

NJC

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: S. K. A., N. Sasidharan, R. Ganguly, L. Dasheng and H. H. Hng, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ03950F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

3-Amino-1,2,4(4H)-oxadiazol-5-one (AOD) and its Nitrogen-Rich Salts: A Class of Insensitive Energetic Materials

A. Sudheer Kumar,^{*a} Sasidharan Nimesh,^a Rakesh Ganguly,^b Dasheng Leow^a and Huey Hoon Hng^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The targeted energetic material 3-amino-1,2,4(4H)-oxadiazol-5-one (AOD) was synthesized from sodium dicyanamide using hydroxylamine hydrochloride in one-step procedure. AOD was prepared by a novel procedure in good yield and characterized using spectroscopic (IR, Raman, NMR) techniques. The high nitrogen-containing hydroxylamine and hydrazine salts of AOD (**3**) were prepared from their respective nitrogen bases in good yields. The solid state structures of the synthesized molecules were confirmed by single X-ray crystallography. 3-amino-1,2,4(4H)-oxadiazol-5-one (AOD, **3**), 3-amino-1,2,4(4H)-oxadiazol-5-one-Hydroxylamine (AOD-HyAm, **5**) and 3-amino-1,2,4(4H)-oxadiazol-5-one-Hydrazine (AOD-Hy, **6**) showed densities of 1.76, 1.73 and 1.64 g/cc respectively. The thermal stabilities of the molecules were assessed by thermogravimetric analysis. Non-isothermal kinetics was performed on the molecules to derive the activation energy. Constant volume combustion energy was determined using oxygen bomb calorimeter and the heat of formation was calculated from the experimental values. Sensitivities of the molecules were measured by using impact and friction tests.

Introduction

For years tetrazoles and their derivatives have been in use as the building blocks for the synthesis of energetic materials.¹ Although tetrazole derivatives show good densities as compared to their analogues with lesser nitrogen atoms, their sensitivities are often not suitable for good practical use.² The incorporation of oxygen containing rings such as oxazoles, may be a good option. The oxadiazole moiety reveals promising energetic properties as shown for furazanes (Figure 1).³

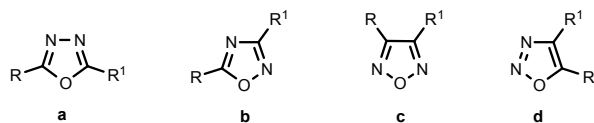


Figure 1. a) 1,3,4 oxadiazole; b) 1,2,4 oxadiazole; c) 1,2,5-oxadiazole (furazane); d) 1,2,3-oxadiazole.

Oxadiazole 'a' and 'b' (Figure 1) are reported frequently in literature, as their rings are fused from a hydroxyamino amide or from a hydrazino amide and an organic acid. They are often used in pharmaceutical applications.⁴ Whereas 'd' is rarely reported due to the rather complex synthetic preparation, as well as the unstable nature of the molecule and they can exist only with substituents.⁵

Although the chemistry of tetrazole and its derivatives is well explored with respect to their properties as explosives^{6a}, the chemistry of 1,2,4-oxadiazol-5(4H)-ones and its salts are largely unknown to the best of our knowledge.

During our investigations, we found that the reported methods to prepare AOD (**3**) involved multi-step synthetic procedures.^{6b-c} The use of toxic methyl mercaptane and expensive methylation agents like dimethyl sulfate or iodomethane make this synthetic strategy cumbersome.

Herein, we report an easy and effective novel one-step synthesis of AOD (**3**) from sodium dicyanamide with hydroxylamine hydrochloride in basic medium. The resultant reaction mixture was acidified (pH=1) using concentrated hydrochloric acid (37%) at 0 °C to obtain AOD (**3**) in good yield. The hydroxylamine (AOD-HyAm, **5**) and hydrazine (AOD-Hy, **6**) salts of AOD were prepared from AOD (**3**) with their respective bases in good yield. The compounds were characterized by spectroscopic (IR, Raman, NMR) methods and the solid state structures of the synthesized compounds were elucidated by X-ray diffraction technique. The thermal stabilities of the molecules were determined by thermogravimetric analysis (TGA). In addition, the detailed thermo-chemical analyses of the synthesized compounds were studied.

