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ARTICLE

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

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Dicarbohydrazide bis[3-(5-nitroimino-1,2,4-triazole)] (DCBNT) was firstly synthesized by ions exchange and salt formation reaction. A combination of single-crystal X-ray diffraction (SXRD), FTIR, ^1H NMR, ^{13}C NMR, and elemental analysis was utilized to analyze the structural character and composition of DCBNT. DCBNT exhibits high detonation velocity of 9234.87 m s^{-1} and detonation pressure of 31.73 GPa calculated by EXPLO5 v6.02 program. In addition, DCBNT was investigated in the aspect of sensitivities (impact sensitivity >40 J, H_{50} value of 90 cm and friction sensitivity is 216 N) and thermal stability (>230 ℃). Moreover, we measured solubility of DCBNT in 12 common solvents by a polythermal method system which demonstrates its poor solubility in common organic solvents and water. These excellent physicochemical properties make DCBNT an environmental-friendly low-sensitive high-energetic explosives.

Introduction

High energy density materials (HEDMs) have been increasingly used in both military and civilian fields for the past two centuries.[1] Nevertheless, for traditional HEDMs, although great progress has been achieved in terms of their performance and behavior,[2-3] it is still difficult to simultaneously show a good balance between the high energetic performance and low sensitivity.[4] So, there has been an urgent requirement for high energy as well as safety, which represents admirable performance, for example good thermal stability, high density, high detonation characteristics, low sensitivity, and good environmental compatibility.[1-13] Specially, environmental adaptability of explosive became more and more important in the harsh war environment. There are only limited number of low-sensitive high-energetic explosives, such as TATB,[14-16] LLM-105,[17-18] FOX-7,[19-21] NTO,[22] etc. has been synthesized. So, there has been a growing interest in the synthesis of new low-sensitive high-energetic explosives.[23-24]

The energetic salts based on nitrogen-rich heterocycles, especially the triazole or tetrazole ring, exhibits intrinsically lower vapor pressure, higher positive heat of formation, better thermal stability, and higher densities than their atomically similar nonionic compounds, so they have unique advantages in many aspects.[11,25-26] What is more, the main decomposition products of these compounds were dinitrogen, which can avoid environmental pollution as well as health risks.[13,27-28] Therefore, these materials, such as TKX-50,[29] MAD-X1[30] and CBNT carbonic dihydrazidinium bis[3-(5-nitroimino-1,2,4-triazolate)][31-32] etc., had achieved considerable attention in recent years.

CBNT is a typical triazole energetic ion salt,[32-33] which consists of one carbonyl hydrazide cation and one BNT^{2-} anion, both are with two charges. The measured density of CBNT is 1.95 g cm^{-3}, the calculated detonation velocity and detonation pressure are 9316.89 m s^{-1} and 33.40 GPa (calculated by EXPLO5 v6.02 program), respectively, so CBNT was considered as an alternative substitution of RDX.[11] However, the single crystal of CBNT is very difficult to obtain and its crystal structure have not been revealed. Since carbonyl hydrazine contains two hydrazine groups, it can receive one or two protons to form monovalent or two valent cations. So, in order to verify whether BNT and carbonyl hydrazine can be combined in different ratios into new energetic salts, and to obtain more assistant information of CBNT, we conducted experiments. The new compound may have similar characteristics and properties compared with CBNT.

In the text, we synthesized a kind of new material dicarbohydrazide bis[3-(5-nitroimino-1,2,4-triazole)] (DCBNT) based on BNT^{2-} anions and monovalent carbonyl hydrazine cations. The synthesis method, crystal structural characterization, thermal properties, detonation performances and solubility of DCBNT have been studied and compared with

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CBNT, which will provide guidance and reference for later research about CBNT and triazole salts.

