Electronic Supplementary Material

A Comparative Study of the Structure, Energetic Performance and Stability of Nitro-NNO-azoxy Substituted Explosives.

Yuan Wang [a], Shenghua Li [a], Yuchuan Li [a], Rubo Zhang*[b], Dong Wang[a] and Siping Pang*[ac]

[a] *School of Materials Science & Engineering,* [b] *School of Chemistry,* [c] *State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081 (China)*

Fax: +86-010-68913038

E-mail: zhangrubo@bit.edu.cn. *(*Rubo Zhang*)*

pangsp@bit.edu.cn *(*Siping Pang*)*

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1. Spectra of 3 and 4

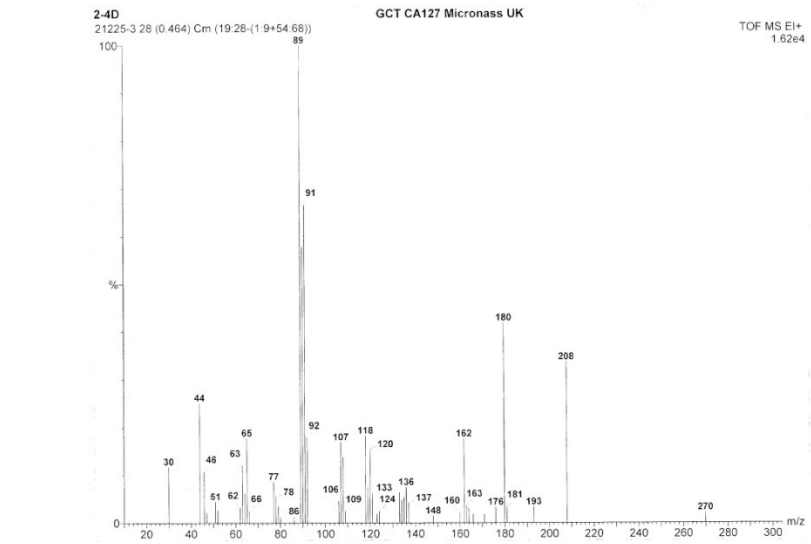


Fig. S1 mass spectrum of **3**

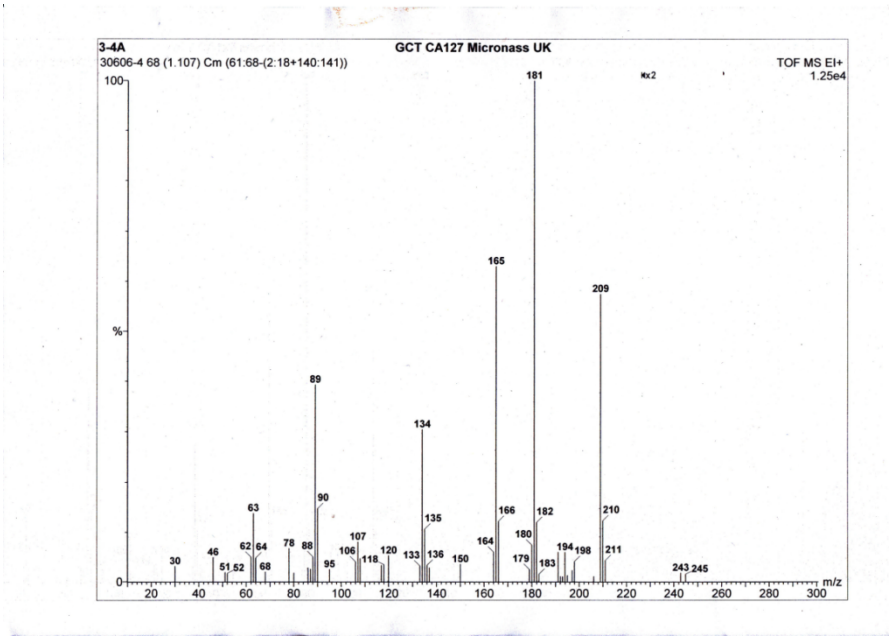


Fig. S2 mass spectrum of **4**

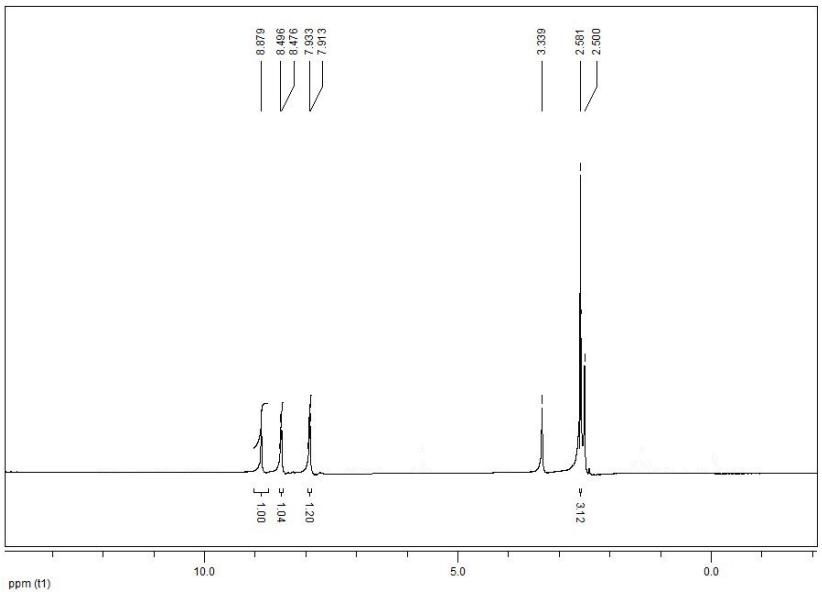


Fig. S3 1H NMR spectrum of **3** (DMSO-d6).

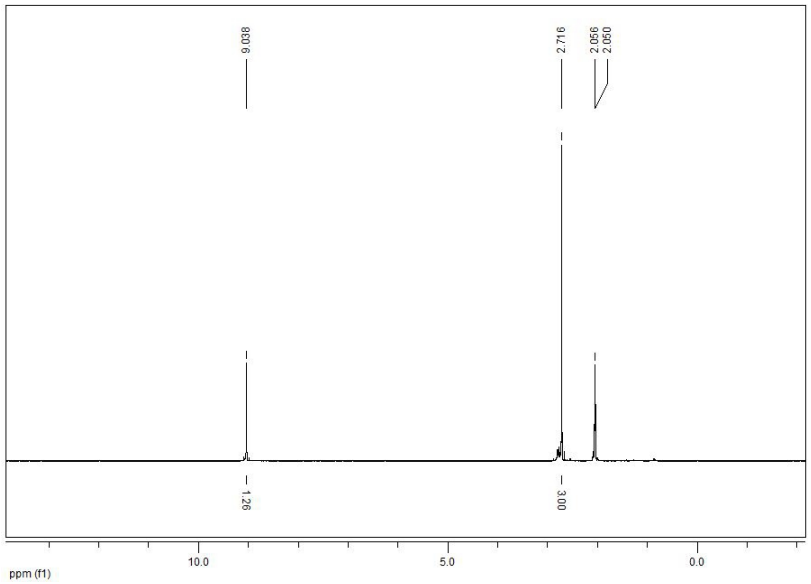


Fig. S4 1H NMR spectrum of **4** (acetone-d6).

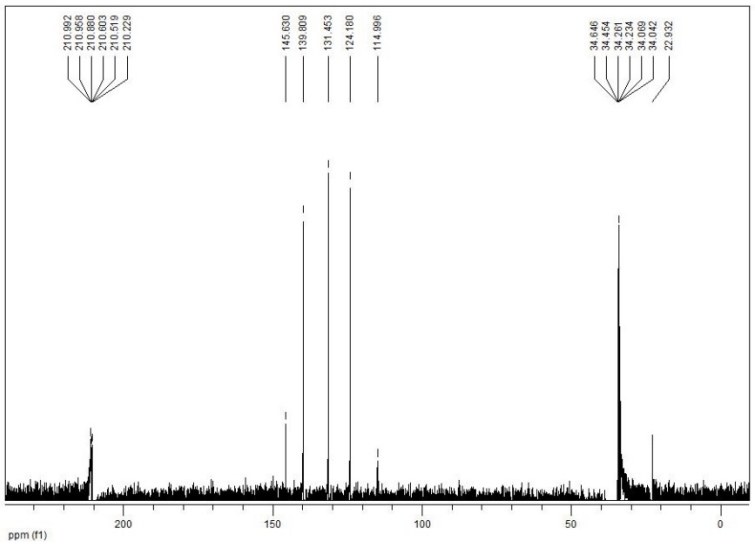


Fig. S5 13C NMR spectrum of **3** (acetone-d6).