Results and Discussion

Synthesis and characterization

AOD (**3**) was synthesized in a one-step procedure (Scheme 1). A solution of sodium dicyanamide was added dropwise to the

^a Energetics Research Institute, Nanyang Technological University, N1-B4a-02, 50 Nanyang Avenue, Singapore 639798. Email: ksudheer@ntu.edu.sg

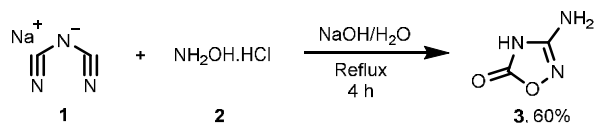
^b NTU-CBC Central Instrumentation Facility, Nanyang Technological University, 21 Nanyang Link, Singapore 637371.

Electronic Supplementary Information (ESI) available: Details of general experimental, characterization of all new compounds, X-ray crystallography data and CCDC numbers for synthesized compounds. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

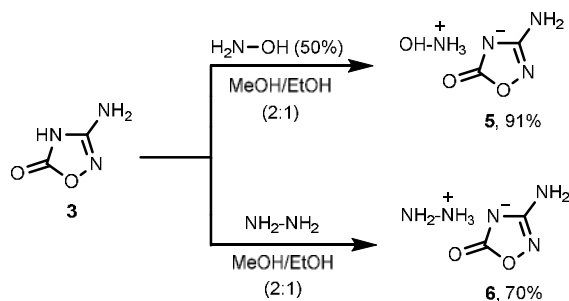
ARTICLE

Journal Name

mixture of hydroxylamine hydrochloride and sodium hydroxide in aqueous medium at 40 °C. Acidification of the mixture with concentrated hydrochloric acid resulted crude AOD (**3**). It was recrystallized from hot methanol to produce white solid in 60% yield. X-ray diffraction analysis confirmed the structure of compound **3** as depicted in Figure 2.

Scheme 1. Novel synthetic route for 3-amino-1,2,4-oxadiazole (**3**).

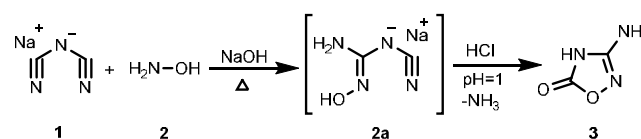
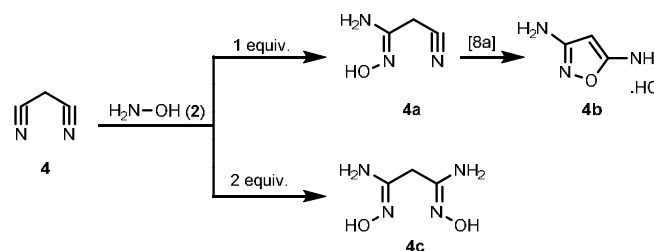
Following the synthesis of AOD (**3**), novel energetic nitrogen-rich salts with hydroxylamine and hydrazine were prepared and characterized (Scheme 2). The highly acidic secondary amine ($-\text{NH}$) proton was deprotonated by the nitrogen bases in simple acid-base reaction to yield the nitrogen-rich salts (**5** and **6**) in quantitative yields. The structures of **5** and **6** were confirmed by single-crystal X-ray diffraction analysis (Figure 2).

Scheme 2. Synthetic route towards AOD salts (**5** and **6**).

The formation of AOD (**3**) occurs via nucleophilic addition of hydroxylamine to one of the cyano group in sodium dicyanamide (**1**) resulting the mono oxime derivative (**2a**), confirmed by the presence of nitrile group (2250 cm^{-1}) in the structure by FT-IR. Finally, the cyclization product (**3**) was observed after acidification ($\text{pH}=1$) with concentrated hydrochloric acid (37%) with the liberation of ammonia and confirmed by the disappearance of the nitrile group in the structure by FT-IR.

Only mono oxime derivative (**2a**) was obtained from compound **1** under 1 or 2 equiv. of hydroxylamine (**2**) as shown in Scheme 3. Contrary to that, mono^{8a-c} and di oxime^{8d} (**4a** and **4c**) resulted when the reaction was performed with malononitrile under the same conditions (Scheme 4). The cyclization might be prompted by the electron rich nature of the central nitrogen atom on sodium dicyanamide (**1**) analogous to the methylene group on malononitrile (**4**). Further cyclization of compound **4a** to **4b** was reported in the

literature.^{8a} The molecular structure of **4c** was confirmed by single X-ray diffraction analysis (Figure 2).