Results and discussion

Synthesis

At present, reports on CBNT are focused on the improvement of synthetic methods. According to Shreeve group's reports,[31,32,33] the synthetic method of H_2BNT has been very mature. More special is that the metathesis reactions of Na_2BNT with monocationic halides in hot water resulted in the formation of corresponding energetic salts. In terms of the synthesis method, H_2BNT was synthesized according to the method of H_2BNT in CBNT. In our study, the NaOH solution was added dropwise to the aqueous solution of H_2BNT instead of the suspension. Next to it, a certain amount of positive monovalent carbohydrazide hydrochloride was added to the Na_2BNT solution at 70 ℃, and the product is washed with cold water, no rest during the period. What is different from Shreeve group's is that Na_2BNT solution was held in air for several days, then an excess of the relevant salts was added to the hot aqueous solution of Na_2BNT and the final product was washed with hot water. The yield of DCBNT in our work was 65%, slightly lower than 87% of CBNT.

The results show that BNT and carbohydrazide can be combined in a ratio of 1:1 or 1:2 by adjusting the valence number of the raw materials and there was not any report before.

Structural description

Table 1. Crystal data and structure refinement for DCBNT

Compound	DCBNT
Empirical formula	C6H18N18O6
Formula weight	436.37
Crystal system	monoclinic
Space group	P 21/n
temperature/K	293(2)
Crystal size [mm3]	0.35×0.25×0.02
a/Å	4.8647(3)
b/Å	25.2903(17)
c/Å	6.7166(5)
α(°)	90
β(°)	99.765(7)
γ(°)	90
V(Å3)	814.36(10)
Z	2
ρcalc g cm^{-3}	1.780
θ(°)	3.181-26.372
F(000)	452
Reflections collected	5101
Index ranges	-6≤h≤5, -31≤k≤30, -8≤l≤7
Rint	0.0686
Data / restraints /	1660 / 4
parameters	144
Final R index [I >2σ(I)]	R1=0.0978, wR2=0.1702
Final R index [all data]	R1=0.1613, wR2=0.1881
GOF on F2	1.091

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DCBNT was fully characterized through FTIR, ^1H NMR, ^{13}C NMR (SI Fig. S1) and EA. Furthermore, single-crystal X-ray diffraction method was used to measure its crystal structure. The IR spectrum of DCBNT can be seen in Fig. S2 in SI. In the ^1H NMR ([D_6] DMSO) spectra, the signal for the N–H proton resonance of the triazole cation occurred at δ = 8.05 ppm (s, brs), and the amino and amide groups of the carbohydrazide are found at δ = 6.15 ppm as a very broad peak (for more details, refer to Fig. S1 in SI). In the ^{13}C NMR spectra, the signals in the ^{13}C NMR ([D_6] DMSO) spectrum of salt were found at δ (ppm) = 160.71 [C=O], 157.04 [CH=N], and 151.07 [C-C] and the shifts corresponding to the cation and anion in this study are in good agreement with previously recorded shifts for the relevant cation and anion (Shreeve et al. 2010;[32] Dippold et al. 2012[33]).

Crystalline carbohydrazide bis[3-(5-nitroimino-1,2,4-triazole)] salt based on BNT^{2-} with a molar ratio of 1:1 has been reported by Shreeve's group.[32] However, by controlling the molar ratios and reaction conditions, the ratios between cations and anions of DCBNT obtained herein was 2:1. DCBNT crystallizes in the monoclinic P 2_1/n space group and contains 2 molecules in the unit cell and has a density of 1.780 g cm^{-3}.

As shown in Fig. 1, DCBNT consists of two carbohydrazide cations and one BNT^{2-} anion, which are linked by ionic bonds and hydrogen bonds. The two hydrogen atoms of the trazole rings (N1 and N1A) are lost in the reaction and transferred to the nitrogen atoms (N7 and N7A) of carbohydrazide, which can be presented as $2[(C_1H_7N_4O)^+](C_4N_{10}O_2)^{2-}$. It was constructed by the effect of hydrogen bonds such as N1–H1···O1 and N1–H1···N6 and π-π interaction to form a stable structure.

