pubs.acs.org/OrgLett

gem-Dinitromethyl-Functionalized 5-Amino-1,3,4-oxadiazolate Derivatives: Alternate Route, Characterization, and Property Analysis

Jinchao Ma, Jiaheng Zhang,* Gregory H. Imler, Damon A. Parrish, and Jean'ne M. Shreeve*



NMR and IR spectroscopy, elemental analysis, and differential scanning calorimetry. Crystal structure analysis, property tests, and theoretical calculations confirm good detonation performance and high mechanical stabilities of the salts.

nergetic materials have been widely used in military and E civilian applications because of their special properties of releasing a large amount of energy quickly. As a growing number of scientists join this study, the field of energetic materials has experienced rapid development in the past few decades.¹⁻⁴ Many novel heterocyclic energetic molecules composed of an energetic framework and some explosive groups have been reported in recent years, and their energetic performance has reached a high level.^{5,6} However, along with the increasing consideration of safety and the availability of energetic materials, the research is no longer a simple successful synthesis and characterization but a move toward structural design, synthesis and property optimization, and application development.⁷⁻¹¹

Before design of an energetic molecule, the properties of its composition and effects on the whole must be analyzed. Oxadiazole, which has played an important role in the synthesis of high energy density materials,¹²⁻¹⁵ includes four isomers, namely, 1,2,5-, 1,2,4-, 1,3,4-, and 1,2,3-oxadiazole (Figure 1).¹⁶⁻¹⁹ Among them, except the unstable 1,2,3oxadiazole, the 1,2,5-, 1,2,4-, and 1,3,4-oxadiazoles have been widely studied as energetic backbones because of their high nitrogen and oxygen content. Especially for 1,3,4-oxadiazole, the distribution of heteroatoms is more uniform, and there is no weak N-O bond (two N-O bonds in 1,2,5-oxadiazole, one N-O bond in 1,2,4-oxadiazole), which helps to ensure that this member will show high stability.^{20,21} The nitro group was used to improve the density and detonation performance. However, the incorporation of multiple nitro groups can significantly reduce the stability of these energetic compounds.



Figure 1. Design selection of energetic molecules.

Cost-effective

Helical assembly of cross structure

For example, trinitromethyl-functionalized compounds often exhibit low thermal and mechanical sensitivities because of the weak trinitromethyl C-N bond and the large space that the three nitro groups occupy. One of the best choices to increase the energy density and enhance stability is the gemdinitromethyl group. Unlike the trinitromethyl group, the gem-dinitromethyl group has a planar structure and a strong C-N bond, which helps to stabilize energetic compounds.²²

In this work, gem-dinitromethyl-1,3,4-oxadiazolate derivatives are obtained by using a new, safer, and more cost-effective

Received: May 7, 2020



\infty ACS Publications

Letter

way. All intermediates and energetic products are fully characterized. Thermal stabilities, impact sensitivities, as well as calculated detonation performance of **AAOD** (ammonium (5-amino-1,3,4-oxadiazol-2-yl)dinitromethanide) and hydroxylammonium salt **8** were determined. The crystal structures of these compounds were determined. High performance coupled with low sensitivity suggest that **8** has good potential as an energy-safe balanced explosive.

As shown in Scheme 1, in the earlier method, the energetic AAOD salt was synthesized from a zwitterionic com-



pound—(5-iminio-4,5-dihydro-1,3,4-oxadiazol-2-yl) dinitromethanide (4)—which was prepared using a four-step synthesis route from commercially available ethyl potassium malonate.²⁵ Among all of the intermediates, the dinitromethyl potassium salts, specifically potassium (5-amino-1,3,4-oxadiazol-2-yl) dinitromethanide (3), have high mechanical sensitivity. Potassium 2-hydrazinyl-1,1-dinitro-2-oxoethan-1ide (2) is unstable and can not be stored for extended periods. For these reasons, the previous method for the synthesis of AAOD was limited by utilization of the formation of unstable intermediates and hidden safety hazards. In this study, the ammonium salt AAOD and the hydroxylammonium salt 8 were obtained from 2-(2-methyl-1,3-dioxolan-2-yl) acetohydrazide $(5)^{26,27}$ following a three-step route. Initially 5-((2-methyl-1,3-dioxolan-2-yl)methyl)-1,3,4-oxadiazol-2amine (6, 88%) resulted from reacting 5 with cyanogen bromide in a solution of potassium bicarbonate. Compound 6 was deprotected by using a 2 M HCl solution and then treated with sodium bicarbonate to give 1-(5-amino-1,3,4-oxadiazol-2yl)propan-2-one (7, 75%) as a white solid. AAOD and 8 were obtained after nitrating 7 and subsequently neutralizing it with the corresponding base. Our process employs inexpensive raw

materials and removes the necessity to utilize unstable intermediates. The detailed description of the synthesis process is given in the experimental section of the Supporting Information (SI).