Scheme 3. Plausible mechanism with sodium dicyanamide (**1**).Scheme 4. Plausible mechanism with malononitrile (**4**).

The structure of AOD (**3**) was characterized by spectroscopic (IR, Raman, NMR) methods. The ^1H and ^{13}C NMR spectra were measured in $\text{DMSO}-d_6$ solvent. The resonance peaks at $\delta = 11.86, 6.19\text{ ppm}$ in ^1H spectrum corresponds to the amino groups in oxadiazole ring. The de-shielding of the resonance peak may be due to the electronic effects of the oxadiazole ring and keto group. The two chemically different carbon atoms in the molecule showed resonance at $\delta = 159.1, 157.5\text{ ppm}$, respectively. The carbon atom of the keto group is the most de-shielded and resonated at $\delta = 159.1$ downfield from TMS. The carbon atom of the oxadiazole ring was less de-shielded and resonated at $\delta = 157.5\text{ ppm}$. FT-IR spectrum revealed absorption peaks at 2250 cm^{-1} of the nitrile stretching mode (**2a**), $3356, 3204\text{ cm}^{-1}$ of N-H stretching, $1686, 1533\text{ cm}^{-1}$ of N-H bending, and $906, 739\text{ cm}^{-1}$ of N-H wag modes of the primary and secondary amino groups (**3**). Raman spectrum showed vibrational modes characteristic of oxadiazole ring. AOD showed stretching bands at $1539\text{ (C}_{\text{tet}}\text{-N-C}_{\text{tr2}})$, 1453 (N=N) , 1264 (N-N) , $1070\text{ (C-N}_{\text{ring str}})$ and $769\text{ (N-N wagging)}\text{ cm}^{-1}$.

Molecular Structure

The structure of AOD (**3**) was ascertained from single crystal X-ray diffraction data. Suitable crystals for analysis were grown by slow evaporation from hot methanol at room temperature and atmospheric pressure. AOD (**3**) crystallized in monoclinic space group C_2c_1 with a cell volume of $381.34(11)\text{ \AA}^3$. From the crystal structure of **3**, it was clear that the O-C bond formation has happened at the keto group carbon. AOD (**3**) showed a nearly planar arrangement of the whole molecule. The hydrogen atoms of the amine moiety are merely tilted from the plane which is spanned by the five-membered ring.

Table 1. Crystal data and refinement for **3**, **4c**, **5** and **6**.

Crystal data	3	4c	5	6
CCDC	1407655	1561177	1560543	1561922
Chemical Formula,	C ₂ H ₃ N ₃ O ₂ ,	C ₂ H ₈ N ₄ O	C ₂ H ₆ N ₄ O ₃ ,	C ₂ H ₇ N ₅ O ₂ ,
M _r	101.07	132.13	134.11	133.13
T (K)	103	100	100	100
Radiation type, λ	Mo Kα,	Mo Kα,	Mo Kα,	Mo Kα,
(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system,	Monoclinic,	Monocli	Monoclini	Orthorho
Space group	C ₁ c ₁	nic, C ₁₂ c ₁	c, P2 ₁ /c	mbic, Pna2 ₁
a, b, c (Å)	9.3860(16), 3.5384(6), 12.154(2)	8.5972(3), 9.4798(3), 14.2271(5)	7.0644(2), 6.1129(2), 12.3876(5)	13.3609(4), 10.8742(4), 3.7046(1)
α, β, γ (°)	90, 109.139(6), 90	90, 96.2613(13), 90	90, 105.6560(12), 90	90, 90, 90
V (Å ³)	381.34(11)	1152.59(7)	515.10(3)	538.24(3)
Z	4	8	4	4
ρ, g cc ⁻¹	1.760	1.523	1.729	1.643
μ, mm ⁻¹	0.156	0.127	0.157	0.141
wR ₂ [all]	0.0875	0.1320	0.0910	0.0730
F(000)	208	560	280	280
Crystal size, mm ³	0.100x0.120x 0.400	0.058x 0.257x0.308	0.068x0.1 57 x0.208	0.040x0.0 80 x0.100
Theta range for data collection, °	3.55 to 31.43	2.88 to 30.98	3.75 to 31.03	2.42 to 27.09
Reflections collected	2638	13893	14096	11594
Independent reflections	1157 [R(int) = 0.0454]	1830 [R(int) = 0.0744]	1625 [R(int) = 0.0460]	1180 [R(int) = 0.0644]
Absorption correction	Multi-Scan	Numeric al Mu Calculat ed	Numerica l Mu Calculat ed	Multi- Scan
Max. and min. transmission	0.9850 and 0.9400	0.731	0.9890 and 0.9680	0.9940 and 0.9860
Refinement method	Full-matrix least-squares on F ²	Full- matrix least- squares on F ²	Full- matrix least- squares on F ²	Full- matrix least- squares on F ²
Refinement Programme	SHELXL- 2014/6 (Sheldrick, 2014)	SHELXL- 2014/7 (Sheldric k, 2014)	SHELXL- 2014/7 (Sheldrick , 2014)	SHELXL- 2016/6 (Sheldrick, 2016)
Data/restraints/par ameters	1157 / 3 / 70	1830 / 0 / 84	1625 / 2 / 90	1180 / 5 / 95
Goodness- of-fit on F ²	1.113	1.085	1.077	1.079

