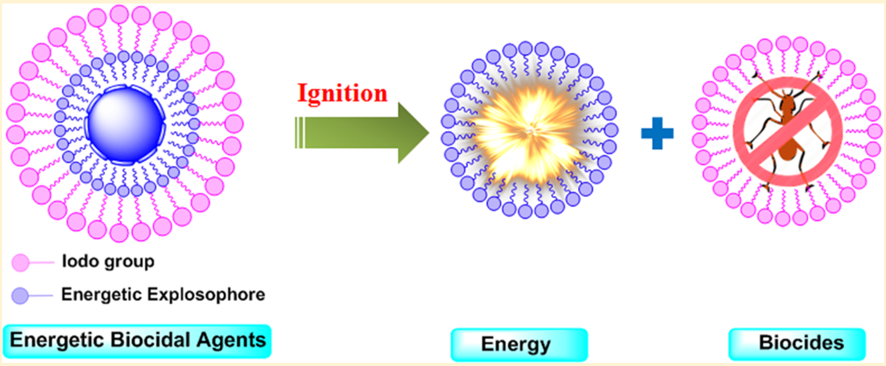
Inorganic Chemistry
Article
Cite This: *Inorg. Chem.* XXXX, XXX, XXX-XXX
pubs.acs.org/IC

Energy and Biocides Storage Compounds: Synthesis and Characterization of Energetic Bridged Bis(triiodoazoles)

Chunlin He,[†] Gang Zhao,[†] Joseph P. Hooper,[‡] and Jean'ne M. Shreeve*[,†]

[†]Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States
[‡]Department of Physics, Naval Postgraduate School, Monterey, California 93943, United States

Supporting Information



ABSTRACT: Energetic bridged triiodopyrazoles and triiodoimidazoles were designed and synthsized by reacting potassium triiodopyrazolate or triiodoimidazolate with corresponding dichloro compounds. All compounds were fully characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analyses. The structure of compound **1** was further confirmed by single-crystal X-ray diffraction. All of the compounds exhibit good thermal stability with decomposition temperatures between 199 and 270 °C and high densities ranging from 2.804 to 3.358 g/cm^3. The detonation performances and the detonation products were calculated by CHEETAH 7. Compound **3** (D_v = 4765 m s^{-1}; P = 17.9 GPa) and compound **7** (D_v = 4841 m s^{-1}; P = 18.5 GPa) show comparable detonation pressure to TNT, and high iodine content makes them promising as energy and biocides storage compounds.

INTRODUCTION

Ongoing threats of bioterrorism highlight the need for Agent Defeat Weapons (ADWs), which can be used not only to eliminate weapons of mass destruction (WMD) in the target but also to destroy or neutralize the active agents released. However, the conventional warheads, which rely on a "thermal kill" mechanism, have limited destructive impact on biological agents while the blast could also have the undesirable effect of airborne dispersal of the biological agents. Thus, it is appropriate to design a new class of materials which could defeat a biological weapon effectively. The preferred materials should have the capacity to store both energy and biocides and release them upon ignition. The energy released will destroy a storage facility and the biocides released can destroy or neutralize the active agents.

Recently, the study of novel energetic biocidal agents has attracted increasing interest among researchers.[1−8] Iodine exhibits high efficiency in killing certain bacteria, amoebic cysts, and viruses.[9] Since iodine-rich compounds which can release iodine upon decomposition or detonation are of increasing interest as potential ingredient candidates for ADWs, many were developed by our research group in the past few years (Figure 1).[4,10−13] Such compounds produce nearly quantitative amounts of gaseous iodine (I_2) upon detonation; therefore, active agents can be neutralized or destroyed effectively.

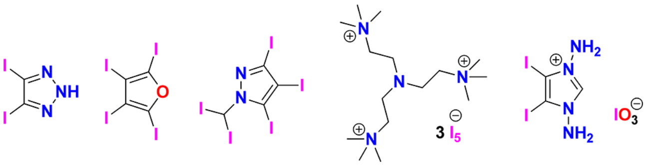


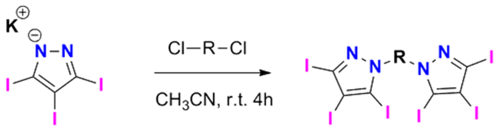
Figure 1. Previously synthesized iodine-rich compounds.