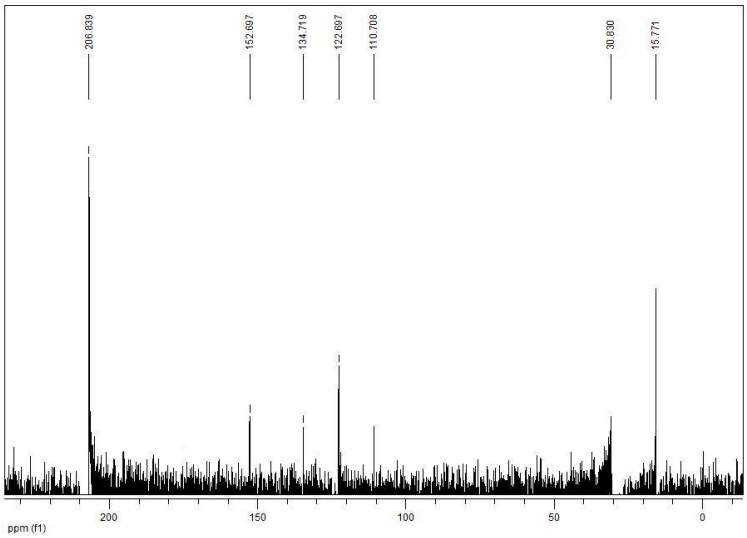


Fig. S6 13C NMR spectrum of **4** (acetone-d6).