Single crystals were grown by the slow evaporation of solution of AOD-HyAm (**5**) in EtOH/MeOH (1:1) solvent at room temperature and atmospheric pressure. AOD-HyAm (**5**) crystallized in monoclinic space group *P2₁/c* with cell volume of 515.10(3) Å³.

AOD-Hy (**6**) was unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 2). Suitable crystals for analysis were grown by slow evaporation from EtOH/MeOH (1:1) solvent at room temperature and atmospheric pressure. AOD-Hy (**6**) crystallized in orthorhombic space group *Pna2₁* with cell volume of 538.24(3) Å³.

The crystallographic data of these compounds (**3**, **4c**, **5** and **6**) are detailed in Table 1. The complete list of hydrogen-bond geometry, bond lengths, bond angles, atom coordinates and thermal displacement parameters can be obtained from ESI.

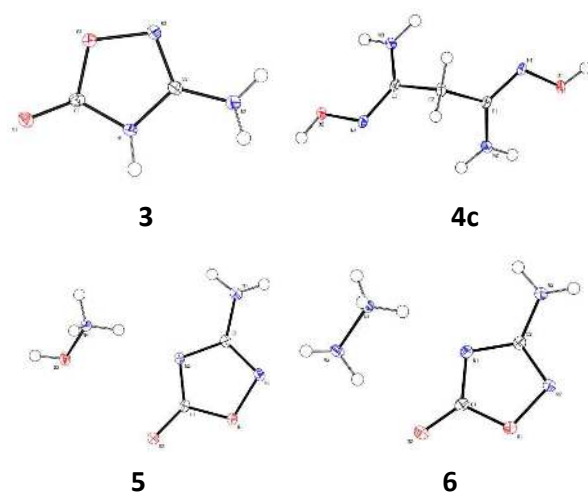


Figure 2. Molecular structures of compounds **3**, **4c**, **5** and **6**; thermal ellipsoids are set at 50% probability and hydrogen atoms are unlabeled for clarity.

Thermo-Chemical Properties

Thermogravimetric Analysis (TGA) was used to assess the thermal stability and decomposition behavior of the molecule. AOD and its salts (less than 2 mg) in aluminium crucibles were subjected to a temperature scanning programme, which involved heating the sample and reference from 50–500 °C under dynamic nitrogen purging environment with a flow rate of 50 mL min⁻¹. The experiments were done at 5 °C min⁻¹ heating rate with empty aluminium crucible as the reference. AOD (**3**), AOD-HyAm (**5**) and AOD-Hy (**6**) showed exothermic decomposition with an onset temperature of 207, 206, 114 °C respectively (Figure 3).

