

Dense Iodine-Rich Compounds with Low Detonation Pressures as Biocidal Agents

Chunlin He, Jiaheng Zhang, and Jean'ne M Shreeve*^[a]

Abstract: Fifteen iodo compounds and six iodyl compounds with an iodine content between 45.3 and 89.0% were prepared. The mono, di, and triiodyl compounds were obtained from the corresponding iodo compound by employing Oxone. All the compounds were characterized by IR, ¹H and ¹³C NMR, elemental analysis, and differential scanning calorimetry (DSC). The impact sensitivity was measured by

using BAM (Bundesamt für Materialforschung) methodology. Based on the calculated heats of formation and experimental densities, the detonation properties and detonation products were predicted by employing Chee-

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tah 6.0. A total percentage of iodine-containing species in wt % (I₂, HI, and I in gas phase) ranged from 46.7 (**21**) to 88.94% (**11**) was found in the detonation products. The high concentration and easy accessibility of iodine and/or iodine-containing species is very important in developing materials suitable as Agent Defeat Weapons (ADWs).

Introduction

During the last few years, interest in developing Agent Defeat Weapons (ADWs) has grown to enable the minimization of the collateral damage arising from chemical and biological weapons.^[1] The low pressure and prolonged high-temperature detonations generated by ADWs destroy storage facilities and the bioagents therein, and, secondarily, utilize the materials arising from the blast to eradicate any harmful airborne agents, which may have resulted. It has been shown that hydroiodic acid (HI) and iodine (I₂) have strong biocidal activity against biological agents.^[2] Therefore, iodine-rich compounds, which could generate HI or I₂ upon detonation, are of interest as ingredient candidates for ADWs.

Polyiodo compounds, such as triiodoimidazole,^[3] tetraiodofuran,^[4] tetraiodopyrrole, and others, have high iodine content, high densities, and good thermal stabilities. However, there is no information about properties, such as impact sensitivity, heat of formation, and detonation properties. The expected low detonation pressures and low energy of these polyiodo compounds make them worthwhile candidates for ADWs (Figure 1).

The iodyl group (-IO₂) is an attractive functional group, which possesses a structure similar to that of the nitro group and which can be produced by oxidizing the corresponding

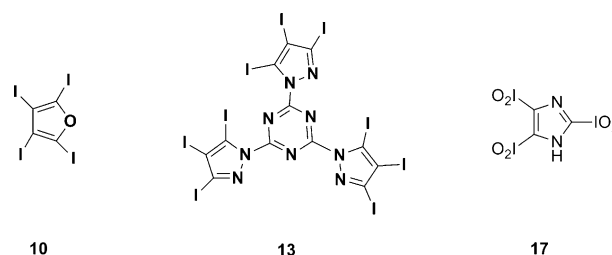


Figure 1. Iodo and iodyl compounds of interest as ADWs.

iodo compound. Iodyl compounds are likely to be more energetic than the corresponding iodo compounds. The densities of ammonium periodate^[5] ($\rho = 3.04 \text{ g cm}^{-3}$) and ammonium iodate ($\rho = 3.30 \text{ g cm}^{-3}$) suggest that such oxohalogen may exhibit useful attributes with higher densities than the perchlorates and also with great effectiveness toward bioagents and with less negative environmental impacts. However, most of the research concerning iodyl compounds is focused on the synthesis and applications of 2-iodylbenzoic acid (IBX) and its analogues based on the advantages provided by their selective, mild, and environmentally friendly properties as oxidizing agents in organic synthesis.^[6] Iodyl pyridines are the only N-heterocyclic iodyl compounds described in the literature to date.^[7] Iodyl-substituted imidazole or pyrazole-based compounds could be of interest because of their high densities and greater thermal stabilities. Although some explosions of iodyl compounds have been reported in the literature,^[8] these materials have not been studied systematically as energetic compounds.

The iodine-rich iodo and iodyl compounds could be interesting ingredient candidates for ADWs (Figure 1). In our continuing search for new energetic compounds, 15 iodo compounds and six iodyl compounds were synthesized by

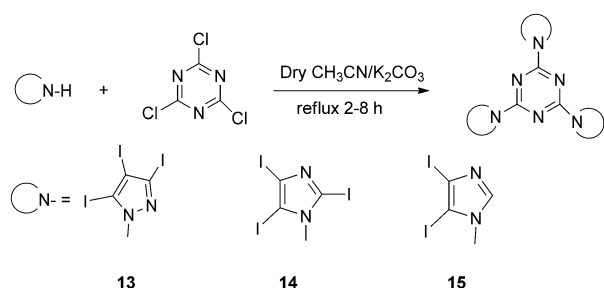
[a] Dr. C. He, J. Zhang, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
Fax: (+1)208-885-9146
E-mail: jshreeve@uidaho.edu

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using straightforward methods and characterized by IR, NMR, elemental analysis, and differential scanning calorimetry (DSC). Measuring densities and determining heats of formation made possible the calculation of detonation properties.