While high iodine content is beneficial for increasing the killing efficiency of biological agents, it also results in a low energy content which may be insufficient to destroy ADWs. The introduction of an energetic explosophore into a molecule should improve the energy level of the target biocidal agents. One strategy often used is partial replacement of iodo groups in the molecules;[10,11] however, due to a limited number of iodo groups in aromatic rings, the substitution of iodine with a nitro

Received: September 4, 2017

DOI: 10.1021/acs.inorgchem.7b02277

Table 1. Synthesis of Energetic Bridged Triiodopyrazoles, 1−4



1 - 4

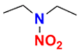
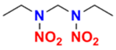
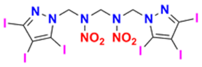
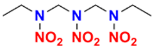
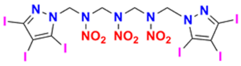
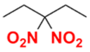
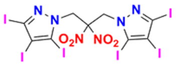
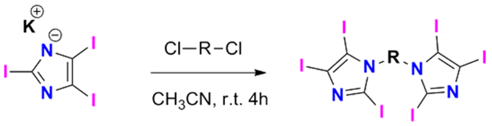
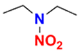
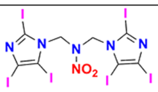
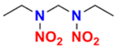
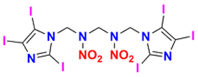
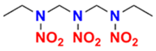
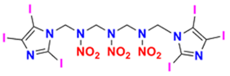
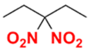
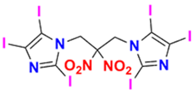
Entry	R	Compounds	Yield (%)
1			82%
2			76%
3			85%
4			63%

Table 2. Synthesis of Energetic Bridged Triiodoimidazoles, 5−8



5 - 8

Entry	R	Compounds	Yield (%)
5			80%
6			70%
7			71%
8			58%

group also decreases iodine content dramatically. The linkage of triiodopyrazole or triiodoimidazole with energetic groups can improve the energy of the molecule and maintain the iodine content at a high level. Inspired by the good thermal stability and detonation performances of nitramine-linked 1,2,4-triazoles, imidazoles, and pyrazoles,[14,15] a series of triiodopyrazoles or triiodoimidazoles linked by 2-nitrazapropane, 2,4-nitrazapentane, 2,4,6-trinitro-2,4,6-triazaheptane, or 2,2-dinitropropane moieties were synthesized. These new compounds provide an efficacious method to store both energy and biocides.

■ RESULTS AND DISCUSSION

Synthesis. Potassium triiodopyrazolate or triiodoimidazolate was prepared *in situ* by reacting a suspension of triiodopyrazole or triiodoimidazole with potassium hydroxide in acetonitrile until a clear solution was achieved. The dichloro compounds, 1,3-dichloro-2-nitrazapropane,[16] 1,5-dichloro-2,4,-nitrazapentane,[17] 1,7-dichloro-2,4,6-trinitro-2,4,6-triazaheptane,[18] and 1,3-dichloro-2,2-dinitropropane,[19] were synthesized according to known methods. The energetic-bridged triiodopyrazoles or triiodoimidazoles (**1**−**8**) were synthesized by adding the dichloro compounds to acetonitrile solution of potassium triiodopyrazolate or triiodoimidazolate, respectively. The reaction mixture was stirred for 4 h at room temperature;

the precipitate was collected by filtration and washed with acetonitrile and water to give the desired product in moderate yield (Tables 1 and 2).

NMR Spectroscopy. All of the new compounds were characterized by ^{1}H and ^{13}C{^{1}H} spectroscopy with [D$_6$]DMSO as solvent. The resonance bands of the protons were observed in the range from 5.46 to 6.24 ppm. In the ^{13}C {^{1}H} NMR spectra, chemical shifts for the methylene group are found between 56.65 and 66.12 ppm. Three peaks were observed for the carbon atoms bonded to iodine, ranging between 88.51 and 110.71 ppm on the pyrazole ring and between 86.59 and 101.03 ppm on the imidazole ring, respectively.

Single-Crystal X-ray Analysis. Suitable single colorless plate crystals were grown by dissolving **1** in THF and the solvent slowly evaporated at room temperature. Compound **1** crystallizes in the monoclinic $P2_1/c$ space group with four formula units per unit cell; its calculated density is 3.413 g cm^{-3} at 173(2) K. The crystal structure of **1** is shown in Figure. 2. All of the bond lengths and angles are in the expected range reported for triiodopyrazole compounds.[7] The crystallographic data and refinement details as well as the packing diagrams are given in the Supporting Information.

