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Supporting Information

3-Trinitromethyl-4-nitro-5-nitramine-1*H*-pyrazole: A High Energy Density Oxidizer

Hualin Xiong[a], Hongwei Yang[a] and Guangbin Cheng[a] *

[a]School of Chemical Engineering, Nanjing University of Science and Technology Nanjing 210094, P. R. China

Email: gcheng@mail.njust.edu.cn

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1. Computational Details

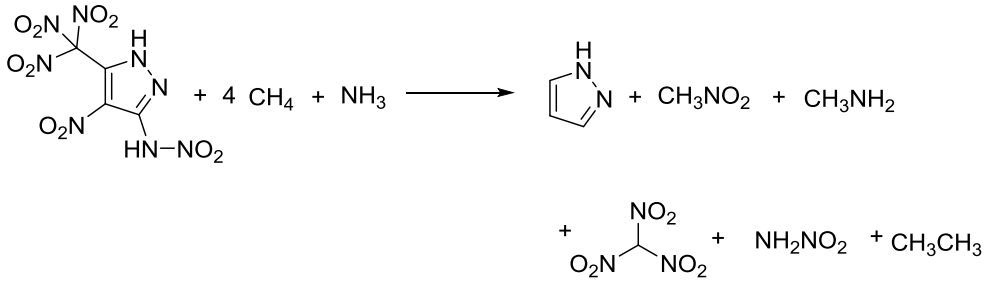
Computations were performed by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yang-Parr (B3LYP) functional with the 6-311+G** basis set.[2-4] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[5] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The predictions of heats of formation (HOF) of compounds used the hybrid DFT-B3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reaction used to derive the HOF of the title compound **5** is in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

$$\Delta H_{298} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R \quad (1)$$

where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298}=\Delta E_{298}+\Delta(PV) =\Delta E_0+\Delta ZPE+\Delta H_T+\Delta nRT \quad (2)$$

where E_0 is the change in total energy between the products and the reactants at 0 K; *ZPE* is the difference between the zero-point energies (*ZPE*) of the products and the reactants at 0 K; H_T is thermal correction from 0 to 298 K. The (*PV*) value in eq (2) is the PV work term. It equals *nRT* for the reactions of ideal gas. For the isodesmic reactions, n = 0, so (*PV*) = 0. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from the experiments or from the high level computing like CBS-4M.



Scheme S1. The isodesmic reactions for calculating heat of formation for **5**

The solid-state enthalpy of formation for compound **5** can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. On the basis of the literature,[6] the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition.[7]

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188[J\ mol^{-1}\ K^{-1}] \quad \text{(equation 1)}$$

Table S1. Calculated zero-point energy (ZPE), thermal correction to enthalpy (H_T), total energy (E_0) and heats of formation (HOF)

Compound	E_0/ a.u.	*ZPE* / kJ mol^{-1}	ΔH_T / kJ mol^{-1}	HOF/kJ mol^{-1}
5	-1343.640616	319.92	53.37	320.2
CH_4	-40.5339263	112.26	10.04	-74.60[b]
NH_3	-56.5826356	86.27	10.05	-45.9[b]
pyrazole	-226.2603313	179.2	12.57	177.4[b]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.4[c]
NH_2NO_2	-261.1248168	98.79	12.39	-3.9[c]
CH_3NO_2	-245.0915559	124.93	11.60	-80.80[b]
CH_3CH_3	-79.8565413	187.31	11.79	-84.01[b]

[a] E_0 in a.u. *ZPE* (vibrational zero-point energy), ΔH_T (thermal correction to enthalpy) and HOF are in kJ mol^{-1}. [b] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.]. [c] Data obtained from CBS-4M calculation in combination with the atomization reaction of the corresponding compound.