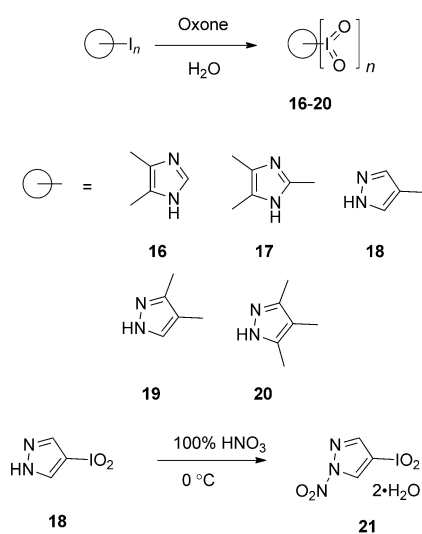
Results and Discussion

Mono-, di-, tri- and tetra-iodo-substituted compounds **1–11** were prepared based on the literature.^[3–4,9] For the preparation of **13–15**, the respective iodo compound (3.5 equiv) was heated at reflux with potassium carbonate (7.7 equiv) in dry CH₃CN under nitrogen for 1 h; then cyanuric chloride (1 equiv) was added, and the solution was heated at reflux for 2–8 h to complete the reaction (Scheme 1).



Scheme 1. Synthesis of compounds **13–15**.

The common oxidants that have been used for preparing iodyl compounds include sodium hypochlorite, sodium periodate, dimethyldioxirane, and Oxone (potassium peroxomonosulfate).^[10] Based on the low cost, commercial availability, good stability, simple handling, and nontoxic nature, Oxone was used in preparation of the iodyl compounds by using a modified method (Scheme 2).^[10b] Although oxidation






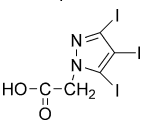



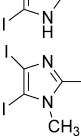



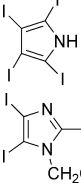
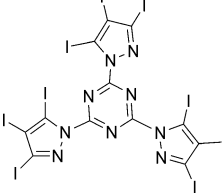
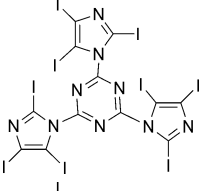
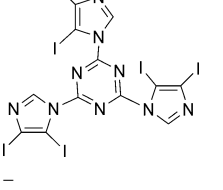
Scheme 2. Preparation of iodyl compounds.

of mono-iodo compounds can be accomplished in aqueous solution at room temperature by using 1.3 equiv Oxone, oxidation of poly-iodo compounds requires temperatures up to 70 °C and often extended reaction times to complete the reactions. All of the iodyl compounds are slightly or totally insoluble in water, which allows them to be precipitated and easily purified by washing with cold water. However, after striving to oxidize all of the 15 iodo compounds, only five iodyl compounds (**16–20**) were obtained successfully. The attempted oxidation reactions of the *N*-acetyl compounds (**4** and **12**), as well as of compounds **13–15** failed due to steric effects with the starting material being recovered; oxidation of **5** and **8** generated products with good solubility in water, which were difficult to isolate. The more energetic iodyl nitropyrazole compound **21** was synthesized by nitrating **18** by using 100% HNO₃ (see the Supporting Information). All of the iodo and iodyl compounds were characterized by IR, NMR, elemental analysis, and (DSC). NMR data were not obtained for **19** and **20** due to lack of solubility in any available solvent. Single crystals suitable for X-ray diffraction analysis were not obtained because solvents suitable for recrystallization could not be found.

Physical properties of the iodo and iodyl compounds are listed in Tables 1 and 2. All of the iodo compounds possess high iodine contents ranging from 65.4 to 89.0% and exhibit densities from 2.39 to 3.90 g cm⁻³. Increase of iodine atom numbers in single heterocyclic rings concomitantly results in increase of density. Iodopyrazoles are more dense than their imidazole analogues; all compounds exhibit good thermal stabilities (≥ 168 °C for **11**). Compounds **1–10** melt before they decompose thermally, whereas **11–15** decompose without melting. The thermal stabilities of trisubstituted triazine compounds (**13–15**) are superior relative to their parent iodo compounds due to their symmetric structures. Methyl derivatives have lower melting points and higher decomposition temperatures, whereas the presence of the carboxylic acid group gives rise to decreased thermal stability and density. The densities of iodyl compounds range between 2.54–3.68 g cm⁻³. Surprisingly, 4-iodopyrazole (**18**) has a higher density than its diiodo analogue, diiodopyrazole (**19**), which may arise from an intramolecular hydrogen bond between O10 and H5 (2.821 Å, Figure 3, dashed line) based on the optimized structure calculated by using the Gaussian 03 program. All iodyl compounds decomposed between 159–227 °C; triiodyl compound **20** is the least thermally stable, whereas compound **16** decomposes at 227 °C probably arising from hydrogen-bond formation as a result of the presence of water as the hemihydrate.