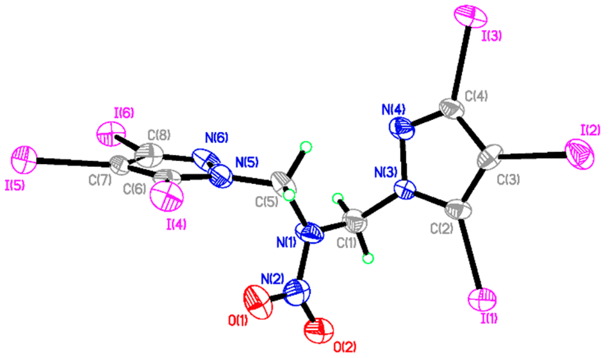


Figure 2. Crystal structure of **1**; thermal ellipsoids are drawn at the 50% probability level.

Thermal Stability. All of the compounds are thermally stabile with decomposition temperatures ranging between 199.4 and 270.2 °C. Introduction of the energetic bridges causes a slight decrease in thermal stability compared to 3,4,5-triiodopyrazole[13] (T_{dec} 282 °C) or 2,4,5-triiodoimidazole[13] (T_{dec} 252 °C). The nitro-aza bridged bistriiodopyrazoles (**1**−**3**) melt before decomposing, while the other compounds decompose without melting (Table 3).

Heat of Formation. The heats of formation were calculated using the Gaussian 03 (Revision E.01) program[20] suite based on isodesmic reactions. For the calculation of iodine compounds, the (15s, 11p, 6d) basis of Stromberg et al.[21] was augmented with another p shell and the five valence sp exponents optimized, resulting in a [5211111111, 411111111, 3111] contraction scheme in conjunction with 6-31+G** for first- and second-row elements. Single point energy (SPE) refinement on the optimized geometries was performed with the use of the MP2/6-311++G** level. The heat of sublimation was calculated based on Trouton's rule[22] by using the equation $\Delta H_{sub} = 0.188 \times T$. Heats of formation for compounds **1**−**8** are in the range between +797.1 (**5**) and +1508.1 kJ mol^{-1} (**3**). The bistriiodopyrazole analogues have slightly higher heats of formation compared to the corresponding bistriiodoimidazoles.

Sensitivities and Detonation Performances. The impact sensitivities were measured using a BAM drop hammer, and the detonation properties were calculated with CHEETAH 7[23] by using the calculated heat of formation and measured density as shown in Table 3. Compounds **1** and **2** have the lowest sensitivity toward impact (10J), and **8** has the highest sensitivity toward impact (4J). The detonation velocities and pressures range from 3767 to 4841 m/s and 9.4 to 18.5 GPa, respectively. Because of the higher densities of bistriimidazoles, slightly higher detonation performances are found compared to their bistriiodopyrazole analogues. An increase in the number of N-NO$_2$ groups aids in improving the energy of the compounds. Compounds **3** (D_v: 4765 m/s, P: 17.9 GPa) and **7** (D_v: 4841 m/s, P: 18.5 GPa) are the most powerful in this series; their detonation pressures are comparable to that of TNT (P: 19.53 GPa).

Detonation Products. In order to determine the ability of these new materials to destroy active agents, the detonation products of **1**−**8** were calculated by using CHEETAH 7 thermochemical code. The major detonation products are listed in Table 4. The bistriiodoimidazole and bistriiodopyrazole isomers release the same major composition of products upon detonation. All of the iodine in these molecules is converted to I$_2$ and HI after ignition (Figure 3), which indicates high efficiency as biocidal agents.

■ CONCLUSIONS

In summary, a series of energetic bridged triiodoimidazoles and triiodopyrazoles were designed and synthesized. Their structures were fully characterized by ^{1}H, ^{13}C NMR, infrared, and elemental analyses. The structure of **1** was determined by single-crystal X-ray diffraction. The combination of an energetic

