Supporting Information

3-(3,5-Dinitrophenyl)-5-amino-1,2,4-oxadiazole: Synthesis, Structure and Properties of a Novel Insensitive Energetic Material

Bin-shan Zhao [a], Bao-long Kuang [a], Mou Sun [b], Ting-wei Wang [a], Chao Zhang [a], Mei-qi Xu [a], Cong Li [a], Zu-jia Lu [a], Jian-guo Zhang [a,*]

[a] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing, 100081, China.
[b] China Wuzhou Engineering Group Co., Ltd., Beijing, 100053, China.

Corresponding author: Jian-guo Zhang, E-mail: zjgbit@bit.edu.cn

Table of Contents:

Experimental Section

Caution!

Some compounds in this work are potential explosives which could be detonated by certain stimuli, although no accident occurred during our experiences, personal protective equipment including gloves, goggles, and safety shield should be pro-vided when appropriate.

Materials and Equipment

All reagents and solvents used in this work were used as received if not otherwise specified. Thermal behaviors were detected by METTLER TOLEDO Thermal Analysis System TGA/DSC 3+ using heating rates 5 ℃ min^{-1} under a nitrogen environment of 80 mL min^{-1}. Infrared spectra were measured with Thermo-Nicolet Nexus 470 FTIR with a measurement range of 4000-400 cm^{-1}, and the resultant transmittance values were defined as 's' for strong, 'm' for medium and 'w' for weak. All NMR spectra were conducted Bruker AVANCE III nuclear magnetic resonance spectrometer at 101 MHz and 400 MHz for ^{13}C NMR and ^{1}H NMR respectively. By using a BAM DFH-10 device with a weight drop of 5 kg, the standard step approach of the drop weight device was used to assess the mechanical sensitivities of the material, including impact sensitivity and friction sensitivity.

Theoretical Method

Post-processing calculations related to wavefunction analysis, such as electrostatic surface potential (ESP) analysis and noncovalent interaction (NCI) analysis, were carried out with the assistance of the Multiwfn program. Predictions of explosive performance, including detonation velocity and pressure, were conducted using EXPLO5.

All the geometry optimizations in this work were initiated using experimental crystal data. These optimizations were conducted using Gaussian 09 at the B3LYP/6-31G* level of theory. Additionally, vibrational analysis was performed to confirm that the optimized structures correspond to energy minima on the potential energy surface.

Enthalpy of Formation Calculation

In this research, calculations of enthalpy of formation are performed based on its definition. Taking the compound $C_aH_bN_cO_d$ as an example, the corresponding general equation for its formation reaction is as follows:

$$aC + \frac{b}{2}H_2 + \frac{c}{2}N_2 + \frac{d}{2}O_2 \rightarrow C_aH_bN_cO_d$$

And the atomization reaction is employed to derive the enthalpy of formation according to the Hess law:

$$C_aH_bN_cO_d \rightarrow aC + bH + cN + dO$$

For the formation reaction, the gas-phase heat of reaction at 298 K can be calculated from the following equation:

$$\Delta_f H(C_aH_bN_cO_d) = a\Delta_f H(C) + b\Delta_f H(H) + c\Delta_f H(N) + d\Delta_f H(O) - \Delta H_{atomization}$$

Where $\Delta_f H(C)$, $\Delta_f H(H)$, $\Delta_f H(N)$ and $\Delta_f H(O)$ are experimental gas phase enthalpies of formation of C, H, N and O atoms; $\Delta H_{atomization}$ is standard reaction enthalpy for atomization reaction, which

can be can be calculated by the following equation:

$\Delta H_{atomization} = aH(C) + bH(H) + cH(N) + dH(O) - H(C_aH_bN_cO_d)$

According to Hess law, the solid-phase enthalpy of formation can be obtained from the gas-phase enthalpy of formation of and the enthalpy of sublimation as follows:

$\Delta H_{solid} = \Delta H_{gas} - \Delta H_{sublimation}$

In this work, we obtained the enthalpy of sublimation using the method of ref. S1:

$$\Delta H_{sublimation} = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + \mathrm{c}$$

Where SA is molecular surface area, υ is equilibrium constant of positive and negative electrostatic potentials at the surface of the molecule and σ_{tot} is variance of total surface electrostatic potential. The details of heats of formation calculation are listed in **Table S1**.

