



## Accepted Article

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# Energetic Materials Trends in 5- and 6-Membered Cyclic Peroxides Containing Hydroperoxy and Hydroxy Substituents

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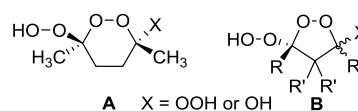
**Abstract:** Ten peroxide compounds based upon the 3,6-di(hydroperoxy)-1,2-dioxane, 2-hydroxy-6-hydroperoxy-1,2-dioxane, 3,5-di(hydroperoxy)-1,2-dioxolane, and 3-hydroxy-5-hydroperoxy-1,2-dioxolane skeletons have been synthesized, structurally characterized, and fully evaluated for their energetic materials properties. The solid state structures of these compounds are dominated by hydrogen bonding interactions involving the hydroperoxy and hydroxy groups. Energetic materials testing shows that most of the compounds are highly sensitive toward impact and friction, with similar properties to highly sensitive peroxides such as triacetone triperoxide. 3,5-Diethyl-5-hydroperoxy-1,2-dioxolan-3-ol (**3b**) and 3,5-dimethyl-5-hydroperoxy-1,2-dioxolan-3-ol (**5b**) have lower impact and friction sensitivities than the other compounds, with values that are appropriate for use as primary explosives.

## Introduction

Peroxo compounds contain one or more O-O bonds and are widely used as polymerization initiators, curing and vulcanizing agents, cross-linking agents, bleaching and disinfecting agents, and homemade explosives.<sup>[1-3]</sup> Until recently, detailed information about the energetic materials properties of peroxides was only available for triacetone triperoxide (TATP), diacetone diperoxide (DADP), hexamethylene triperoxide diamine (HMTD), and methyl ethyl ketone peroxide (MEKP).<sup>[1-3]</sup> TATP, DADP, HMTD, and MEKP are very sensitive and can explode violently upon routine handling. As such, there are no military and civilian applications of peroxide explosives. However, TATP is easily synthesized and is frequently used as a homemade explosive in terrorist attacks.<sup>[1,2]</sup> Based upon the well-documented high sensitivities of TATP, DADP, HMTD, and MEKP, organic peroxides remain largely unexplored as energetic materials.

We are interested in exploring the limits of oxygen atom incorporation into organic compounds, with the aim of

synthesizing low sensitivity, oxygen-rich compounds that might be used as explosives and high energy dense oxidizers.<sup>[4]</sup> We recently reported new classes of organic peroxides that are much less sensitive toward stimuli than TATP, DADP, HMTD, and MEKP.<sup>[5-7]</sup> In particular, cyclic and bicyclic compounds containing two geminal hydroperoxy groups have appropriate sensitivity values for use as primary explosives,<sup>[5]</sup> and nitroaromatic peroxy acids have low enough sensitivities to be classified as secondary energetic materials.<sup>[6]</sup> There have been several reports of organic peroxides with O:C ratios of >1, but most of these compounds are reported to decompose readily or explode violently.<sup>[8]</sup> Herein, we report the synthesis, structure, and energetic properties of a series of oxygen-rich compounds based upon the 6-hydroperoxy-1,2-dioxane (**A**) and 5-hydroperoxy-1,2-dioxolane (**B**) skeletons, where X is OOH or OH (Chart 1). Compounds where X is OOH are very sensitive, with impact, friction, and electrostatic discharge sensitivities that are similar to TATP, DADP, HMTD, and MEKP. Several compounds where X is OH exhibit lower sensitivities, without a significant loss in the energetic materials performance. We have also carried out calculations to understand the solid state interactions that contribute to sensitivity differences.



**Chart 1.** Six-membered (**A**) and five-membered (**B**) peroxides studied herein.

## Results and Discussion

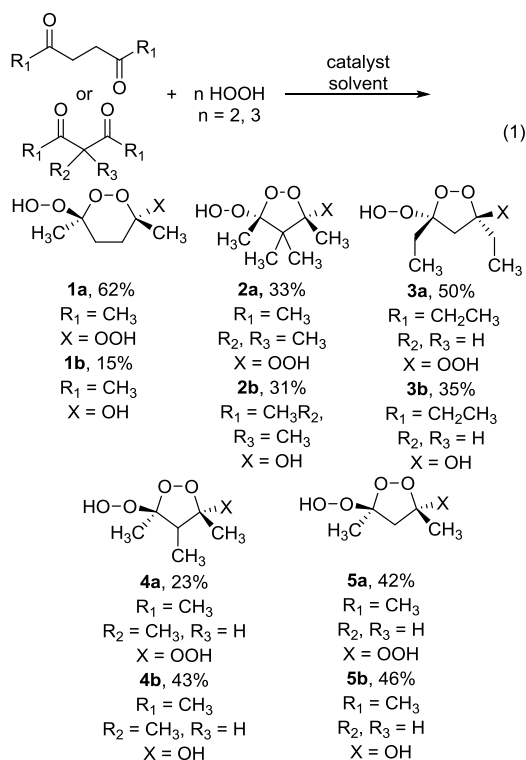
Compounds **1-5** were prepared upon treatment of  $\gamma$ - or  $\beta$ -diketones with 50 wt. % aqueous  $\text{H}_2\text{O}_2$  in the presence of the catalysts  $\text{I}_2$ ,  $\text{H}_2\text{SO}_4$ , or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at or below room temperature (Equation 1).<sup>[9-11]</sup> Compounds **1a**,<sup>[10]</sup> **5a**,<sup>[9b,11]</sup> and **5b**<sup>[11]</sup> were reported previously, and **2b** was briefly mentioned in one of our recent papers.<sup>[7]</sup> The other compounds have not been previously reported. The indicated yields are for the optimum syntheses. Compounds **3a** and **5a** were obtained upon treatment of the diketones with a catalytic amount of concentrated  $\text{H}_2\text{SO}_4$  and were recrystallized to afford pure materials. Reactions using catalytic  $\text{I}_2$  or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  gave variable mixtures of **1a-5a** and **1b-5b**, with the former generally predominating. These mixtures were easily separated by silica gel column chromatography to afford the pure compounds. In this way, **1a**, **2a**, **2b**, **3b**, **4a**, and **4b** were obtained using catalytic  $\text{I}_2$  and **1b** and **5b** were synthesized with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . Further efforts to optimize the

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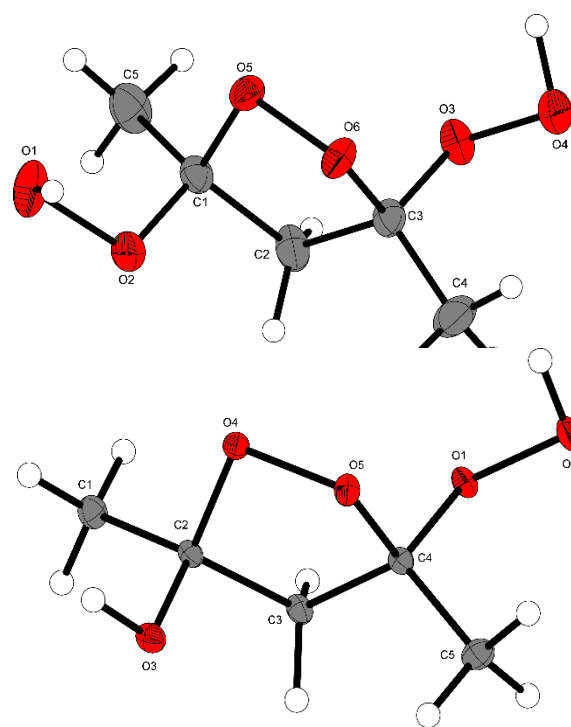
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syntheses of **1-5** were not made, because of their energetic nature and the facile separations by column chromatography. The structures and compositions of **1-5** were established by a combination of spectral and analytical data and by X-ray crystal structure determinations of all compounds except **1b**, which exists as an oil. The relative stereochemistries of **1-5** were obtained from the X-ray crystal structures. Compounds **1-5** showed the expected resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and the infrared spectra were consistent with the structures. The  $^{13}\text{C}$  NMR resonances of the oxygen-substituted carbon atoms were the most diagnostic spectroscopic feature. In **1a**, this resonance appeared at 109.3 ppm. In **1b**, the C(OO)(OOH) carbon atom resonated at 107.2 ppm, while the C(OO)(OH) carbon atom appeared at 100.0 ppm. For the five-membered ring compounds **2a-5a**, the C(OO)(OOH) carbon atom resonated between 113.4 and 115.6 ppm. For **2b-5b**, the C(OO)(OOH) and C(OO)(OH) carbon atom resonances were observed between 113.7 and 115.9 ppm and 106.5 and 108.6 ppm, respectively.



