Boron Peroxides

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Stable Boron Peroxides with a Subporphyrinato Ligand

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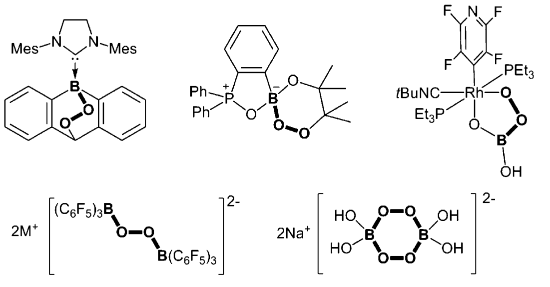
Abstract: *Subporphyrin B-peroxides have been synthesized in good yields by acid-catalyzed exchange reactions of subporphyrin B-methoxide with the corresponding hydroperoxides. Thermal dimerization of the subporphyrin B-hydroperoxide provided the peroxo-bridged bis(subporphyrin) quantitatively. These subporphyrin B-peroxides are fairly stable under ambient conditions, which allowed their isolation and full characterization as the first examples of structurally authenticated boron hydroperoxides, acyclic boron organylperoxides, and neutral peroxo-bridged diboron species. The subporphyrin B-peroxides thus prepared were investigated through their crystal structures, IR spectra, and cyclic voltammograms as well as by DFT calculations. The subporphyrin B-hydroperoxide oxidizes triphenylphosphine quantitatively to triphenylphosphine oxide.*

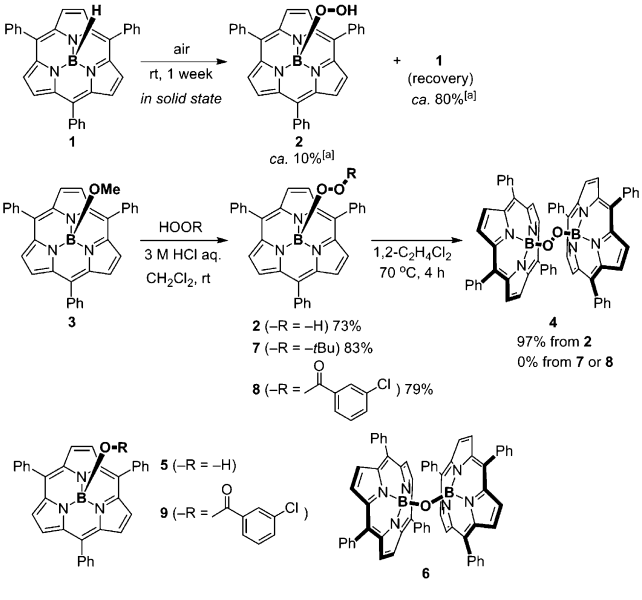


Scheme 1. Structurally characterized boron peroxides. Mes = mesityl.

Boron peroxides are important boronic species that have been proposed to be intermediates during the oxidation of alkylboranes to alkylborates,[1] radical chain reactions initiated by the combined use of BEt_3 and O_2,[2] and transition-metal-catalyzed oxidative homocoupling of arylboronic acids.[3] In addition, sodium perborate is widely used as a mild oxidant[4] and an industrial bleaching agent.[5] Therefore, the chemical behaviors of boron peroxides in oxidation processes have been extensively studied by NMR, ESR, and IR spectroscopy, mass spectrometry, as well as calorimetry.[6] Despite these efforts, full characterization of boron peroxides has been hampered, mainly because of their tendency to undergo explosive decomposition. To the best of our knowledge, there are only five examples of structurally characterized boron peroxides (Scheme 1),[7] which, with the exception of sodium perborate, were prepared by trapping highly reactive boron compounds with molecular oxygen.[5] These boron peroxides are not suitable for systematic investigations on the nature of the B-O-O bonding, and thus a new and reliable synthetic procedure is highly desired for the synthesis of a series of stable boron peroxides.

In recent years, subporphyrinatoboron(III) (hereafter referred to as subporphyrin) complexes have emerged as a new class of functional molecules,[8–11] most of which are chemically stable, because the boron atom is tightly embedded in a small cavity of a divalent and tridentate subporphyrinato ligand. Subporphyrins have been shown to undergo facile axial exchange reactions.[11] We attempted to take advantage of these reactivities to synthesize subporphyrin *B*-peroxides.