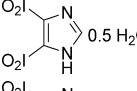
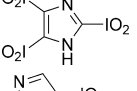
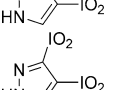
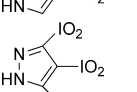
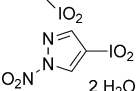
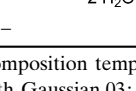
Impact-sensitivity (IS) measurements were made by using standard BAM techniques.^[11] All the iodo compounds have relatively low IS (≥ 28 J); however, the iodyl compounds have IS ranging between 2 to 40 J. Compound **16** showed an impact sensitivity lower than expected, which arises from the presence of water involved in extensive hydrogen-bond formations (Figure 2). Water of hydration in **21** also improves the IS to some extent. For pyrazole–iodyl derivatives, the greater the number of iodyl groups present in the com-

Table 1. Physical properties of iodo compounds.

Comp.	Structure	$T_m^{[a]}$ [°C]	$T_d^{[b]}$ [°C]	$\rho^{[c]}$ [g cm ⁻³]	$\Delta H_f^{[d]}$ [kJ mol ⁻¹]	ΔH_f° [kJ g ⁻¹]	OB ^[e] [%]	$D^{[f]}$ [m s ⁻¹]	$P^{[g]}$ [GPa]	Iodine [%]
1		109	229	2.48	337.3	1.74	-61.8	4210	9.46	65.4
2		160	290	3.14	400.3	1.25	-35.0	3475	7.63	79.4
3		220	282	3.38	461.1	1.03	-23.3	2859	5.32	85.4
4		237	247	3.27	396.4	0.79	-30.2	4049	11.41	75.6
5		137	220	2.39	288.0	1.48	-61.8	3912	7.82	65.4
6		197	233	3.09	351.9	1.10	-35.0	3298	6.68	79.4
7		191	252	3.27	416.0	0.93	-23.3	2646	4.37	85.4
8		153	318	3.26	477.0	1.04	-26.1	3137	6.35	82.8
9		204	397	3.94	547.1	0.93	-136.1	2304	4.03	86.4
10		163	261	3.83	341.0	0.60	-19.6	2417	4.29	88.8
11		[h]	168	3.62	449.9	0.79	-23.8	2253	3.27	89.0
12		[h]	180	3.00	360.6	0.72	-30.2	3658	8.74	75.6
13		[h]	355	3.30	2019.6	1.43	-27.2	3223	6.64	80.9
14		[h]	315	3.10	1881.3	1.33	-27.2	2894	5.07	80.8
15		[h]	386	3.05	1250.9	1.21	-39.4	3554	7.22	73.6
TNT	-	[h]	295	1.65	-67	-0.3	-31.7	6881	19.53	-

[a] Melting point; [b] decomposition temperature; [c] density measured by gas pycnometer (25°C); [d] heat of formation calculated with Gaussian 03; [e] oxygen balances; [f] calculated detonation velocities with Cheetah 6.0; [g] calculated detonation pressures with Cheetah 6.0; and [h] decompose before melting.

Table 2. Physical properties of iodyl compounds.

Comp.	Structure	$T_d^{[a]}$ [°C]	$\rho^{[b]}$ [g cm ⁻³]	$\Delta H_f^{[c]}$ [kJ mol ⁻¹]	ΔH_f° [kJ g ⁻¹]	OB ^[d] [%]	$D^{[e]}$ [m s ⁻¹]	$P^{[f]}$ [GPa]	Iodine [%]	IS ^[g] [J]
16	 0.5 H ₂ O	227	2.85	-388.8	-1.01	-12.2	4129	9.89	64.6	> 40
17		183	3.68	-669.3	-1.23	-1.5	4946	17.60	70.3	5
18		201	2.99	-24.2	-0.11	-24.8	5505	19.09	56.2	2
19		188	2.87	-336.9	-0.88	-12.5	4457	12.22	66.1	4
20		159	3.54	-647.3	-1.19	-1.5	4746	15.79	70.3	7
21	 2 H ₂ O	179	2.54	94.9	0.35	-15.6	6166	23.11	45.3	12
TNT	-	295	1.65	-67	-0.3	-31.7	6881	19.53	-	15