The X-ray crystal structures of **1a** and **2-5** were determined to obtain molecular structures and to understand intermolecular interactions. Table 1 gives crystal data for **1a** and **2-5** and Figure 1 shows representative perspective views of **5a** and **5b**, along with selected bond lengths and angles. The X-ray crystal structures of **1a** and **2-5** are contained in the supporting information. Compounds **1a** and **3-5** exhibit anti arrangement of the oxygen substituents within the rings, most likely to minimize steric interactions between the alkyl groups. By contrast, the oxygen groups in **2a** and **2b** are syn. The cyclic peroxide O-O bond lengths in **1a** and **2-5** range from 1.4613(8) Å in **1a** to

1.4956(9) and 1.493(2) Å in **2a** and **2b**, respectively. The syn-oxygen substituents and four methyl groups on the rings in **2a** and **2b** may introduce strain into the 5-membered rings that cause the slightly longer O-O bond lengths, compared to **3-5**. The O-O bond lengths in the OOH substituents fall within the narrow range of 1.4575(2) to 1.465(2) Å. These values are very similar to the O-O bond lengths in recent compounds reported by our group that contain OOH substituents.<sup>[5,6]</sup> Solid state densities range from 1.328 to 1.474 g/cm<sup>3</sup> (Table 1). The dihydroperoxy compounds **2a-5a** have slightly higher densities than the corresponding hydroperoxy compounds **2b-5b**, consistent with their higher molecular weights.

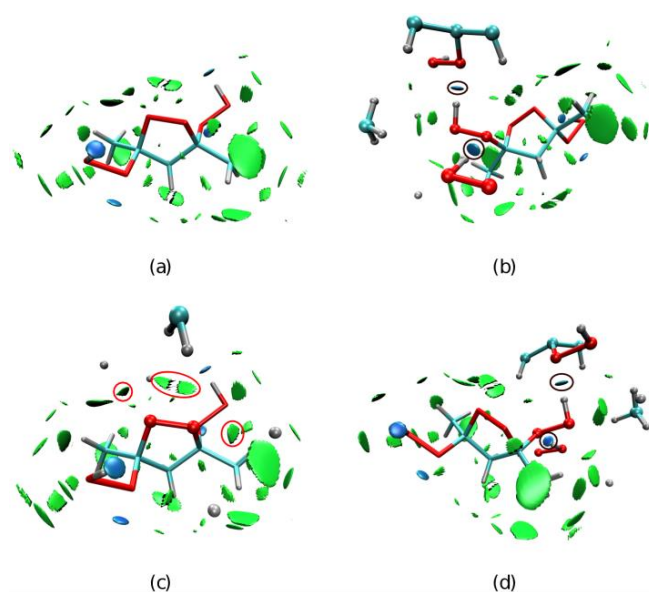


**Figure 1.** Perspective views of **5a** (top) and **5b** (bottom). Selected bond lengths (Å): **5a**, O1-O2 1.458(1), O3-O4 1.460(1), O5-O6 1.475(1); **5b**, O1-O2 1.4638(6), O5-O6 1.4783(6).

Tables S1-S9 and Figures S1-S9 in the supporting information document the intermolecular interactions in **1a** and **2-5**. The intermolecular interactions in these compounds are dominated by O $\cdots$ H and O $\cdots$ O contacts that are within the van der Waals radii of these atoms (2.62 Å for O $\cdots$ H, 3.04 Å for O $\cdots$ O).<sup>[12]</sup> As expected, these O $\cdots$ H and O $\cdots$ O close contacts occur through hydrogen bond formation involving the OOH and OH groups. The lattices in **1a** and **2-5** are composed of various O-H $\cdots$ O hydrogen bonded motifs, including 1-dimensional chains (**1a**), dimers (**2a**, **2b**, **3b**), two-dimensional sheets (**3a**, **4a**, **4b**, **5a**), and tetramers (**5b**). Compounds **1a**, **2a**, **2b**, **4b**, and **5b** contain one or more H $\cdots$ H close contacts, **2b**, **4a**, **4b**, and **5b** each exhibit one or more C $\cdots$ H close contacts, and **3a** and **4a** each have one close C $\cdots$ O close contact. The H $\cdots$ H, C $\cdots$ H, and C $\cdots$ O close contacts appear to arise through maximization of the

hydrogen bond networks associated with the OOH and OH groups.

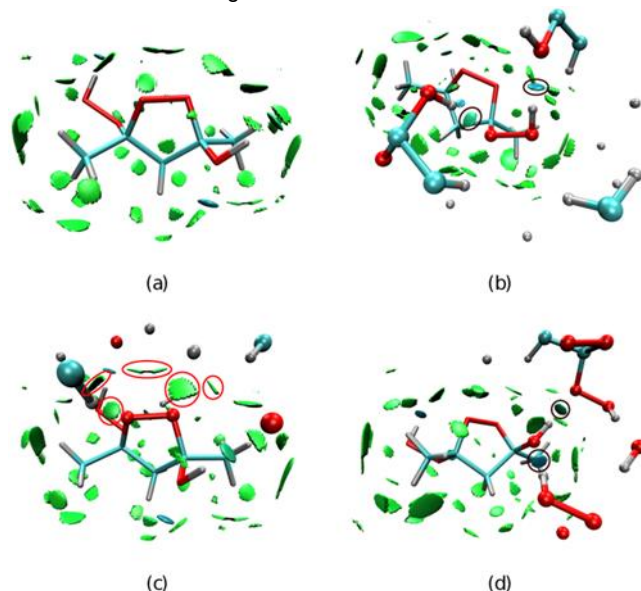
Electronic structure calculations can be used to determine the strength of stabilizing intermolecular interactions within the crystal lattice. Representative compounds **5a** and **5b** were chosen for these studies. Stabilization energies for **5a** and **5b** were calculated to be -89.0 and -89.4 kJ/mol, respectively. Because the lattice energies of these two crystals are nearly identical, a non-covalent interaction (NCI) analysis<sup>[13]</sup> was performed on **5a** and **5b** to gain further insights into the interactions within the crystal lattices. Attractive interactions (and the neighboring atoms responsible) around each functional group in **5a** and **5b** are shown in Figures 2 and 3, respectively. Key interactions within the lattice are circled and the surfaces are color coded based on the strength of the interactions. The color scale used for the NCI surfaces varies between weakly attractive (green) and strongly attractive (dark blue). The OOH groups in **5a** form a zigzag two-dimensional [OOH...]<sub>n</sub> hydrogen bond donor-acceptor chain across the crystal. The OOH and OH groups in **5b** form a tetrameric [OH...OOH]<sub>2</sub> hydrogen bond donor-acceptor ring (see supporting information). The peroxide bonds in the C<sub>3</sub>O<sub>2</sub> rings of **5a** and **5b** show only weak CH...O interactions in the X-ray crystal structures. Our calculations confirm the presence of four weak CH...O close contacts in **5a** between the core ring oxygen atoms and a ring C-H bond and a methyl group from another molecule. In **5b**, calculations show six CH...O close contacts between the core ring oxygen atoms and methyl groups from adjacent molecules. The C...H and C...O close contacts that are observed in the crystal structure of **5b** are not observed as attractive in the calculations, suggesting very weak interactions at best. The nearly identical calculated lattice energies for **5a** and **5b** suggest that intermolecular interactions alone cannot explain the observed sensitivity differences (vide infra).



