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**Peroxides**

# Highly Energetic, Low Sensitivity Aromatic Peroxy Acids

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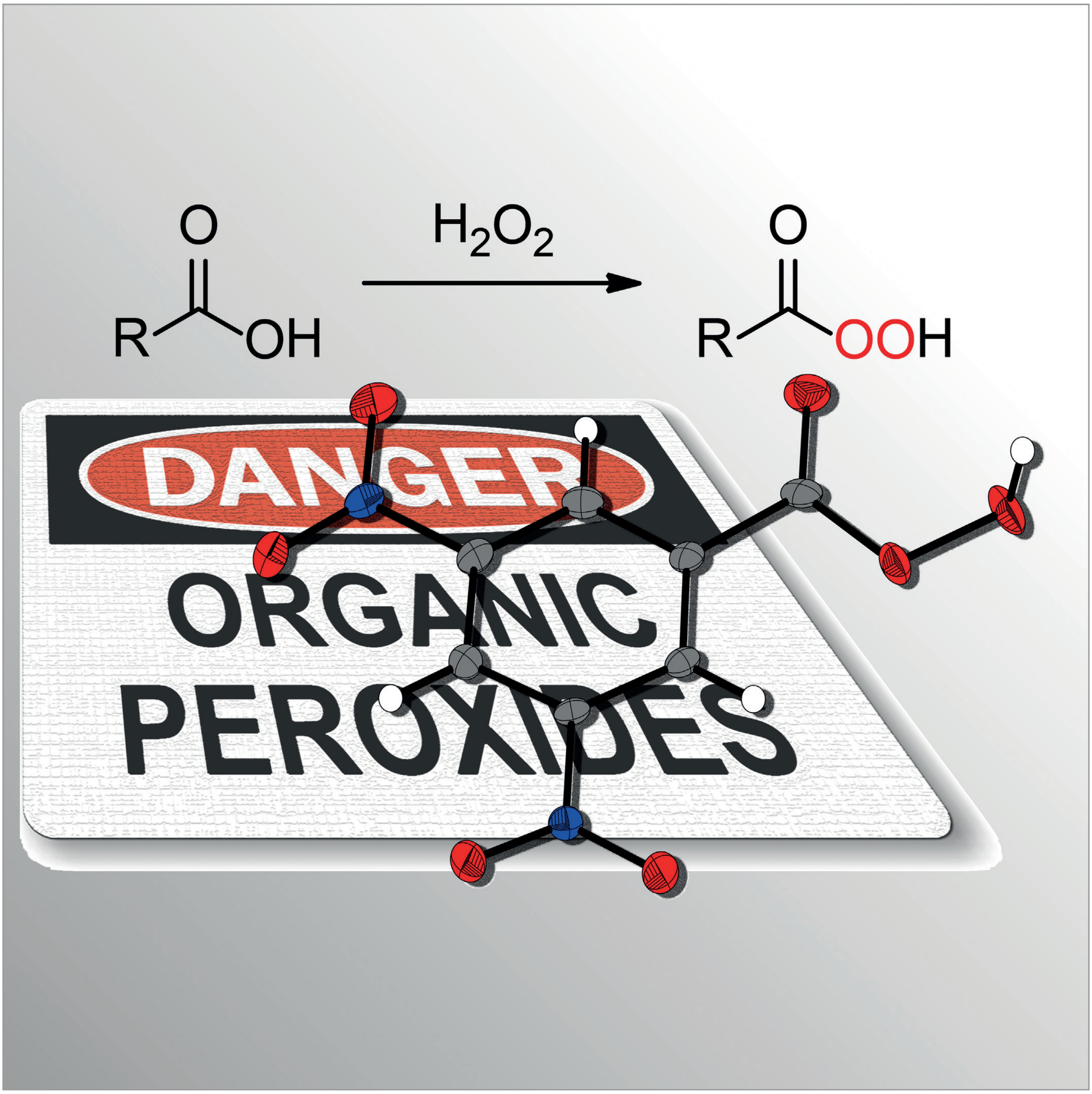
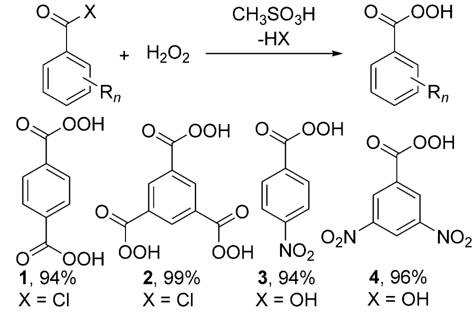


