

Electronic Supplementary Information

Synthesis, characterization and property analysis: a novel energetic ionic salt of dicarbohydrazide bis[3-(5-nitroimino-1,2,4-triazole)]

Jianrong Ren,^{a,b} Dong Chen,^b Guijuan Fan,^b Ying Xiong,^b Zhenqi Zhang,^b Yanwu Yu,^{a*} Hongzhen Li^{b*}

^a College of Environment and Safety Engineering, North University of China, Taiyuan 030051, China

^b Institute of Chemical Materials, China Academy of Engineering Physics, Sichuan, Mianyang 621900, China.

Corresponding author: Dr. Hongzhen Li, E-mail: hongzhenli@caep.cn and Dr. Yanwu Yu, E-mail: yyw7711@sina.cn.

Table of Contents:

1.1. Chemicals and Equipments

1.2. Synthesis

1.3. X-ray crystallography

1.4. Non-isothermal kinetics

1.5. Sensitivity test

1.6. Molar enthalpy of formation and oxygen balance

1.7. Solubility test

References

1.1. Chemicals and Equipments

All reagents were purchased commercially and used without further purification. ^1H and ^{13}C spectra were recorded on a 400 MHz (Bruker AVANCE 400) or 600 MHz (Bruker AVANCE 600) nuclear magnetic resonance spectrometer. Infrared (IR) spectra were measured on SHIMADZU IRTracer-100 FT-IR spectrometer in the range of $4000\text{-}400\text{ cm}^{-1}$ as KBr pellets at $25\text{ }^\circ\text{C}$. Transmittance values are qualitatively described as strong (s), medium (m) and weak (w). TG and DSC analysis were conducted on a Mettler Toledo TGA/DSC 2 instrument with the linear heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. Single crystal X-ray diffraction data were tested in a Rigaku supernova Single X-ray Diffractometer area detector ($\text{Mo K}\alpha$, 0.71073 \AA). Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer ($\text{Cu K}\alpha$, 1.5418 \AA). The sensitivity to impact stimuli was determined by the standard staircase method applying fall hammer apparatus of BAM DFH-10 with a 10 kg drop weight¹. The friction sensitivity was determined on a BAM FSKM-10 apparatus by following the BAM method².

1.2. Synthesis

CAUTION! All the compounds in every scheme should be handled with extreme care, although no incidents occurred during preparation and manipulation. Additional proper protective precautions like face shield, leather coat, earthed equipment and shoes, Kevlar gloves should be used when working with these compounds.

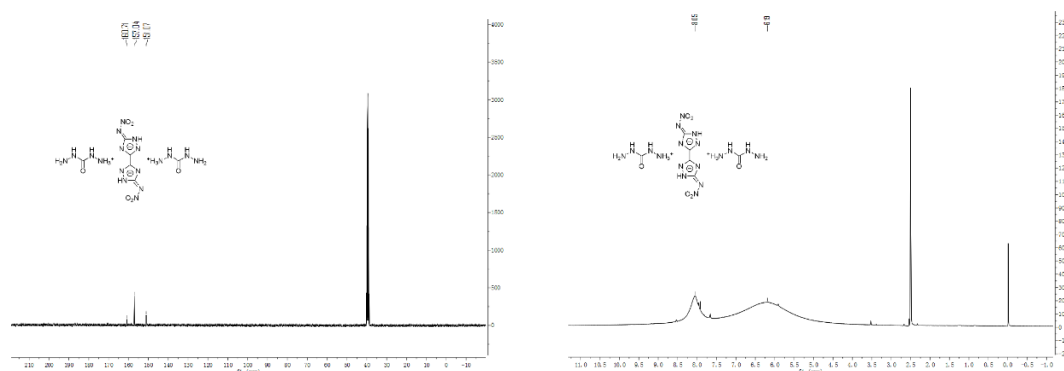


Fig. S1 The ^{13}C NMR spectrum and ^1H NMR spectrum of DCBNT.

