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Synthesis and thermal behavior of a fused, tricyclic pyridine-based energetic material: 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-*e*]tetra-zolo[1,5-*a*]pyridine-3-oxide

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A fused, tricyclic pyridine-based energetic material: 4-amino-5nitro-[1,2,5]oxadiazolo[3,4-*e*]tetrazolo[1,5-*a*]pyridine-3-oxide

(ANTP) was first synthesized through a two-step reaction from commercially available reagents with a total yield of 75%, namely the azidonation of 4-amino-2,6-dichloro-3,5-dinitropyridine with nitrogen elimination and ring closure, followed by another azidonation and azido-tetrazolo tautomerism. Its structure was determined by single X-ray diffraction. The crystal of ANTP is orthorhombic, space group $P2_12_12_1$ with crystal parameters of a=8.9130(18) Å, b=14.057(3) Å, c=6.5730(13)Å, V=823.5(3) Å³, Z=4, F(000)=480. It exhibits a surprisingly high density (1.92 g/cm³ at 293 K), low thermal stability, a positive heat of formation and good detonation properties.

The synthesis of compounds based on the pyridine ring as energetic materials has been the focus of our group for the past few years. The difficulty of synthesizing nitroheteroaromatic systems may be attributed to their electron deficiency, making electrophilic aromatic substitution problematic.¹ By the addition of electron donating substituents to the pyridine ring, especially the amino group, nitration may proceed easily. Besides, by the use of an alternating array of amino and nitro-groups attaching to the pyridine ring, density and thermal stability may increase.²

Poor detonation performance of pyridine-based energetic materials is a concern that also needs to be considered.² One of the current synthetic strategies has focused on incorporating nitrogen-rich heterocycles into the pyridine ring. The tetrazole ring form a unique class of energetic materials, which have a large number of N-N and C-N bonds, deriving most of their energy from their very high positive heats of formation rather than from oxidation of the carbon backbone, as with traditional energetic materials.³ The high nitrogen

content typically leads to high densities, and the low amount of hydrogen and carbon, and also allows for a good oxygen balance to be achieved more easily. Moreover, substituting a furoxan ring for a nitro, the density and detonation velocity can increase about 0.06-0.08g/cm³ and 300m/s, respectively.⁴

Few studies have been conducted on the combination of energetic groups to form a fused, tricyclic or tetracyclic ring system. Typical examples including benzotrifuroxan (1a), 2,3,5,6-tetranitro-4H,9H-dipyrazolo[1,5-a:5',1'-d][1,3,5]triazine (1b),^e and 2,9-dinitrobis([1,2,4]triazolo)[1,5-d:5',1'f[[1,2,3,4]tetrazine (1c)⁷ are shown in Fig. 1. In our continuous effort to seek energetic compounds by incorporating different energetic fragments into a single heterocyclic pyridine ring, we present the facile synthesis of a fused, tricyclic pyridine-based energetic material i.e., 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4e]tetrazolo[1,5-a]pyridine-3-oxide (name as ANTP). The prepared compound is characterized by X-ray diffraction (XRD), multinuclear nuclear magnetic resonance (NMR) spectroscopy, thermogravimetry and differential scanning calorimetry (TG-DSC). In addition, quantum chemical calculations are used to predict the energetic properties of ANTP.



Fig. 1 Representative examples of fused and tricyclic or tetracyclic energetic materials

In 1990, Wilson reported the preparation of a series of disubtituted pyridines including nitro/tetrazole, nitro/furoxano, or tetrazole/furoxano (Fig. 2, a-g).⁸ In 2005, a kind of trisubstituted pyridine derivative, i.e., 7-nitrotetrazole[1,5-*a*]furazano[4,5-*b*]pyridine-1-oxide (Fig. 2, NFP) was obtained.⁹

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As

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shown

in



Scheme

1,

4-amino-5-nitro-

[1,2,5]oxadiazolo[3,4-e]tetrazolo[1,5-a]pyridine-3-oxide (ANTP) was readily prepared through a two-step reaction from commercially available reagents, containing amino/nitro/tetrazole/furoxano moieties. In the first step, an intermediate 4-amino-2,6-dichloro-3,5-dinitropyridine (ADNP) was easily obtained through a dinitration reaction by treating 4-animo-2,6-dichloropyridine with concentrated sulfuric acid and potassium nitrate for 30 min at 50 2 and then pouring the mixture into ice water, achieving a high yield of 70 wt%. Thereafter, a one-pot of diazido reaction followed from ADNP and excess sodium azide in acetone to give the target product ANTP as a grass green solid (yield: 90 wt%). This facile synthesis approach has proven to be successful, yielding a novel high-density energetic material with adequate purity, easy operation, mild reaction conditions, and allows further scale-up to the production scale.