2. Crystallographic data for 5

Table S2 Crystallographic data for **5**

Empirical Formula	C4H2N8O10
Formula Weight	322.14
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.7073(4)
b/Å	8.8246(7)
c/Å	18.6187(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1102.03(13)
Z	4
ρ (calc) mg/mm^3	1.942
Absorptioncoefficient m/mm^{-1}	0.192
F(000)	648.0
Crystal size/mm^3	0.32 ×0.26 ×0.2
2Θ range for data collection	6.362 to 52.9 °
Index ranges	$-8 \le h \le 8$, $-10 \le h \le 10$, $-22 \le h \le 22$
Reflections collected	12743
Independent reflections	2249[R(int)=0.067]
Data/restraints/parameters	2249/0/205
Goodness-of-fit on F^2	1.041

Final R indexes [I>=2σ (I)]	0.0356, 0.0634
Final R indexes [all data]	0.0589, 0.0698
CCDC	1847087

Table S3 Selected bond lengths [Å] and angles [°] for compound **5**

O1-N4	1.231(4)	N2-C1	1.338(4)
O2-N4	1.210(4)	N3-N4	1.369(4)
O3-N5	1.226(3)	N3-C1	1.371(4)
O4-N5	1.238(3)	N5-C2	1.419(4)
O5-N6	1.214(4)	N6-C4	1.535(4)
O6-N6	1.206(4)	N7-C4	1.537(4)
O7-N7	1.212(4)	N8-C4	1.546(4)
O8-N7	1.208(3)	N2-H2A	0.81(4)
O9-N8	1.210(4)	N3-H3A	0.81(3)
O10-N8	1.209(3)	C1-C2	1.382(4)
N1-N2	1.348(4)	C2-C3	1.415(4)
N1-C3	1.322(4)	C3-C4	1.477(4)
N2-N1-C3	105.3(3)	C1-N2-H2A	129(2)
N1-N2-C1	113.2(2)	N4-N3-H3A	115(2)
N4-N3-C1	122.5(3)	C1-N3-H3A	119(2)
O1-N4-O2	126.7(3)	N3-C1-C2	128.3(3)
O1-N4-N3	116.9(3)	N2-C1-N3	125.8(3)
O2-N4-N3	116.3(3)	N2-C1-C2	105.8(2)
O3-N5-O4	123.9(3)	N5-C2-C3	128.1(3)
O3-N5-C2	118.6(3)	C1-C2-C3	105.4(3)
O4-N5-C2	117.6(3)	N5-C2-C1	126.5(3)
O5-N6-O6	127.3(3)	N1-C3-C2	110.4(3)
O5-N6-C4	116.0(2)	N1-C3-C4	118.9(3)
O6-N6-C4	116.6(2)	C2-C3-C4	130.6(3)
O7-N7-O8	128.1(3)	N7-C4-C3	109.7(2)
O7-N7-C4	116.2(3)	N8-C4-C3	112.5(2)
O8-N7-C4	115.6(2)	N7-C4-N8	105.7(2)
O9-N8-O10	127.5(3)	N6-C4-N7	106.1(2)
O9-N8-C4	117.5(3)	N6-C4-N8	107.9(2)
O10-N8-C4	114.9(2)	N6-C4-C3	114.3(2)
N1-N2-H2A	118(2)	O3-N5-C2-C3	-178.3(3)
C3-N1-N2-C1	1.8(3)	O4-N5-C2-C1	-177.9(3)
N2-N1-C3-C2	-1.1(3)	O5-N6-C4-C3	159.9(3)
N2-N1-C3-C4	-177.3(2)	O6-N6-C4-N8	106.6(3)
N1-N2-C1-N3	-178.4(3)	O5-N6-C4-N8	-74.1(3)
N1-N2-C1-C2	-1.7(3)	O6-N6-C4-C3	-19.5(4)
C1-N3-N4-O1	12.2(4)	O6-N6-C4-N7	-140.5(3)
C1-N3-N4-O2	-169.5(3)	O5-N6-C4-N7	38.8(3)
N4-N3-C1-N2	-45.8(4)	O7-N7-C4-C3	102.8(3)