[a] Decomposition temperature; [b] density measured by gas pycnometer (25°C); [c] heat of formation calculated with Gaussian 03; [d] oxygen balances; [e] calculated detonation velocities with Cheetah 6.0; [f] calculated detonation pressures with Cheetah 6.0; and [g] impact sensitivities measured by BAM drophammer.

compound, the lower the impact sensitivity. Based on electrostatic-potential (ESP) calculations, **18** has wider and stronger positive potentials, and **20** has the weakest positive potentials compared to **18** and **19**, which suggests that **18** should be the most sensitive and **20**—the least sensitive to impact. The calculated results are in agreement with the experimental results. With the exception of **10** and **11**, which have impact sensitivities of 35 and 28 J, respectively, the ISs of all of the iodo compounds exceed 40 J (Tables 1 and 2).

The heats of formation for all the compounds were calculated by using Gaussian 03 program suite, by constructing

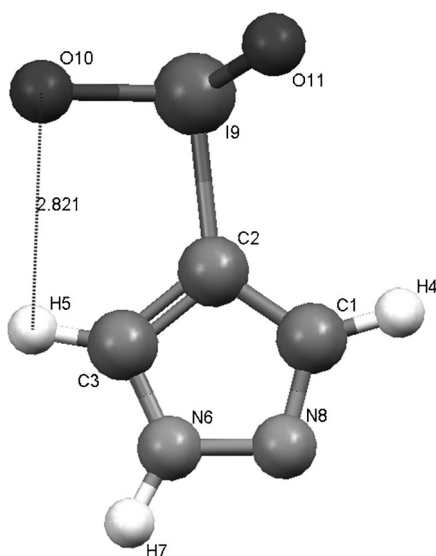


Figure 2. Intramolecular hydrogen bond in 4-iodopyrazole (B3LYP/6-31G+**).

isodesmic reactions, and are summarized in Tables 1 and 2.^[12] For iodine-containing species, the (15s, 11p, 6d) basis of Stromberg et al.^[13] 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 MP2/6-311++G** level. Corresponding iodine sets were constructed in MP2 method by using all-electron calculations and quasi-relativistic energy-adjusted spin-orbit-averaged seven-valence-elec-

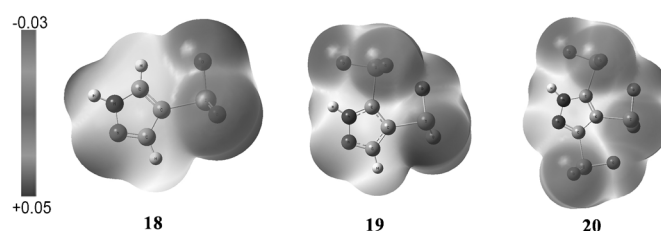


Figure 3. Electrostatic potentials (ESPs) of **18**, **19**, and **20** for the 0.001 electron bohr⁻³ ranging from -0.03 to +0.05 hartrees.

tron effective-core potentials (ECPs).^[14] The heat of formation of iodobenzene was calculated, and the results are in good agreement with the experimental data (see the Supporting Information). As shown in Table 1, all of the iodo compounds have positive heats of formation that range between 288.0–2019.6 kJ mol⁻¹. The heats of formation increase when the number of iodine atoms increases; each time an additional iodine atom was introduced into a pyrazole or imidazole ring, the heat of formation of the molecule increased by 62–64 kJ mol⁻¹. However, all of the iodyl compounds, except **21** with a positive value of 94.9 kJ mol⁻¹, exhibited negative heats of formation. The value became more negative with the increasing number of iodyl groups in the molecule. By using the calculated values of the heats of formation and the experimental values for the densities, the detonation velocities (D) and detonation pressures (P) were calculated by using the Cheetah 6.0 program. All the compounds have low detonation pressures, which range between 3.27 to 23.11 GPa and detonation velocities between 2253 to 6166 m s⁻¹. Except for **21**, which has detonation properties comparable to TNT, the other compounds exhibited low detonation pressures and velocities, which are desirable for

ADWs. However, the values of the detonation properties increase when the number of iodyl groups increases; introduction of a nitro group by N-nitration enhances the magnitude of the detonation properties markedly and also decreases the density to some extent.

The detonation products formed were predicted by using Cheetah 6.0 under Chapman–Jouguet condition and are listed in Table 3. After detonation, most iodine atoms in the

Table 3. Major detonation products of iodo or iodyl compounds [wt%, kg kg⁻¹].