Scheme 1. Synthetic route of ANTP.

Azido-substituted pyridines are known to undergo azidotetrazolo tautomerism that is attributed to the stabilization of the tetrazole form due to the electron-deficient nature of the pyridine ring.¹⁰ MS analysis indicated that only **4** existed in the mono-chrolo and furoxan form, followed by another azidonation and tetrazole tautomerism, proving that 4-amino-2,6-dichloro-3,5-dinitropyridine didn't undergo the di-azido form (Scheme 3), but a mono-azido reaction with dinitrogen elimination and ring closure process(Scheme 2). And the transformation from compound **2** to **4** or compound **4** to ANTP occurred too fast for compounds **3** or **5** to be observed on MS analysis.



Scheme 2. Hypothetical synthetic route of ANTP.

ANTP has low or no solubility in most organic solvents, such as methanol, acetonitrile, chloroform. However, it can be easily dissolved in *N*,*N*-dimethylformamide, and afford a grass green strip shaped crystal suitable for X-ray diffraction. The structure is shown in Fig. 3 and crystallographic data are summarized in Table 1. ANTP crystallized in the orthorhombic

crystal system and belongs to $P2_12_12_1$ space group with four molecules per unit cell. Delocalization of the charge density is evident, for the bond lengths of C1-N4 (1.320 Å), C4-N7 (1.321 Å), C5-N8 (1.307 Å) lie between average single and double C-N bonds (1.47 Å and 1.22 Å, respectively),¹¹ forming a big π -conjugated structure of the molecule.



Fig. 3 Crystal structure of ANTP. **a** Single-crystal X-ray structure of ANTP with labeling (thermal ellipsoid plot: 30%). Dashed lines indicate hydrogen bonding. **b** Crystal packing of ANTP viewing down the unit cell axis c.

Table 1 Crystal data and structure refinement of ANT						
Formula	$C_5H_2N_8O_4$					
FW	238.15					
Crystal size/mm	0.20					
Crystal system	Orthorhombic					
Space group	P2 ₁ 2 ₁ 2 ₁					
a/ Å	8.9130(18)					
<i>b/</i> Å	14.057(3)					
c/ Å	6.5730(13)					
<i>V/</i> Å ³	823.5(3)					
Ζ	4					
<i>D_c</i> /(g⋅cm ⁻³)	1.921					
μ/mm^{-1}	0.168					
<i>т/</i> к	293(2)					
λ(ΜοΚα) / Å	0.71073					
Reflections collected	1739					
Unique reflections	1509					
Rint	0.0249					
Parameters	154					
$S \text{ on } F^2$	1.068					
$R_1 \left(l > 2\sigma(l) \right)$	0.0456					
$\omega R_2 \left(l > 2\sigma(l) \right)$	0.1156					
R ₁ (all data)	0.0570					
ωR_2 (all data)	0.1277					
CCDC	1566496					

ANTP displays a surprisingly high crystal density of 1.921 g/cm³ at 293 K mainly due to its planar molecular structure. The six-membered pyridine ring is nearly planar, building a basic aromatic system, which can be seen by the torsion angles C1-C2-C3-C4 and C1-N1-C5-C4 of -1.940(426)° and 1.919(436)°, respectively. The tetrazole ring and the furoxan ring are also nearly planar, of which the torsion angles N1-N2-N3-N4 and C5-N8-O4-N7 are -0.345(350)° and -0.187(314)°, respectively. The angle of plane between the pyridine ring and the tetrazole ring is 2.287(97)°, while angle of plane between the pyridine ring, the

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furoxan ring, and the tetrazole ring formed a tight fused-ring system. Intramolecular molecular hydrogen bonds can be found between the hydrogen atom of the amino group and the oxygen atom of the nitro group and the furoxan group. As shown in Fig. 2, the H6A...O2 and H6B...O3 distance amounts to 2.038 Å and 2.324 Å, respectively.

The TG-DSC analysis was carried out at a heating rate of 10 \square /min from 50 \square to 500 \square under N₂ atmosphere. The TG-DSC curves showed in Fig.4 reveal that there are two intense exothermic signal with a DSC peak exotherm of 149.58 \square and 200.35 \square , which corresponds to the thermal decomposition of ANTP. The TG curve showed that ANTP starts to decompose at approximately 134 \square in the first stage, and again decompose at almost 190 \square in the second stage with a total mass loss of 98%. These results demonstrate that ANTP exhibits a lower decomposition temperature comparable to that of NFP¹⁰ and RDX (160 \square and 210 \square , respectively).



