Supplementary Information

Constructing insensitive heat-resistant energetic materials via the hydrazo bridge mediated resonance-assisted hydrogen bonds

#Xing Zhang,[a,b] #Linhu Pan,[a,b] Min Li,[c] Jianquan Jing,[a,b] Honglei Xia,[a,b,*] and Qinghua Zhang[a,b,*]

[a] *School of Astronautics, Northwestern Polytechnical University, Xi'an 710065, China*

[b] *National Key Laboratory of Solid Propulsion, Northwestern Polytechnical University, Xi'an 710065, China*

[c] *State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

# *These authors contributed equally to this work*

**Corresponding author*

E-mail: xia_honglei@nwpu.edu.cn (Honglei Xia); qinghuazhang@nwpu.edu.cn (Qinghua Zhang)

1 Materials and characterization methods

All reagents and solvents were obtained from commercial resources and were used as received. The Bruker Advance 400 NMR spectrometer was used at 100 MHz, with Sulphuric Acid-D_2 (D_2SO_4) as the solvent, the ^{13}C NMR spectra of the sample was tested. LC-MS spectra were recorded on ThermoFisher-UltiMate 3000 HPLC and Thermo Scientific-Q Exactive mass spectrometer with electrospray ionization (ESI). The DSC measurements were carried out on a Netzsch STA449F5 simultaneous thermal analyser at a heating rate of 5, 10, 15, 20 °C·min^{-1}, respectively. Impact and friction sensitivity measurements were made using a standard BAM Fall hammer and a BAM friction tester. The non-isothermal thermal decomposition kinetics of compound HDP was also analyzed using Kissinger and Ozawa methods. The Kissinger equation and the Ozawa equation are as follows:[1,2]

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/(RT_p) \qquad (1)$$

$$\ln\beta = \ln(AR/E_a) - E_a/(RT_p) \qquad (2)$$

where β represents the heating rate, K·min^{-1}; T_p is the decomposition peak temperature, K; E_a is the activation energy, kJ·mol^{-1}; A represents the pre-exponential factor; R is the ideal gas constant, 8.314 J mol^{-1}·K^{-1}.

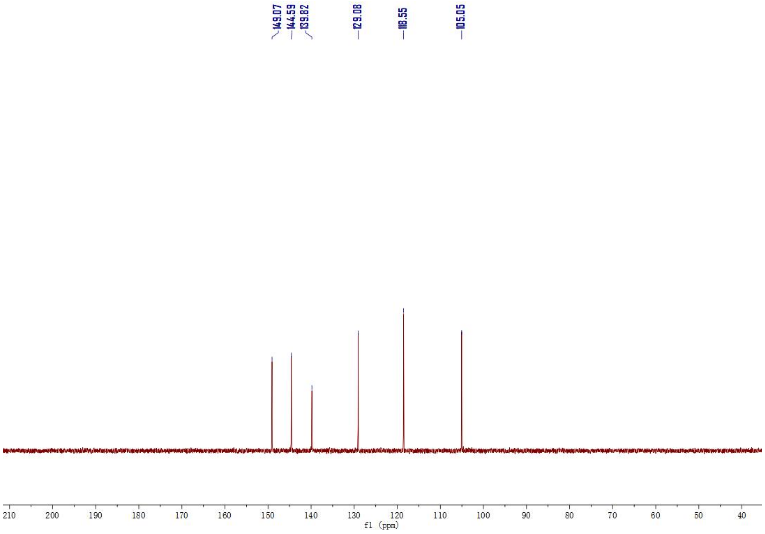


Fig. S1. ^{13}C NMR of compound HDP (D_2SO_4).

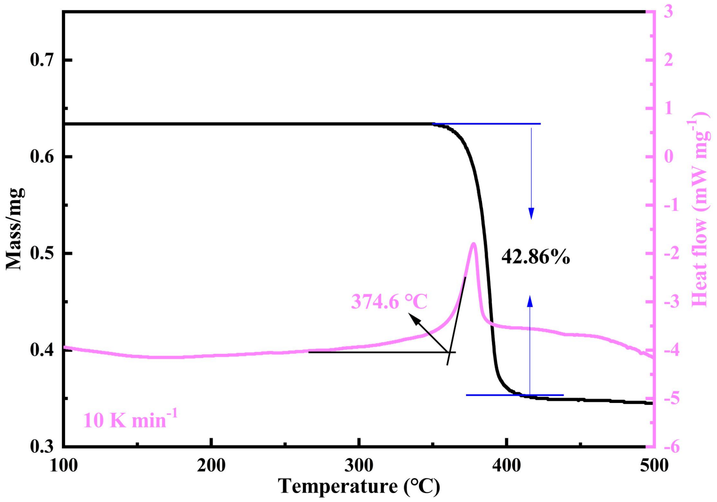


Fig. S2. DSC/TG curves of HDP at a heating rate of 10 K·min^{-1}.