**Abstract:** The synthesis, structure, and energetic materials properties of a series of aromatic peroxy acid compounds are described. Benzene-1,3,5-tris(carboperoxoic) acid is a highly sensitive primary energetic material, with impact and friction sensitivities similar to those of triacetone triperoxide. By contrast, benzene-1,4-bis(carboperoxoic) acid, 4-nitrobenzoperoxoic acid, and 3,5-dinitrobenzoperoxoic acid are much less sensitive, with impact and friction sensitivities close to those of the secondary energetic material 2,4,6-trinitrotoluene. Additionally, the calculated detonation velocities of 3,5-dinitrobenzoperoxoic acid and 2,4,6-trinitrobenzoperoxoic acid exceed that of 2,4,6-trinitrotoluene. The solid-state structure of 3,5-dinitrobenzoperoxoic acid contains intermolecular O-H···O hydrogen bonds and numerous N···O, C···O, and O···O close contacts. These attractive lattice interactions may account for the less sensitive nature of 3,5-dinitrobenzoperoxoic acid.

The compounds triacetone triperoxide (TATP), diacetone diperoxide (DADP), hexamethylene triperoxide diamine (HMTD), and methyl ethyl ketone peroxide (MEKP) are the only peroxides for which detailed energetic materials properties have been determined.[1–3] These peroxides are extremely sensitive to stimuli and are dangerous to handle.[1–3] Other issues include a low decomposition temperature for HMTD (75 °C),[1a] high volatilities for TATP and DADP,[1,2] and calculated detonation velocities for TATP (6168 m s$^{-1}$), DADP (6773 m s$^{-1}$), and MEKP (6191 m s$^{-1}$) that are much lower than those of high nitrogen explosives such as RDX (8750 m s$^{-1}$) and HMX (9100 m s$^{-1}$).[1a] These issues, particularly the high sensitivities, have prohibited military and civilian energetic materials applications of TATP, DADP, HMTD, and MEKP. Moreover, the high sensitivities have likely limited more extensive exploration of peroxo compounds as energetic materials. Peroxo-based compounds might serve as useful explosives if their sensitivities can be adjusted to optimum levels for specific applications and also to allow safe handling. A recent report demonstrated that co-crystals of DADP and 1,3,5-triiodo-2,4,6-trinitrobenzene (TITNB) have reduced impact sensitivity compared to both pure DADP and TITNB, because of I···O close contacts in the co-crystals.[4] We have also recently described the synthesis, structure, and energetic materials properties of oxygen-rich organic compounds containing bis(hydroperoxy)-methylene groups that are less sensitive than TATP, DADP, HTMD, and MEKP.[5] Herein, we report the synthesis, structure, and energetic materials properties of four aromatic peroxy acids. Remarkably, three of these compounds have low sensitivities, very high energy contents, and have properties appropriate for application as secondary energetic materials. These are the first peroxide-based compounds that can be classified as secondary explosives. Structural data point to stabilization of the labile oxygen–oxygen bonds through hydrogen bonding and intermolecular N···O, C···O, and O···O close contacts.