Comp.	N ₂ [g]	I ₂ [g]	HI [g]	I [g]	C [s]	CO [g]	CO ₂ [g]
1	11.92	25.54	36.64	1.34	16.21	–	–
2	8.07	40.11	33.83	4.45	10.60	–	–
3	6.22	52.07	22.87	10.34	8.00	–	–
4	4.88	46.08	23.83	5.24	9.73	1.33	4.07
5	12.19	26.17	36.41	1.21	16.07	–	–
6	8.08	41.62	33.19	3.74	10.58	–	–
7	6.23	53.40	22.99	8.92	8.00	–	–
8	5.48	42.37	34.53	4.96	9.67	–	–
9	–	63.30	–	23.07	7.94	–	–
10	–	68.18	–	20.62	6.99	1.70	2.52
11	2.43	59.70	19.25	9.99	8.37	–	–
12	5.07	42.13	26.99	5.96	7.62	2.24	3.92
13	8.93	64.89	–	15.98	10.21	–	–
14	8.93	64.81	–	16.06	10.21	–	–
15	11.88	48.00	22.84	2.61	13.80	–	–
16	6.94	49.69	14.13	2.33	3.93	0.72	18.03
17	4.87	65.45	3.61	1.24	0.28	0.05	22.45
18	10.40	46.00	9.96	0.17	13.05	0.04	7.23
19	6.77	51.06	12.91	2.17	3.88	0.62	17.87
20	4.89	63.48	4.89	1.94	0.23	0.14	22.49
21	12.05	34.08	11.57	1.05	–	2.57	21.18

molecule were found to be I₂, HI, and I, which are strong biocides. The molecule with more hydrogen atoms formed a high weight percentage of HI. The species CO₂ and CO in wt% increased as a function of the increase in oxygen balance. The sum of iodine-containing species in wt% (I₂, HI, and I in gas phase) ranges between 46.7 (21) to 88.94% (11) as shown in Figure 4. The high percentage of those strong biocides in the detonation products makes them promising candidates for bioagent-defeat materials.

Conclusion

Fifteen iodo and six iodyl compounds were synthesized by using straightforward methods. All the compounds were characterized by IR, ¹H and ¹³C NMR, elemental analysis, and DSC. The detonation products together with physical and detonation properties were obtained. The uniquely high density, the high I₂, HI, and I concentrations present in the detonation products, and the low detonation pressures make these materials promising candidates for ingredients in ADWs. Compound 16 might be used as an oxidant in organic synthesis due to its insensitive properties. The iodyl compounds, which have high densities, good thermal stabilities, and IS properties could be considered as primary explosives.

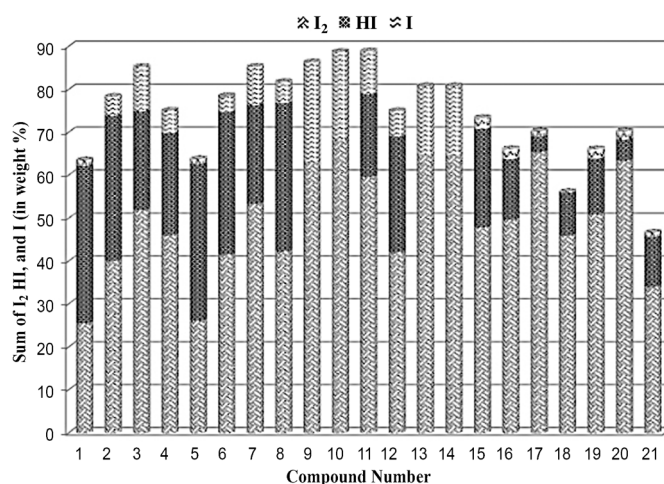


Figure 4. The sum of iodine-containing species in the detonation products (weight percent).

Experimental Section

CAUTION!!! Although no problems have been encountered during these syntheses, all the iodyl compounds described herein are potential energetic compounds and tend to explode under certain conditions. Appropriate safety precautions should be kept during handling.

General methods: Reagents were commercially available from Aldrich and Acros Organics and used as received. ¹H and ¹³C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300 and 75.48 MHz, respectively, by using [D₆]DMSO unless otherwise stated. The melting and decomposition points were obtained on a differential-scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5°C min⁻¹. TGA (TA Instruments Co., model 50) measurements were carried out by heating samples at 10°C min⁻¹ from 25 to 600°C. IR spectra were recorded by using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities of the iodyl compounds were measured at 25°C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental-analyses data were obtained by using an Exeter CE-440 elemental analyzer. 4,5-Diiodoimidazole,^[3] 2,4,5-triiodoimidazole,^[3] 4-iodopyrazole,^[9a] 3,4-diiodopyrazole,^[9b] and 3,4,5-triiodopyrazole^[9b] were prepared according to literature procedures.