Partial bond lengths and angles of DCBNT are given in SI Table S1. In the BNT^{2-} anion, the data about bonds show that the N1-C2(1.360 Å) and N4-C1(1.380 Å) bond lengths in the azole ring are closer to the standard bond length of the C=N double bond(1.35 Å) than to that of the C-N single bond (1.47 Å), whereas the N1-C1(1.342 Å), N2-C2(1.307 Å) and N3-C1(1.318 Å) bond lengths are considerably longer than the C≡N triple bond (1.16 Å) but slightly shorter than the C=N double bond. The N2-N3 and N4-N5 bond lengths are 1.366 and 1.316 respectively, which are between N-N single bond (1.45 Å) and N=N double bond (1.25 Å). The bond lengths of remaining bonds are also all within the range of formal C-C, N-O single and double bonds (C-C: 1.54 Å, C=C: 1.34 Å; N-O: 1.46 Å, N=O: 1.14 Å). These results support the presence of some multiple-bond character, demonstrating that the trazole rings and $N-NO_2$ exist as delocalized π system.

Besides, the data of crystal (SI Table S2) show that the molecule is symmetric along C2-C2#, because the bond lengths and angles on both sides are the consistent. Moreover, the torsion angle of ammonium nitrates base in the plane of the triazole rings as shown by N5-N4-C1-N3 is 3.4(6) °, which means that the ammonium nitrate base and the triazole ring are incompatible. The torsion of N3-N2-C2-C2 and C1-N1-C2-C2 are -179.5(4) °, -180.0(6) ° respectively, indicted that two triazole rings in DCBNT anion exhibit coplanar arrangement. What's more, in addition to the surface of N9-N8-C3-O3 (178.1

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(6) °), incoplanar features can also be observed in carbonylhydrazine cations from the data of angle for DCBNT.

Hydrogen bond is an important influence factor on the molecular packing and crystal structure, thus it can help to increase the thermal stability and density, meanwhile decrease the sensitivity of the ionic salts.[25, 34-35] As shown in Fig. 2, there are a lot of intramolecular hydrogen bonds on carbonyl hydrazine cation, for example, comparatively stronger hydrogen bonds N7-H7C···N4(D···A: 2.806 Å; D–H···A: 172.06 °), N7-H7A···O1(D···A: 2.925 Å; D–H···A: 157.90 °), connected to the carbonyl hydrazine cation with triazole ring and ammonium nitrate on triazole ring. Meanwhile, the hydrogen bonds between the anion-anion and the cation-cation belong to N3-H···N2 and N9-H9A···O3, respectively, each molecule is both the proton donor and the proton acceptor of the hydrogen bonds. Hydrogen bond information is displayed in Table 2. Besides hydrogen bonds interactions, there are π-π stacking interaction (black dash) between closest BNT^{2-}s. In addition, BNT^{2-}s are connected by $carbohydrazide^{+}$ in the b-axis to form wavy-like chains that are parallel to each other (Fig. 3). It is obviously that strong intermolecular hydrogen bond interactions may be responsible for the good thermal stability of DCBNT. At the same time, the wave-live structure enables DCBNT to have low impact sensitivity.[36,37-39] The huge three-dimensional network structure of DCBNT is as shown in Fig. 2.

Table 2. Hydrogen bonds present in DCBNT.

D-H…A	d(D-H)/Å	d(H…A)/Å	d(D…A)/Å	<(DHA)/°
N3-H3…N2	0.860	2.396	2.966(54)	124.157(283)
N6-H6…O3	0.860	2.009	2.690(58)	135.326(319)
N7-H7A…O1	0.890	2.081	2.923(60)	157.897(276)
N7-H7A…O2	0.890	2.489	3.170(58)	133.719(271)
N7-H7B…N1	0.890	2.412	3.089(58)	133.076(268)
N7-H7C…N4	0.890	1.922	2.806(53)	172.062(281)
N8-H8…O2	0.860	2.240	2.970(59)	142.700(325)
N9-H9A…O3	0.895	2.416	3.256(85)	156.501(1848)

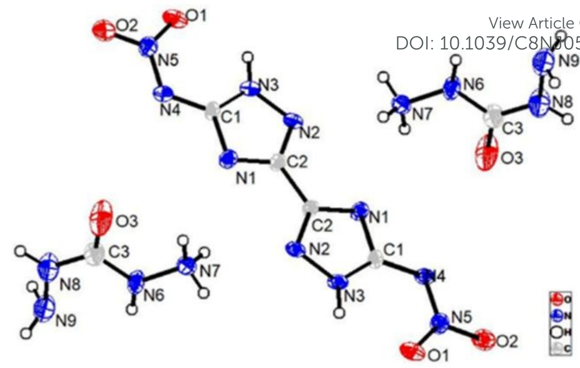

Fig. 1 Representation of the solid-state molecular structure of DCBNT, molecular structure thermal ellipsoids are shown at the 50% probability level.