Fig. 4 TG-DSC curves of ANTP

Comparison of ANTP analogous was determined by differential scanning calorimetric (DSC) measurements. As shown in Fig. 5 and 6, conclusions may be drawn that pyridotetrazolo may decompose at about 150-160 , and pyridofuroxan at more or less 200 .



Fig. 5 Comparison of ANTP analogous determined by DSC measurements



Fig. 6 Several pyridofuroxan analogous

Calculations were carried out using the Gaussian 09 suite of programs.¹² The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with the 6-31G^{**} basis set.¹³ All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

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(1)

The heat of formation $\Delta H_{f,298}$ at 298 K of ANTP was computed by from the following equation (1) using isodesmic reactions (Scheme 3).

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

Where $\Delta H_{f,R}$ and $\Delta H_{f,P}$ are the HOFs of reactants and products at 298 K, respectively.

Scheme 3 Isodesmic reaction of ANTP.

ANTP exhibits a very positive heat of formation, and estimated to be 908 kJ/mol (see Supporting Information), mainly due to its high nitrogen content (47%). The crystal density value of ANTP is much higher than those of polynitro energetic materials (TNT, RDX and TATB). The detonation pressure (P) and velocity (D) were calculated based on traditional Chapman-Jouget thermodynamic detonation theory. As shown in Table 2, the calculated detonation velocity and pressure of ANTP are 8838 m/s and 36.01 GPa, respectively, which are superior to that of TNT (P=19.53 GPa, D=6881 m/s) and TATB (P=31.15 GPa, D=8114 m/s), but exceeds to that of RDX (P=33.92 GPa, D=8600 m/s). In addition to the detonation properties, the impact and friction sensitivities of ANTP were determined using a standard BAM fall hammer and a BAM friction tester, respectively.¹⁸ As can be seen in Table 2, ANTP with an impact sensitivity of 3 J and a friction sensitivity of 100 N, is more sensitive than RDX and HMX (7.4 J, 120 N).

Table 2 Comparison of physical properties of ANTP and some important energetic materials

		ANTP	TNT ^a	RDX ^a	TATB	HMX ^a		
	Formula	$C_5H_2N_8O_4$	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_6H_6N_6O_6$	$C_4H_8N_8O$		
						8		
	$T_{\rm m}/{}^{\circ}{\rm C}^{b}$	-	81	205	-	275		
	$T_{dec}/^{\circ}C^{c}$	134	-	-	318	-		
	N(%) ^d	47.06	18.50	37.84	32.55	37.84		
	OB/%	-47.1	-74.0	-21.6	-55.8	-21.6		
	$\rho/(g \cdot cm^{-3})^{e}$	1.921	1.654	1.806	1.937	1.910		
	$\Delta H_{\rm f}/(\rm kJ\cdot mol^{-1})^{f}$	908	-67	63	-140	75		
	P/GPa ^g	36.01	19.53	33.92	31.15	39.63		
	<i>D/</i> (m·s ⁻¹) ^{<i>h</i>}	8838	6881	8600	8114	9320		
	IS ⁱ /J	3	39	7.4	50	7.4		
	FS ⁱ /N	100	353	120	360	120		
	^a Ref 14-17. ^b Me	Ref 14-17. ^b Melting point. ^c Decomposition point. ^d Nitrogen content. ^e Density.						
^f Heat of formation. ^g Detonation pressure. ^h Detonation velocity. ¹ Impact						act		
	sensitivity. ⁷ Friction sensitivity.							



In conclusion, we have synthesized a fused, tricyclic energetic pyridine-based material: 4-amino-5-nitro-[1,2,5]oxadiazolo[3,4-e]tetra-zolo[1,5-a]pyridine-3-oxide

