Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2023

Supporting Information (SI)

Exploring for high-energy and low-sensitivity energetic compound based on experiment and DFT studies

Qiaoli Li[a], *Shenshen Li*[a], *Jijun Xiao*[a*]

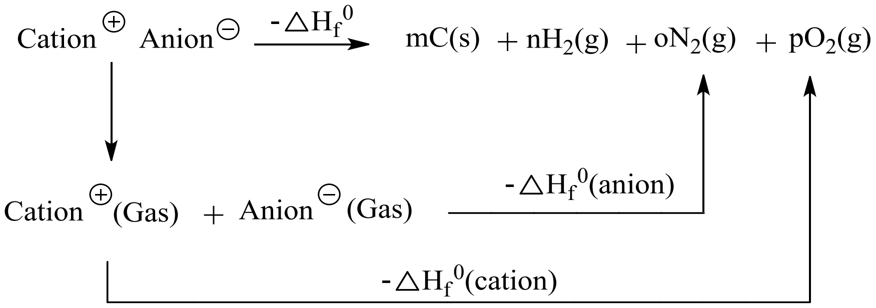
a. Molecules and Materials Computation Institute, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

Table of Content

1. Computational details

Heats of formation calculations

The calculation was performed by using the Gaussian 09 program package[1]. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional[2] with 6-311+G** basis set.[3, 4] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of these compounds were computed through appropriate isodesmic reactions (Scheme S1). All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The heats of formation of DHADAT is calculated based on the simplified formula of Born-Haber energy cycle.



$$\Delta H_f \text{ (salt,298 K)} = \Delta H_f \text{ (cation,298 K)} + \Delta Hf \text{ (anion,298 K)} - \Delta HL$$
$$\Delta H_L = U_{POT} + [p(nM/2 - 2) + q(nX/2 - 2)]RT$$
$$U_{POT} \text{ (kJ mol-1)} = \gamma \text{ } (\rho m/Mm)1/3 + \delta$$

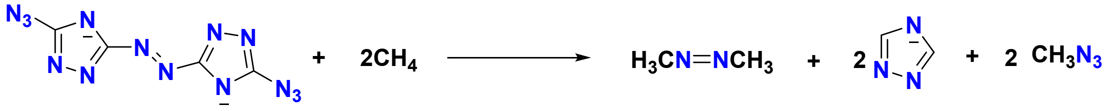
As for ΔHf (anion,298 K), The change of enthalpy for the reactions at 298 K can be expressed as Equation 1

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \qquad \text{(Equation 1)}$$

where $\sum \Delta_f H_P$ and $\sum \Delta_f H_R$ are the ΔHf of reactants and products at 298 K, respectively, and ΔH298 can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E0 + \Delta ZPE + \Delta HT + \Delta nRT \qquad \text{(Equation 2)}$$

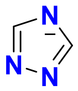
where ΔE0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔHT is thermal correction from 0 to 298 K. The Δ(PV) value in Equation 2 is the PV work term. It equals Δ(nRT) for the reactions of ideal gas. For the isodesmic reaction, Δn = 0, so Δ(PV) = 0. On the left side of Equation 1, apart from target compound, all the others are called reference compounds. The ΔHf of reference compounds is available either from the experiments or from the high-level computing such as CBS-4M.



1^{2-}

Scheme S1 Isodesmic and tautomeric reactions to compute the HOF.

Table S1 Total energy and heat of formation for the reference compounds

	E_0/a.u.	ZPE / kJ·mol^{-1}	ΔH_T / kJ mol^{-1}	HOF / kJ mol^{-1}
1^{2-}	-918.98929	221.05	40.15	1181.29
CH_4	-40.40707	112.26	10.04	-74.60
CH_3NH_2	-95.89385	160.78	11.64	-22.50
CH3NNCH3	-189.33	211.85	16.32	147.85
	-241.7400602	115.36	11.368415	91
NH_3	-56.45483	86.27	10.05	-45.90

First-principles calculations

The calculations based on dispersion-corrected density generalized function theory (DFT-D) in this paper were performed by using the Vienna Ab initio Simulation Package (VASP) code.[5, 6] The projector augmented wave (PAW) method[7] was applied in describing the interaction between the core and valence electrons. To handle the exchange correlation interaction among electrons, the Perdew, Burke, and Ernzerh of (PBE) functional plus the addition of Grimme's D3 dispersion correction (PBE+D3)[8] was utilized. The cutoff energy of plane waves was set to be as 400 eV. The Gamma-centered 1×7×2 Monkhorst-Pack k-point mesh were employed during the geometry optimizations. And the convergence criterion in the geometry optimization for the Hellmann-Feynman force acting on each atom and the total energy of the system were set to be less than 0.02 eV/Å and 10^{-5} eV, respectively. The finite difference method in VASP[9] was applied to the calculation of the mechanical properties of the material.