References

[S1] P. Politzer, J. S. Murray, M. Edward Grice, M. Desalvo, E. Miller, Molecular Physics 1997, 91, 923-928.

Supplementary Figures S1-S8

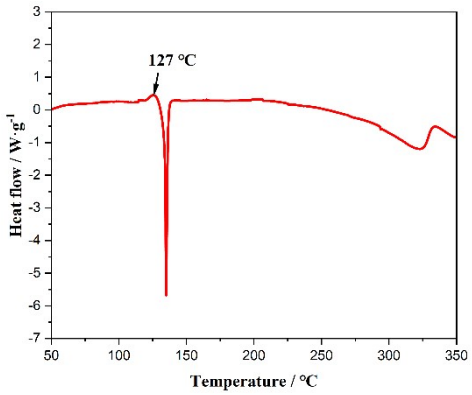

Fig. S1 The DSC curve of compound **2** in the open system

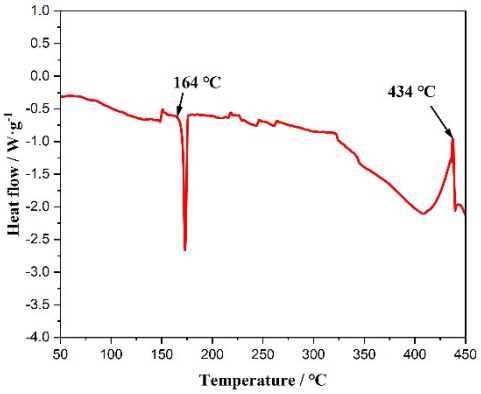

Fig. S2 The DSC curve of compound **3** in the open system

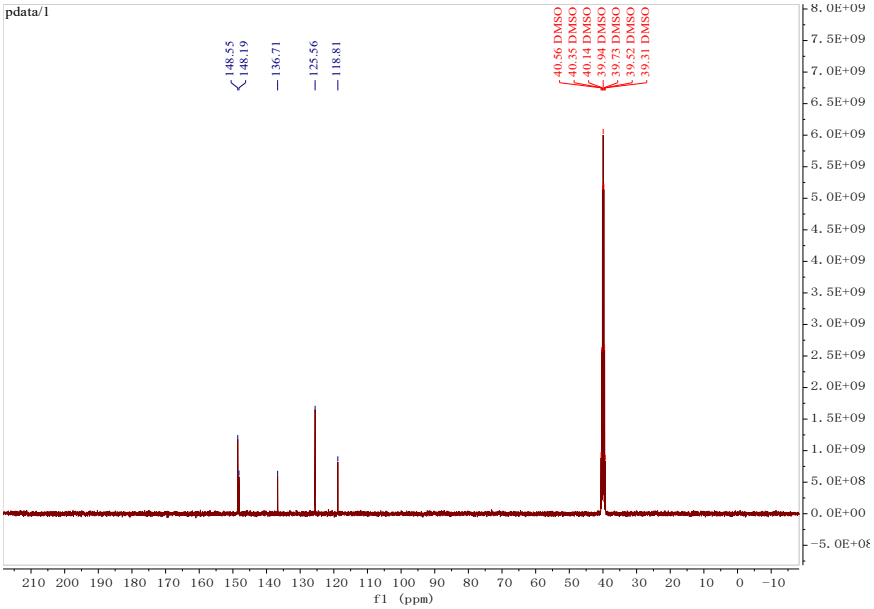

Fig. S3 The ^{13}C NMR spectroscopy of compound **1**