4-Iodopyrazole (1):^[9a] Compound was prepared according to the literature method, yield 65%. M.p.: 109°C; *T*_{decomp} 229°C; ¹H NMR: 13.13, 7.77 ppm; IR (KBr): $\tilde{\nu}$ = 3115, 3040, 2954, 2911, 2846, 1533, 1364, 1321, 1261, 1175, 1142, 1032, 935, 872, 811, 649, 608 cm⁻¹.

4, 5-Diiodopyrazole (2):^[9b] Compound was prepared according to the literature method; product was washed with aqueous ammonia and air dried, yield 40%. M.p.: 160°C; *T*_{decomp} 290°C; ¹H NMR: 13.49, 7.83 ppm; IR (KBr): $\tilde{\nu}$ = 3126, 3022, 2926, 2850, 2781, 2709, 1323, 1254, 1175, 1059, 968, 942, 854, 806, 604 cm⁻¹.

3,4,5-Triiodopyrazole (3):^[9b] Yield 10%. M.p.: 220°C; *T*_{decomp} 282°C; ¹H NMR: 13.94 ppm; IR (KBr): $\tilde{\nu}$ = 3073, 2949, 2872, 2816, 2731, 1512, 1315, 1242, 1131, 961, 854, 807, 604, 447 cm⁻¹.

3, 4, 5-Triiodopyrazolyl-1-acetic acid (4):^[9b] Yield 72%. M.p.: 237°C; *T*_{decomp} 247°C; ¹H NMR: 13.48, 5.09 ppm.

4(5)-Iodoimidazole (5):^[15] Yield 93%. M.p.: 137°C; *T*_{decomp} 220°C; ¹H NMR: 7.31, 7.62 ppm; IR (KBr): $\tilde{\nu}$ = 3442, 3105, 2997, 2875, 2805, 2683, 2641, 2600, 1795, 1435, 1291, 1166, 1128, 1070, 955, 820, 620, 495 cm⁻¹.

4, 5-Diiodoimidazole (6):^[3] Compound was prepared according to the literature method, recrystallized from EtOH and water, yield 42%. M.p.: 197°C; *T*_{decomp} 233°C; ¹H NMR: 12.90, 7.77 ppm; IR (KBr): $\tilde{\nu}$ = 3078, 2960, 2776, 2648, 2584, 2480, 1812, 1639, 1542, 1454, 1285, 1271, 1179, 1152, 955, 918, 818, 654, 620 cm⁻¹.

2,4,5-Triiodoimidazole (7):^[3] Compound was prepared according to the literature method by using four equivalents of I₂, recrystallized from 95% EtOH, yield 90%. M.p.: 191°C; *T*_{decomp} 252°C; ¹H NMR: 13.34 ppm; IR (KBr): $\tilde{\nu}$ = 3421, 3026, 2930, 2831, 2741, 2644, 2583, 1503, 1374, 1269, 1161, 971, 656, 436 cm⁻¹.

1-Methyl-2,4,5-triiodoimidazole (8): Modification of a literature procedure:^[16] potassium carbonate (0.61 g, 4.4 mmol) and 2,4,5-triiodoimidazole (0.90 g, 2 mmol) were added to CH₃CN (10 mL); CH₃I (0.14 mL, 2.2 mmol) was then added slowly to the mixture. The reaction mixture was stirred overnight, then poured into 30 g ice water, filtered, and dried to give 0.88 g of white solid (yield 95%). M.p.: 153°C; *T*_{decomp} 318°C; ¹H NMR: 3.65 ppm; ¹³C NMR: 39.33, 88.49, 94.74, 97.50 ppm; IR (KBr): $\tilde{\nu}$ = 2932, 1431, 1373, 1343, 1190, 1099, 1067, 947, 706, 422 cm⁻¹; elemental analysis calcd for C₃H₃I₃N₂ (447.8): C 10.45, H 0.66, N 6.09; found: C 10.47, H 0.60, N 5.80.

Tetraiodothiophene (9):^[17] Starting from 2-iodothiophene by using a modified method (yield 85%). M.p. 203°C; *T*_{decomp} 397°C; IR (KBr): $\tilde{\nu}$ = 1648, 1433, 1362, 1219, 1169, 1027, 954, 696 cm⁻¹; elemental analysis calcd for C₄I₄S (587.7): C, 8.17; H, 0; N, 0; found: C, 8.14; H, 0; N, 0.78.