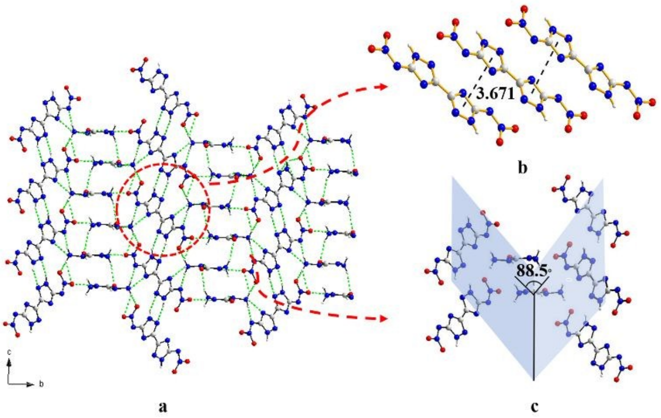

Fig. 2 (a)Intermolecular hydrogen bonds in DCBNT represented by green dashes, (b)π-π interaction of DCBNT represented by black dashes, (c) Plane angle.

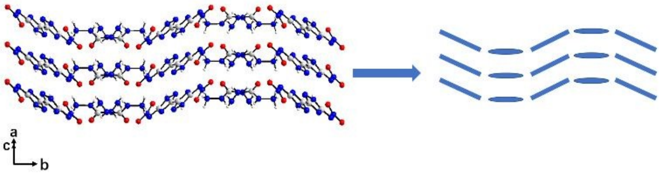

Fig. 3 Wave-like staking of DCBNT.

Thermal decomposition

The thermal stability is significant feature for energetic materials, because it is directly related to the thermal safety and further applications. Therefore, the thermal stability of DCBNT was investigated by TG-DSC at a heating rate of 10 °C min^{-1} in flowing high purity nitrogen, the test temperature range is 0–400 °C. The TG-DSC curves for DCBNT are shown in Fig. 4.

Fig. 4 shows that there are three obvious mass-loss stages (stages I–III) in TG curve, corresponding to the three peaks in DSC curves. For TG curve stage I begins from about 205.33 ℃ and stops at about 235.35 ℃, accompanying 19.59% mass-loss, with the summit peaks in DSC curves at about 232 ℃, corresponding to the main exothermic peak. Then two subordinate exothermic peaks followed, correspond to the stage II and Ⅲ. Stage II begins followed by stage I and stops at about 266 ℃, accompanied by about 22% mass-loss, after that is stage III with about 10% mass-loss, which attributes to the continue decomposition of carbonylhydrazine in DCBNT. Moreover, DCBNT has higher main decomposition peak 232 ℃ than CBNT (222 ℃),[32] means that the thermal stability of DCBNT is better than that of CBNT.

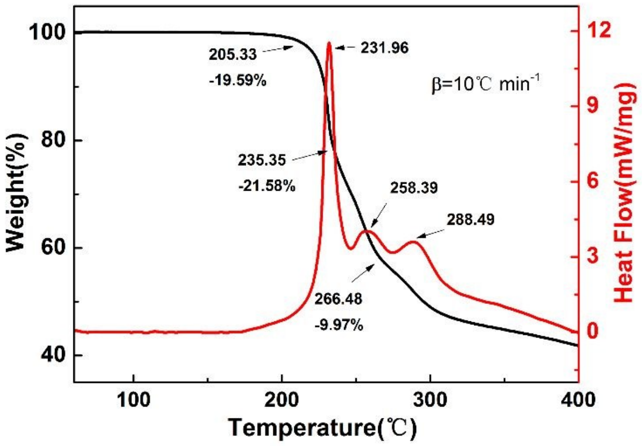

Fig. 4 TG-DSC curve for DCBNT.