**Figure 2.** Attractive intermolecular interactions between **5a** and nearest neighbors within 4 Å. Strongly attractive interactions are shown in blue and weaker interactions are green. Surfaces are shown for (a) the whole molecule,

(b) the first OOH group, (c) the central COOC group (CH...O distance: 2.8-3.0 Å), and (d) the second OOH group. Key interactions (black: hydrogen bond, red: CH...O contacts) are circled for each functional group. Neighboring atoms within 3.5 Å of each functional group are shown to highlight the atoms responsible for the intermolecular interactions.

The thermal behavior of **1-5** was studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). As shown in Table 2, decomposition onset temperatures by DTA range from 82 to 133 °C, except for **2a** and **2b**, which show decomposition onsets at 64 and 67 °C, respectively. The syn arrangements of the oxygen ring substituents in **2a** and **2b** and their long ring O-O bond lengths may correlate with their lower decomposition temperatures. Compound **5b** is the most thermally stable, with a decomposition temperature of 133 °C. CBS-4M electronic enthalpies were calculated with the Gaussian09 software package.<sup>[14]</sup> The heats of formation range from -542.7 to -509.1 kJ/kg for **1a-5a** and -646.5 to -590.7 kJ/kg for **1b-5b** (Table 2). Dihydroperoxy compounds **1a-5a** have more positive heats of formation values than the corresponding hydroperoxy compounds **1b-5b**, consistent with the larger number of weak O-O bonds in **1a-5a**.



**Figure 3.** Attractive intermolecular interactions between structure **5b** and nearest neighbors within 4 Å. Strongly attractive interactions are shown in blue and weaker interactions are green. Surfaces are shown for (a) the whole molecule, (b) the OOH group, (c) the central COOC group (CH...O distance: 2.6-2.9 Å), and (d) the OH group. Key interactions (black: hydrogen bond, red: CH...O contacts) are circled for each functional group. Neighboring atoms within 3.5 Å of each functional group are shown to highlight the atoms responsible for the intermolecular interactions.

Impact, friction, and electrostatic discharge sensitivities were determined with a BAM drop hammer, a BAM friction tester, and an electrostatic discharge tester using standard test methods.<sup>[15]</sup> Sensitivity classifications are based on the "UN Recommendations on the Transport of Dangerous Goods".<sup>[16]</sup> Energetic performance data were calculated using the EXPLO5

V6.02 software.<sup>[17]</sup> As shown in Table 2, impact and friction sensitivities for **1a-5a** are  $\leq 2$  J and  $< 5$  N, respectively. Accordingly, these compounds are “very sensitive” toward impact and “extremely sensitive” toward friction.<sup>[16]</sup> These values

are similar to those of TATP and DADP,<sup>[1-3]</sup> and thus **1a-5a** must be

**Table 1.** Crystal data and structure refinement for **1a** and **2-5**.

|   | <b>1a</b>                                     | <b>2a,2b</b>  | <b>3a,3b</b>  | <b>4a,4b</b>  | <b>5a,5b</b>  |
|---|---|---|---|---|---|
| Formula   | C <sub>5</sub> H <sub>10</sub> O <sub>7</sub> | C <sub>14</sub> H <sub>28</sub> O <sub>12</sub> , C <sub>7</sub> H <sub>14</sub> O <sub>5</sub> | C <sub>7</sub> H <sub>14</sub> O <sub>6</sub> , C <sub>7</sub> H <sub>14</sub> O <sub>5</sub> | C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> , C <sub>6</sub> H <sub>12</sub> O <sub>5</sub> | C <sub>5</sub> H <sub>10</sub> O <sub>6</sub> , C <sub>5</sub> H <sub>10</sub> O <sub>5</sub> |
| <i>M<sub>r</sub></i>                                    | 182.13  | 388.36, 178.18  | 194.18, 178.18  | 180.16, 164.16  | 166.13, 150.13  |
| Crystal system  | tetragonal                                    | orthorhombic,<br>monoclinic   | monoclinic,<br>orthorhombic   | orthorhombic,<br>monoclinic   | monoclinic,<br>monoclinic   |
| Space group   | I4bar   | Pbca, P2 <sub>1</sub> /n  | P2 <sub>1</sub> /n, Pbca  | Pbca, P2 <sub>1</sub> /n  | P2 <sub>1</sub> /n, P2 <sub>1</sub> /n  |
| <i>a</i> [Å]  | 14.0266(7)                                    | 12.6452(16),<br>8.811(2)  | 5.6429(3),<br>9.9659(7)   | 8.1894(6),<br>7.6155(5)   | 5.5729(5),<br>8.6193(6)   |
| <i>b</i> [Å]  | 14.0266(7)                                    | 12.5922(15),<br>8.8031(18)  | 17.6201(9),<br>10.7296(7)   | 6.6753(4),<br>11.9510(8)  | 15.4498(12),<br>8.7945(6)   |
| <i>c</i> [Å]  | 8.7135(5)                                     | 23.364(3),<br>11.281(3)   | 9.1491(5),<br>16.6680(12)   | 30.7184(19),<br>9.3339(6)   | 8.7244(7),<br>9.2016(6)   |
| $\beta$ [°]   | ---   | ---, 95.900(14)   | 90.610(3), ---  | ---, 113.494(3)   | 90.055(4),<br>104.0770(10)  |
| <i>V</i> [Å <sup>3</sup> ]                              | 1714.3(2)                                     | 3720.3(8), 70.4(3)  | 909.63(8),<br>1782.3(2)   | 1679.27(19),<br>779.08(9)   | 751.17(11),<br>676.56(8)  |
| <i>Z</i>  | 8   | 8, 4  | 4, 8  | 8, 4  | 4, 4  |
| <i>D<sub>c</sub></i> [g cm <sup>-3</sup> ]              | 1.411   | 1.387, 1.360  | 1.418, 1.328  | 1.425, 1.400  | 1.469, 1.474  |
| $\mu$ (Mo-K $\alpha$ ) [mm <sup>-1</sup> ]              | 0.136   | 0.122, 0.166  | 0.125, 0.113  | 0.129, 0.123  | 0.138, 0.134  |
| <i>T</i> [K]  | 100(2)  | 100(2), 100(2)  | 100(2), 100(2)  | 100(2), 100(2)  | 100(2), 100(2)  |
| Observed reflections                                    | 5455  | 5148, 2047  | 4490, 4760  | 1437, 2728  | 3631, 3774  |
| Parameters  | 117   | 255, 119  | 126, 117  | 118, 109  | 108, 99   |
| GOF   | 0.620   | 1.040, 1.199  | 1.111, 1.033  | 1.201, 1.094  | 1.959, 0.948  |
| <i>R<sub>f</sub></i> <sup>[a], [b]</sup>                | 0.0321 (0.0293)                               | 0.0400 (0.0305),<br>0.0593 (0.0485)   | 0.0521 (0.0380),<br>0.0357 (0.0301)   | 0.0487 (0.0450),<br>0.0466 (0.0357)   | 0.0803 (0.0618),<br>0.0448 (0.0362)   |
| <i>wR<sub>2</sub></i> <sup>[c]</sup>                    | 0.0883 (0.0838)                               | 0.0822 (0.0761),<br>0.1371 (0.1319)   | 0.1093 (0.1032),<br>0.0915 (0.0866)   | 0.1254 (0.1236),<br>0.0941 (0.0890)   | 0.2333 (0.2203),<br>0.1261 (0.1169)   |
| Largest difference in peak and hole [eÅ <sup>-3</sup> ] | 0.356 and -0.271                              | 0.364 and -0.195,<br>0.374 and -0.324   | 0.473 and -0.286,<br>0.449 and -0.283   | 0.395 and -0.221,<br>0.426 and -0.293   | 0.513 and -0.548,<br>0.548 and -0.223   |

