_{f,\ gas} - \Delta H_{sub}$$

The ΔH_{sub} can be calculated using the corresponding molecular surface area (A) and the electrostatic interaction index ($\mu\sigma_{tot}^2$) of energetic compounds.

$$\Delta H_{sub} = \alpha A^2 + \beta(v\sigma_{tot}^2)^{0.5} + \gamma$$

The correlation coefficients α(0.000627), β(1.650087), and γ(2.966078) in the equation were determined by Rice.

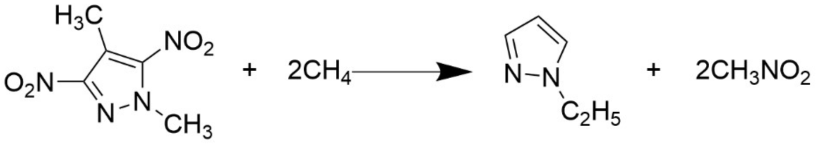
The $\Delta H_{f,gas}$ is calculated by the isodesmic reaction method. The following is an introduction to the isodesmic reaction method.

The isodesmic reaction method, based on Hess's law, predicts the gas-phase heat of formation of molecules by designing isodesmic reactions. The standard reaction enthalpy change is expressed as follows:

$$\sum \Delta_r H^0 = \sum \Delta_f H^0(Products) - \sum \Delta_f H^0(Reactants)$$

In the equation, $\Delta_f H^0$(Products) and $\Delta_f H^0$(Reactants) represent the heats of formation of the products and reactants, respectively. The standard reaction enthalpy change can be obtained from quantum chemical calculations. With known heat of formation data for the other components, the standard heat of formation for a specific component can be determined. The key to this method lies in designing a reasonable isodesmic reaction, where the number of electron pairs and chemical bonds of a given type is conserved before and after the reaction. This conservation helps to cancel out errors arising from the approximate treatment of electron correlation in solving quantum mechanical equations.

The specific calculation process for the standard molar enthalpy of formation in the gas phase is as follows. The isodesmic reaction we designed is shown below:



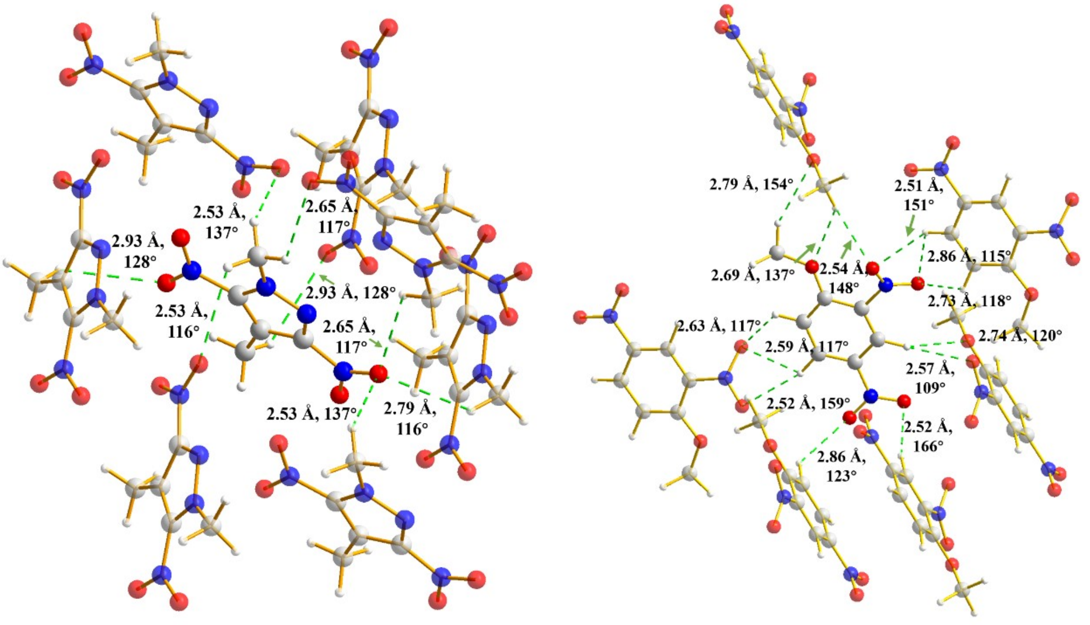
To calculate the standard molar enthalpy change (Δ_rH^0) of this reaction, i.e., to compute the enthalpy (H) of each reactant and product under standard conditions, the Gaussian 09 program was employed. First, geometric structure optimization was carried out using the B3LYP functional with the 6-31+G(d,p) basis set. The thermal correction (ΔH) to enthalpy at 298 K were obtained from the frequency calculations (with scaled frequencies). Subsequently, single-point energy (SPE) calculations were performed using the B2PLYP-D3 functional with the def2-TZVP basis set. The enthalpy of each compound was obtained by summing the results from the two steps.

The experimentally observed standard molar enthalpies of formation (Δ_fH^0) for methane, 1-ethylpyrazole, and nitromethane are known, and the standard molar enthalpy of formation of DMDNP in the gas phase was ultimately determined. The calculation results for each key step are shown in the table below.

Table S2. Calculation results for key steps for DMDNP.

Parameters	DMDNP	CH_4	1-Ethylpyrazole	CH_3NO_2
ΔH/ Hartree	-713.6052	-40.4833	-304.6826	-244.9502
SPE/ Hartree	0.144231	0.049286	0.136232	0.054915
ΔH+SPE/ Hartree	-713.4639	-40.435	-304.549	-244.8964
Δ_rH^0/ Hartree	0.00793638			
Δ_fH^0(exp)/ kJ·mol^{-1}		-74.6	132.6	-74.3
Δ_fH^0(g,calcd)/ kJ·mol^{-1}	154.037	-	-	-

5. The hydrogen-bonding networks in DMDNP and DNAN



DMDNP **DNAN**

Fig. S2 Comparative view of the hydrogen-bonding networks in DMDNP and DNAN, with interaction distances (Å) and angles indicated.

Table S3. Statistics of intermolecular C–H···O hydrogen bonds around a central molecule in DMDNP and DNAN crystals.

Compounds	Number of H-bonds	Average H···A distance / Å	Average D–H···A angle / °
DMDNP	7	2.70	124
DNAN	13	2.66	134