**Scheme 1.** Synthesis of **1**–**4**.

Peroxy acids **1**–**4** were prepared in high yields, as depicted in Scheme 1. Compounds **3** and **4** were prepared by literature procedures entailing treatment of the carboxylic acids with 84 % H$_2$O$_2$ in the presence of methanesulfonic acid.[6] Compounds **1** and **2** were prepared under similar conditions from the acid chlorides and 84 % H$_2$O$_2$.[7] Importantly, **1**–**4** precipitate from the reaction solutions upon cooling to near 0 °C and can be isolated as pure materials by filtration and subsequent air drying. Minimal synthetic manipulation is a great advantage in the synthesis of highly energetic compounds. Attempts to prepare peroxy acids using the acid chlorides derived from 1,2,4,5-benzene tetracarboxylic acid and mellitic acid led to violent reactions upon addition of H$_2$O$_2$, and the desired compounds could not be isolated. Compounds **1**–**4** were characterized with $^{1}$H and $^{13}$C NMR spectroscopy, infrared spectroscopy, and elemental analyses.[7] Additionally, the X-ray crystal structures of **1**·DMF and **4** were determined.[7] Crystals of **1**·DMF were used only for the X-ray experiment, whereas solvent-free **1** was used for all other measurements.

A perspective view of **4** is shown in Figure 1. The bond lengths in **4** are normal. The density of **4** is 1.748 g cm$^{-3}$ at 100 K, which is higher than those of orthorhombic (1.704 g cm$^{-3}$ at 123 K) and monoclinic (1.713 g cm$^{-3}$ at 100 K) 2,4,6-trinitrotoluene (TNT).[8] Because the formula weights of **4** and TNT are almost identical, **4** packs more efficiently than TNT in the solid state. TNT does not contain any strong hydrogen bonds, and only van der Waals forces are present.[8] The asymmetric unit of **4** consists of two molecules situated in an edge-to-face fashion, with a close contact of 2.988 Å between an oxygen atom of a nitro group in one molecule and the π-face of a ring C–H carbon atom in the other molecule. The lattice contains intermolecular O-H···O hydrogen bonds, in addition to numerous N···O (2.993–3.054 Å), C···O (3.043–3.215 Å), and O···O (2.670–3.029 Å) close contacts that are within the van der Waals radii for N···O (3.07 Å), C···O (3.22 Å), and O···O (3.04 Å).[9]

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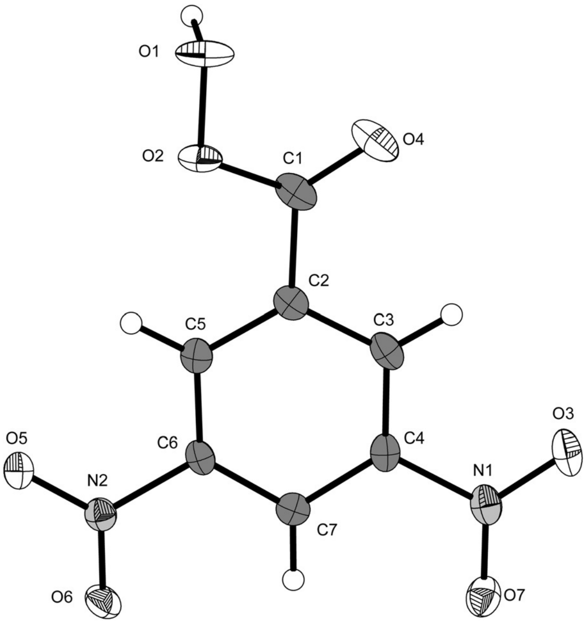


**Figure 1.** X-ray crystal structure of **4**. Selected bond lengths (Å): O1–O2 1.447(3), O2–C1 1.342(4), O4–C1 1.196(4).

Recent studies of energetic materials have shown that such close contacts are attractive because the dispersion forces are larger than the repulsive Coulombic forces.[10] Dissociation energies of O···O close contacts are similar to those of weak hydrogen bonds (3–13 kJ mol$^{-1}$).[10] Accordingly, much of the lattice energy in **4** arises from non-bonded interactions. Additionally, these non-bonded attractive interactions contribute to the high solid state density of **4**.

The thermal behaviour of **1**–**4** was studied using thermogravimetric analysis and differential thermal analysis. The compounds show decomposition onsets ranging from 132 to 160 °C (Table 1). A 200 mg sample of **4** was reported to explode just above its melting point of 112 °C.[6b] We observed no explosions with **4** up to 150 °C, but extreme care should be used when handling this compound. CBS-4M electronic enthalpies were calculated with the Gaussian 09 software package to obtain heats of formation values using the atomization equation.[11] The values are all exothermic, but **3** and **4** have the most positive heats of formation.