Crystals of AAOD (293 K) suitable for single-crystal X-ray diffraction were obtained by dissolving AAOD in a small amount of methanol and allowing the solvent to slowly evaporate. The unit cell of AAOD contains four formula moieties, with a crystal density of 1.750 g cm⁻³ at 293 K (SI). To further examine the structures of **3**, **4**, and **AAOD** (173 K) as well as to evaluate the differences between them, crystal data of 3. 4. and AAOD (173 K) were studied.²⁵ The structures of these gem-dinitromethyl-functionalized 5-amino-1,3,4-oxadiazoles are a cross-shaped conformation, in which the dihedral angles between the gem-dinitromethyl group and oxadiazole are 75.9° (3), 83.9° (4), 78.3° (AAOD (173 K)), and 79.0° (AAOD (293 K)), respectively. In general, a planar configuration helps to improve molecular stability;^{28,29} thus compound 4 with a high degree of molecular distortion likely generates hot spots when mechanically stimulated. The free space per molecule in the unit cells of 3, 4, and AAOD (173 K) is 21, 44, and 50 $Å^3$, respectively. In light of a sensitivityfree space relationship, the sensitivity value of these compounds will decrease according to 3 > 4 > AAOD (173) K).

From a crystallographic perspective, layer by layer stacking is beneficial to improve the stability of energetic materials (Figure 2). However, the premise of layer by layer stacking



Figure 2. Planar/cross structures form 2-D and 3-D cube layer by layer stacking with different arrangements, respectively.

is planar molecular structure. For dinitro-1,3,4-oxadiazole derivatives, which all possess cross structures, an interesting 3-D cube layer by layer assembly was found.³³ gem-Dinitromethyl-1,3,4-oxadiazolates form a columnar body through spiral arrangements in a certain direction, and columnar bodies are arranged to form a 3-D layer. This interesting arrangement is believed to help the compounds have optimal balance between stability and performance.

As seen from Figure 3, these materials all exhibit 3-D cube structures. Moreover, each 3-D cube of these materials consists of molecules arranged in two distinct ways. For the layered structure, the interlayer distance is an important parameter that affects the density and even the performance of the compound. The average distances between neighboring cubes are 5.0250 Å (3), 4.1344 Å (4), 4.9541 Å (AAOD (173 K)), and 4.9681 Å (AAOD (293 K)), respectively. Compound 4 with small intermolecular spacing is likely to be more dense. In the cubes of 3 and AAOD, two neighboring molecules generate a large





Figure 3. (a1)-(d1) Molecular structures of 3, 4, AAOD (173 K), and AAOD (293 K); (a2)-(d2) three-dimensional packing diagrams of 3, 4, AAOD (173 K), and AAOD (293 K) along [001]; and (a3)-(d3) helical structures of 3, 4, AAOD (173 K), and AAOD (293 K) along [100].

and open quadrilateral channel along the [100] direction. The distances between the neighboring channels in the same cube were 7.5626 Å (3), 6.1121 Å (4), 7.8116 Å (AAOD (173 K)), and 7.8993 Å (AAOD (293 K)), respectively. The length of the quadrilateral channels varied between 4.3513 and 4.4388 Å. The width of quadrilateral channels ranged between 3.3456 and 3.5042 Å. However, 4 is arranged slightly differently from 3 and AAOD, with the channel being small because the molecules creating the channel were closely packed. Seen from

the [100] direction, molecules in two different directions in each quadrilateral channel were stacked in a helical shape, and the molecular distances in the vertical direction were 9.6783 Å (3), 13.2779 Å (4), 9.9589 Å (AAOD (173 K)), and 9.9694 Å (AAOD (293 K)), respectively.