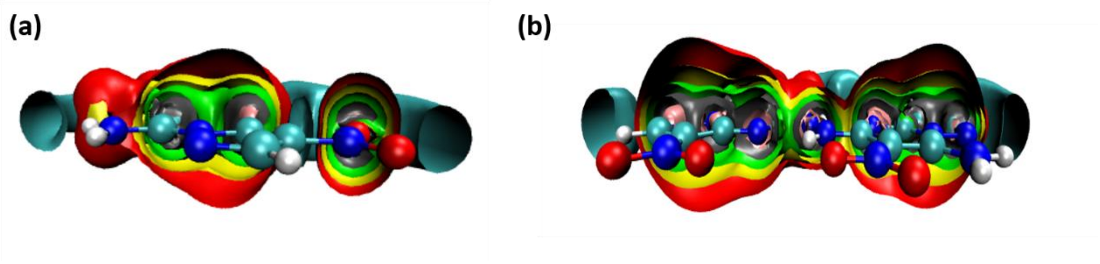


Fig. S3. Clipping plane of HDP for multiple isochemcal shielding surfaces (ICSS; at 2 ppm in red, at 6 ppm in yellow, at 10 ppm in blue, at 15 ppm in green, at 20 ppm in pink, and at -1 ppm in black).

Table S1. Kinetic parameters obtained using the Kissinger and Ozawa methods.

β/K·min^{-1}	T_P/K	Kissinger method			Ozawa method	
		E_K/kJ mol^{-1}	InA	R	E_O/kJ mol^{-1}	R
5	651.15	204.98	12.90	0.98	216.00	0.99
10	664.15					
15	668.15					
20	675.15					

Table S2. HOMO−LUMO gaps of HDP, TATB, LLM-105, HNS, PYX.

Compound	HOMO/eV	LUMO/eV	Gap/eV
HDP	-6.697	-3.379	3.318
TATB	-7.661	-3.321	4.340
LLM-105	-7.233	-3.758	3.475

HNS	-8.388	-4.294	4.094
PYX	-8.24583	-4.726851	3.519

2 X-ray crystallography

Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo-Kα monochromated radiation (λ=0.71073 Å). The crystal structure was solved by direct method. The structure was refined on F^2 by full-matrix least-squares methods using the Olex2 1.2 script package. All non-hydrogen atoms were refined anisotropoically.

Table S3. Crystal data and structure refinement for HDP·DMF.

Crystal	**HDP**·DMF
CCDC number	2419061
Empirical formula	$C_{12}H_8N_{14}O_8$
Formula weight	476.06
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a [Å]	4.5534(5)
b [Å]	11.8134(10)
c [Å]	12.2013(9)
α [°]	81.384(7)
β [°]	88.616(7)
γ [°]	81.965(8)
Volume	642.54(10)
Z	1
ρ(g cm^{-3})	1.609
F(000)	322
Crystal size (mm^3)	0.02×0.02×0.02
Theta range for data collection	3.6590 to 71.9060°
Index ranges	$-5 \leq h \leq 5$, $-14 \leq k \leq 14$, $-15 \leq l \leq 14$
Final R indices [I>2σ(I)]	$R_1 = 0.0740$, $wR_2 = 0.1774$

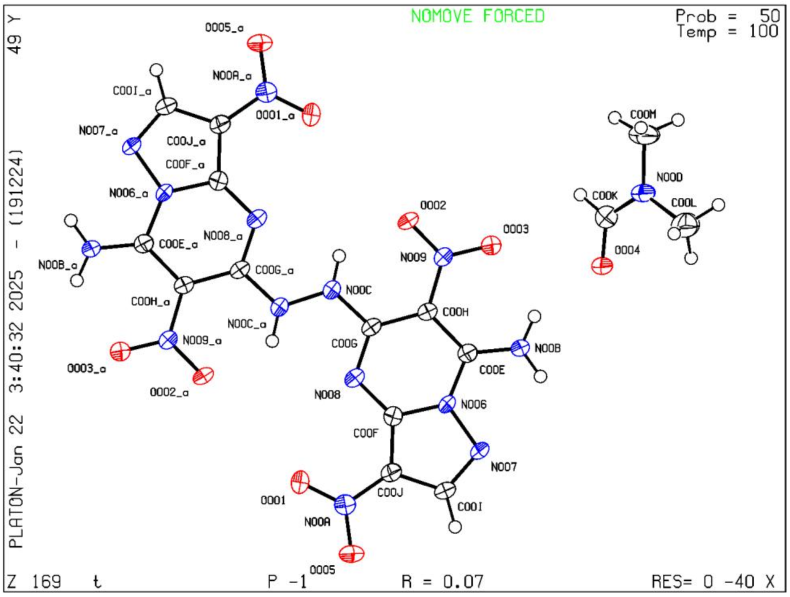


Fig. S4. Molecular structure of HDP·DMF with the thermal ellipsoids set at 50% probability level.