Table S2. The experimental and calculated lattice constants (Å) for **DHADAT**.

Methods	*a* (Å)	*b* (Å)	*c* (Å)	*B* (°)	*V* (Å^3)
Experimental	23.190	3.611	16.033	93.4	1340.3

Theoretical	23.131	3.574	15.986	93.5	1319.0
Errors	-0.25%	-1.04%	-0.29%	+0.10%	-1.58%

Table S3 The bond lengths (Å) and bond angles (°) for **DHADAT** crystal by calculation and experiment.

Bond lengths (Å)			Bond angles (°)		
	Experimental	Theoretical		Experimental	Theoretical
N1-C1	1.395(3)	1.375	C1-N2 -C2	99.6(2)	100.6
N2-C2	1.338(4)	1.340	N1-C1-N2	127.9(2)	128.9
N2-C1	1.362(4)	1.369	N4-N3 -C1	106.4(2)	106.7
N3-C1	1.330(4)	1.352	N1-C1-N3	118.1(2)	118.2
N3-N4	1.365(3)	1.352	N3-N4-C2	103.9(2)	104.6
N4-C2	1.340(4)	1.357	N2-C1 -N3	114.1(2)	112.9
N5-N6	1.248(4)	1.233	N6-N5 -C2	113.5(3)	117.2
N5-C2	1.406(4)	1.399	N2-C2 -N4	116.0(2)	115.1
N6-N7	1.141(4)	1.148	N5-N6 -N7	172.9(4)	172.4
N8-N9	1.442(4)	1.448	N2-C2 -N5	120.7(3)	122.0
			N4-C2 -N5	123.3(3)	122.8

2. The experiment and crystallographic data

Experimental section

Caution! Although we experienced no explosion in handling these energetic materials, the use of small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^{1}H and ^{13}C NMR spectra are recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300 and 75.0 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of 5°C min^{-1}. IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.05).

X-ray crystallography

The data for **DHADAT**•H_2O was collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated CuKa (λ= 1.54178 nm) at 193 K. The data collection and the initial unit cell refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in **Table S4.**

Table S4 Crystallographic Data for **DHADAT**•H_2O

	DHADAT •H_2O
Empirical formula	$C_4H_{12}N_{18}O$
Formula weight	328.32
Temperature/K	193
Crystal system	monoclinic
Space group	C2/c
a/Å	23.1895(12)
b/Å	3.6111(2)
c/Å	16.0327(9)
α/°	90
β/°	93.365(4)
γ/°	90
Volume/Å^3	1340.26(13)
Z	4
ρ_{calc} g/cm^3	1.627
μ/mm^{-1}	1.130
F(000)	680.0
Crystal size/mm^3	0.13 × 0.11× 0.10
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.638 to 137.414
Index ranges	-28≤h≤27, -4≤k≤4, --14≤l≤19
Reflections collected	4691
Independent reflections	1238 [Rint=0.0708, Rsigma=0.0675]
Data/restraints/parameters	1238/0/115
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0633, wR_2 =0.1614
Final R indexes [all data]	R_1 = 0.0840, wR_2 = 0.1801
Largest diff. peak/hole / e Å^{-3}	0.53/-0.40

CCDC	2268374

Table S5 Bond distance of compound **DHADAT**

parameter	Å	parameter	Å
N8-H8A	0.87(4)	N4 -C2	1.340(4)
N8 -H8B	0.87(5)	N5-N6	1.248(4)
N9-H9B	0.9100	N5-C2	1.406(4)
N9-H9C	0.9100	N6 -N7	1.141(4)
N9-H9A	0.9100	N8 -N9	1.442(4)

Table S6 Bond angle of compound **DHADAT**

parameter	°	parameter	°
H9B-N9-H9C	109.00	H8A-N8-H8B	116(3)
N1 -C1-N2	127.9(2)	N8 -N9-H9A	109.00
N1-C1 -N3	118.1(2)	N8 -N9-H9B	109.00
N2 -C1 -N3	114.1(2)	N8 -N9 -H9C	109.00
N2 -C2 -N4	116.0(2)	H9A-N9-H9B	109.00
N2 -C2-N5	120.7(3)	H9A-N9 -H9C	109.00
N4 -C2 -N5	123.3(3)		