N4-N3-C1-C2	138.4(3)	O7-N7-C4-N8	-18.8(3)
O3-N5-C2-C1	1.9(4)	O7-N7-C4-N6	-133.2(3)
O4-N5-C2-C3	1.9(4)	O9-N8-C4-N7	-86.1(3)
O8-N7-C4-N8	163.5(2)	O10-N8-C4-C3	-28.1(3)
O8-N7-C4-C3	-75.0(3)	O9-N8-C4-C3	154.2(3)
O8-N7-C4-N6	49.0(3)	O10-N8-C4-N6	-155.2(2)
C1 -C2-C3-N1	0.1(3)	O9 -N8-C4-N6	27.1(3)
N5 -C2-C3-N1	-179.7(3)	O10-N8-C4-N7	91.6(3)
C1 -C2-C3-C4	175.8(3)	N3 -C1-C2-N5	-2.7(5)
N1 -C3-C4-N8	123.9(3)	N3 -C1-C2-C3	177.4(3)
C2 -C3-C4-N7	-168.7(3)	N2 -C1-C2-C3	0.9(3)
C2 -C3-C4-N8	-51.4(4)	N2 -C1-C2-N5	-179.2(3)
C2 -C3-C4-N6	72.2(4)	N5 -C2-C3-C4	-4.1(5)
N1 -C3-C4-N6	-112.5(3)	N1 -C3-C4-N7	6.6(4)

Table S4 Hydrogen bonds for compound **5**

D—H ⋯A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N2-- H2A ⋯O1	0.81(4)	2.46(3)	2.757(4)	103(3)
N2-- H2A ⋯O1^{i}	0.81(4)	2.19(4)	2.936(4)	155(3)
N3-- H3A ⋯O3	0.81(3)	2.33(4)	2.819(3)	120(3)
N3-- H3A ⋯O4^{ii}	0.81(3)	2.20(3)	2.968(3)	159(3)