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>Values in parentheses for reflections with  $I > 2\sigma(I)$ . <sup>c</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

handled with great care. Compounds **1b-5b** each contain one fewer oxygen atom and one fewer peroxide linkage than the corresponding compounds **1a-5a**. Compounds **1b**, **2b**, and **4b** have impact sensitivities of  $< 2$  J, whereas **3b** and **5b** each has an impact sensitivity of 3 J. The central ring carbon atoms in **2b** and **4b** are substituted with one or two methyl groups, while these carbon atoms are unsubstituted in **3b** and **5b**. The ring substitution thus might influence impact sensitivity. Compounds **3b** and **5b** are less sensitive toward impact than **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, **4b**, and **5a**, although they are still classified as “very sensitive” according to the UN classification. The friction

sensitivities decrease in the order **1b** (5 N)  $>$  **2b** (6 N)  $>$  **3b** (14 N)  $>$  **4b**, **5b** (40 N). Compounds **1b** and **2b** are classified as “extremely sensitive” toward friction, while **3b-5b** are “very sensitive”. The electrostatic discharge sensitivity values of **1-5** are greater than what can be generated by the human body (0.025 J).<sup>[1b]</sup>

Compounds **1a-5a** have calculated detonation velocity values ( $V_{Det}$ ) that increase from 6350 m/s in **1a** to 6694 m/s in **5a**. The  $V_{Det}$  value trend in **1a-5a** correlates approximately with the increasing solid state densities. For comparison, **2b-5b** have calculated  $V_{Det}$  values of **3b** (5954 m/s)  $<$  **2b** (6100 m/s)  $<$  **4b**

(6103 m/s) < **5b** (6461 m/s). This trend exactly mirrors the order of increasing solid state density values in Table 2. Compounds

**Table 2.** Sensitivities and energetic performance of peroxo-based oxygen-rich compounds **1-5**.

|  | <b>1a,1b</b>    | <b>2a,2b</b>    | <b>3a,3b</b>    | <b>4a,4b</b>    | <b>5a,5b</b>    |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|
| IS <sup>a</sup> (J)                    | <1,1            | <1,2            | 2,3             | <1,1            | <1,3            |
| FS <sup>b</sup> (N)                    | <5,5            | <5,6            | <5,14           | <5,40           | <5,40           |
| ESD <sup>c</sup> (J)                   | 0.15,oil n.d.   | 0.065,0.10      | 0.15,0.20       | 0.10,0.20       | 0.5,0.15        |
| Ω <sup>d</sup> (%)                     | -106.57,-126.70 | -123.59,-143.67 | -123.59,-143.67 | -106.57,-126.70 | -86.68,-106.57  |
| T <sub>Dec</sub> <sup>e</sup> (°C)     | 124,131         | 64,67           | 129,95          | 96,82           | 118,133         |
| ρ <sup>f</sup> (g/cm <sup>3</sup> )    | 1.411, oil n.d. | 1.387,1.360     | 1.418,1.328     | 1.425,1.400     | 1.469,1.474     |
| Δ <sub>f</sub> H <sup>o</sup> (kJ/kg)  | -541.2,-627.2   | -542.7,-646.5   | -538.7,-641.6   | -529.6,-615.4   | -509.1,-590.7   |
| Δ <sub>f</sub> U <sup>o</sup> (kJ/kg)  | -2945.3,-3692.2 | -2667.1,-3496.1 | -2646.7,-3468.9 | -2816.0,-3620.5 | -2945.3,-3810.5 |
| Explo V6.02:                           |                 |                 |                 |                 |                 |
| Δ <sub>Ex</sub> U <sup>o</sup> (kJ/kg) | -4885,---       | -4748,-3498     | -4783,-3517     | -4952,-3780     | -5133,-4572     |
| P <sub>CJ</sub> <sup>j</sup> (kbar)    | 130,---         | 124,104         | 132,98          | 134,109         | 154,136         |
| V <sub>Det</sub> <sup>k</sup> (m/s)    | 6350,---        | 6357,6100       | 6501,5954       | 6511,6103       | 6694,6461       |
| V <sub>o</sub> <sup>l</sup> (L/kg)     | 853,---         | 871,876         | 869,878         | 853,864         | 840,842         |

<sup>a</sup>BAM drophammer. <sup>b</sup>BAM friction. <sup>c</sup>Electrostatic discharge sensitivity. <sup>d</sup>Oxygen balance. <sup>e</sup>Decomposition onset temperature from DTA (5 °C min<sup>-1</sup>). <sup>f</sup>Low temperature X-ray densities. Values at 298 K were calculated from the low-temperature X-ray values using the equation: (ρ<sub>298K</sub> = ρ<sub>T</sub> / (1+α<sub>v</sub>(298-T<sub>0</sub>); α<sub>v</sub> = 1.5 · 10<sup>-4</sup> K<sup>-1</sup>) <sup>g</sup>Calculated molar enthalpy of formation. <sup>h</sup>Energy of formation <sup>i</sup>Total energy of detonation. <sup>j</sup>Detonation pressure. <sup>k</sup>Detonation velocity. <sup>l</sup>Volume of detonation products.

and **5b** have the highest V<sub>Det</sub> values (6694, 6461 m/s), the highest solid state densities (1.469, 1.474 g/cm<sup>3</sup>), and the highest oxygen:carbon ratios (1.20, 1.00) among the series **1-5**.

Table 3 lists selected energetic materials properties for TNT, TATP, and Pb(N<sub>3</sub>)<sub>2</sub>, to provide comparisons for **1-5**. TNT is classified as a relatively insensitive secondary explosive, TATP is a very sensitive primary explosive, and Pb(N<sub>3</sub>)<sub>2</sub> is a widely used primary explosive.<sup>[1b]</sup> Typical sensitivity values for primary explosives are ≤ 4 J (impact), ≤ 10 N (friction), and 0.002-0.20 J (ESD), whereas the related values for secondary explosives are ≥ 4 J (impact), ≥ 50 N (friction), and ≥ 0.1 J (ESD).<sup>[1b]</sup> The impact sensitivities of **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, **4b**, and **5a** are ≤ 2 J, which are in the range of the value for highly sensitive TATP (the lowest value of our drophammer is 1 J). The impact sensitivities of **3b** and **5b** are both 3 J, which makes them slightly less sensitive than the others and similar to the value for the widely used primary explosive Pb(N<sub>3</sub>)<sub>2</sub>. Compounds **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, **4b**, and **5a** have friction sensitivities that are ≤ 6 N, which are within the typical range for primary explosives and are similar to the value for Pb(N<sub>3</sub>)<sub>2</sub> (5 N is the lower limit for our friction sensitivity apparatus). By contrast, the friction sensitivity values for **3b** (14 N), **4b** (40 N), and **5b** (40 N) are in between those for typical primary and secondary explosives, but are still “very sensitive” according to the UN classifications. Among **1-5**, **3b**

and **5b** stand out as having reduced impact and friction sensitivities. For comparison, our recently reported organic peroxides containing geminal hydroperoxy groups have impact and friction sensitivities of 1-3 J and ≤ 5 N, respectively, and were the first peroxides that exhibit safe primary explosive properties.<sup>[5]</sup> The related sensitivity values for **3b** and **5b** are similar to or better than the geminal hydroperoxy compounds. Thus, **3b** and **5b** have useful sensitivities for application as primary energetic materials. The thermal decomposition temperatures would need to be improved to > 150 °C for widescale practical use.