Recently, we synthesized meso-triphenylsubporphyrin *B*-hydride **1** as a stable boron hydride.[11f] In the course of this study, we observed slow formation of subporphyrin *B*-hydroperoxide **2** from **1** under aerobic conditions.[12] Exposure of **1** in the solid state to air for one week caused its conversion into **2** in about 10% yield (Scheme 2). To our surprise, **2** is fairly stable under ambient conditions and can be manipulated like usual organic molecules. It then occurred to us that



Scheme 2. Synthesis of subporphyrinatoboron(III) peroxides and structures of related subporphyrinatoboron(III) complexes. [a] Yields were determined by ^{1}H NMR spectroscopy, using 1,1,2,2-tetrachloroethane as an internal standard.

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2 might be prepared by an axial exchange reaction of subporphyrins with hydrogen peroxide. After extensive screening of the reaction conditions, we found that **2** could actually be synthesized in 73% yield by the reaction of subporphyrin *B*-methoxide **3** with a mixture of hydrogen peroxide and HCl. In addition, we found that simply heating **2** at 70°C for 4 h gave peroxo-bridged subporphyrin dimer **4** in 97% yield. It is noteworthy that the reactivity of **2** contrasts that of subporphyrin *B*-hydroxide **5**, since heating **5** under the same conditions did not produce the μ-oxo-bridged subporphyrin dimer **6**.[11c] The unique reactivity of **2** may be ascribed to the high nucleophilic character of the *B*-hydroperoxide moiety. It is also noteworthy that dimer **4** is stable, but **6** is promptly hydrolyzed in the presence of water or on silica gel. Subporphyrin *B*-peroxides **7** and **8** were prepared in 83 and 79% yield by the reaction of **3** with *tert*-butylhydroperoxide and *m*-chloroperbenzoic acid, respectively. *B*-Peroxides **7** and **8** are also fairly stable under aerobic conditions, but do not undergo thermal dimerization to **4**. These results suggest that the formation of **4** from **2** did not proceed through a radical mechanism involving homolytic cleavage followed by recombination of the O−O bond, but through an ionic mechanism, that is, nucleophilic trapping of a borenium cation intermediate.[11d]

High-resolution atmospheric pressure chemical ionization time-of-flight mass spectrometry (HR-APCI-TOF-MS) operating in a negative ion mode revealed the parent anion signal of **2** to be at $m/z = 502.1746$ (calculated for $[C_{33}H_{21}{}^{11}BN_3O_2]^- = 502.1738$) with an isotropic distribution consistent with the chemical composition. Similarly, HR-APCI-TOF-MS showed the parent ion signals of boron peroxides **4**, **7**, and **8** (see the Supporting Information). The ^{1}H NMR spectrum of **2** is consistent with its C_{3v}-symmetric 14π-electron aromatic structure, with a singlet at 8.16 ppm corresponding to the pyrrolic β-protons and a singlet at 4.18 ppm corresponding to the peroxy proton. The ^{11}B NMR spectrum of **2** displays a sharp singlet at −14.1 ppm. On the other hand, the ^{1}H and ^{11}B NMR spectra of **5** exhibit signals for the β-protons and the central boron atom at 8.12 and −15.6 ppm, respectively. These spectral data indicate that the hydroperoxo ligand is more electron withdrawing than the hydroxo ligand. In the case of **4**, signals corresponding to the β-protons and the central boron atom are shifted upfield to 7.74 ppm and −15.8 ppm, respectively, as a result of the ring current effect of aromatic subporphyrin moieties.

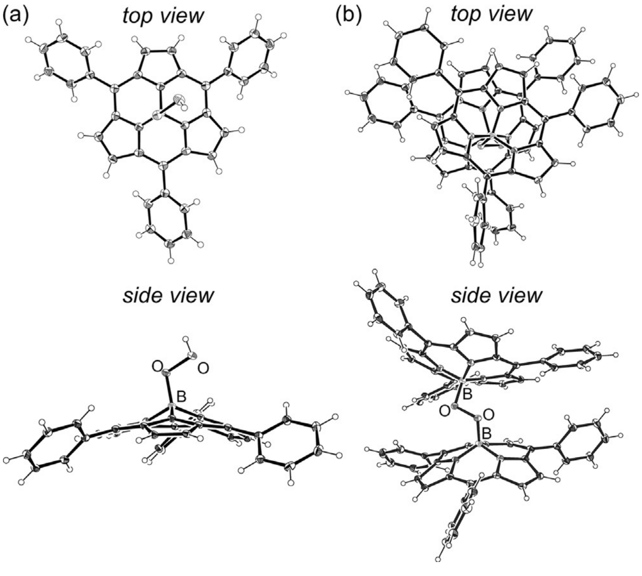


Figure 1. X-ray crystal structures of a) **2** and b) **4**. Thermal ellipsoids are scaled to 50% probability. Solvent molecules are omitted for clarity. **2** revealed a face-to-face packing of dimers through two intermolecular hydrogen-bonding interactions of the O-O-H units. See Figure S8-7 for details.