Table 3. Physicochemical Properties of Compounds 1−8

compd	T_d[a] (°C)	d[b] (g/cm^3)	ΔH_f°[c] (kJ/mol)	D_v[d] (m/s)	P[e] (Gpa)	% iodine	IS[f] (J)
1	220.0[g]/270.2	3.265	864.8	3767	9.5	77.89	10
2	242.0[g]/243.9	2.941	1164.6	4321	12.4	72.40	10
3	239.3[g]/244.6	2.804	1508.1	4765	17.9	67.64	8
4	218.1	2.920	858.6	3818	9.4	74.53	5
5	199.4	3.358	797.1	3840	9.9	77.89	9
6	220.8	3.021	1129.3	4409	13.1	72.40	5
7	234.3	2.851	1436.1	4841	18.5	67.64	5
8	205.0	2.983	822.5	3869	9.8	74.53	4
TNT	80.4[g]/ 295	1.65	−31.70	6881	19.53	0	15

[a] Decomposition temperature (onset). [b] Measured density at 25 °C. [c] Calculated heat of formation. [d] Detonation velocity calculated with CHEETAH 7. [e] Detonation pressure calculated with CHEETAH 7. [f] Impact sensitivity measured via BAM method. [g] Melting point.

Table 4. Calculated Major Decomposition Products (in Weight Percent) at T = 298 K, P = 1 atm

compd	N_2 (g)	I_2 (g)	HI (g)	C (s)	CH_4 (g)	CO_2 (g)
1	8.6	77.11	0.78	7.39	1.61	4.49
2	10.66	71.54	0.86	6.31	2.25	8.35
3	12.44	66.73	0.91	5.37	2.82	11.71
4	8.22	73.76	0.77	7.08	1.54	8.60
5	8.6	77.11	0.78	7.39	1.61	4.49
6	10.66	71.54	0.86	6.31	2.25	8.35
7	12.44	66.73	0.91	5.37	2.82	11.71
8	8.22	73.76	0.77	7.08	1.54	8.60

bridge with an iodine-rich aromatic compound provides an efficient way for the storage of both energy and biocide. Compounds **3** and **7** exhibit detonation performances comparable with that of TNT, suggesting great potential as ingredient candidates as biocidal agents.

EXPERIMENTAL SECTION

General Methods. Reagents purchased from Aldrich, Acros Organics, and AK Scientific were used as received. ^1H and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively. Chemical shifts in the ^{13}C spectra are reported relative to Me_4Si. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q20) at a heating rate of 5 °C/min. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet AVATAR 370 FTIR. Densities were determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer or Elmentar vario MICRO cube elemental analyzer. Impact sensitivity measurements were made using a standard BAM Fallhammer.

The starting materials 3,4,5-triiodopyrazole,[7] 2,4,5-triiodoimidazole,[24] 1,3-dichloro-2-nitrazapropane,[16] 1,5-dichloro-2,4,-2,4-nitrazapentane,[17] 1,7-dichloro-2,4,6-trinitro-2,4,6-triazaheptane,[18] and 1,3-dichloro-2,2-dinitropropane[19] were prepared according to the literature.

General Procedures to Synthesize Energetic-Bridged Triiodazoles. To a suspension of triiodopyrazole or triiodoimidazole (0.98 g, 2.2 mmol) in acetonitrile (10 mL) was added potassium hydroxide (0.14 g, 2.5 mmol). With stirring, the suspension slowly became a clear solution. After stirring for another 10 min, the solution was filtered to remove the excess potassium hydroxide, and the filtrate was transferred into a 25 mL round-bottom flask. The dichloro compound (1 mmol) in acetonitrile (5 mL) was added in one portion. The reaction mixture was stirred for 4 h at room temperature. The precipitate formed was collected by filtration, washed with acetonitrile (2 mL), and then with water (2 mL). The solid was air-dried to give the target compound.

1,3-Bis(3,4,5-triiodopyrazolyl)-2-nitrazapropane (**1**). Yield: 82%. M.P. 242.0 °C; T_{dec}: 243.9 °C; IR (cm^{-1}) ν = 3036, 3002, 1545, 1436, 1406, 1364, 1306, 1292, 1277, 1243, 1228, 1172, 1097, 1024, 975, 943, 859, 778, 748, 672, 648, 614, 497; ^1H NMR (DMSO-d6): 6.24 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 65.51, 88.84, 99.62; 110.52. EA ($C_8H_4I_6N_6O_2$, 977.58): Calcd, C: 9.83; H: 0.41; N: 8.60; Found, C: 9.87; H: 0.47; N: 8.52.