Non-isothermal kinetics

In this work, Kissinger's method (Kissinger[40]) and Ozawa Doyle's method (Doyle 1961[41]; Ozawa 1965[42]) were applied to determine the kinetic parameters of the exothermic decomposition process of DCBNT. The apparent activation energy (E) and the pre-exponential factor (A) was universally applied in this field, depending on the peak temperatures measured at four different heating rates of 5, 10, 15, and 20 ℃ min^{-1} (Fig. 5 and SI).

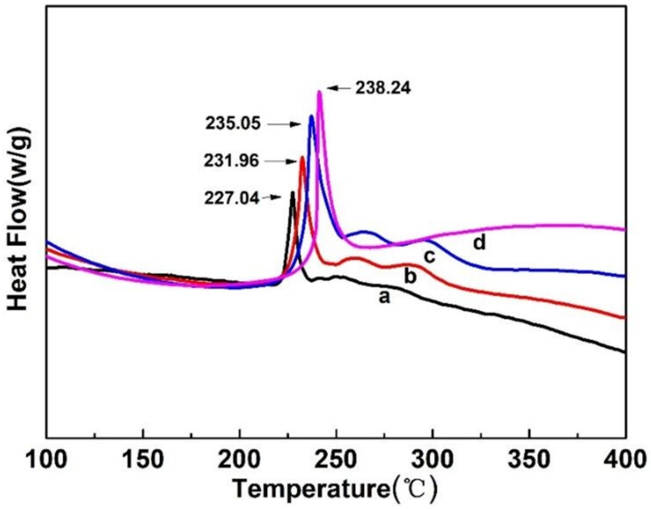

Fig. 5 DSC curves for DCBNT. Heating rate (℃ min^{-1}): (a) 5, (b) 10, (c) 15, (d) 20.

The calculated results using both methods include linear correlation coefficient r_K and r_O are shown Table 3. It can be found that the exothermic peak Tp shifts to higher temperatures as the heating rate increases and the good linear correlation coefficients are 0.9922(r_K) and 0.9927(r_O) respectively, which are very close to 1. It is demonstrating that the results are credible. The activation energy E obtained by Kissinger's method and Ozawa-Doyle's are 258.37 and 253.70 kJ mol^{-1}, which agree well with each other. Accordingly, the Arrhenius equations for DCBNT can be expressed by Ea (average of Ek and Eo) and lnA, as shown in equation (1):

$$\ln k = 54.800 - 256.035 \times \frac{10^3}{RT} \qquad (1)$$

The equations can be used to estimate the rate constants for the thermal decomposition processes of compound DCBNT and predict its thermal decomposition mechanisms.

Table 3. The calculated kinetic parameters for the first exothermic decomposition processes of DCBNT

β(℃ min^{-1})	T_P (℃ min^{-1})	Kissinger			Ozawa	
		E_K	lnA	r_K	E_O	r_O
5	227.04	258.37	54.80	0.992	253.70	0.993
10	231.96					
15	235.05					
20	238.24					

In order to fully evaluate the thermal stabilities of the energetic salts, the self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (Tb), are necessary for energetic compounds. The values ($T_0$0, Te0 and Tp0) of the initial temperature point corresponding to β →0 are also obtained by equation (2). The values of T_{SADT} and T_b for compounds DCBNT are obtained by equations (3) and (4). The values of the propellants are listed in SI Table S3.

$$T_{(O,e\ or\ P)} = T_{(00,e0\ or\ P0)i} + n\beta_i + m\beta_i^2 \quad i = 1\ to\ 4 \qquad (1)$$

$$T_{SADT} = T_{e0} \qquad (2)$$

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0}}}{2R} \qquad (3)$$

The T_{SADT} and T_b values of DCBNT are 217.9 ℃ and 218.7 ℃ respectively, higher than that of commonly used explosives like FOX-7(206.0 and 207.1 ℃).[21] and CBNT (207.4 ℃ and 214.2 ℃),[31] which indicates DCBNT has the higher resistance to heat and better thermal safety than CBNT and TOX-7 under the same condition. Moreover, the values of T_{SADT} and T_b over 210 ℃ mean that DCBNT has good thermal stability.