The peak temperature from the DTA thermograms was utilized for non-isothermal kinetic analysis. Peak values (*T_p*), from thermograms run at four different heating rates were used to generate the kinetic parameters with Kissinger and Ozawa methods. As observed for many energetic materials, the decomposition temperature of both the compounds increased as the heating rate increased. In order to have good correlation, the *E_a* value obtained by Ozawa method was

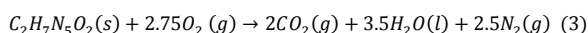
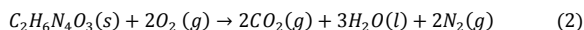
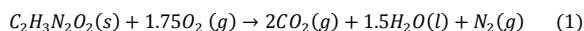
ARTICLE

Journal Name

refined as per the ASTM E-698 standard.^{7a} A correlation factor D , was introduced to refine the Ozawa relation as laid out by Ozawa-Flynn-Wall. The factor was based on the value of E_a/RT . The E_a value from refined Ozawa-Flynn-Wall relation correlated well with that of the Kissinger relation.^{7b-c} The trend in activation energy gave indication of the thermal stability of molecules. AOD-HyAm (**5**) with the highest thermal stability showed the highest activation energies among the three molecules. Table 2 assimilates the E_a and $\ln A$ values derived from these two relations for the molecules. A representative depiction of Kissinger and Ozawa plots of **3**, **5** and **6** can be obtained from ESI.

Constant Volume Calorimetry

Constant volume combustion energy of AOD (**3**), AOD-HyAm (**5**) and AOD-Hy (**6**) were experimentally calculated using a Parr bomb calorimeter. The total energy on combustion, $\Delta_c U$ inside an oxygen bomb was recorded to be -2073.9 (AOD), -1682.5 (AOD-HyAm), and -2484.5 (AOD-Hy) cal g⁻¹. The enthalpy of combustion was calculated from the relation, $\Delta_c H = \Delta_c U + \Delta nRT$, where ΔnRT is the correction factor for gas volume increase. The standard energies of formation ($\Delta_f H^\circ$) were back calculated from $\Delta_c H$, on the basis of the combustion relation equations (1, 2 & 3). The calculated heats of formation values were -343.5 (AOD), -705.3 (AOD-HyAm) and -407.9 (AOD-Hy) kJ mol⁻¹.



Sensitivities of **3**, **5** and **6** towards impact (IS) and friction (FS) were measured. Measurements were made using a standard BAM Fall hammer with 2 kg drop weight and BAM friction J tester. The synthesized nitrogen-rich derivatives **3** (IS: >20 J;

FS: >360 N), **5** (IS: >20 J; FS: >360 N) and **6** (IS: >20 J; FS: 192 N) were found to be insensitive towards impact and friction, suggesting the potential use of these molecules as insensitive energetic materials in gas generators/mono propellant additives.

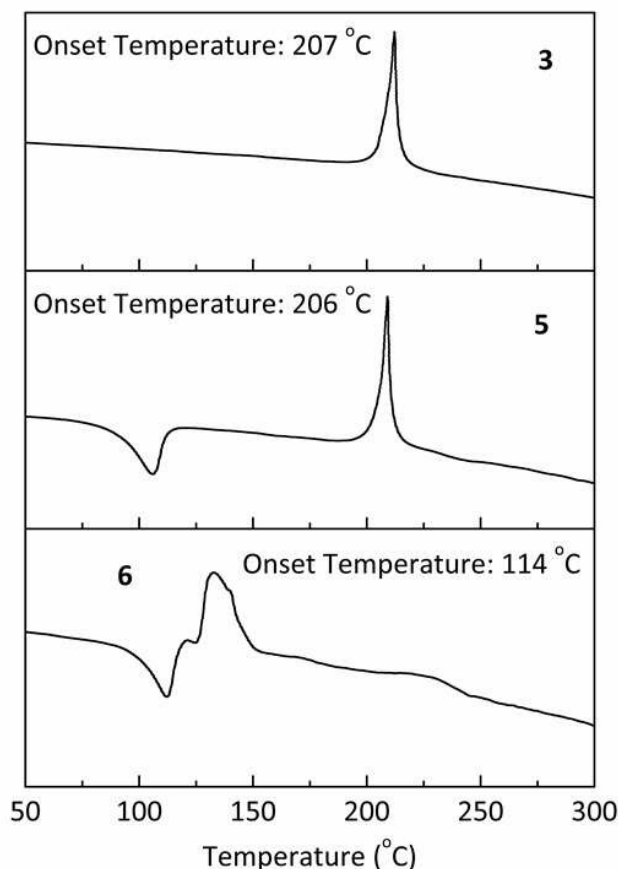


Figure 3. TGA plots of **3**, **5** and **6** (heating rate of 5 °C min⁻¹).