1,5-Bis(3,4,5-triiodopyrazolyl)-2,4-nitrazapentane (**2**). Yield: 76%. M.P. 220.0 °C; T_{dec}: 270.4 °C; IR (cm^{-1}) ν = 3030, 2917, 1562, 1547, 1436, 1409, 1397, 1316, 1273, 1243, 1220, 1168, 1117, 1064, 1021, 975, 924, 868, 759, 650, 632, 605, 477; ^1H NMR (DMSO-d6): 6.07 (2H, s, CH_2); 6.20 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 64.66, 66.01, 88.51, 99.52; 110.42. EA ($C_9H_6I_6N_8O_4$, 1051.62): Calcd, C: 10.28; H: 0.58; N: 10.66; Found, C: 10.32; H: 0.55; N: 10.56.

1,7-Bis(3,4,5-triiodopyrazolyl)-2,4,6-trinitro-2,4,6-triazaheptane (**3**). Yield: 85%. M.P. 239.3 °C; T_{dec}: 244.6 °C; IR (cm^{-1}) ν = 3032, 1560, 1437, 1409, 1315, 1273, 1230, 1168, 1135, 1088, 1021, 974, 928, 857, 762, 709, 643, 619, 606; ^1H NMR (DMSO-d6): 5.98 (4H, s, CH_2); 6.20 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 64.51, 66.04, 88.52, 100.06; 110.71. EA ($C_{10}H_8I_6N_{10}O_6$, 1125.66): Calcd, C: 10.67; H: 0.72; N: 12.44; Found, C: 10.24; H: 0.56; N: 12.14.

1,3-Bis(3,4,5-triiodopyrazolyl)-2,2-dinitropropane (**4**). Yield: 63%. T_{dec}: 218.1 °C; IR (cm^{-1}) ν = 3190, 2845, 1680, 1631, 1566, 1541, 1504, 1460, 1422, 1339, 1284, 1193, 1154, 1143, 1106, 1066, 1034, 1004, 975, 943, 755, 706, 669, 538; ^1H NMR (DMSO-d6): 5.60 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 53.23, 85.97, 97.27; 106.88; 130.69. EA ($C_9H_4I_6N_6O_4$, 1021.59): Calcd, C: 10.58; H: 0.39; N: 8.23; Found, C: 10.36; H: 0.45; N: 8.13.

1,3-Bis(2,4,5-triiodoimidazolyl)-2-nitrazapropane (**5**). Yield: 80%. T_{dec}: 199.4 °C; IR (cm^{-1}) ν = 2999, 2921, 1561, 1452, 1388, 1277, 1247, 1174, 1114, 962, 767, 658; ^1H NMR (DMSO-d6): 6.04 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 64.62, 87.84, 96.93, 101.03; EA ($C_8H_4I_6N_6O_2$, 977.58): Calcd, C: 9.83; H: 0.41; N: 8.60; Found, C: 10.07; H: 0.46; N: 8.73.

1,5-Bis(2,4,5-triiodoimidazolyl)-2,4-nitrazapentane (**6**). Yield: 70%. T_{dec}: 220.8 °C; IR (cm^{-1}) ν = 3019, 2917, 1561, 1439, 1421, 1390, 1316, 1282, 1176, 1121, 1100, 962, 927, 859, 769, 657, 629; ^1H

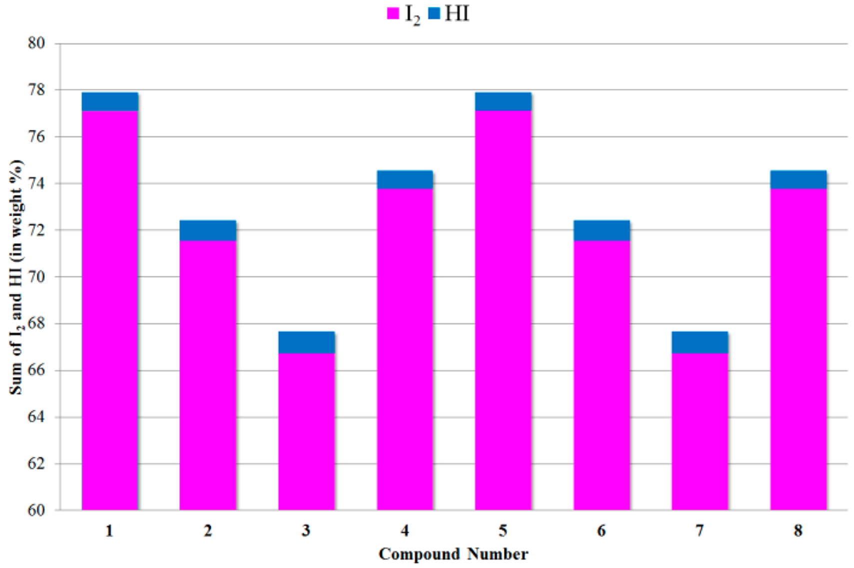


Figure 3. Sum of I_2 and HI in the decomposition products (weight percent).