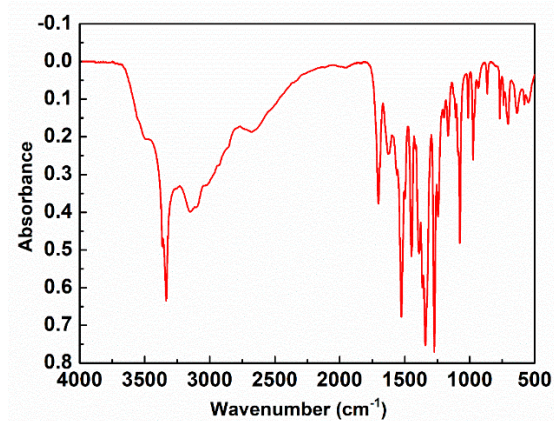


Fig. S2 IR curves for DCBNT.

1.3. X-ray crystallography

Suitable crystals were chosen and placed in a Rigaku supernova Single X-ray Diffractometer area detector using graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at 293(2) K. Its structures were solved by direct methods and successive Fourier difference syntheses using the SHELXTL software suite. Hydrogen atoms attached to oxygen were placed from difference Fourier maps and were refined using riding model. Torsion angle of DCBNT are given in Table S1.

Table S1 Torsion angle /° of DCBNT.

| | |
|-------------|-----------|
| C2 N2 N3 C1 | -0.5(5) |
| C1 N4 N5 O1 | 2.9(7) |
| C1 N4 N5 O2 | -176.9(4) |
| N2 N3 C1 N1 | 0.7(6) |
| N2 N3 C1 N4 | 177.9(5) |
| C2 N1 C1 N3 | -0.5(5) |
| C2 N1 C1 N4 | -178.2(4) |
| N5 N4 C1 N3 | 3.4(8) |
| N5 N4 C1 N1 | -179.5(4) |
| N3 N2 C2 N1 | 0.2(5) |
| N3 N2 C2 C2 | -179.6(5) |
| C1 N1 C2 N2 | 0.2(5) |
| C1 N1 C2 C2 | -180.0(6) |
| N9 N8 C3 O3 | 178.1(6) |
| N9 N8 C3 N6 | -2.4(9) |
| N7 N6 C3 O3 | -6.4(8) |
| N7 N6 C3 N8 | 174.0(6) |

Table S2 Selected bond lengths /Å and angles /° for DCBNT.

| Bond length | | | | Bond angle | | | |
|-------------|----------|--------|-----------|------------|----------|------------|----------|
| O1-N5 | 1.255(5) | N6-C3 | 1.334(6) | C1-N1-C2 | 102.1(4) | N2-C2-C2 | 122.8(5) |
| O2-N5 | 1.261(5) | N6-N7 | 1.409(5) | C2-N2-N3 | 101.7(4) | N1-C2-C2 | 121.6(5) |
| N1-C1 | 1.342(6) | N6-H6 | 0.8600 | C1-N3-N2 | 110.8(4) | C3-N6-N7 | 117.8(4) |
| N1-C2 | 1.360(6) | N7-H7A | 0.8900 | C1-N3-H3 | 124.6 | C3-N6-H6 | 121.1 |
| N2-C2 | 1.307(6) | N8-C3 | 1.315(7) | N5-N4-C1 | 117.2(4) | N6-N7-H7A | 109.5 |
| N2-N3 | 1.366(5) | N8-N9 | 1.411(7) | O1-N5-O2 | 120.6(4) | C3-N8-N9 | 121.0(5) |
| N3-C1 | 1.318(6) | N8-H8 | 0.8600 | O1-N5-N4 | 123.2(4) | C3-N8-H8 | 119.5 |
| N3-H3 | 0.8600 | N9-H9A | 0.894(10) | O2-N5-N4 | 116.4(4) | N8-N9-H9A | 105(4) |
| N4-N5 | 1.316(6) | | | N3-C1-N1 | 109.7(4) | N8-N9-H9B | 94(3) |
| N4-C1 | 1.381(6) | | | N3-C1-N4 | 132.1(4) | H9A-N9-H9B | 128(4) |
| C2-C2 | 1.462(9) | | | N1-C1-N4 | 118.1(4) | O3-C3-N8 | 124.3(5) |
| O3-C3 | 1.234(6) | | | N2-C2-N1 | 115.6(4) | O3-C3-N6 | 119.4(5) |
| | | | | N8-C3-N6 | 116.3(5) | | |