Table 2. Non-isothermal kinetic analysis data using Kissinger and Ozawa methods for **3**, **5** and **6**.

β (°C min ⁻¹) ^a	Onset Temperature (°C) ^b			Peak Temperature, T_p (°C) ^c			Frequency factor (LnA, min ⁻¹)			E_a Kissinger (kJ mol ⁻¹) ^d			E_a Ozawa (kJ mol ⁻¹) ^e		
	3	5	6	3	5	6	3	5	6	3	5	6	3	5	6
2	194	195	111	201.3	198.9	117.1	22.5	29.3	17.1	96.1	122.4	61.3	99.1	124.0	64.7
4	204	205	113	214.4	211.8	129.4									
6	210	207	116	220.1	215.6	135.3									
8	213	211	118	228.3	222.1	143.2									

a) DTA Heating rate; b) Onset temperature of decomposition from DTA thermograms; c) Peak temperature of decomposition from DTA thermograms; d) Activation energy calculated from Kissinger equation; e) Activation energy calculated from Ozawa method.

Conclusions

The 3-amino-1,2,4-oxadiazole (**3**) was prepared by novel one-step procedure in good yield. The hydroxylamine and hydrazine salts of AOD (**5** and **6**) were synthesized from AOD

(**3**) in good yields. These compounds were characterized by spectroscopic (IR, Raman, NMR) methods and the solid-state structures of most of these compounds were determined by using single crystal X-ray diffraction techniques. The synthesized compounds AOD (**3**), AOD-HyAm (**5**) and AOD-Hy (**6**) exhibited densities of 1.76, 1.73, 1.64 g/cc respectively. The

thermal behavior and non-isothermal kinetics performed on the molecules revealed good thermal stability and activation energies for decomposition. The molar enthalpies of formation of the synthesized molecules were determined from bomb calorimetric measurements. The synthesized compounds were insensitive towards impact and friction. As AOD (3) is energetic similar to 5-amino-(1H)- tetrazole (AT) and insensitive, further derivatization of AOD (3) is ongoing in our laboratory and will be reported in the future.

Caution!

Although we have not experienced any safety issues in handling or during synthesis; in any case, AOD and its salts should be handled with care by using proper safety precautions. Safety shields, safety glasses, face shields, leather gloves, and protective clothing, such as leather suits, and ear plugs must be worn. Ignoring safety precautions can lead to serious injury.

Conflicts of interest

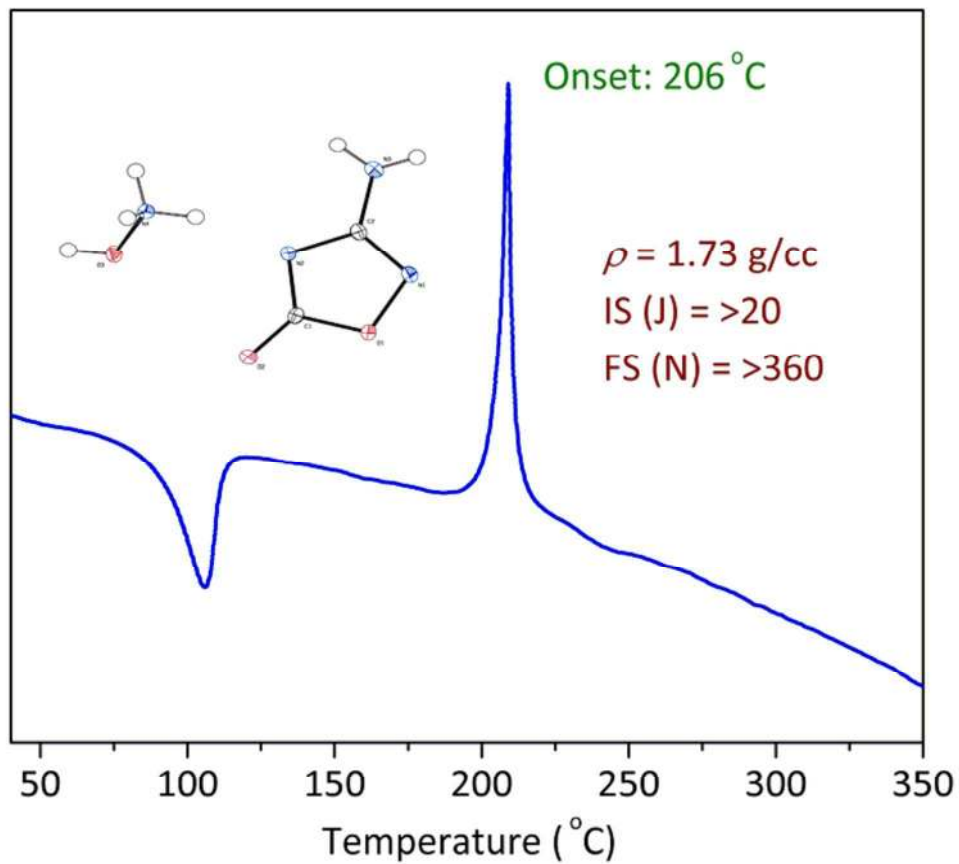
There are no conflicts of interest to declare.