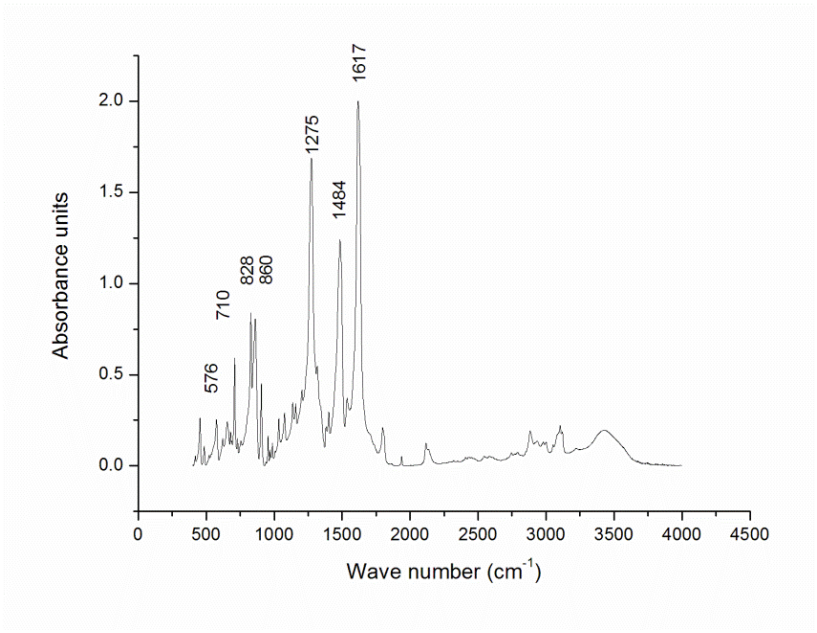


Fig. S7 IR spectrum of **3**

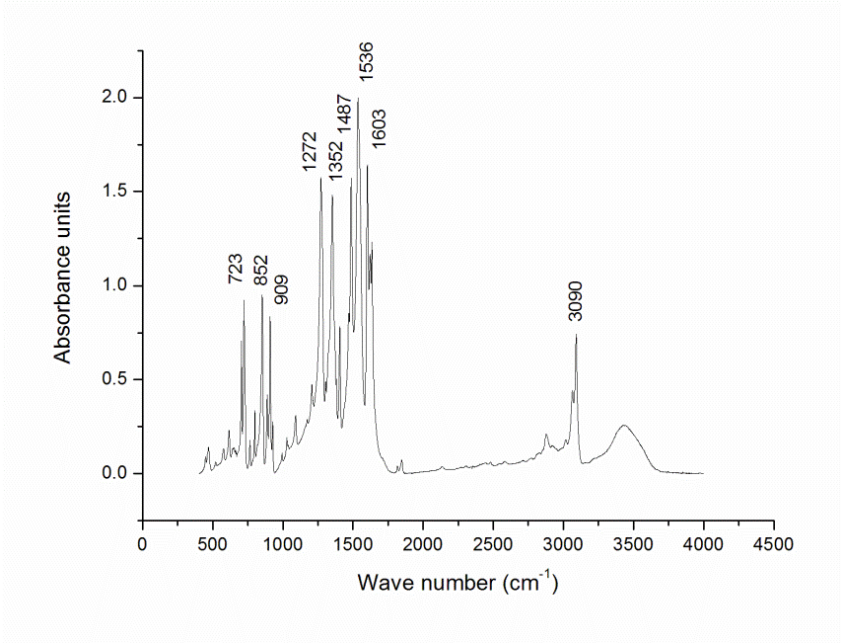
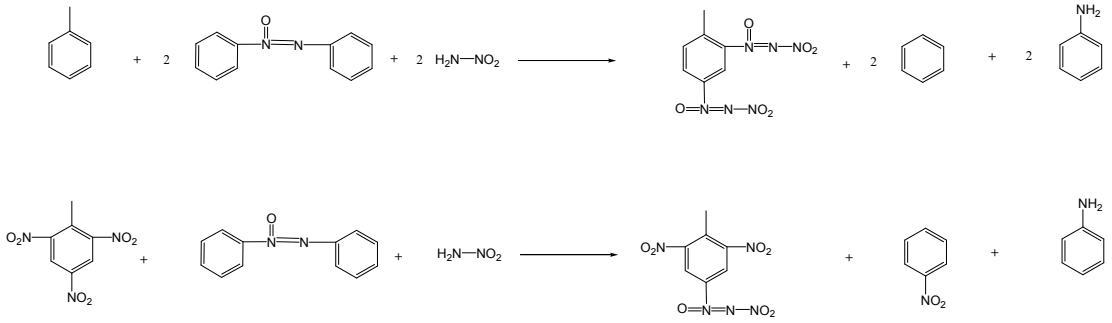


Fig. S8 IR spectrum of **4**

2. X-Ray Diffraction

The single crystals of **1** and **2** were mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoKα radiation (λ= 0.71073 Å). Data were collected by the ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined with theoretical calculations and refined with an isotropic vibration factor.

3. Heat of formation



Scheme S1 isodesmic reactions of **3** and **4**.

For the isodesmic reactions, heat of reaction (ΔH_{298K}) can be calculated according to the following equation:

$\Delta H_{298K} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R}$

Where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the heats of formation for reactants and products at 298.15K, respectively. At the same time, ΔH_{298K} can be also obtained from the following expression:

$\Delta H_{298K} = \Delta E_{298K} - \Delta(PV)$

$= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta(nRT)$

Where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies of the products and the reactants; ΔH_T is thermal correction from 0K to 298.15K. Consequently, the heat of formation can be worked out by using ΔH_{298} and heats of formation of other reactants and products. The data in needed can be obtained from literatures and handbooks.

Table S1 The gas-phase heat of formation (HOF) of title compounds.

	toluene	TNT	Ph-NO=N-Ph	H_2N-NO_2	**3**	**4**	Ph	Ph-NO_2	Ph-NH_2
ΔE_0+ΔZPE +ΔH_T/a.u.	-271.43	-884.89	-647.73	-260.98	-1049.59	-1069.48	-232.14	-436.63	-287.47
HOF(g) /kJ·mol^{-1}	50.1	-80.5	342	342	537.5	168.1	82.9	68.53	87.03

$$\Delta H(Solid) = \Delta H(Gas) - \Delta H(Sublimation)$$

$$\Delta H(Sublimation) = a(SA)^2 + b\sqrt{\sigma_{Tot}^2 \nu} + c$$

Table S2 heats of sublimation and their calculating parameters.

	SA/Å^2	σ^2_{tot} /(kcal•mol)^2	ν	H(S)/ kJ·mol^{-1}	HOF(S) /kJ·mol^{-1}
3	263.39	99.88	0.2128	121.80	415.70
4	251.64	108.26	0.1691	112.74	55.35

4. Sensitivity

The impact sensitivity was tested on a type 12 tooling according to "up and down" method. A 2.5 kg weight was dropped from a set height onto a 20 mg sample placed on 150 grit garnet sandpaper. Each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. 50 drops were made from different heights, and an explosion or non-explosion was recorded to determine the results. RDX was considered as a reference compound, the impact sensitivity of RDX is 7 J.

The friction sensitivity was tested on a FSKM 50/20K apparatus produced by OZM Research. The sample was placed between the porcelain plate and peg. The weight of leading at least one ignition in six times was recorded. Tested results for **3** and **4** are 120 N and 160 N respectively.