Safety and detonation properties

Detonation velocity (υ_D) and detonation pressure (P) were important parameters of energetic properties. The detonation velocity (υ_D) and the detonation pressure (P) of DCBNT were

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evaluated using EXPLO5 (v6.02) based on the measured ambient temperature density (1.780 g cm^{-3}) and the calculated heat of formation(Δ_fH). The Δ_fH of DCBNT was calculated by the isodesmic reaction approach using Gaussian 03 (Revision D.01) suite program and was estimated to be 528.1 kJ mol^{-1} (see SI), which was first reported. As shown in Table 4, the calculated detonation velocity and detonation pressure of DCBNT are 9235 m s^{-1} and 31.7 GPa, respectively. The detonation velocity is quite similar to that of HMX (9221 m s^{-1}) and much superior to those of TATB (8114 m s^{-1}), RDX (8878 m s^{-1}) and LLM-105 (8560 m s^{-1}). Due to the relatively low OB (51.38%), the detonation pressure of DCBNT (31.7 GPa) is lower than those listed in the Table 4 but is comparable to TATB (32.4 GPa). This exhibits DCBNT has superior detonation performance.

Sensitivity should be necessarily investigated because it is closely linked with the safe handling and applying of explosives. Results are shown in Table 4 and showed that the impact sensitivity of DCBNT is very low (IS>40 J and H_{50} =90 cm), which are comparable to CBNT, LLM-105 and FOX-7, meanwhile much lower than typical nitroamine explosives like HMX and RDX (32 cm and 26 cm) and TKX-50 (41 cm). The friction sensitivity of DCBNT is slightly higher than that of CBNT, but far lower than RDX and HMX, these attributes to the wave-like chain crystal structure with π-π stacking interaction.[39, 43-44] Additionally, DCBNT has higher decomposition temperature (232 ℃) than CBNT (222 ℃), RDX (210 ℃), TKX-50 (221 ℃) and FOX-7 (220 ℃), which means that it has better thermal stability. So, DCBNT can serve as a promising candidates for RDX.[11]

Table 4. Physicochemical and energetic properties of DCBNT and comparison with TATB, RDX, HMX, CBNT, LLM-105 and FOX-7,[45] TKX-50.[46]

compound	ρ[a]	T_d[b]	Δ_fH	P[d]	D[e]	H_{50}[f]	FS[g]	IS[h]	OB[i]
TATB	1.94	360	-139.5	32.4	8114	320	>360	>60	-55.81
RDX	1.80	210	86.3	34.9	8878	26	120	7.5	-21.61
HMX	1.90	279	116.1	39.2	9221	32	120	7.5	-21.62
CBNT	1.95	222	47[c]	33.4	9317	89	195	38	-46.24
DCBNT	1.78	232	528.1[c]	31.7	9235	90	216	>40	-51.38
TKX-50	1.918	221	446.6[c]	42.4	9698	41	-	20	-27.12
LLM-105	1.91	342	-12.0	33.4	8560	117	>360	28.7	-37.04
FOX-7	1.88	220	-188.9	35.9	9000	126	>360	24.7	-21.62

[a] Density measured by gas pycnometer (25 °C). [b] Decomposition temperature(onset). [c] Calculated molar enthalpy of formation. [d] Detonation pressure (calculated with EXPLO5 v6.02). [e] Detonation velocity (calculated with EXPLO5 v6.02). [f] Impact sensitivity.[47] [g] Friction sensitivity evaluated by a BAM friction tester. [h] Impact sensitivity evaluated by a standard BAM fall-hammer. [i] Oxygen balance (based on CO_2) for CaHbOcNd; 1600(c-2a-b/2)/MW (MW=molecular weight).