Table S7 Torsion angles of compound **DHADAT**

parameter	°	parameter	°
N4 -N3 -C1-N1	-179.2(2)	C2 -N2-C1 -N1	179.4(3)
N4-N3 -C1-N2	0.4(3)	C2-N2-C1-N3	-0.2(3)
N3-N4-C2-N2	0.3(3)	C1-N2-C2-N4	-0.1(3)
N3-N4-C2 -N5	179.6(2)	C1 -N2-C2-N5	-179.4(2)
N6 -N5-C2-N2	-176.6(2)	C1 -N3-N4-C2	-0.4(3)
N6-N5-C2-N4	4.1(4)		

Table S8 Hydrogen bonds of compound **DHADAT**

D-H···A	d(D-H)/Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/ °
O1- H1A···N3	0.8700	1.9700	2.767(3)	152.00
O1-H1B···N3	0.8700	1.9400	2.767(3)	159.00
N8-H8B ···N4	0.87(5)	2.28(4)	3.093(4)	157(3)
N9-H9A··· N2	0.9100	2.0000	2.846(3)	154.00
N9- H9B···O1	0.9100	1.9400	2.784(3)	153.00
N9-H9C···N8	0.9100	2.0000	2.913(3)	176.00

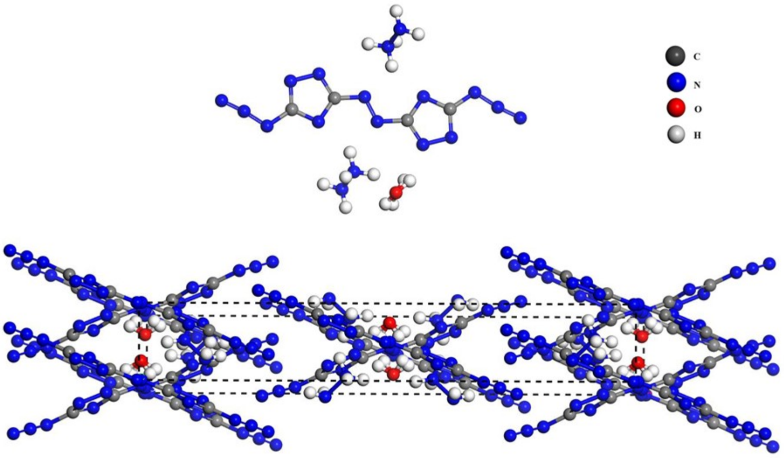


Figure S1. The crystal and molecular structure of **DHADAT**.

3． ^{1}H ,^{13}C NMR spectra and TG-DSC curves of new compounds

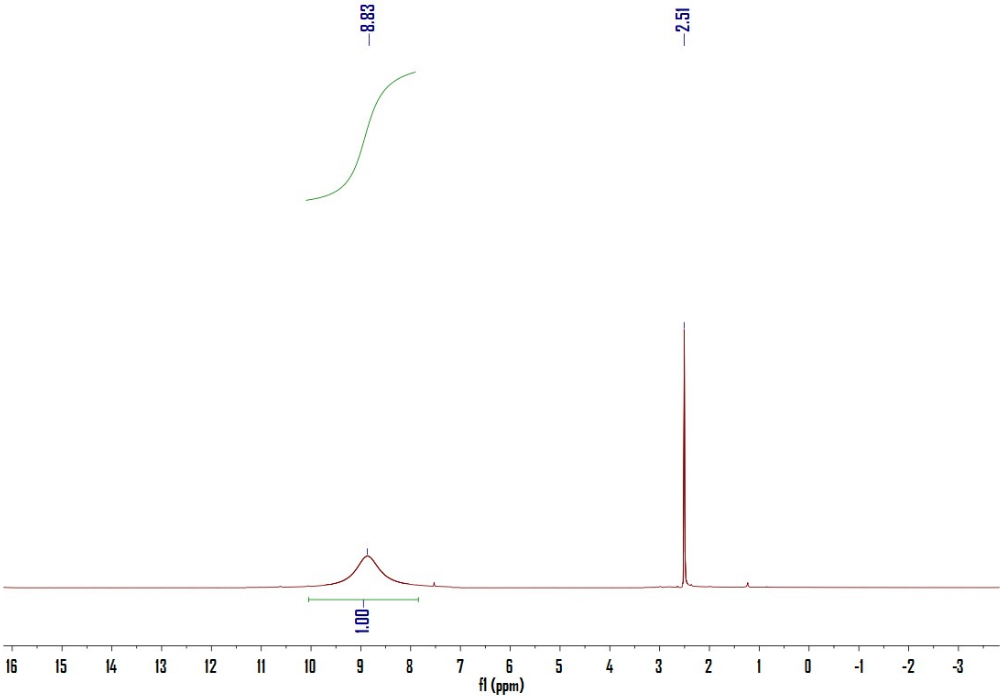


Figure S2^{1}H NMR spectra (500MHz) of **DHADAT** in [D$_6$] DMSO at 25 ^{o}C.