Table 1 gives detailed energetic test results for **1** and **3**–**5**. Impact, friction, and sensitivity toward electrostatic discharge were determined with a drop hammer, friction tester, and electrostatic discharge tester, respectively, using standard Bundesanstalt für Materialforschung und –prüfung (BAM) and electrostatic methods.[12] Sensitivity classifications are based on the "UN Recommendations on the Transport of Dangerous Goods".[13] Energetic performance was calculated using the EXPLO5 V6.02 software.[14] Compound **2** has an impact sensitivity of 1 J, a friction sensitivity of 5 N, and an electrostatic discharge of 0.025 J.[7] This electrostatic discharge value is close to what can be created by the human body (≤0.02 J),[1b] so **2** must be handled with great care. Compounds **1**, **3**, and **4** have impact sensitivity values of 10 (**1**) and 9 (**3**, **4**) J and friction sensitivity values of 288 (**1**) and 360 (**3**, **4**) N. The calculated detonation performance values increase in going from **1** to **4**. The calculated detonation pressure ($P_{CJ}$) range from 88 kbar for **1** to 213 kbar for **4**. The calculated detonation velocities increase from 5262 to 7217 m s$^{-1}$ for **1** and **4**, respectively.

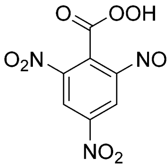
**Table 1.** Sensitivities and energetic performance of **1** and **3**–**5**.

| | **1** | **3** | **4** | **5** |
|---|---|---|---|---|
| Formula | $C_8H_6O_6$ | $C_8H_6O_6$ | $C_7H_4N_2O_7$ | $C_7H_3N_3O_9$ |
| FW [g mol$^{-1}$] | 198.14 | 183.12 | 228.11 | 271.11 |
| IS [J][a] | 10 | 9 | 9 | — |
| FS [N][b] | 288 | 360 | 360 | – |
| ESD [J][c] | 0.1 | 0.1 | 0.1 | – |
| $\Omega_{CO2}$ [%][d] | −105.0 | −100.5 | −63.13 | −38.4 |
| $T_{Dec}$ [°C][e] | 160 | 141 | 132 | – |
| $\rho$ [g cm$^{-3}$][f] | 1.423 | 1.586[m] | 1.748 | 1.80[n] |
| $\Delta_f H^\circ$ [kJ mol$^{-1}$][g] | −584.1 | −324.3 | −310.9 | −275.5 |
| $\Delta_{Ex} U^\circ$ [kJ kg$^{-1}$][h,i] | −3373 | −3590 | −4660 | −5243 |
| $P_{CJ}$ [kbar][h,j] | 88 | 133 | 213 | 269 |
| $V_{Det}$ [m s$^{-1}$][h,k] | 5262 | 6176 | 7217 | 7885 |
| $V_o$ [L kg$^{-1}$][h,l] | 598 | 628 | 596 | 619 |

[a] BAM drophammer. [b] BAM friction. [c] Electrostatic discharge sensitivity. [d] Oxygen balance for $CO_2$. [e] Decomposition temperature from DTA (5 °C min$^{-1}$). [f] Density from X-ray diffraction for **1**·DMF and **4** at −173 °C. [g] Calculated molar enthalpy of formation. [h] Calculated using EXPLO5V6.02. [i] Total energy of detonation. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of detonation products. [m] Published crystal density.[14] [n] Estimated density at 25 °C.

The extremely high performance values and low sensitivity of **4** prompted us to consider the more highly nitrated peroxy acid **5**. Synthetic approaches to **5** are ongoing, but the performance parameters were calculated using EXPLO5.[14] Using an estimated solid-state density of 1.80 g cm$^{-3}$ based upon those of **3**[15] and **4**, the calculated detonation pressure of **5** is 269 kbar and the calculated detonation velocity is 7885 m s$^{-1}$.