DOI: 10.1021/acs.inorgchem.7b02277
Inorg. Chem. XXXX, XXX, XXX−XXX

NMR (DMSO-d6): 6.05 (4H, s, CH_2); 6.08 (2H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 65.42, 68.09, 88.36, 96.98; 100.22. EA ($C_9H_6I_6N_8O_4$, 1051.62): Calcd, C: 10.28; H: 0.58; N: 10.66; Found, C: 10.08; H: 0.54; N: 10.20.

1,7-Bis(2,4,5-triiodoimidazolyl)-2,4,6-trinitro-2,4,6-triazaheptane (***7***). Yield: 71%. M.P. T_{dec}: 234.3 °C; IR (cm^{-1}) ν = 3015, 2925, 1561, 1443, 1390, 1278, 1174, 1136, 1105, 969, 927, 763, 610; ^1H NMR (DMSO-d6): 5.94 (4H, s, CH_2); 6.02 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 65.47, 66.12, 87.78, 96.60; 100.29. EA ($C_{10}H_8I_6N_{10}O_6$, 1125.66): Calcd, C: 10.67; H: 0.72; N: 12.44; Found, C: 10.98; H: 0.63; N: 12.85.

1,3-Bis(2,4,5-triiodoimidazolyl)-2,2-dinitropropane (***8***). Yield: 58%. T_{dec}: 205.0 °C; IR (cm^{-1}) ν = 2983, 2925, 1476, 1435, 1413, 1360, 1313, 1249, 1189, 1139, 963, 763, 726, 704, 619; ^1H NMR (DMSO-d6): 5.46 (4H, s, CH_2); ^{13}C NMR (DMSO-d6): δ 50.65, 86.59; 94.92, 98.62, 130.04. EA ($C_9H_4I_6N_6O_4$, 1021.59): Calcd, C: 10.58; H: 0.39; N: 8.23; Found, C: 9.07; H: 0.43; N: 7.19.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02277.

> X-ray crystal diffraction data and crystal structures for compound **1**, NMR spectra, crystallographic data, Gaussian calculations (PDF)

Accession Codes

CCDC 1561448 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 Author

*E-mail: jshreeve@uidaho.edu.

ORCID

Joseph P. Hooper: 0000-0003-4899-1934
Jean'ne M. Shreeve: 0000-0001-8622-4897

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (N00014-16-1-2089) and the Defense Threat Reduction Agency (HDTRA 1-15-1-0028). The authors thank the M. J. Murdock Charitable Trust, Vancouver, WA (Reference No.: 2014120: MNL:11/20/2014), for funds to purchase a 500 MHz NMR spectrometer. We are indebted to Dr. Richard Staples for crystal structure.

■ DEDICATION

Remembering Professor Malcolm MacKenzie Renfrew.

■ REFERENCES

(1) Knott, A.; Stamatis, D.; Svingala, F.; Lightstone, J.; Miller, K.; Bensman, M.; Bohmke, M. Subscale testing of prompt agent defeat formulations. *AIP Conf. Proc.* **2015**, *1793*, 040035.

(2) Wang, S.; Schoenitz, M.; Dreizin, E. L. Mechanically alloyed magnesium−boron−iodine composite powders. *J. Mater. Sci.* **2016**, *51*, 3585−3591.

(3) Wang, S.; Abraham, A.; Zhong, Z.; Schoenitz, M.; Dreizin, E. L. Ignition and combustion of boron-based Al·B·I_2 and Mg·B·I_2 composites. *Chem. Eng. J.* **2016**, *293*, 112−117.

(4) He, C.; Hooper, J. P.; Shreeve, J. M. Iodine-Rich imidazolium iodate and periodate salts: en route to single-Based biocidal agents. *Inorg. Chem.* **2016**, *55*, 12844−12850.