1.4. Non-isothermal kinetics

| | | | | | | | | | | | | |
|----|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 9 | | | | | | | | | | | |
| 10 | 217.1 | 223.4 | 231.96 | 215.2 | 217.0 | 221.7 | 218.6 | 258.3 | 0.992 | 54.80 | 253.7 | 0.992 |
| | 1 | 0 | | 3 | 9 | 4 | 6 | 7 | 2 | 0 | 0 | 7 |
| 15 | 219.3 | 226.1 | 235.05 | | | | | | | | | |
| | 0 | 0 | | | | | | | | | | |
| 20 | 219.8 | 229.6 | 238.24 | | | | | | | | | |
| | 1 | 9 | | | | | | | | | | |

Subscript K: Kissinger's method. Subscript O: Ozawa-Doyle's method.

1.5. Sensitivity test

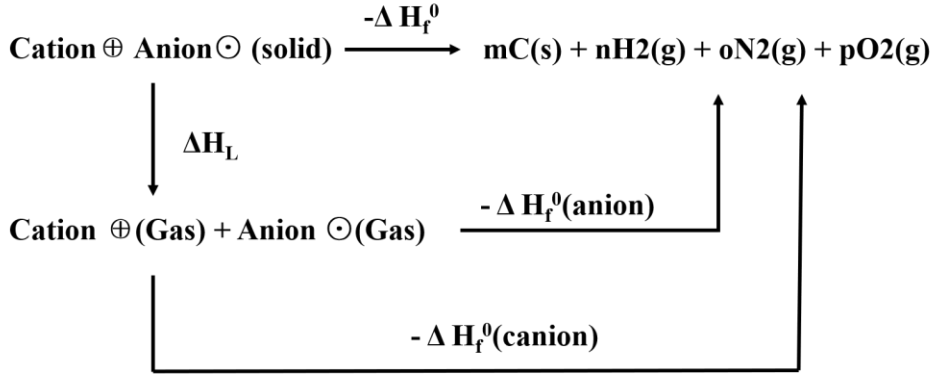
Impact sensitivity was determined by fall hammer apparatus of BAM DFH-10. About twenty milligrams of tested compounds were shifted into an iron cap and was hit by 10 kg drop hammer. The impact sensitivity value of DCBNT was > 40 J.

Friction sensitivity of DCBNT was measured by applying BAM FSKM-10 using about 20 mg sample. No friction sensitivities are observed up to 216 N for DCBNT.

Impact sensitivity was also determined by fall hammer apparatus of GJB5891.22-2006. The characteristic falling height method is based on the quality of the fixed falling hammer. The impact sensitivity of DCBNT was tested by the corresponding drop hammer height (H_{50}) at 50% probability of explosion.

1.6. Molar enthalpy of formation and oxygen balance

Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O . For a compound with the molecular formula of CaHbOcNd , $\text{OB} (\%) = 1600[(c - 2a - b/2)/MW]$. The charge distributions, the molecular orbital analyses, the isomers of DCBNT were calculated using high-level density functional theory calculation (B3LYP/6-311+G (d,p)) with the Gaussian 03 program. All the structures were characterized to be true local energy minima on the potential energy surface without negative eigenvalues in the vibrational frequency analysis. The heat of formation of salts were calculated using the Gaussian 03 (Revision D.01) suite of programs. The geometric optimization of the structures and frequency analyses were carried out using B3-LYP functional with the 6-31+G(d,p) basis set; single-point energy was calculated at the MP2(full)/6-311++G(d,p) level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme S1 Born-Haber cycle for the formation of energetic salts.