In Table 1, some key physical properties, such as thermal stability, density, and detonation performance, are given for the energetic materials. The onset decomposition temperature of **AAOD** is 195 °C, which is slightly lower than the literature value (202 °C).²⁵ The hydroxylammonium salt 8 has a lower thermal stability than **AAOD**, decomposing readily at 145 °C; however, the value was higher than that of the zwitterionic 4 (138 °C). As shown in Figure 4, the sharper peak of 8



Figure 4. DSC curves of compounds AAOD and 8.

compared to that of **AAOD** implies a more intense exothermic reaction than that of **AAOD**. The thermal stability of these new compounds is less than that of cyclotrimethylene trinitramine (RDX, 220 $^{\circ}$ C) and 1,1-diamino-2,2-dinitroethene (FOX-7, 204 $^{\circ}$ C).

The densities of AAOD and 8 were determined experimentally at room temperature using a gas pycnometer. The density of 8 (1.88 g cm⁻³) is higher than that of AAOD (1.75 g cm^{-3}) and comparable to traditional explosives FOX-7 (1.88 g cm⁻³) and RDX (1.82 g cm⁻³). The gas-phase heats of formation were calculated by the Gaussian 03 suite of programs with isodesmic reactions.³⁶ Based on the experimental densities and the calculated heats of formation, detonation velocities and detonation pressures were calculated using EXPLO5 (v6.01).³⁷ Benefiting from the existence of the oxadiazole backbone, 8 and AAOD have larger $\Delta_{f}H$ values $(-0.14 \text{ to } -0.36 \text{ kJ g}^{-1})$ than FOX-7 $(-0.88 \text{ kJ g}^{-1})$ but much lower than RDX (0.36 kJ $g^{-1}).$ The calculated heat of formation (-0.36 kJ g⁻¹), detonation velocity (8365 m s⁻¹), and detonation pressure (29.1 GPa) of AAOD were slightly lower than those reported in the literature ($\Delta_t H = -0.36$ kJ g^{-1} , D = 8554 m s⁻¹, P = 30.1 GPa) because of the lower experimental density value used.²⁵ As shown in Figure 5a, the calculated detonation velocity and pressure of 8 are 8956 m s⁻¹ and 37.1 GPa, respectively, which are slightly higher than those of FOX-7 ($D = 8870 \text{ m s}^{-1}$, P = 34.0 GPa) and RDX (D =8748 m s⁻¹, P = 34.9 GPa) and comparable to the highly dense 3 ($D = 9035 \text{ m s}^{-1}$, P = 33.0 GPa) and zwitterionic 4 (D =8828 m s⁻¹, P = 34.6 GPa).

The experimental impact and friction sensitivity values were determined with standard BAM drop hammer and friction tester techniques.³⁸ **AAOD** has almost the same friction (160 N) and impact sensitivity values (22 J) as those given in the

pubs.acs.org/OrgLett

	H+	
		- 1
LC.		-

Table 1. Physical ar	nd Detonation Propertie	s of the Reported	Compounds in	Comparison wit	h FOX-7 and RDX
	1		1	1	

compd.	$T_{\rm d}^{\ a} [^{\circ}{\rm C}]$	ρ^{b} [g cm ⁻³]	$\Delta_{\rm f} H^c \; [\rm kJ \; mol^{-1}/\rm kJ \; g^{-1}]$	D^d [m s ⁻¹]	P ^e [GPa]	$\mathrm{IS}^{f}[\mathrm{J}]$	$FS^{g}[N]$
AAOD	195	1.75	-73.9/-0.36	8365	29.1	22	160
8	145	1.88	-30.3/-0.14	8956	37.1	30	240
3 ^{<i>h</i>}	235	2.051 ^{<i>i</i>}	-203.2/-0.89	9035	33.0	10	80
4 ^{<i>h</i>}	138	1.872^{i}	62.0/0.33	8828	34.6	25	120
AAOD ^h	202	1.776 ^{<i>i</i>}	-72.2/-0.35	8554	30.1	20	160
FOX-7 ^j	220	1.88	-130.0/-0.88	8870	34.0	25	340
RDX^{k}	204	1.82	80.0/0.36	8748	34.9	7.4	120

^{*a*}Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). ^{*b*}Measured densities at room temperature. ^{*c*}Calculated heat of formation (gas phase). ^{*d*}Calculated detonation velocity. ^{*e*}Calculated detonation pressure. ^{*f*}Impact sensitivity. ^{*g*}Friction sensitivity. ^{*h*}Ref 25. ^{*i*}Crystal density at 173 K. ^{*j*}Ref 34. ^{*k*}ref 35.





literature (IS = 20 J, FS = 160 N).²⁵ For 8, the impact and friction sensitivity were 30 and 240 J (Figure 5b), respectively, showing that it is more insensitive than other derivatives and RDX (IS = 7.4 J, FS = 120 N).