There are no clear structural features that account for the lower impact and friction sensitivities of **3b** and **5b**, compared to the others. The calculated lattice energies of **5a** and **5b** are nearly identical, and are dominated by O-H...O hydrogen bonds. Less sensitive **3b** and **5b** each contain an unsubstituted central ring carbon atom, compared to alkyl substitution in more sensitive **2** and **4**. The lower alkyl content in **3b** and **5b** may afford more efficient packing by reducing steric bulk around the oxygen atoms, thereby decreasing the sensitivities slightly by leaving less room for motion of the weak O-O bonds in the crystal. Alkyl substitution on the central ring carbon atom may lead to increased ring strain, which may weaken the ring O-O bond slightly and thus increase sensitivity. Moreover, **1a-5a**

each contain three peroxide groups per molecule, while **1b-5b** contain only two peroxide groups per molecule. Hence, the probability of breaking a weak O-O bond is higher in **1a-5a**, compared to the corresponding **1b-5b** analogs, thereby making **1a-5a** more sensitive toward stimuli. Despite the lower oxygen contents in **2b-5b**, the calculated detonation velocities are only 3.6-9.2% lower than the **2a-5a** analogs and **5b** is only 3.6% lower than **5a**. Thus, the decreased sensitivity in **5b**, relative to **5a**, is only associated with a small decrease in the detonation velocity.

**Table 3.** Selected sensitivities and energetic performance for TNT, TATP, and Pb(N<sub>3</sub>)<sub>2</sub>.

|                            | TNT <sup>[a]</sup> | TATP <sup>[b]</sup> | Pb(N <sub>3</sub> ) <sub>2</sub> <sup>[c]</sup> |
|----------------------------|--------------------|---------------------|---|
| IS (J)                     | 15                 | 0.3                 | 2.5-4   |
| FS (N)                     | 353                | 0.1                 | <1  |
| ESD (J)                    | 0.57               | 0.16                | 0.005   |
| Ω <sub>CO2</sub> (%)       | -73.96             | -151.2              |   |
| T <sub>Dec</sub> (°C)      | 240                | 150-160             |   |
| ρ (g/cm <sup>3</sup> )     | 1.704,<br>1.713    | 1.25                |   |
| Δ <sub>f</sub> H° (kJ/mol) | -70.6              | -631.4              |   |
| P <sub>Ci</sub> (kbar)     | 190                | 108                 | 343   |
| V <sub>Det</sub> (m/s)     | 6900               | 6315                | 4600-5100                                       |
| V <sub>o</sub> (L/kg)      | 825                | 916                 |   |

[a] Data are taken from ref. [5]. [b] Data taken from ref. [7]. [c] Data taken from ref. [1b].

## Conclusions

The cyclic peroxide compounds **1-5** were synthesized in 15-62% yields by simple synthetic methods entailing treatment of γ- or β-diketones with concentrated aqueous H<sub>2</sub>O<sub>2</sub> using the catalysts I<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, or SnCl<sub>2</sub>·2H<sub>2</sub>O. Compounds **3a** and **5a** were obtained as pure compounds upon crystallization, whereas the others were obtained as mixtures (**1a/1b**, **2a/2b**, **3a/3b**, **4a/4b**, **5a/5b**) that were easily separated by column chromatography. All compounds except for **1b** were characterized by X-ray crystallography. The solid state structures are dominated by hydrogen bonding involving the OOH and OH groups. The solid state densities range from 1.328 to 1.474 g cm<sup>-3</sup>, which are high for organic peroxides. Compounds **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, **4b**, and **5a** are very sensitive toward impact (≤ 2 J) and friction (≤ 6 N) and should thus be treated as primary explosives. By contrast, **3b** and **5b** are less sensitive than the others, with impact sensitivities of 3 J and friction sensitivities of 14 and 40 N, respectively. Compounds **5a** and **5b** were studied by NCI to

probe solid state interactions that could explain their differing sensitivities. Surprisingly, calculated stabilization energies for **5a** and **5b** are identical, suggesting that solid state interactions alone cannot explain the sensitivity differences. The lower sensitivities of **3b** and **5b** are proposed to arise from their lower ring alkyl substitution and concomitant tighter packing of the peroxy groups, as well as the presence of three peroxy groups in **1a-5a**, compared to two peroxy groups in **1b-5b**. Compounds **3b** and **5b** have useful sensitivity values for application as primary explosives, although their decomposition temperatures (95, 133 °C) are likely too low for widespread practical applications. The present study greatly increases the number of organic peroxides whose detailed energetic properties are described.<sup>[1-3,5-7]</sup>

## Experimental Section

**Experimental Details.** The syntheses of **1-5** were carried at room temperature under ambient atmosphere in appropriately sized round-bottomed flasks. Chemicals were purchased from Sigma-Aldrich, Acros Organics, EMD, or Alfa Aesar and were used without further purification. ACS grade solvents were obtained from EMD and Fisher Scientific. The synthesis of **5a**<sup>[10]</sup> was carried out using a modified published procedure. Silica gel 60, 230–400 mesh (EMD Chemicals) was used to perform silica gel column chromatography. ASTM TLC plates precoated with silica gel 60 F<sub>254</sub> (250 μm layer thickness) were used for thin-layer chromatography (TLC). TLC spots were observed using a UV lamp and/or a potassium permanganate solution as a stain (3 g KMnO<sub>4</sub>, 20 g K<sub>2</sub>CO<sub>3</sub>, 5 mL 5% w/v aqueous NaOH, 300 mL H<sub>2</sub>O). The spots on the stained TLC plates were visualized after heating with a heat gun. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at 400 MHz and 101 MHz, respectively, in CD<sub>3</sub>OD as indicated and were referenced to the residual proton and carbon resonances of the solvent (<sup>1</sup>H δ = 3.31 ppm, <sup>13</sup>C δ = 49.00 ppm). Mass spectra were obtained on an electrospray time-of-flight high-resolution Waters Micromass LCT Premier XE mass spectrometer. Infrared spectra were obtained from a Shimadzu MIRacle 10 IRAffinity-1 equipped with a single reflection ATR accessory. Melting points were determined on an Electrothermal IA 9300 melting point apparatus and are uncorrected. The decomposition characteristics were studied by TGA and DTA, which were carried out with a SDT-2960 TGA/DTA instrument. Decomposition points were determined on an OZM Research DTA 552 Ex instrument.

**CAUTION!** Organic peroxides **1-5** are sensitive and highly explosive and require handling with extreme care. The H<sub>2</sub>O<sub>2</sub> solutions are strong oxidizers that may cause explosions. Reactions and manipulations should be run in fume hoods behind blast shields. Personal safety gear should include a face shield, leather gloves, a leather apron, hearing protection, and plastic spatulas. Peroxide compounds should not come into contact with strong acids, metal salts, or easily oxidized species. All reactions should be run at or below room temperature and performed on small scales.