Table S4. Selected bond lengths for compound HDP·DMF.

Bond	Length/Å	Bond	Length/Å
O001–N00A	1.241(4)	N009–C00H	1.408(5)
O002–N009	1.249(4)	N00A–C00J	1.407(5)
O003–N009	1.227(4)	O001–N00A	1.241(4)
O005–N00A	1.238(4)	O002–N009	1.249(4)
N006–N007	1.404(4)	O003–N009	1.227(4)
N006–C00F	1.374(5)	O005–N00A	1.238(4)
N007–C00I	1.312(5)	C00F–C00J	1.395(5)
N008–C00F	1.339(5)	N006–N007	1.404(4)
N008–C00G	1.326(5)	N00C–N00C	1.326(6)

Table S5. Selected bond angles for compound HDP·DMF.

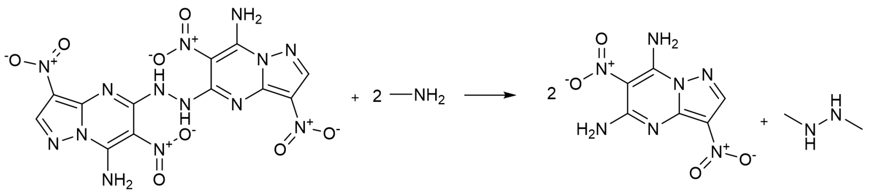
Bond	Angle/(°)	Bond	Angle/(°)
C00E–N006–N007	122.8(3)	C00G–N008–C00F	116.2(3)
C00E–N006–C00F	124.6(3)	C00K–N00D–C00L	119.9(4)
C00F–N006–N007	112.6(3)	O003–N009–C00H	119.8(3)
C00I–N007–N006	103.7(3)	O001–N00A–C00J	118.6(3)
N006–C00E–C00H	113.7(3)	O005–N00A–O001	123.5(3)
N00B–C00E–N006	117.3(3)	O005–N00A–C00J	117.9(3)
N00B–C00E–C00H	128.5(3)	C00F–C00J–N00A	126.7(3)
N008–C00F–C00J	132.7(4)	C00F–C00J–C00I	106.3(3)
N008–C00F–N006	122.7(3)	C00I–C00J–N00A	127.0(3)

Table S6. Selected torsion angles for compound HDP·DMF.

Bond	**Angle/(˚)**	**Bond**	**Angle/(˚)**
C00G–N008–C00F–N006	-1.8(6)	N00C–C00G–C00H–C00E	-179.4(4)
C00G–N008–C00F–C00J	178.3(5)	N00C–N00C–C00G–C00H	179.8(5)
N00C–N00C–C00G–N008	0.2(7)	O001–N00A–C00J–C00I	-177.2(4)
N00C–N00C–C00G–C00H	179.8(5)	N006–C00E–C00H–N009	179.2(4)

3 Calculation procedures

Computations were carried out by using the Gaussian09 suite of programs[3]. The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals[4] with 6-31+G** basis set[5]. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Then, the single-point energies of optimized structures were accessed under the level of MP2/6-311++G**. The predictions of heats of formation (HOF) were implemented via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of these compounds are in Scheme S1. The detonation performance of compound HDP was further calculated by using the EXPLO5 (v6.05) software[6].



Scheme S1. Isodemic reaction for computing the HOF.

In addition, the enthalpy of sublimation and solid-state formation based on the equation[7]: $\Delta H_{\mathrm{sub}}=Aa^2 + b\sqrt{v\sigma_{tot}^2} + c$. All the results are shown in the following TableS7-S9:

Table S7. The enthalpy of gaseous, sublimation and solid phase formation of **HDP**.