Tetraiodofuran (10):^[4] Prepared according to the literature (yield 52%). M.p. 163°C; *T*_{decomp} 261°C; ¹³C NMR: 106.2; 94.1 ppm; IR (KBr): $\tilde{\nu}$ = 1700, 1497, 1444, 1242, 1084, 962, cm⁻¹; elemental analysis calcd for C₄H₄I₄N: C 8.40, H 0, N 0; found: C 8.38, H 0.03, N 0.10.

Tetraiodopyrrole (11): The same method as was used for **10** (yield 47%). *T*_{decomp} 168°C; ¹H NMR: 12.3 ppm; ¹³C NMR: 86.7; 79.7 ppm; IR (KBr): $\tilde{\nu}$ = 3431, 1530, 1375, 1292, 1170, 1027, 963, 897, 865, 772, 667 cm⁻¹; elemental calcd for C₄I₄O (571.7): C 8.42, H 0.18, N 2.45; found: C 8.68, H 0.17, N 2.46.

2,4,5-Triiodoimidazolyl-1-acetic acid (12): The mixture of potassium carbonate (0.61 g, 4.4 mmol), 2,4,5-triiodoimidazole (0.90 g, 2 mmol), and bromoacetate (2.2 mmol) in 2-ethoxyethanol (25 mL) was heated at 100°C for 16 h; the suspension was filtered, and the filtrate was evaporated under reduced pressure. The residue was dissolved in water, the solution was filtered, and the filtrate was acidified to pH 1 to give 2,4,5-triiodoimidazolyl-1-acetic acid (0.75 g, yield 69%). *T*_{decomp} 179°C; ¹H NMR: 4.79, 13.53 ppm; IR (KBr): $\tilde{\nu}$ = 3427, 1717, 1458, 1418, 1356, 1328, 1238, 1173, 982, 889, 803, 669, 446 cm⁻¹; elemental analysis calcd for C₃H₃I₃N₂O₂ (503.8): C 11.92, H 0.60, N 5.56; found: C 11.95, H 0.60, N 5.48.

General procedure for preparing tris(3, 4, 5-triiodopyraolyl)-2, 4, 6-triazine (**13**), tris(2, 4, 5-triiodoimidazolyl)-2, 4, 6-triazine (**14**), and tris(4, 5-diiodoimidazolyl)-2, 4, 6-triazine (**15**): The respective iodo compound (3.5 equiv) and potassium carbonate (7.7 equiv) were heated at reflux in CH₃CN for 1 h; then cyanuric chloride (1 equiv) was added in portions, and heating was continued for 2–8 h to complete the reaction. The reaction mixture was cooled to RT, filtered, and the filter cake was washed with CH₃CN, followed by water. Then it was air dried to give the expected product.

Tris(3,4,5-triiodopyraolyl)-2,4,6-triazine (13): yield 80%; *T*_{decomp} 355°C; ¹³C NMR: 162.9; 118.0; 98.56; 98.50 ppm; elemental analysis calcd for C₁₂I₉N₉ (1412.3): C 10.21, H 0, N 8.93; found: C 10.49, H 0.11, N 8.08.

Tris(2,4,5-triiodoimidazolyl)-2,4,6-triazine (14): yield 85%; *T*_{decomp} 386°C; ¹³C NMR: 162.4; 106.1; 95.2; 86.6 ppm; IR (KBr): $\tilde{\nu}$ = 1547, 1456, 1382, 1274, 1163, 1065, 945, 808, 688, 648 cm⁻¹; elemental analysis calcd for C₁₂I₉N₉ (1412.3): C 10.21, H 0, N 8.93; found: C 10.23, H 0.02, N 8.57.

Tris(4,5-diiodoimidazolyl)-2,4,6-triazine (15): yield 73%; M.p. 386°C (decomp); ¹H NMR: 9.00 ppm; ¹³C NMR: 160.9, 143.0, 106.2, 81.7 ppm; elemental analysis calcd for C₁₂H₃I₆N₉ (1049.8): C 13.93, H 0.29, N 12.18; found: C 14.24, H 0.31, N 11.89.

General procedure for preparing iodyl compounds: Oxone (0.8 g, 1.3 mmol) was dissolved in H₂O (5 mL) at room temperature, then mono-iodo compound (1 mmol) was added in portions. The reaction mixture was stirred for 3 h, the precipitate formed was collected by filtration, washed with cold water (2 mL), then with acetone (1 mL), and air dried. Double or triple quantities of Oxone and water were needed to prepare di- or tri-iodyl compounds, heating at 70°C, and stirring overnight were required to complete the reaction.