**Computational Methods.** Intermolecular interactions between compounds **5a** and **5b** and all neighbors within 4 Å of the central molecule were calculated. Symmetry adapted perturbation theory (SAPT)<sup>[18,19]</sup> was employed to calculate intermolecular interactions of the compound-neighbor pairs at the SAPT2+3/6-31++G(d,p) level of theory. The total lattice stabilization energy was estimated by the sum of the pairwise energies,

$$E_{x,lat} = \frac{1}{2} \sum E_{x,j},$$

where  $E_{x,lat}$  is the total lattice stabilization energy of compound  $x$ , and  $E_{x,j}$  is the intermolecular interaction energy of structure  $x$  with neighbor  $j$ . In addition to the lattice energies, NCI surfaces were generated using the crystal structures for compounds **5a** and **5b** and all nearest neighbors within 4 Å. Each surface was created using the NCIPLOT software package,<sup>[13]</sup> with an isovalue of 0.3 and a reduced density cutoff of 0.07 a.u. Due to the large size of the system, precalculated atomic densities were used to represent the total molecular electron density. The NCI surfaces were then post-processed (see supporting information) to display only surfaces that are due to the attractive intermolecular interactions.

**3,6-Dihydroperoxy-3,6-dimethyl-1,2-dioxane (1a).** To a solution of  $I_2$  (0.102 g, 0.400 mmol) in  $CH_3CN$  (5 mL) was added a 50 wt. % aqueous solution of  $H_2O_2$  (1.4 mL, 24 mmol) and 2,5-hexanedione (0.24 mL, 2.0 mmol). The resultant mixture was stirred for 24 h at ambient temperature. The solvent and volatile components were removed under reduced pressure, and the resultant residue was dissolved in methanol (10 mL). Storage of this solution at  $-29$  °C for 24 h led to crystallization, and afforded **1a** (0.225 g, 62%) as thick, colorless plates after decanting of the methanol solvent and brief vacuum drying. mp 128–130 °C (lit<sup>[10]</sup> 131 °C).  $^1H$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = OOH resonance not observed due to exchange with  $CD_3OD$ , 1.89–1.77 (m, 2H), 1.60–1.47 (m, 2H), 1.38 (s, 6H,  $CH_3$ ) ppm.  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = 109.29 (C), 27.97 ( $CH_2$ ), 19.05 ( $CH_3$ ) ppm. IR ( $\nu$ ,  $cm^{-1}$ ): 3332 (broad, m), 3300 (broad, m), 3277 (broad, m), 3246 (broad, m), 2999 (w), 2947 (w), 1439 (m), 1377 (s), 1344 (m), 1272 (m), 1250 (w), 1157 (m), 1120 (s), 1062 (s), 1022 (w), 960 (w), 924 (w), 893 (w), 862 (s), 761 (w). Anal. Calcd for  $C_6H_{12}O_6$ : C, 40.00; H, 6.71. Found: C, 40.35; H, 6.76. TGA/DTA decomposition onset/max: 124/126 °C.

**6-Hydroperoxy-3,6-dimethyl-1,2-dioxan-3-ol (1b).** To a stirred solution of 2,5-hexanedione (0.24 mL, 2.0 mmol) in  $CH_3CN$  (10 mL) was added  $SnCl_2 \cdot 2H_2O$  (0.090 g, 0.400 mmol) at ambient temperature. Then, a 50 wt. % aqueous solution of  $H_2O_2$  (0.6 mL, 10 mmol) was added and the mixture was stirred at ambient temperature for 18 h. At this point, distilled water (30 mL) was added and the aqueous phase was extracted with three 20 mL portions of ethyl acetate. The combined organic layers were dried over anhydrous magnesium sulfate, filtered through a fluted filter paper, and then the resulting solution was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography with 4:1 dichloromethane:ethyl acetate to afford **1b** ( $R_f$  = 0.25, 0.048 g, 15%) as a colorless oil.  $^1H$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = OOH and OH resonances not observed due to exchange with  $CD_3OD$ , 1.80–1.96 (m, 2H), 1.61–1.78 (m, 1H), 1.44–1.60 (m, 1H), 1.40 (s, 3H,  $CH_3$ ), 1.30 (s, 3H,  $CH_3$ ) ppm.  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = 107.21 (C(OOH)), 100.04 (C(OH)), 30.02 ( $CH_2$ ), 26.99 ( $CH_2$ ), 22.52 ( $CH_3$ ), 18.08 ( $CH_3$ ) ppm. IR ( $\nu$ ,  $cm^{-1}$ ): 3399 (broad, m), 2992 (w), 2972 (w), 2943 (w), 2870 (w), 1703 (w), 1634 (w), 1449 (m), 1400 (m), 1377 (m), 1337 (m), 1256 (m), 1231 (m), 1167 (m), 1148 (m), 1115 (s), 1070 (s), 1024 (w), 964 (m), 943 (m), 881 (w), 849 (s), 766 (w), 743 (w). Anal. Calcd for  $C_8H_{12}O_5$ : C, 43.90; H, 7.37. Found: C, 43.60; H, 7.35. TGA/DTA decomposition onset/max: 131/134 °C.

**3,5-Dihydroperoxy-3,4,4,5-tetramethyl-1,2-dioxolane (2a).** A solution of  $I_2$  (0.103 g, 0.400 mmol) in  $CH_3CN$  (10 mL) was treated with a 50 wt. % aqueous solution of  $H_2O_2$  (0.7 mL, 12 mmol), followed by 3,3-dimethylpentane-2,4-dione (0.26 mL, 2 mmol). The mixture was then stirred at ambient temperature for 5 h. At this point, the solution was concentrated under reduced pressure, and the residue was dissolved in dichloromethane (10 mL). The resulting solution was filtered through a pad of anhydrous  $Na_2SO_4$  to remove water. The dichloromethane

solution was again concentrated and the product was purified by silica gel column chromatography with 9:1 dichloromethane:ethyl acetate, followed by 4:1 dichloromethane:ethyl acetate, to afford **2a** ( $R_f$  = 0.20 in 9:1 dichloromethane:ethyl acetate,  $R_f$  = 0.30 in 4:1 dichloromethane:ethyl acetate, 0.129 g, 33%) as a white solid. Colorless polygons of **2a** were grown by slow evaporation of a diethyl ether solution. Crystals of **2a** exploded at 84 °C in the capillary tube upon attempting to measure the mp.  $^1H$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = OOH resonance not observed due to exchange with  $CD_3OD$ , 1.45 (s, 6H,  $CH_3$ ), 1.16 (s, 3H,  $CH_3$ ), 1.01 (s, 3H,  $CH_3$ ) ppm.  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = 113.62 (C(OOH)), 60.69 (C), 24.06 ( $CH_3$ ), 15.99 ( $CH_3$ ), 15.33 ( $CH_3$ ) ppm. IR ( $\nu$ ,  $cm^{-1}$ ): 3414 (broad, m), 3011 (w), 2956 (w), 2523 (m), 1456 (m), 1396 (m), 1377 (m), 1267 (w), 1221 (w), 1142 (m), 1098 (s), 1043 (w), 951 (w), 925 (w), 887 (s), 849 (m), 798 (w), 732 (w). Anal. Calcd for  $C_7H_{14}O_6$ : C, 43.30; H, 7.27. Found: C, 42.99; H, 7.10. TGA/DTA decomposition onset/max: 64/65 °C.