Notes and references

- 1 T. M. Klapötke, *Chemistry of High Energy Materials*, 1st Ed., de Gruyter Verlag, Berlin, 2009, ISBN 3110207451.
- 2 T. M. Klapötke, R. Alsfasser, C. Janiak, H. J. Meyer and E. Riedel, *Modern Inorg. Chem.*, 3rd Ed., de Gruyter Verlag, Berlin, 2007, ISBN 978-3-11-019060-1.
- 3 a) M. D. Coburn, *J. Heterocycl. Chem.*, 1968, **5**, 83; b) J. W. Grate and G. C. Frye in *Sensors Update*, Wiley-VCH, Weinheim, 1996, **2**, 10.
- 4 K. Rehse and S. Bade, *Arch. Pharm. Pharm. Med. Chem.*, 1996, **329**, 535.
- 5 M. T. Nguyen, A. F. Hegarty and J. Elguero, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 713.
- 6 a) J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, Wiley-VCH, Weinheim, 2010; b) T. Suyama, N. Ozawa and N. Suzuki, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 307; c) D. Y. Ra, N. S. Cho, S. K. Kang and E. S. Choi, *Bull. Korean Chem. Soc.*, 1998, **19**, 880.
- 7 a) *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*, ASTM Designation E698–99, 1999; b) T. Ozawa, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1881; c) H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702.
- 8 a) W. J. Fanshawe, V. J. Bauer and S. R. Safir, *J. Org. Chem.*, 1965, **30**, 2862; b) V. N. Yarovenko, V. Z. Shirinyan, I. V. Zavarzin and M. M. Krayushkin, *Russ. Chem. Bull.*, 1994, **43**, 114; c) V. Andrianov and A. Ereemeev, *Synth. Commun.*, 1992, **22**, 453; d) H. Schmidtman, *Chem. Ber.*, 1896, **29**, 1168.
- 9 N. Kommu, M. Balaraju, V. D. Ghule and A. K. Sahoo, *J. Mater. Chem. A*, 2017, **5**, 7366.
- 10 a) P. Yin, J. Zhang, C. He, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2014, **2**, 3200; b) C. He, J. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2013, **1**, 2863; c) Y. Gao, C. Ye, B. Twamley and J. M. Shreeve, *Chem. Eur. J.*, 2006, **12**, 9010; d) R. P. Singh and J. M. Shreeve, *Chem. Eur. J.*, 2011, **17**, 11876.
- 11 a) N. Kommu, V. D. Ghule, A. S. Kumar and A. K. Sahoo, *Chem. Asian. J.*, 2014, **9**, 166; b) N. Kommu, A. S. Kumar, J. Raveendra, V. D. Ghule and A. K. Sahoo, *Asian J. Org. Chem.*, 2016, **5**, 138.
- 12 a) Q. Zhang and J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2013, **52**, 2; b) G. H. Tao, B. Twamley and J. M. Shreeve, *J. Mater. Chem.*, 2009, **19**, 5850; c) C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley and J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2006, **45**, 7262; d) R. P. Singh and J. M. Shreeve, *Chem. Eur. J.*, 2011, **17**, 11876.