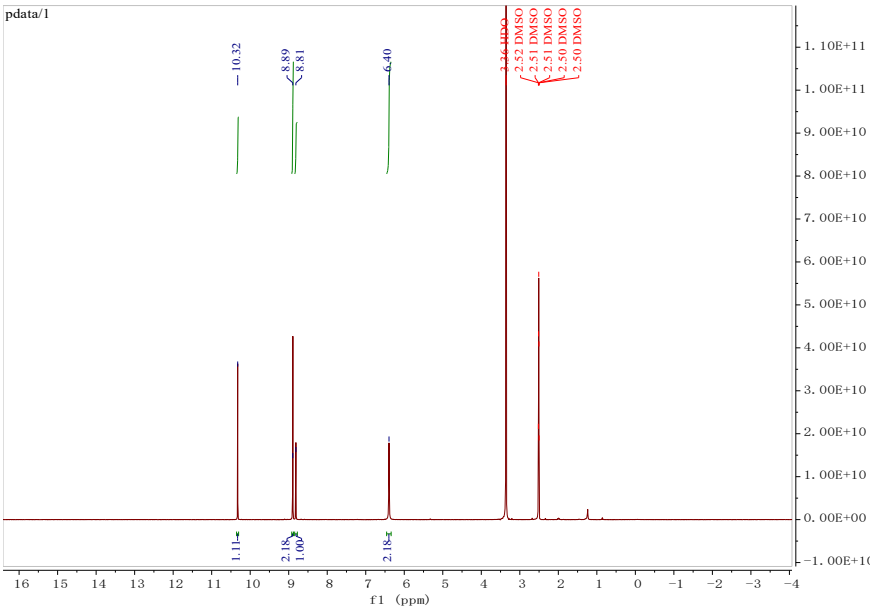

Fig. S4 The ^{1}H NMR spectroscopy of compound **1**

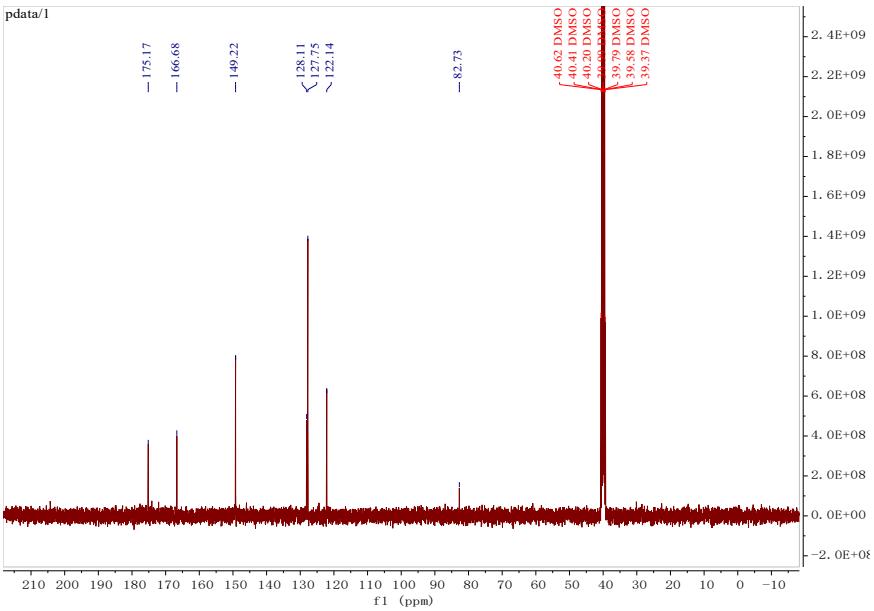

Fig. S5 The ^{13}C NMR spectroscopy of compound **2**

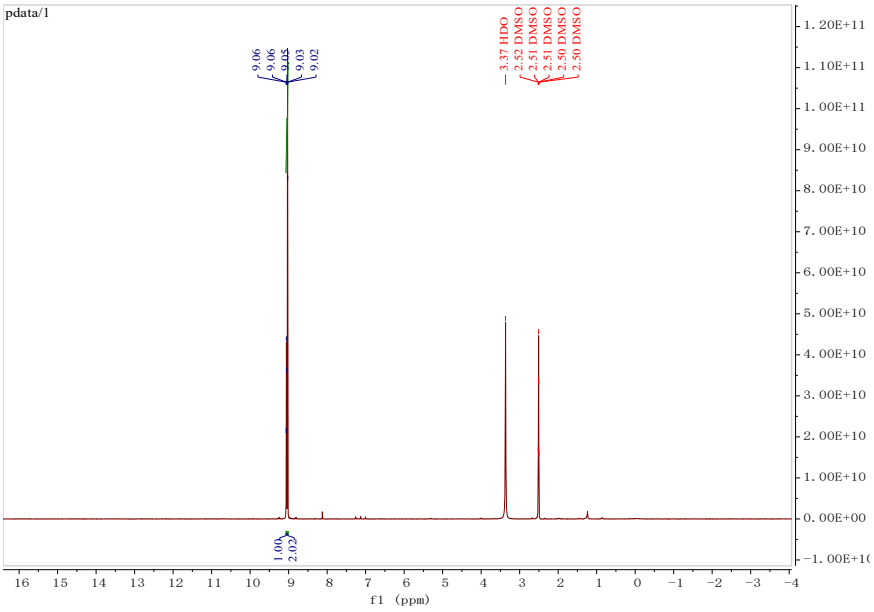

Fig. S6 The ^{1}H NMR spectroscopy of compound **2**

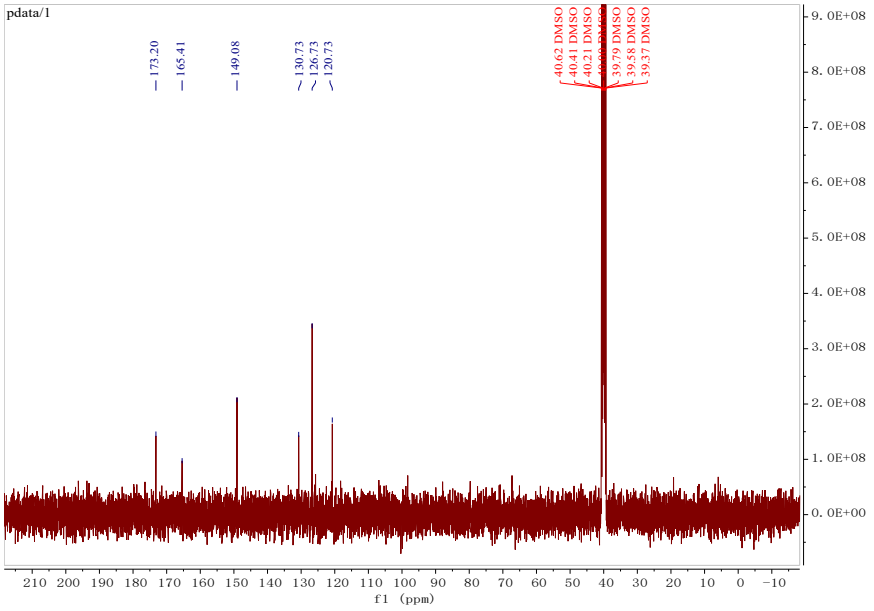

Fig. S7 The ^{13}C NMR spectroscopy of compound **3**

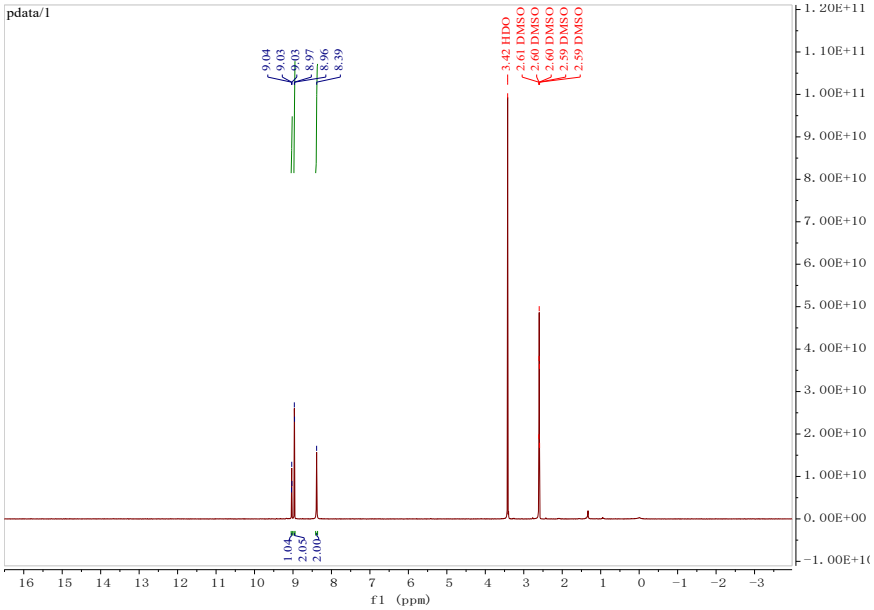

Fig. S8 The ^{1}H NMR spectroscopy of compound **3**

Supplementary Tables S1-S5

Table S1: Details of heats of formation calculation

Comp.	**2**	**3**
Electronic energy / Hartree	-2320.244903	-957.5314208
ZPE / Hartree	0.131433	0.148717
ZPE scale factor	0.977	0.977
H_{cor} / Hartree	0.019009	0.016211
H_f (gas) / kJ mol^{-1}	91.6	92.7
Area / Å^2	304	242.5
$\nu\sigma_{tot}^2$ / kcal mol^{-1}	26.324	41.871
H_{sub} / kJ mol^{-1}	219.7	164.8
H_f(solid) / kJ mol^{-1}	-128.1	-72.1