**5-Hydroperoxy-3,4,4,5-tetramethyl-1,2-dioxolan-3-ol (2b).** To a solution of  $I_2$  (0.102 g, 0.400 mmol) in  $CH_3CN$  (10 mL) was added a 50 wt. % aqueous solution of  $H_2O_2$  (0.7 mL, 12 mmol), followed by 3,3-dimethylpentane-2,4-dione (0.26 mL, 2.0 mmol). The mixture was then stirred at ambient temperature for 5 h. At this point, the solution was concentrated under reduced pressure, and the residue was dissolved in dichloromethane (10 mL). The resulting solution was filtered through a pad of anhydrous  $Na_2SO_4$  to remove water. The decanted dichloromethane solution was again concentrated and the product was purified by silica gel column chromatography with 9:1 dichloromethane:ethyl acetate to afford **2b** ( $R_f$  = 0.50, 0.111 g, 31%) as a white solid. Colorless polygons of **2b** were obtained from 2:1 dichloromethane:methanol at  $-29$  °C: mp 79–81 °C.  $^1H$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = OOH and OH resonances not observed due to exchange with  $CD_3OD$ , 1.48 (s, 3H,  $CH_3$ ), 1.31 (s, 3H,  $CH_3$ ), 1.11 (s, 3H,  $CH_3$ ), 1.09 (s, 3H,  $CH_3$ ) ppm.  $^{13}C$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = 114.86 (C(OOH)), 108.05 (C(OH)), 59.73 (C), 23.41 ( $CH_3$ ), 18.72 ( $CH_3$ ), 16.94 ( $CH_3$ ), 14.41 ( $CH_3$ ) ppm. IR ( $\nu$ ,  $cm^{-1}$ ): 3455 (m), 3260 (broad, m), 3005 (w), 2943 (w), 2874 (w), 2555 (w), 2419 (w), 1454 (m), 1396 (m), 1375 (m), 1279 (w), 1253 (w), 1213 (m), 1140 (s), 1115 (s), 1098 (s), 1063 (m), 943 (m), 916 (m), 880 (s), 851 (m), 810 (w), 791 (w), 734 (w). Anal. Calcd for  $C_7H_{14}O_5$ : C, 47.19; H, 7.92. Found: C, 47.20; H, 7.93. TGA/DTA decomposition onset/max: 67/68 °C.

**3,5-Diethyl-3,5-dihydroperoxy-1,2-dioxolane (3a).** To a 50 wt. % aqueous solution of  $H_2O_2$  (1.20 mL, 19.2 mmol) was added concentrated  $H_2SO_4$  (0.038 g, 0.400 mmol), followed by heptane-3,5-dione (0.41 mL, 3.0 mmol) in a dropwise fashion at 0 °C. The mixture was then stirred for 1 h at 0 °C. The reaction solution was then concentrated under reduced pressure to afford a crude white solid. This solid was crystallized by slow evaporation of a diethyl ether solution to afford **3a** (0.290 g, 50%) as colorless, thick needle-like crystals: mp 118–120 °C.  $^1H$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = OOH resonance not observed due to exchange with  $CD_3OD$ , 2.49 (s, 2H), 1.96–2.10 (m, 2H), 1.62–1.75 (m, 2H), 0.99 (t, 6H,  $J$  = 7.6 Hz,  $CH_3$ ) ppm.  $^{13}C$  NMR ( $CD_3OD$ , 23 °C):  $\delta$  = 115.61 (C), 48.43 (ring  $CH_2$ ), 24.92 ( $CH_2$ ), 9.26 ( $CH_3$ ) ppm. IR ( $\nu$ ,  $cm^{-1}$ ): 3377 (m, broad), 2982 (w), 2947 (w), 2885 (w), 2511 (w), 1462 (m), 1443 (w), 1425 (w), 1383 (w), 1341 (m), 1321 (m), 1275 (w), 1219 (m), 1159 (s), 1121 (m), 1084 (m), 1020 (m), 1003 (m), 984 (w), 953 (s), 895 (w), 876 (w), 847 (w), 826 (w), 787 (s), 736 (w). Anal. Calcd for  $C_7H_{14}O_6$ : C, 43.30; H, 7.27. Found: C, 43.40; H, 7.37. TGA/DTA decomposition onset/max: 129/132 °C.

**3,5-Diethyl-5-hydroperoxy-1,2-dioxolan-3-ol (3b).** To a stirred solution of  $I_2$  (0.103 g, 0.400 mmol) in  $CH_3CN$  (10 mL) was added a 50 wt. % aqueous solution of  $H_2O_2$  (0.7 mL, 12 mmol) at ambient temperature. To this solution was added heptane-3,5-dione (0.26 mL, 1.9 mmol) and the mixture was stirred at ambient temperature for 5 h. At this point, the solution was concentrated under reduced pressure, and the



residue was dissolved in dichloromethane (10 mL). The resulting solution was filtered through a pad of anhydrous  $\text{Na}_2\text{SO}_4$  to remove water. The decanted dichloromethane solution was again concentrated and the product was purified by silica gel column chromatography with dichloromethane followed by 4:1 dichloromethane:ethyl acetate to afford **3b** ( $R_f = 0.45$ , 0.126 g, 35%) as a white solid. Colorless plate-like crystals were obtained by slow evaporation from a 10:1 mixture of toluene:diethyl ether. mp 79–81 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = \text{OOH}$  and  $\text{OH}$  resonances not observed due to exchange with  $\text{CD}_3\text{OD}$ , 2.47 (q, 2H,  $J = 10.0$  Hz,  $\text{CH}_2$ ), 2.05–2.17 (s, 1H), 1.66–1.81 (m, 3H), 1.00 (t, 6H,  $J = 7.6$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = 115.93$  (C(OOH)), 108.57 (C(OH)), 51.79 ( $\text{CH}_2$ ), 30.07 ( $\text{CH}_2$ ), 25.17 ( $\text{CH}_2$ ), 9.40 ( $\text{CH}_3$ ), 9.35 ( $\text{CH}_3$ ) ppm. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3410 (broad, m), 3333 (broad, m), 2982 (m), 2947 (w), 2887 (w), 2797 (w), 2359 (s), 2160 (w), 2023 (w), 1973 (w), 1742 (w), 1690 (m), 1647 (w), 1551 (m), 1526 (m), 1458 (m), 1406 (m), 1306 (m), 1260 (m), 1213 (w), 1163 (m), 1113 (m), 1072 (m), 1018 (m), 934 (m), 899 (m), 851 (m), 800 (m), 718 (m). Anal. Calcd for  $\text{C}_7\text{H}_{14}\text{O}_5$ : C, 47.19; H, 7.92. Found: C, 46.98; H, 7.89. TGA/DTA decomposition onset/max: 95/98 °C.

**3,5-Dihydroperoxy-3,4,5-trimethyl-1,2-dioxolane (4a).** To a stirred solution of  $\text{I}_2$  (0.103 g, 0.400 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was added a 50 wt. % aqueous solution of  $\text{H}_2\text{O}_2$  (0.7 mL, 12 mmol) at ambient temperature. To this solution was added 3-methyl-2,4-pentanedione (0.23 mL, 2.0 mmol) and the mixture was stirred at ambient temperature for 5 h. At this point, the reaction mixture was concentrated under reduced pressure and was dissolved in dichloromethane (10 mL). The resulting solution was filtered through a pad of anhydrous  $\text{Na}_2\text{SO}_4$  to remove water. The dichloromethane solution was again concentrated under reduced pressure and the crude product mixture was purified by silica gel column chromatography with 9:1 dichloromethane:ethyl acetate to obtain **4a** ( $R_f = 0.20$ , 0.083 g, 23%) as a white solid. Colorless polygons of **4a** were obtained at -29 °C from a 2:1 mixture of toluene:dichloromethane. mp 59–61 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = \text{OOH}$  resonance not observed due to exchange with  $\text{CD}_3\text{OD}$ , 2.70 (q, 1H,  $J = 8.0$  Hz,  $\text{CH}$ ), 1.50 (s, 3H,  $\text{CH}_3$ ), 1.39 (s, 3H,  $\text{CH}_3$ ), 1.06 (d, 6H,  $J = 8.0$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = 114.86$  (C), 113.00 (C), 57.08 (CH), 16.69 ( $\text{CH}_3$ ), 16.14 ( $\text{CH}_3$ ), 9.18 ( $\text{CH}_3$ ) ppm. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3410 (broad, m), 3364 (broad, m), 2999 (w), 2945 (w), 1713 (w), 1628 (w), 1464 (m), 1439 (m), 1377 (s), 1337 (m), 1263 (w), 1229 (w), 1165 (s), 1124 (m), 1086 (s), 1047 (m), 1009 (m), 947 (w), 874 (s), 802 (m), 754 (w). Anal. Calcd for  $\text{C}_6\text{H}_{12}\text{O}_6$ : C, 40.00; H, 6.71. Found: C, 39.68; H, 6.63. TGA/DTA decomposition onset/max: 96/98 °C.