Solubility

Knowledge the solubility of explosive in different solvents is necessary for the purifying and application， as well as preparing high-quality crystals of explosive. This study measured the solubility of DCBNT in 12 common solvents: water (H_2O), dimethyl sulfoxide (DMSO), N, N-diethylformamide (DEF), N, N-dimethylformamide (DMF), 1,4-butyrolactone (BL), methanol (MeOH), ethanol (EtOH), acetone, chloroform (TCM), dioxane, acetonitrile, ethyl acetate (EA). The solubility results are listed in Table 5 and solubility test device diagram is shown in SI.

Table 5. Solubility of DCBNT in various solvents at 25 ℃

Sovent	DMSO	Water	EtOH	BL	DEF	Chloroform
Solubility (mg/100mL solvent)	670	75	35	24	17	<15
Solvent	Dioxane	EA	Acetonitrile	MeOH	Acetone	DMF
Solubility (mg/100mL solvent)	<15	<15	<15	<15	<15	-

Table 5 shows that DCBNT exhibits a relatively poor solubility in these solvents. Though the solubility value of DCBNT in DMSO is highest, the solubility is only 670 mg per 100ml DMSO at 25 ℃. By construct, DCBNT exhibited a much lower solubility of below 15 mg per 100 ml in most organic solvents including chloroform, dioxane, ethyl acetate, acetonitrile, methanol and acetone. Even in water, DCBNT was only slightly soluble at 25 ℃ (about 1/90 of the solubility in DMSO).

Conclusions

In this study, DCBNT was synthesized and fully characterized by single-crystal X-ray diffraction (SXRD), FTIR, ^{1}H NMR and ^{13}C NMR, and elemental analysis were also introduced to analyse its structural characterization and composition. Thermal properties for the title salt was determined by TG-DSC analysis as well as the calculation of non-isothermal kinetic parameters. In addition, detonation parameters (e.g. detonation velocity and pressure) of the target compound were computed using EXPLO5 v6.02 based on the calculated heat of formation and density. The results show that DCBNT exhibits a density of 1.780 g cm^{-3} and calculated detonation velocity and detonation pressure with 9234.87 m s^{-1} and 31.71 GPa, respectively. DCBNT exhibited good thermal stabilities as the decomposition peak temperatures were over 230 °C. The activation energy was 258.37 kJ mol^{-1} and 253.70 kJ mol^{-1} calculated by Kissinger's method and Ozawa–Doyle's method, respectively. Impact and friction sensitivities were also tested, and the results indicated that these salts both have low sensitivities (impact sensitivity >40 J and friction sensitivity is 216 N). The high thermal stability, low sensitivity toward impact and friction with the good detonation properties make DCBNT a potential king of low-sensitive high-energic explosive.

Experimental

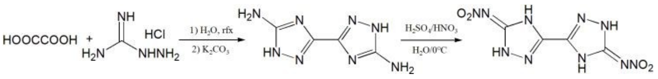
CAUTION! All the compounds in every scheme should be handled with extreme care, although no incidents occurred during preparation and manipulation. Additional proper protective precautions like face shield, leather coat, earthed equipment and shoes, Kevlar gloves should be used when working with these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

Materials and Instrument

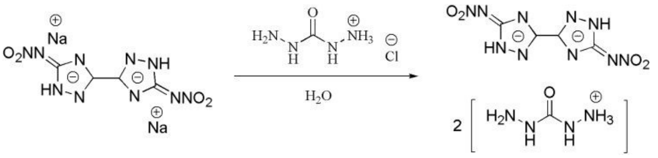
All reagents were purchased commercially and used without further purification. Distilled water was prepared in our laboratory and used throughout. ^1H and ^{13}C spectra were recorded on a 400 MHz (Bruker AVANCE 400) or 600 MHz (Bruker AVANCE 600) nuclear magnetic resonance spectrometer. Infrared (IR) spectra were measured on SHIMADZU IRTracer-100 FT-IR spectrometer in the range of 4000-400 cm^{-1} as KBr pellets at 25 ℃. Transmittance values are qualitatively described as strong (s), medium (m) and weak (w). Elemental analyses (C, H, N) were carried out on an elemental analyzer (Vario EL Cube, Germany). TG and DSC analysis were conducted on differential scanning calorimeter-thermal gravity instrument (TGA/DSC2, METTLER TOLEDO STAR^e system) at the heating rate of 10 ℃ min^{-1}. Single crystal X-ray diffraction data were tested in a Rigaku supernova Single X-ray Diffractometer area detector (Mo Kα, 0.71073 Å). The solubility of DCBNT was collected by the CrystalSCAN system (E1320, United Kingdom He., Ltd.). The mass of the solid was weighted using an analytical balance (CP225D, Sartorius, Germany) with the accuracy of 10^{-4} g. The temperature of the mixture was controlled by circulating oil solution from a thermostat (Huber CC1-505wl vpc55, Germany) with an uncertainty of u(T) = 0.01 °C.