Based on a Born-Haber energy cycle (Scheme S1), the molar enthalpy of formation of a salt can be simplified by the formula:

$$\Delta H_f^0(\text{ionic salt, 293K}) = \Delta H_f^0(\text{cation, 293K}) + \Delta H_f^0(\text{anion, 293 K}) - \Delta H_L$$

where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al.⁶ as:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (6)$$

where n_M and n_X depend on the nature of the ions M_p^+ and X_q^- , respectively, and are equal to 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (equation (7)) has the form

$$U_{POT} \text{ (kJ/mol)} = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (7)$$

where M_m is the chemical formula mass of the ionic material, e. g, and the coefficients γ kJ mol⁻¹ cm and δ kJ mol⁻¹ are assigned literature value.^{6,7}

1.7. Solubility test

A certain amount of DCBNT samples were added to a PTFE-coated glass vial with 60 mL solvent which was equipped with a magnetic agitator. The dissolution of DCBNT was monitored using turbidity sensor and temperature sensor during the whole heating process. The mixture was heated at a rate of 0.5 °C min⁻¹ first. With temperature increasing, the DCBNT solid is dissolved gradually. when the turbidity value starts to decrease, the heating rate is slowed down to 0.2 °C min⁻¹. When the turbidity reached its minimum and remained a constant meaning a full dissolution. And the temperature at that moment is the "T". To reduce the deviations, each experiment was carried out for three times and an average value of the three measurements was considered as the measured one. The estimated relative standard uncertainty of the temperature was less than 0.003.

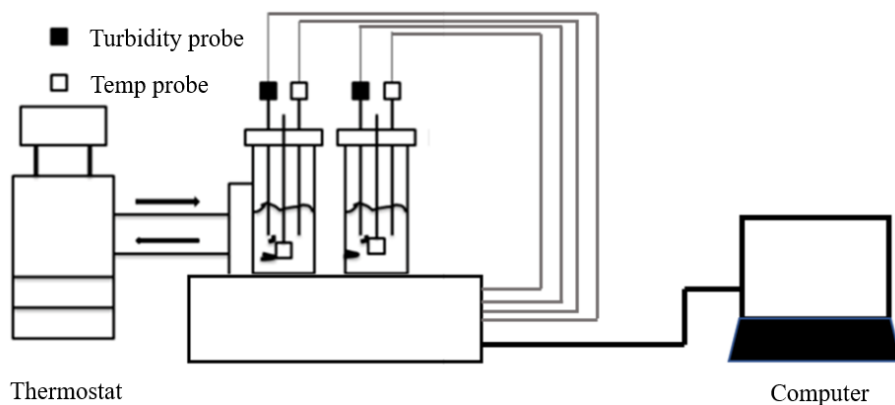


Fig. S4 Solubility test device diagram.

References

1. R. Meyer and J. Kohler (Eds.), *Explosives*, 4th ed. Revised and extended, VCH Publishers, New York. 1993, 149–150.
2. R. Meyer and J. Kohler (Eds.), *Explosives*, 4th ed. Revised and extended, VCH Publishers, New York. 1993, 197–199.
3. H. E. Kissinger, Reaction Kinetics in Differential Thermal Analysis. *Anal Chem* 1969, 2060-2069.
4. T. Ozawa, *Bull Chem Soc Jpn*, 1965, **38**, 1881-1883.
5. C. D. Doyle, Kinetic Analysis of Thermogravimetric Data. *JOURNAL OF APPLIED POLYMER SCIENCE* 1961, 285-292.
6. H. D. B. Jenkins, L. Glasser, *Inorg. Chem.* 2002, **41**, 4378-4388.
7. G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures. 1997.