**5-Hydroperoxy-3,4,5-trimethyl-1,2-dioxolan-3-ol (4b).** The crude product from the synthesis of **4a** was further eluted with 4:1 dichloromethane:ethyl acetate to afford **4b** ( $R_f = 0.2$ , 0.140 g, 43%) as a white solid. Colorless hexagons of **4b** were obtained at -29 °C from a 5:1 mixture of toluene:diethyl ether: mp 71–73 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = \text{OOH}$  and  $\text{OH}$  resonances not observed due to exchange with  $\text{CD}_3\text{OD}$ , 2.48 (q, 1H,  $J = 7.6$  Hz,  $\text{CH}$ ), 1.42 (s, 3H,  $\text{CH}_3$ ), 1.41 (s, 3H,  $\text{CH}_3$ ), 1.06 (d, 6H,  $J = 7.2$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = 115.18$  (C(OOH)), 107.01 (C(OH)), 57.02 (CH), 21.63 ( $\text{CH}_3$ ), 16.09 ( $\text{CH}_3$ ), 10.24 ( $\text{CH}_3$ ) ppm. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3445 (broad, m), 3296 (broad, m), 2995 (w), 2947 (w), 2888 (w), 1649 (w), 1622 (w), 1558 (m), 1510 (w), 1467 (m), 1383 (s), 1342 (w), 1290 (w), 1263 (w), 1209 (m), 1171 (s), 1124 (s), 1084 (s), 1011 (m), 949 (s), 854 (s), 797 (m), 758 (m). Anal. Calcd for  $\text{C}_6\text{H}_{12}\text{O}_5$ : C, 43.90; H, 7.37. Found: C, 43.71; H, 7.45. TGA/DTA decomposition onset/max: 82/87 °C.

**3,5-Dihydroperoxy-3,5-dimethyl-1,2-dioxolane (5a).** A 50 mL round bottomed flask was cooled to 0 °C and was charged with a magnetic stir bar, a 50 wt. % aqueous solution of  $\text{H}_2\text{O}_2$  (0.6 mL, 9.6 mmol), and concentrated  $\text{H}_2\text{SO}_4$  (0.019 g, 0.194 mmol). To this solution

was added 2,4-pentanedione (0.32 mL, 3.1 mmol) in a dropwise fashion. The mixture was then stirred for 1 h at 0 °C and was kept in a refrigerator (2–8 °C) for 18 h. Then, the reaction mixture was added to a separatory funnel, and was extracted with three 5 mL portions of diethyl ether. The separated diethyl ether mixture was dried over anhydrous magnesium sulfate, filtered through a Whatman No. 1 filter paper, and the diethyl ether was removed under reduced pressure to afford 0.295 g of a white solid. Crystallization of this crude solid from a 20:1 dichloromethane:ethyl acetate mixture afforded **5a** as colorless polygons (0.209 g, 42%). mp 98–100 °C (lit<sup>[9b]</sup> 98–100 °C).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = \text{OOH}$  resonance not observed due to exchange with  $\text{CD}_3\text{OD}$ , 2.61 (s, 2H,  $\text{CH}_2$ ), 1.52 (s, 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = 113.42$  (C), 52.69 ( $\text{CH}_2$ ), 18.14 ( $\text{CH}_3$ ) ppm. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3362 (m, broad), 3003 (w), 2953 (w), 1431 (m), 1379 (m), 1329 (m), 1225 (m), 1167 (s), 1088 (m), 1028 (w), 953 (w), 920 (w), 889 (w), 849 (m), 820 (w), 789 (m), 750 (w). Anal. Calcd for  $\text{C}_5\text{H}_{10}\text{O}_6$ : C, 36.15; H, 6.07. Found: C, 36.07; H, 5.98. TGA/DTA decomposition onset/max: 118/121 °C.

**5-Hydroperoxy-3,5-dimethyl-1,2-dioxolan-3-ol (5b).** To a stirred solution of 2,4-pentanedione (0.21 mL, 2.0 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was added  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.090 g, 0.400 mmol) at room temperature. Then, a 50 wt. % aqueous solution of  $\text{H}_2\text{O}_2$  (0.6 mL, 10 mmol) was added and the mixture was stirred at ambient temperature for 24 h. At this point, distilled water (30 mL) was added to the reaction mixture and the products were extracted with two 20 mL portions of ethyl acetate. The separated organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered through a fluted filter paper, and was concentrated under reduced pressure. The product was purified by silica gel column chromatography with 4:1 dichloromethane:ethyl acetate to afford **5b** ( $R_f = 0.30$ , 0.137 g, 46%) as a white solid. Colorless polygons of **5b** were grown by slow evaporation of a diethyl ether solution. mp 112–114 °C (lit<sup>[11b]</sup> 110–112 °C).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = \text{OOH}$  and  $\text{OH}$  resonances not observed due to exchange with  $\text{CD}_3\text{OD}$ , 2.58 (s, 2H,  $\text{CH}_2$ ), 1.58 (s, 3H,  $\text{CH}_3$ ), 1.47 (s, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 23 °C):  $\delta = 113.69$  (C(OOH)), 106.53 (C(OH)), 56.11 ( $\text{CH}_2$ ), 22.80 ( $\text{CH}_3$ ), 18.54 ( $\text{CH}_3$ ) ppm. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3439 (broad, m), 3260 (broad, m), 3005 (w), 2956 (w), 2835 (s), 1439 (m), 1381 (m), 1331 (m), 1308 (m), 1217 (m), 1173 (s), 1078 (m), 1057 (m), 959 (m), 918 (w), 883 (w), 845 (s), 808 (s), 799 (s). Anal. Calcd for  $\text{C}_5\text{H}_{10}\text{O}_5$ : C, 40.00; H, 6.71. Found: C, 40.35; H, 6.66. TGA/DTA decomposition onset/max: 133/147 °C.

**X-ray Crystal Structure Determinations of 1a and 2-5.** Single crystals were grown as described in the experimental procedures. CCDC 1487198–1487206 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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**Keywords:** peroxides • sensitivities • structure elucidation • energetic materials • NMR spectroscopy

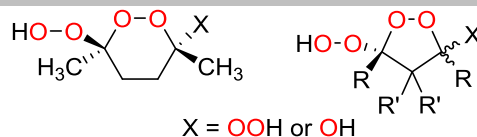
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## Entry for the Table of Contents

## FULL PAPER

**Oxygen-rich** 5- and 6-membered cyclic peroxides have been prepared and fully characterized, including by X-ray crystallography, electronic structure calculations, and detailed energetic materials testing. Most compounds are highly sensitive toward impact and friction, but two compounds where X = OH have reduced sensitivities.

**Peroxide Explosives**

*Nipuni-Dhanesha H. Gamage, Benedikt Stiasny, Eric G. Kraz, Jörg Stierstorfer, Philip D. Martin, G. Andrés Cisneros, Thomas M. Klapötke,\* and Charles H. Winter\**

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**Energetic Materials Trends in 5- and 6-Membered Cyclic Peroxides Containing Hydroperoxy and Hydroxy Substituents**

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