Synthetic procedures

The synthetic routes to the target compounds are outlined in Scheme 1 and Scheme 2.



Scheme 1 Synthesis of compound BNT.



Scheme 2 Synthesis of compound DCBNT.

Bis[3-(5-amino-1,2,4-triazole)] (**BNT**): BNT was prepared according to the literature procedure.[27,33, 36]

Preparation of carbonyl hydrazine hydrochloride: 3.69 g (41 mmol) carbohydrazide was added to 10 ml water, then added 25% 10ml hydrochloric acid (8.3 g, 224 mmol concentrated hydrochloric acid, about 6.4 ml, diluted with water to 10 ml) when the temperature raised to 70 °C. Dring via rotary evaporation method to remove water, then 5.13 g white solid was obtained (melting point is 219.7 ℃).

Preparation of Dicarbohydrazide bis[3-(5-nitroimino-1,2,4-triazole)]: 5.8 g (22.7 mmol) BNT was dissolved in 30 ml water, then added 2M 30 ml NaOH 60 mmol dropwise, the mixture was stirred to dissolve completely. 5.2 g (41 mmol, 1: 1, mol) prepared carbohydrazide hydrochloride were added to the reaction solution when the temperature was raised to 70 °C, then a large amount of white solid appeared. The resulting solution was refluxed 1.5 h, and filtered while cool to give corresponding salt, which was washed several times with cold water and dried in vacuo at 60 ℃. Yield: 65%.^1H NMR(600 MHz, DMSO- d $_6$, 25 ℃) δ=6.19, 8.05 ppm; ^{13}C NMR(150 MHz, DMSO- d $_6$, 25℃) δ=151.07, 157.04, 160.71 ppm. IR (KBr): υ (cm^{-1}) =3501(w), 3365(s), 3335(s), 3153(w), 3098(w), 3024(w), 2926(w), 2854(w), 2668(w), 1953(w), 1702(s), 1630(m), 1566(w), 1524(s), 1493(w), 1448(s), 1387(m), 1363(w), 1339(s), 1274(s), 1246(m), 1200(w), 1166(m), 1113(s), 1080(s), 1013(m), 972(s), 933(w), 869(m), 766(m), 739(w), 709(m), 639(m), 583(w), 546(w), 472(w), 443(m), 416(w). Anal. Calcd. for $C_6H_{18}N_{18}O_6$: C,16.44; H, 4.11; N, 57.53; Found: C, 16.35; H, 4.08, N, 57.61.

X-ray crystallography

Suitable crystals were chosen and placed in a Rigaku supernova Single X-ray Diffractometer area detector using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) 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. Data collection parameters and refinement statistics were given in Table 1.

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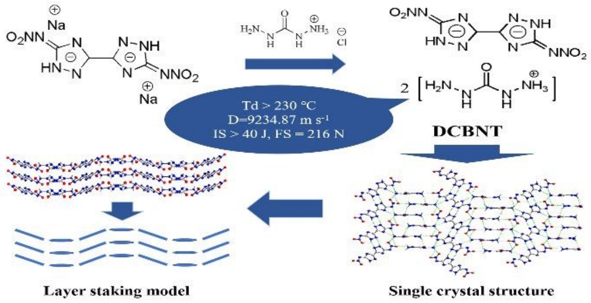

DCBNT, a new compound, exhibits low friction and impact sensitivities, good thermal stability, promising detonation pressure and detonation velocity.