In summary, the *gem*-dinitromethyl-functionalized 5-amino-1,3,4-oxadiazolate-based energetic salts **AAOD** and **8** were synthesized according to a new route, using less-expensive raw materials and a safer process. Remarkable 3-D cube layer by layer stacking and quadrilateral channels as well as helical structures were observed from crystal structure analyses of **3**, **4**, and **AAOD**. The interesting and structurally compact assembly imparts these compounds with a good balance between high energy density and stability. The hydroxylammonium salt **8** has a high density (1.88 g cm⁻³) and good detonation properties ($D = 8956 \text{ m s}^{-1}$, P = 37.1 GPa), comparable to those of FOX-7 ($D = 8870 \text{ m s}^{-1}$, P = 34.0 GPa), and low impact sensitivities (IS = 30 J, FS = 240 N), which indicate its potential as a highperformance insensitive explosive.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01569.

Synthesis, calculation detail, crystal refinements, NMR spectra, IR spectra, DSC plots (PDF)

Accession Codes

CCDC 1957886 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Jean'ne M. Shreeve Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States; orcid.org/0000-0001-8622-4897; Email: jshreeve@ uidaho.edu; Fax: (+1) 208-885-9146
- Jiaheng Zhang Zhuhai Institute of Advanced Technology Chinese Academy of Sciences, Biomaterials Research Center, Zhuhai 519003, China; Research Centre of Flexible Printed Electronic Technology, Harbin Institute of Technology, Shenzhen 518055, China; orcid.org/0000-0002-2377-9796; Email: jzhang@uidaho.edu

Authors

- Jinchao Ma Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States; Zhuhai Institute of Advanced Technology Chinese Academy of Sciences, Biomaterials Research Center, Zhuhai 519003, China
- Gregory H. Imler Naval Research Laboratory, Washington, D.C. 20375, United States; Occid.org/0000-0002-9686-9186
- **Damon A. Parrish** Naval Research Laboratory, Washington, D.C. 20375, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01569

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Office of Naval Research (N00014-16-1-2089) and the Defense Threat Reduction Agency (HDTRA 1-15-1-0028).

Organic Letters

REFERENCES

- (1) Gao, H.; Zhang, Q.; Shreeve, J. M. J. Mater. Chem. A 2020, 8, 4193-4216.
- (2) Wang, P.; Xu, Y.; Lin, Q.; Lu, M. Chem. Soc. Rev. 2018, 47, 7522-7538.
- (3) Lewczuk, R. Propellants, Explos., Pyrotech. 2018, 43, 436-444.

(4) He, P.; Zhang, J.; Yin, X.; Wu, J.; Wu, L.; Zhou, Z.; Zhang, T. Chem. - Eur. J. 2016, 22, 7670–85.

(5) Zhang, W.; Zhang, J.; Deng, M.; Qi, X.; Nie, F.; Zhang, Q. Nat. Commun. 2017, 8, 181.

(6) Hu, L.; Yin, P.; Zhao, G.; He, C.; Imler, G. H.; Parrish, D. A.; Gao, H.; Shreeve, J. M. J. Am. Chem. Soc. 2018, 140, 15001–15007.

(7) Barton, L. M.; Edwards, J. T.; Johnson, E. C.; Bukowski, E. J.; Sausa, R. C.; Byrd, E. F. C.; Orlicki, J. A.; Sabatini, J. J.; Baran, P. S. J.

 Am. Chem. Soc. 2019, 141, 12531–12535.

(8) Tang, Y.; Huang, W.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. J. Am. Chem. Soc. 2020, 142, 7153–7160.

(9) Song, S.; Wang, Y.; Wang, K.; Chen, F.; Zhang, Q. J. Mater. Chem. A 2020, 8, 5975-5985.

(10) Xu, Y.; Tian, L.; Li, D.; Wang, P.; Lu, M. J. Mater. Chem. A **2019**, 7, 12468–12479.