- 13 a) K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Piotrowski, K. Polborn, R. L. Willer and J. J. Weigand, *J. Org. Chem.*, 2006, **71**, 1295; b) M. J. Crawford, K. Karaghiosoff, T. M. Klapötke and F. A. Martin, *Inorg. Chem.*, 2009, **48**, 1731; c) M. V. Denffer, T. M. Klapötke, G. Kramer, G. Spiess and J. Welch, *Propellants. Explos. Pyrotech.*, 2005, **30**, 191; d) J. C. G. Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Lohnwitz, P. Mayer, H. Noth, K. Polborn, C. J. Rohbogner, M. Suter and J. J. Weigand, *Inorg. Chem.*, 2005, **44**, 4237; e) K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Piotrowski, K. Polborn, R. L. Willer and J. J. Weigand, *J. Org. Chem.*, 2006, **71**, 1295.
- 14 a) A. S. Kumar, N. Kommu, V. D. Ghule and A. K. Sahoo, *J. Mater. Chem. A*, 2014, **2**, 7917; b) A. S. Kumar, V. D. Ghule, S. Subrahmanyam and A. K. Sahoo, *Chem. Eur. J.*, 2013, **19**, 509.
- 15 a) V. D. Ghule, D. Srinivas and K. Muralidharan, *Asian J. Org. Chem.*, 2013, **2**, 662; b) a) Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu and Si. P. Pang, *J. Am. Chem. Soc.*, 2010, **132**, 12172.
- 16 a) S. Nimesh and H. G. Ang, *Propellants Explos. Pyrotech.*, 2015, **40**, 426; b) S. Nimesh and A. G. Rajendran, *Propellants Explos. Pyrotech.*, 2012, **37**, 267.
- 17 a) R. Damavarapu, *Propellants Explos. Pyrotech.*, 2010, **35**, 395; b) R. Damavarapu, C. R. Surapaneni, N. Gelber, R. G. Duddu and P. R. Dave, U. S. Patent 7304164, 2007.
- 18 a) C. M. Sabate, E. Jeanneau and J. Stierstorfer, *Z. Anorg. Allg. Chem.*, 2011, **637**, 1490; b) T. M. Klapötke and C. M. Sabate, *Chem. Mater.*, 2008, **20**, 1750; c) T. M. Klapötke, C. M. Sabate and J. Stierstorfer, *New J. Chem.*, 2009, **33**, 136; d) T. M. Klapötke, C. M. Sabate and J. Stierstorfer, *Z. Anorg. Allg. Chem.*, 2008, **634**, 1867.
- 19 a) A. Shlomovich, T. Pechersky, A. Cohen, Q. L. Yan, M. Kosa, N. Petrutik, N. Tal, A. Aizikovich and M. Gozin, *Dalton Trans.*, 2017, **46**, 5994; b) A. Cohen, Q. L. Yan, A. Shlomovich, A. Aizikovich, N. Petrutik and M. Gozin, *RSC Adv.*, 2015, **5**, 106971; c) A. Aizikovich, A. Shlomovich, A. Cohen and M. Gozin, *Dalton Trans.*, 2015, **44**, 13939.
- 20 a) G. Cheng, X. Li, X. Qi and C. Lv, *J. Energetic Mater.*, 2010, **28**, 35; b) X. Qi, G. Cheng, C. Lv and D. Qian, *Synth. Commun.*, 2008, **38**, 537; c) G. Cheng, X. Qi and C. Lv, *Cent. Eur. J. Energ. Mater.*, 2007, **4**, 59; d) X. Qi, G. Cheng, C. Lv and D. Qian, *Cent. Eur. J. Energ. Mater.*, 2007, **4**, 105.

The 3-amino-1,2,4(4*H*)-oxadiazole-5-one and its nitrogen-rich salts are synthesized in good yield. The compounds show promise as insensitive energetic ingredients.

Insensitive Nitrogen-Rich Energetic Materials



168x159mm (600 x 600 DPI)