Symmetry Code: i: -1/2+x, 1/2-y,2-z, ii: 1-x,-1/2+y,3/2-z

3. ^{1}H NMR and ^{13}C NMR of compound 5

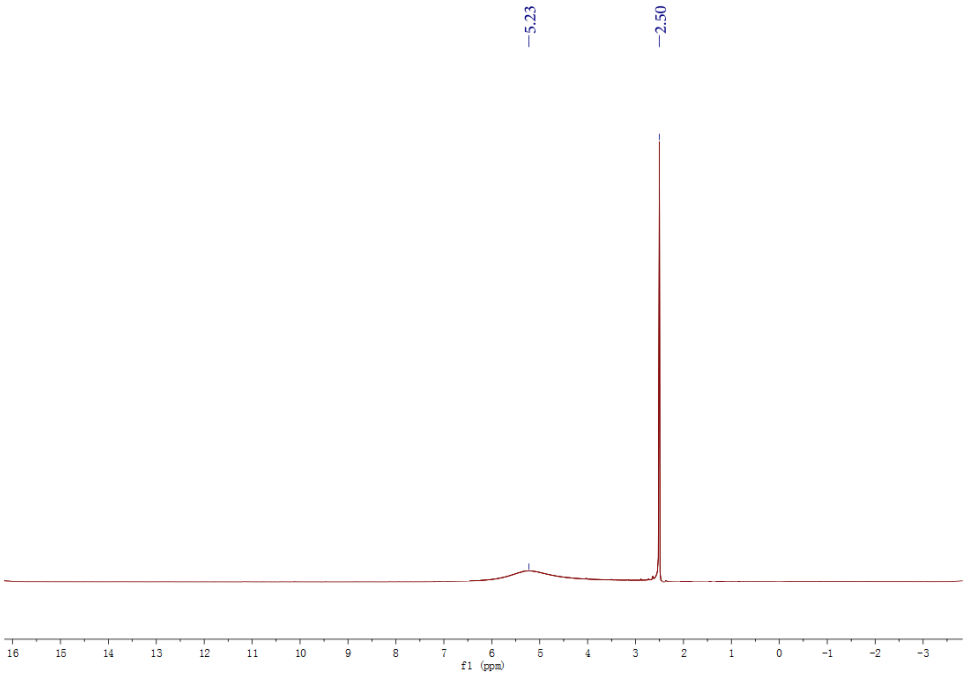


Figure S1. ^{1}H NMR spectra in DMSO-d_6 for 5

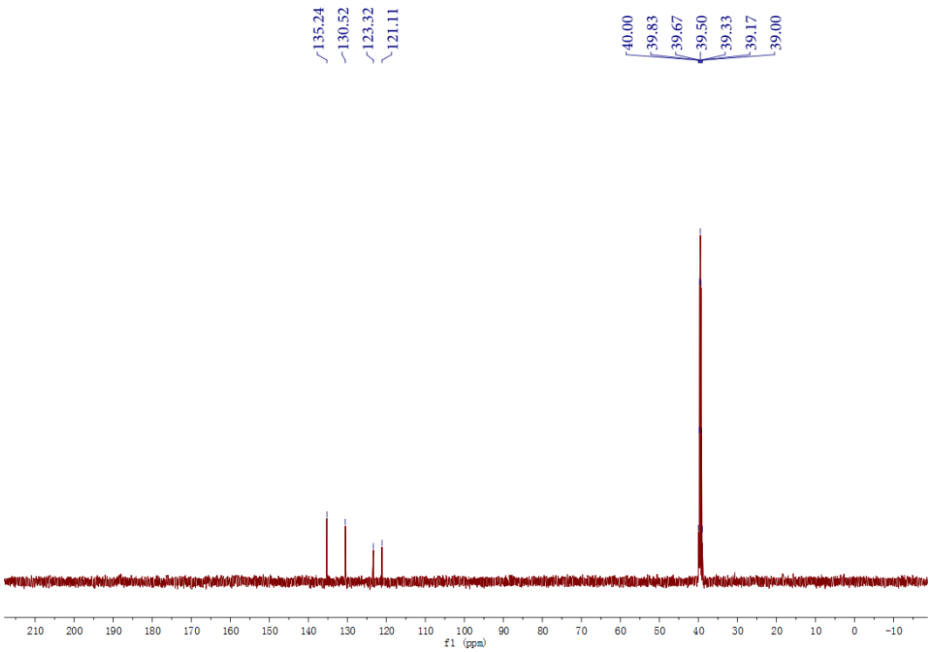


Figure S2. ^{13}C NMR spectra in DMSO-d_6 for 5

4. The DSC Plots of compounds 5

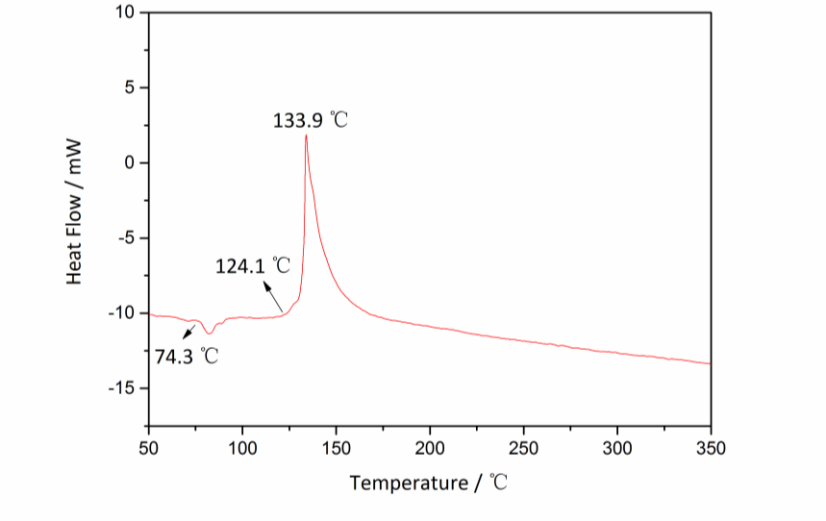


Figure S3. The DSC curve of compound 5 measured at a heating rate of 5 ℃ min^{-1}

5. References

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