Compound	Enthalpy of gaseous Formation (kJ/mol)	Enthalpy of sublimation (kJ/mol)	Enthalpy of formation in the solid state (kJ/mol)
HDP	64.7239283	64.7239283	586.5659878

Table S8. The optimized Cartesian coordinates.

element	x coordinates	y coordinates	Z coordinates
H	6.89466700	0.88359600	-0.00010400
O	-3.46225000	-3.15755600	-0.00015000
O	-0.25526900	3.22541500	-0.00025800
O	-2.10278100	4.37777400	0.00008100
O	-5.65303800	-3.28298100	-0.00001900
N	-4.30403100	0.92960700	0.00010200
N	-5.68005200	0.81874600	0.00013000
N	-2.31002700	-0.37188300	-0.00005100
N	-1.49453500	3.28744500	-0.00013200
N	-4.58684700	-2.64954900	-0.00011400
N	-4.43533500	3.21638900	0.00011000
H	-5.43872700	3.08011200	0.00011600
H	-3.98628600	4.12438900	0.00004000
N	-0.27221100	0.63072300	0.00033800
H	0.37195200	1.42098200	0.00005400
C	-3.66194000	2.13651800	0.00008200
C	-3.63779000	-0.29246500	-0.00001800
C	-1.61287400	0.76869000	0.00000900
C	-2.24359200	2.07849500	0.00001600
C	-5.88962000	-0.48703500	0.00003400
H	-6.89460700	-0.88371300	0.00004200
C	-4.68408300	-1.22990600	-0.00004100
O	3.46238000	3.15754800	0.00020500
O	0.25514900	-3.22518700	0.00021400
O	2.10253100	-4.37775900	-0.00012500
O	5.65316300	3.28291100	0.00004000
N	4.30403800	-0.92964900	-0.00011000
N	5.68006300	-0.81882700	-0.00015900
N	2.31007300	0.37190000	0.00006600
N	1.49440700	-3.28736000	0.00016800
N	4.58695800	2.64950300	0.00007000
N	4.43529500	-3.21642500	-0.00011100
H	5.43868900	-3.08016000	-0.00013400
H	3.98623200	-4.12441800	-0.00002000
N	0.27222900	-0.63067900	-0.00027800
H	-0.37193700	-1.42093600	-0.00001200
C	3.66191500	-2.13654300	-0.00007600
C	3.63783400	0.29244400	0.00001200
C	1.61289100	-0.76865400	0.00002200
C	2.24356500	-2.07847400	0.00001200
C	5.88966800	0.48694700	-0.00007700
C	4.68415400	1.22985600	0.00001000

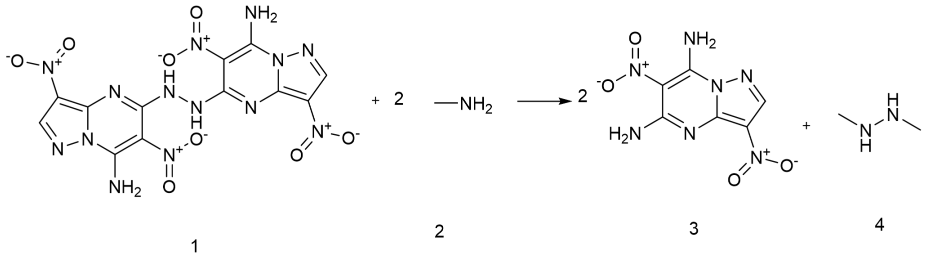


Table S9. The energies and gas phase data for all compounds used in the isodesmic reaction.

	1	2	3	4
Enthalpy at low accuracy (Hartree)	-1825.5586	-95.5263	-913.3822	-189.8533
Enthalpy of formation at high accuracy (kJ/mol)		-18.9214	249.5000	97.3164

References

[1] U. R. Nair, G. M. Gore, R. Sivabalan, S. J. Pawar, S. N. Asthana and S. Venugopalan, Preparation and thermal studies on tetrani-trodibenzo tetraazapentalene (TACOT): A thermally stable high explosive. *J. Hazard. Mater*., 2007, **143**, 500−505.

[2] H. E. Kissinger, Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem*., 1957, **29**, 1702−1706.

[3] M. J. Frisch, et al. Gaussian 09, Revision D.01 (Gaussian, Inc., Wallingford CT, 2013).

[4] A. D. Becke. Density-functional thermochemistry. III. The role of exact exchange. J Phys Chem, 1993, 98, 5648-5652; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J Phys Chem*., 1994, **98**, 11623-11627.

[5] P. C. Hariharan, J. A. Pople. The influence of polarization functions on molecular orbital hydrogenation energies. *Theorefica Chimica Acta.*, 1973, **28**, 213-222.

[6] M. Sućeska, EXPLO5 Program, Version 6.05; Brodarski Institute: Zagreb, Croatia, 2020.

[7] F. C. Byrd, R. M Betsy. Improved Prediction of Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations. *J. Phys. Chem. A*., 2006, **110**, 3, 1005-1013.