Table 1: Bond lengths [Å] and the sums of N-B-N angles [°].

Compound	O-O	B-O	B-N[a]	Sum of $\measuredangle_{\mathrm{NBN}}$
4[b] (*B*-OO*B*)	1.484	1.450	1.494	316.4
7[b,c] (*B*-OO*t*Bu)	1.475	1.457	1.491	316.9
2 (*B*-OOH)	1.469	1.468	1.484	319.4
8 (*B*-OOCOAr)	1.466	1.493	1.479	320.4
6[b,d] (*B*-O*B*)	–	1.415	1.515	310.1
3[b,c,e] (*B*-OMe)	–	1.436	1.497	313.9
5[b,c] (*B*-OH)	–	1.447	1.498	313.8
9[b,c] (*B*-OCOAr)	–	1.500	1.483	318.6

[a] Mean bond lengths of three B−N bonds. [b] Mean values of two subporphyrinatoboron moieties are represented. [c] The asymmetric unit contains two independent subporphyrinatoboron molecules. [d] Ref. [9b]. [e] Ref. [11c]. *B* = meso-triphenylsubporphyrinatoboron, Ar = 3-chlorophenyl.

The structures of **2**, **4**, **7**, and **8** have all been revealed by single-crystal X-ray diffraction analysis. The structures of **2** and **4** are shown in Figure 1.[13] To the best of our knowledge, these are the first crystal structures of acyclic and neutral boron peroxides. The solid-state structures of **5** and 3-chlorobenzoyloxyboron **9** were also determined for comparison. Selected bond lengths and the sums of three N-B-N angles of **2**–**9** are summarized in Table 1. The O-O bond lengths of **2**, **4**, **7**, and **8** are in the range of 1.466 to 1.484 Å, which are comparable to those of the previously reported boron peroxides (1.456–1.497 Å). Curiously, the O-O bond lengths increase in the order **8** < **2** < **7** < **4**, namely, with an increasing electron-donating ability of the peroxy substituents. This trend can be understood in terms of increasing electronic repulsions between the lone pairs of electrons on the oxygen atoms as a result of the electron-donating substituents.[14]

The B-O bond length of **2** is longer than that of **5**, while the average B-N length of **2** is shorter than that of **5**. In addition, the sum of the three N-B-N angles of **2** is larger than that of **5**. These data suggest that **2** may have more ion pair character and consist of a borenium cation and peroxyanion. In other words, the s-orbital character of the boron center of **2** is larger than that of **5**. Similarly, *tert*-butylperoxide **7** and peroxo-bridged diboron **4** show larger s-orbital characters than *B*-methoxide **3** and μ-oxo-bridged diboron **6**, respectively. The s-orbital characters of **8** and **9** are larger than those of **2** and **7**, which comes from the higher stabilities of the benzoate and perbenzoate groups. The s-orbital characters of the central boron atoms increase in the order of **4** < **7** < **2** < **8**, opposite to the trend of the O−O bond lengths. Density functional theory (DFT) calculations were performed on **2**–**9** by using the Gaussian 09 package, and the optimized structures were obtained after geometry optimizations at the B3LYP/6-31G(d) level (Figure S10-1).[15] The calculated structures are in good agreement with the crystal structures, thereby supporting the above arguments.

The electrochemical properties of the subporphyrin *B*-peroxides were examined by cyclic voltammetry (Figure S9). The first one-electron reductions of the *B*-peroxides are all quasi-irreversible, thus suggesting that the one-electron reduction induces O−O bond cleavage. The first reduction potentials are positively shifted in the order **4** (−1.97 V) < **7** (−1.94 V) < **2** (−1.81 V) < **8** (−1.70 V), again reflecting the electron-donating abilities of the peroxy substituents. These differences are also supported by calculations of the molecular orbital energies (Figure S10-2).