- Notes and references
 d ring
 P. F. Pagoria, G. S. Lee, A. R. Mitchell and R. D. Schmidt, trazolo
 Thermochimica Acta, 2002, 384, 187.
 - C. Ma, Z. Liu, X. Xu, and Q. Yao, Chinese Journal of Organic Chemistry, 2014, 34, 1288.
 H. Gao and L. M. Shreeve, *Chemical Reviews* 2011 111 7377.
 - H. Gao and J. M. Shreeve, *Chemical Reviews*, 2011, **111**, 7377.
 - 4 Y. Zhang, C. Zhou, B. Wang, Y. Zhou, K. Xu, S. Jia and F. Zhao, Propellants, Explosives, Pyrotechnics, 2014, **39**, 809.
 - 5 Bailey A S, and Case J R, *Tetrahedron*, 1958, **3**, 113.
 - 6 P. Yin, J. Zhang, G. H. Imler, D. A. Parrish and J. M. Shreeve, Angewandte Chemie International Edition, 2017, 56, 8834.
 - 7 D. E. Chavez, J. C. Bottaro, M. Petrie and D. A. Parrish, Angewandte Chemie, 2015, **127**, 13165.
 - 8 C. K. Lowe-Ma, R. A. Nissan and W. S. Wilson, *The Journal of Organic Chemistry*, 1990, **55**, 3755.
 - 10 M. H. V. Huynh, M. A. Hiskey, D. E. Chavez and R. D. Gilardi, Journal of Energetic Materials, 2005, 23, 99.
 - 11 J. Zhang, S. Dharavath, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Journal of the American Chemical Society*, 2016, **138**, 7500.
 - 12 M. J. Frisch, et al. Gaussian 09, Revision D. 01 (Gaussian Inc., 2009).
 - 13 X. Li, R. Zhang and X. Zhang, *Journal of Hazardous Materials*, 2010, **183**, 622.
 - 14 D. M. Badgujar, M. B. Talawar, S. N. Asthana and P. P. Mahulikar, *Journal of Hazardous Materials*, 2008, **151**, 289.
 - 15 G. H. Tao, B. Twamley and J. M. Shreeve, Journal of Materials Chemistry, 2009, 19, 5850.
 - 16 P. He, L. Wu, J. Wu, Q. Wang, Z. Li, M. Gozin, and J. Zhang, Chemistry-A European Journal, 2017, 23, 11159.
 - 17 P. Yin, L. A. Mitchell, D. A. Parrish, and J. M. Shreeve, *Chemistry -An Asian Journal*, 2017, **12**, 378.
 - 18 Test methods according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, United Nations Publication, New York, 4th edn, 2003; 13.4.2 Test 3 (ii) BAM Fall hammer, pp. 75-82; 13.5.1 Test 3: BAM friction apparatus, pp. 104-107.

(ANTP) starting from 4-amino-2,6-dichloropyridine, followed by nitration, azidonation, nitrogen elimination and ring closure, and again azidonation and azido-tetrazolo tautomerism. ANTP displays a high density (1.92 g/cm³ at 293 K), low thermal stability, and is predicted to be a high performance energetic material.

Experimental

Caution: Some compounds are energetic materials that tend to explode under certain conditions. Proper protective measures (work with small quantities, safety glassed, face shields) should be observed.

General: Melting point was measured on an X-4 melting point apparatus and was uncorrected. ¹H NMR and ¹³C NMR were recorded on a Bruker Avance Spectrometer. The coupling constants (*J*) were reported in hertz (Hz). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analyses were carried out on a Perkin-Elmer instrument. Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was conducted on a Q600SDT.

Synthesis of 2. A solution of 4-amino-2,6-dichloropyridine (0.81 g, 5 mmol) in concentrated sulfuric acid (10 mL) was stirred vigorously at room temperature and treated portionwise with potassium nitrate (1.52 g, 15 mmol). Then the mixture was heated to 50 \Box for 30 min. After pouring over ice water, the precipitate solid was filtered, washed with cold water and dried. Yield: yellow solid, 0.88 g (70%). m.p. 159-161 \Box ; ¹H NMR (DMSO-*d*₆, 500 MHz): δ 8.25 (s, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ 142.39, 141.03, 132.00; Anal. Calcd. for C₅H₂Cl₂N₄O₄: C, 23.74; H, 0.80; N, 22.14; found: C, 23.65; H, 1.02; N, 22.19%; MS (ESI) *m/z*: 250.87: 252.86: 254.87= 9: 6: 1 (M-H).

Synthesis of 6.

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4-amino-2,6-dichloro-3,5-dinitropyridine (1.26 g, 5 mmol) was dissolved in acetone (15 mL) and sodium azide (0.98 g, 15 mmol) was added portionwise at room temperature, then heated up to 30 □ for another 30 min. The mixture was distilled under reduced pressure, dissolved with water (15 mL), extracted with ethyl acetate (2×25 mL), The combined organic layers were dried over MgSO₄ and solvent evaporated. Yield: yellow solid, 1.07 g (90%). *T*_{dec}: 150 □; ¹H NMR (DMSO-*d*₆, 400 MHz): δ 10.17 (s, 1H), 9.50 (s, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 148.96, 144.27, 141.87, 111.17, 105.06; Anal. Calcd. for C₅H₂N₈O₄: C, 25.22; H, 0.85; N, 47.06; found: C, 25.10; H, 1.01; N, 47.22%; MS (ESI) *m/z*: 236.96(M-H).

Conflicts of interest

There are no conflicts to declare.

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A table of contents entry

Combination of nitro, amino, tetrazole, furoxano with pyridine gave a novel fused, tricyclic energetic material with good detonation properties.