(11) Huang, C.; Yang, Z.; Li, Y.; Zheng, B.; Yan, Q.; Guan, L.; Luo, G.; Li, S.; Nie, F. Chem. Eng. J. 2020, 383, 383.

(12) Fischer, D.; Klapötke, T. M.; Reymann, M.; Stierstorfer, J.; Völkl, M. B. R. New J. Chem. 2015, 39, 1619–1627.

- (13) Yu, Q.; Yin, P.; Zhang, J.; He, C.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. J. Am. Chem. Soc. **2017**, *139*, 8816–8819.
- (14) Fu, Z.; Su, R.; Wang, Y.; Wang, Y. F.; Zeng, W.; Xiao, N.; Wu, Y.; Zhou, Z.; Chen, J.; Chen, F. X. *Chem. Eur. J.* **2012**, *18*, 1886–9.
- (15) Yan, C.; Wang, K.; Liu, T.; Yang, H.; Cheng, G.; Zhang, Q. Dalton Trans 2017, 46, 14210–14218.
- (16) Wei, H.; He, C.; Zhang, J.; Shreeve, J. M. Angew. Chem., Int. Ed. 2015, 54, 9367-9371.

(17) Xiong, H.; Yang, H.; Lei, C.; Yang, P.; Hu, W.; Cheng, G. Dalton Trans 2019, 48, 14705-14711.

(18) Lu, T.; Wang, C.; Wang, G.; Wang, S.; Song, J.; Yin, H.; Fan, G.; Chen, F. New J. Chem. **2019**, 43, 13330–13333.

- (19) Yu, Q.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Chem. Eur. J. 2017, 23, 17682–17686.
- (20) Dacons, J. C.; Sitzmann, M. E. J. J. Heterocycl. Chem. 1977, 14, 1151–1155.
- (21) Klapötke, T. M.; Witkowski, T. G. ChemPlusChem 2016, 81, 357–360.

(22) Lei, C.; Yang, H.; Cheng, G. Dalton Trans 2020, 49, 1660-1667.

(23) Ma, J.; Tang, J.; Yang, H.; Yi, Z.; Wu, G.; Zhu, S.; Zhang, W.;

Li, Y.; Cheng, G. ACS Appl. Mater. Interfaces 2019, 11, 26053-26059.

(24) Zhang, J.; Zhang, J.; Parrish, D. A.; Shreeve, J. M. J. Mater. Chem. A 2018, 6, 22705-22712.

(25) Liu, T.; Liao, S.; Song, S.; Wang, K.; Jin, Y.; Zhang, Q. Chem. Commun. 2020, 56, 209–212.

(26) Liu, Z.; Fang, L.; Zhang, H.; Gou, S.; Chen, Li. Bioorg. Med. Chem. 2017, 25, 2387–2398.

- (27) Kübel, B. Monatsh. Chem. 1982, 113, 793-803.
- (28) Yin, P.; Zhang, J.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Angew. Chem., Int. Ed. 2017, 56, 8834–8838.
- (29) Piercey, D. G.; Chavez, D. E.; Scott, B. L.; Imler, G. H.; Parrish, D. A. Angew. Chem., Int. Ed. **2016**, 55, 15315–15318.
- (30) Politzer, P.; Murray, J. S. J. Mol. Model. 2014, 20, 2223.
- (31) Politzer, P.; Murray, J. S. J. Mol. Model. 2015, 21, 25.

(32) Zeman, S.; Liu, N.; Jungová, M.; Hussein, A. K.; Yan, Q.-L. Defence Technology **2018**, *14*, 93–98.

(33) Sun, Q.; Shen, C.; Li, X.; Lin, Q.; Lu, M. Cryst. Growth Des. 2017, 17, 6105–6110.

- (34) Bellamy, A. J. Struct. Bonding (Berlin) 2007, 125, 1.
- (35) Gao, H.; Shreeve, J. M. Angew. Chem., Int. Ed. 2015, 54, 6335–6338.
- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.;

Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanavakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision E.01; Gaussian, Inc.: Wallingford, CT, 2003.

(37) Súceska, M. *EXPLOS* 6.01; Brodarski Institute: Zagreb, Croatia, 2013.

(38) United Nations. Recommendations on the Transport of Dangerous Goods. *Manual of Tests and Criteria*, 5th rev. ed.; United Nations Publication: New York, 2009.