4,5-Di-iodylimidazole hemidyrate (16): Yield 64.3%; M.p. 124°C (-H₂O), *T*_{decomp} 228°C; ¹H NMR: 8.38 ppm (d, CH); ¹³C NMR: 141.3 (C-IO₂), 85.9 ppm (C=N); IR (KBr): $\tilde{\nu}$ = 3462 (OH), 3148 (NH), 3050, 2914, 2820, 2747, 2577, 1871, 1643, 1566, 1148, 1101, 1065, 887, 822 (I=O), 617, 513 cm⁻¹; elemental analysis calcd for C₃H₂N₂I₂O₄·0.5H₂O (392.9): C 9.17, H 0.77, N 7.13; found: C 9.53, H 0.86, N 7.21.

2,4,5-Tri-iodylimidazole (17): Yield 55.6%; *T*_{decomp} 183°C; IR (KBr): $\tilde{\nu}$ = 3447 (NH), 1655, 1439, 1324, 1277, 1215, 1175, 982, 473 cm⁻¹; elemental analysis calcd for C₃H₁N₂I₃O₆ (541.8) C 6.65, H 0.19, N 5.17; found: C 7.06, H 0.13, N 5.27.

4-Iodylpyrazole (18): Yield 72.6%; *T*_{decomp} 201°C; ¹H NMR (300 MHz, D₂O) 8.25 ppm (s, CH); ¹³C NMR (300 MHz, D₂O) 136.0 (C-IO₂), 124.9 ppm (C=N); IR (KBr): $\tilde{\nu}$ = 3160 (NH), 3096, 3055, 2963, 2872, 2829, 1558, 1482, 1380, 1329, 1171, 1153, 1031, 957, 838, 802, 773 (I=O), 725, 615 cm⁻¹; elemental calcd for C₃H₃N₂IO₂ (226.0): C 15.95, H 1.34, N 12.40; found: C 16.08, H 1.22, N 11.86.

3,4-Di-iodylpyrazole(19): Yield 73.4%; *T*_{decomp} 188°C; IR (KBr): $\tilde{\nu}$ = 3229 (NH), 3142, 2975, 2911, 1630, 1501, 1443, 1351, 1247, 1154, 1097, 1061, 970, 931, 727 (I=O), 687, 613 cm⁻¹; elemental analysis calcd for C₃H₂N₂I₂O₄ (383.9): C 9.39, H 0.53, N 7.30; found: C 9.13, H 0.78, N 6.86.

3,4,5-Tri-iodylpyrazole (20): Yield 73.4%; *T*_{decomp} 159°C; IR (KBr): $\tilde{\nu}$ = 3162, 3140 (NH), 2923, 1568, 1522, 1451, 1395, 1349, 1327, 1209, 1161, 1049, 972, 931, 854, 822, 787 (I=O), 604 cm⁻¹; elemental analysis calcd for C₃H₁N₂I₃O₆·2.5H₂O (586.8): C 6.14, H 1.03, N 4.77; found: C 6.23, H 0.91, N 4.40.

Procedure for preparing N-nitro-4-iodylpyrazole (21): 4-Iodopyrazole (0.1 g) was added in portions to HNO₃ (2 mL 100%) with cooling. The reaction mixture was stirred at 0°C for 1.5 h, and then poured into ice water (5 g). The solid was formed, then collected by filtration and dried in vacuum to give 0.108 g of white solid (yield 92%).

N-nitro-4-iodylpyrazole dihydrate (21): *T*_{decomp} 132 (H₂O) 179°C; ¹H NMR: 8.05, 8.10 ppm; IR (KBr): 3392 (OH), 1630, 1381, 1184, 1128, 1042, 947, 854, 741 (I=O), 602 cm⁻¹; elemental analysis calcd for C₃H₂N₃I₁O₄·2H₂O (307.0): C 11.74, H 1.97, N 13.69; found: C 11.73, H, 1.81, N 13.03.

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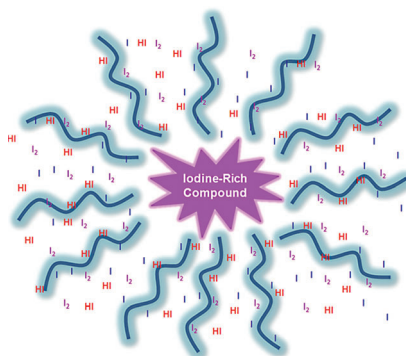
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Density Functional Calculations

C. He, J. Zhang,

J. M. Shreeve* ■■■■-■■■■

 **Dense Iodine-Rich Compounds with Low Detonation Pressures as Biocidal Agents**



Agent Defeat Weapons: Fifteen iodo compounds and six iodyl compounds with an iodine content between 45.3 and 89.0% were synthesized. The high concentration and easy accessibility of iodine and/or iodine-containing species is very important in developing materials suitable as agent defeat weapons (see figure).