The present work documents the energetic materials properties of peroxy acids **1**–**5**. Compound **2** is "very sensitive" and "extremely sensitive" to impact and friction, respectively, according to the UN recommendations,[13] with values that are in the same range as those of TATP.[1,2] By contrast, **1**, **3**, and **4** are much less sensitive than **2**, TATP, DADP, HMTD, and MEKP. According to the UN Recommendations,[13] **1**, **3**, and **4** are "sensitive" toward impact and "less sensitive" to "insensitive" toward friction. These impact and friction sensitivity values are very similar to those of TNT, which is a widely used secondary explosive.[1] Hence, **1**, **3**, and **4** can also be classified as secondary explosives. These are the first peroxide-based secondary explosives. Moreover, the detonation velocity of **4** (7217 m s$^{-1}$) exceeds that of TNT (6900 m s$^{-1}$). The detonation velocity of **5** (7885 m s$^{-1}$) is much higher than those of **4** and TNT, but is less than that of RDX (8750 m s$^{-1}$).[1] Hence, **4** and **5** are powerful explosives, which likely arises from higher solid-state densities compared to TATP, DADP, HMTD, and MEKP.[1–3]



**5**

There is no single structural feature in **1**, **3**, and **4** that can explain their reduced sensitivities relative to **2**, TATP, DADP, HMTD, and MEKP. Low sensitivity, high energy explosives tend to pack in layered structures with hydrogen bonds within each layer, but only weak van der Waals interactions between the layers.[10] These materials can absorb shocks by allowing interlayer sliding without covalent bond breaking.[10c] By contrast, high sensitivity, high energy explosives tend to have structures that do not allow facile dissipation of shocks, which leads to hot spots, covalent bond breaking, and explosions.[10b] Compound **3** contains a wave-like packing arrangement,[7,15] which has been previously proposed as a structural motif that allows shock dissipation in low sensitivity, high energy explosives.[10c] The lattice of **3** contains O-H···O hydrogen bonds, three O···O close contacts (2.740–2.965 Å), and one N···O close contact (3.063 Å).[7,15] Examination of the packing in **4** does not show a layered structure like those observed in low sensitivity, high energy explosives.[10c] The low sensitivity of **4** may arise from the presence of intermolecular O-H···O hydrogen bonds and the numerous N···O (5 interactions), C···O (5 interactions), and O···O (7 interactions) close contacts, which stabilize the lattice and could allow dissipation of shock without covalent bond breaking. In this vein, the reduced sensitivity of DADP/TITNB co-crystals was proposed to originate from attractive I···O close contacts that stabilize the covalent oxygen–oxygen and iodine–carbon bonds.[4] As comparisons, the solid-state structures of highly sensitive DADP and TATP have no O···O close contacts, and contain only very weak O···H and C···H interactions.[2b,7] Features in **3** and **4** that are lacking in DADP and TATP include the O-H···O hydrogen bonding and the N···O, C···O, and O···O close contacts. We propose that these structural motifs stabilize the lattices and contribute to the low sensitivities of **1**, **3**, and **4**. In particular, the O···O close contacts in **4** likely stabilize the labile oxygen–oxygen bonds and make bond cleavage less favorable. The sterically unconstrained nature of the oxygen and nitrogen atoms in peroxy acid and nitro groups allows more intermolecular close contacts, relative to the peroxo groups in DADP and TATP.

As a cautionary note, **4** has been suggested a "safe" oxygen transfer reagent for epoxidations and other oxygen transfer reactions.[6b] The highly energetic nature of **4** advises against its large-scale synthesis. Finally, there is significant interest in the development of high-energy dense oxidizers to replace ammonium perchlorate.[1] Though the oxygen balances of **1**–**5** are all negative (−105 to −38%) and ammonium perchlorate is positive (34%[1]), the present work suggests that incorporation of peroxy acid groups in energetic materials structures can make the oxygen balance more positive without increasing sensitivity and decreasing performance. It has been reported that the active oxygen content of **4** is reduced from 93.5% to 84.0% upon standing at ambient temperature for 80 days.[6b] Accordingly, further studies are needed to explore the thermal stability, sensitivity upon heating, and chemical compatibility of peroxy acid derivatives as potential explosives.

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**Keywords:** explosives · hydrogen bonding · peroxides · sensitivities · structure elucidation

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