Table S2: Crystallographic data for compound **2**

CCDC	2279208
Formula	$C_9H_3Cl_3N_4O_5$
Formula weight	353.50
Temperature / K	120.1(2)
Crystal system	monoclinic
Space group	$P2_1$
a / Å	5.4240(8)
b / Å	10.6544(14)
c / Å	11.243(7)
α/°	90.00
β/°	101.40(3)
γ/°	90.00
Volume / Å^3	636.9(4)
Z	2
ρ_{calc} / g cm^{-3}	1.843
μ / mm^{-1}	0.747
F(000)	352
Crystal size / mm^3	0.29 × 0.15 × 0.15
Crystal shape	rod
Crystal color	colorless
R1	0.0463
wR2	0.0732
Data/restraints/parameters	2421/1/190
Goodness-of-fit on F2	0.998
Flack Parameters	-0.15(7)
Completeness	0.9975

Table S3: Crystallographic data for compound **3**

CCDC	2279209
Formula	$C_8H_5N_5O_5$
Formula weight	251.17
Temperature / K	116.7(9)
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	6.8806(4)
b / Å	14.1354(8)
c / Å	10.3877(5)
α/°	90.00
β/°	103.677(5)
γ/°	90.00
Volume / Å^3	981.66(9)
Z	4
ρ_{calc} / g cm^{-3}	1.699
μ / mm^{-1}	0.145
F(000)	512
Crystal size / mm^3	0.23 × 0.22 × 0.22
Crystal shape	rod
Crystal color	grayish yellow
R1	0.0732
wR2	0.1161
Data/restraints/parameters	1895/0/163
Goodness-of-fit on F2	1.046
Flack Parameters	N
Completeness	0.9973

Table S4: Optimized Cartesian coordinates of compound **2**

Atom	x	y	z
C1	-0.314784	6.15747	-0.246106
C2	0.531457	7.133733	-1.027361
C3	1.460397	8.384383	-2.403012
C4	1.759423	9.070873	-3.667159
C5	0.974862	8.807542	-4.796158
C6	2.82047	9.983382	-3.748702
C7	1.268592	9.464375	-5.987046
C8	3.07207	10.61278	-4.961792
C9	2.312323	10.374266	-6.102579
H1	0.151653	8.10562	-4.750607
H2	3.440891	10.202772	-2.88835
H2	2.525001	10.874969	-7.037399
N1	0.427749	7.477132	-2.271141
N2	2.151844	8.5809	-1.302354
N3	0.438594	9.184738	-7.178285
N4	4.191637	11.575123	-5.046372
O1	1.532437	7.743324	-0.374599
O2	0.72255	9.779823	-8.21397
O3	-0.477085	8.376749	-7.048994
O4	4.388301	12.114659	-6.131505
O5	4.846605	11.767647	-4.025686
Cl1	0.750786	4.846219	0.38035
Cl2	-1.578675	5.465572	-1.294067
Cl3	-1.071996	7.031048	1.136195

Table S5: Optimized Cartesian coordinates of compound **3**

Atom	x	y	z
C1	-1.395571	8.319351	8.900618
C2	0.325892	8.80059	9.957489
C3	1.307616	8.875042	11.050762
C4	2.509445	9.578156	10.889217
C5	1.034459	8.234874	12.264794
C6	3.410099	9.624056	11.947132
C7	1.968645	8.310236	13.293905
C8	3.168868	8.998616	13.166439
H1	-3.162664	7.320976	9.050041
H2	-2.887493	8.094517	7.510727
H3	2.741056	10.080758	9.958279
H4	0.110248	7.688552	12.402948
H5	3.882964	9.046477	13.97701
N1	0.536402	9.384171	8.800112
N2	-0.861208	8.120977	10.081112
N3	-2.580478	7.877446	8.445133
N4	4.676225	10.366024	11.774161
N5	1.675905	7.632815	14.573598
O1	-0.638353	9.059142	8.070609
O2	5.451434	10.388886	12.726985
O3	4.868885	10.910088	10.689841
O4	2.519098	7.716477	15.463134
O5	0.608524	7.030771	14.663154