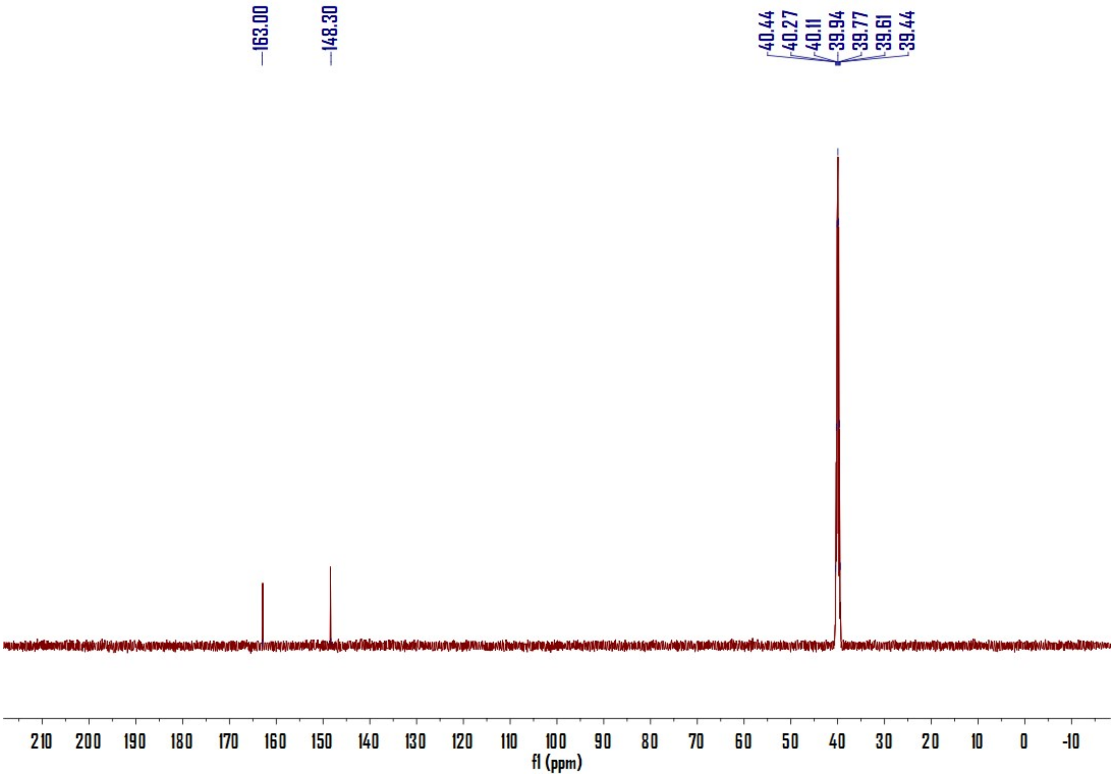


Figure S3^{13}C NMR spectra (125 MHz) of **DHADAT** in [D6] DMSO at 25 °C.

1. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Zakrzewski V. G., Montgomery J. A., Stratmann R. E., Burant J. C., Dapprich S., Millam J. M., Daniels A. D., Kudin K. N., Strain M. C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G. A., Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman P., Cioslowski J., Ortiz J. V., Baboul A. G., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R. L., Fox D. J., Keith T., Laham M. A., Peng C. Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Andres J. L., Gonzalez C., Head M. G., Replogle E. S., Pople J. A. Gaussian 09, revision A. 01. Gaussian, Inc.: Wallingford, CT, 2009.
2. Becke A. D., Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
3. Stephens P. J., Devlin F. J., Chabalowski C. F. and F. M. J., Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields., *J. Phys. Chem.*, 1994, **98**, 11623-11627.
4. H. P. C. and P. J. A., The influence of polarization functions on molecular orbital hydrogenation energies., *Theoretica Chimica Acta.*, 1973, **28**, 213-222.
5. G. Kresse and J. Furthmiiller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp. Mater. Sci.*, 1996, **6**, 15-50.

6. W. Kohn and L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.*, 1965, **140**, A1133-A1138.
7. G. Kresse, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 1999, **59**, 1758-1775.
8. A. M. Ganose, C. N. Savory and D. O. Scanlon, $(CH_3NH_3)_2Pb(SCN)_2I_2$: a more stable structural motif for hybrid halide photovoltaics?, *J. Phys. Chem. Lett.*, 2015, **6**, 4594-4598.
9. Y. Le Page and P. Saxe, Symmetry-general least-squares extraction of elastic data for strained materials fromab initiocalculations of stress, *Phys. Rev. B*, 2002, **65**, 104104.