(5) Bennion, J. C.; Vogt, L.; Tuckerman, M. E.; Matzger, A. J. Isostructural cocrystals of 1,3,5-trinitrobenzene assembled by halogen bonding. *Cryst. Growth Des.* **2016**, *16*, 4688−4693.

(6) Wang, H.; Jian, G.; Zhou, W.; DeLisio, J. B.; Lee, V. T.; Zachariah, M. R. Metal iodate-based energetic composites and their combustion and biocidal performance. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17363−17370.

(7) Chand, D.; Shreeve, J. M. Versatile polyiodopyrazoles: synthesis and biocidal promise. *Chem. Commun.* **2015**, *51*, 3438−3441.

(8) Fischer, D.; Klapötke, T. M.; Stierstorfer, J. Synthesis and characterization of guanidinium difluoroiodate, $[C(NH_2)_3]^+[IF_2O_2]^-$ and its evaluation as an ingredient in agent defeat weapons. *Z. Anorg. Allg. Chem.* **2011**, *637*, 660−665.

(9) Kaiho, T. *Iodine Chemistry and Applications*; John Wiley & Sons, Inc.: New York, 2015.

(10) Chand, D.; He, C.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Electrophilic iodination: a gateway to high iodine compounds and energetic materials. *Dalton Trans.* **2016**, *45*, 13827−13833.

(11) Chand, D.; He, C.; Hooper, J. P.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Mono- and diiodo-1,2,3-triazoles and their mono nitro derivatives. *Dalton Trans.* **2016**, *45*, 9684−9688.

(12) He, C.; Parrish, D. A.; Shreeve, J. M. Alkyl ammonium cation stabilized biocidal polyiodides with adaptable high density and low pressure. *Chem. - Eur. J.* **2014**, *20*, 6699−6706.

(13) He, C.; Zhang, J.; Shreeve, J. M. Dense iodine-rich compounds with low detonation pressures as biocidal agents. *Chem. - Eur. J.* **2013**, *19*, 7503−7509.

(14) Klapötke, T. M.; Penger, A.; Pflüger, C.; Stierstorfer, J.; Sućeska, M. Advanced open-chain nitramines as energetic materials: heterocyclic-substituted 1,3-dichloro-2-nitrazapropane. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4667−4678.

(15) Zhang, J.; He, C.; Parrish, D. A.; Shreeve, J. M. Nitramines with varying sensitivities: functionalized dipyrazolyl- N-nitromethanamines as energetic materials. *Chem. - Eur. J.* **2013**, *19*, 8929−8936.

(16) Il'yasov, S. G.; Danilova, E. O. Preparation of 1,3-diazido-2-nitro-2-azapropane from urea. *Propellants, Explos., Pyrotech.* **2012**, *37*, 427−431.

(17) Highsmith, T. K.; Hanks, J. M.; Velarde, S. P.; Bottaro, J. C. Process for the synthesis and recovery of nitramines. Patent WO2002060881A1, 2002.

(18) Klapötke, T. M.; Krumm, B.; Steemann, F. X. Preparation, characterization, and sensitivity data of some azidomethyl nitramines. *Propellants, Explos., Pyrotech.* **2009**, *34*, 13−23.

(19) Borgardt, F. G.; Seeler, A. K.; Noble, P. Aliphatic polynitro compounds. I. synthesis of 1,1,1-trinitrochloroethane and its rearrangement to dipotassium tetranitroethane. *J. Org. Chem.* **1966**, *31*, 2806−2811.

(20) 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.; Nanayakkara, 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, 2004.

(21) Strömberg, A.; Gropen, O.; Wahlgren, U. Gaussian basis sets for the fourth-row main group elements, In−Xe. *J. Comput. Chem.* **1983**, *4*, 181.

(22) Westwell, M. S.; Searle, M. S.; Wales, D. J.; Williams, D. H. Empirical correlations between thermodynamic properties and intermolecular forces. *J. Am. Chem. Soc.* **1995**, *117*, 5013−5015.

(23) Bastea, S.; Fried, L. E.; Glaeseman, K. R.; Howard, W. M.; Kuo, I. F. W.; Souers, P. C.; Vitello, P. A. *Cheetah 7.0 thermochemical code*; Lawrence Livermore National Laboratory: Livermore, CA; 2012.

(24) Katritzky, A. R.; Cundy, D. J.; Chen, J. Polyiodoimidazoles and their nitration products. *J. Energ. Mater.* **1993**, *11*, 345−352.