The infrared and Raman spectra of subporphyrin *B*-peroxides were measured. DFT frequency calculations were conducted to simulate the infrared spectra, thereby allowing the B-O stretching vibrations of **2**, **4**, **7**, and **8** at 966, 972, 992, and 970 cm^{-1}, respectively, to be assigned (Figures S7-1 and S7-2). These B-O bands are at lower frequencies than that of **5** (1105 cm^{-1}), but at higher frequencies than those of **3** (954 cm^{-1}) and **9** (909 cm^{-1}). These results indicate that the B-O stretching vibrational frequencies increase in the order B-O-R < B-O-O-R < B-O-H, as the size of the substituents on the oxygen atom decreases. The O-H stretching band of **2** was observed at 3373 cm^{-1}, which is lower than that of **5** (3634 cm^{-1}), which suggests that the O−H bond of **2** is weaker than that in **5**. The Raman spectra of the subporphyrin *B*-peroxides were measured to directly observe the O-O stretching vibration. As a consequence of the relatively intense fluorescence and facile decomposition of **2**, **4**, and **8** under the measurement conditions, their Raman spectra were difficult to observe. However, a rather clear Raman spectrum was obtained for the *tert*-butylperoxide **7**. The frequencies of the experimentally observed Raman feature of **7** is linearly correlated with the calculated Raman-active vibration modes (Figure S7-3). The σ-bond character of O−O bond leads to a small polarizability of the O-O stretching modes and hence the almost suppressed Raman peaks near 900–1000 cm^{-1}, where O-O stretching is predicted to be observed. However, as a result of coupling with the backbone vibration of the subporphyrin macrocycle, slightly allowed Raman peaks of **7** have been observed as broad signals around 900 nm.

The UV/Vis absorption and fluorescence spectra of **2**, **7**, and **8** in CH_2Cl_2 are quite similar to those of **3** and **5**, with their Soret-like bands at 372–374 nm, Q-like bands at 460–461 and 484–485 nm, and fluorescence maxima at 519–521 nm (Figure 2, see also Figures S5-1 and S5-2). On the other hand, peroxo-bridged dimer **4** and μ-oxo-bridged diboron **6** revealed blue-shifted Soret-like bands at 364 and 363 nm, respectively. Since the two subporphyrin subunits of **4** and **6** are in proximity, the energy shifts of the Soret bands were attributed to excitonic coupling between the subporphyrin moieties. We performed time-correlated single-photon counting (Figure S5-4) to obtain the lifetimes of the excited singlet state. The fluorescence decay profile of **2** fitted well with a single exponential function with a time constant of $\tau_f =$ 2.8 ns, which was quite similar to that of **3** ($\tau_f = 2.95$ ns), while a slightly shorter lifetime constant of $\tau_f = 2.3$ ns was obtained for **4**. These observations are consistent with the results obtained by femtosecond transient absorption measurements, where the excited species of **2** and **4** were found to decay with time constants of 2.8 and 2.3 ns, respectively.

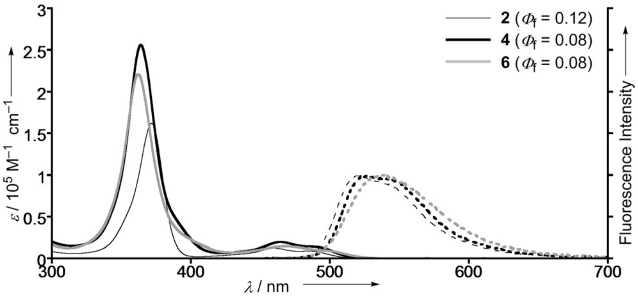
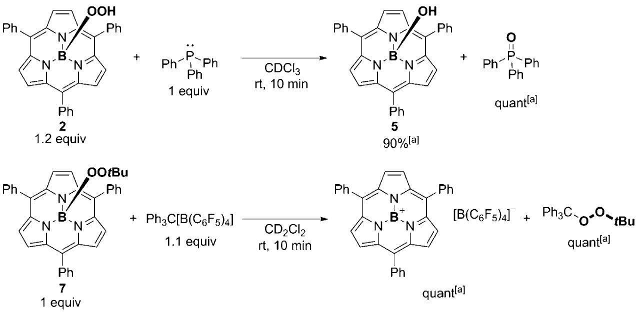


Figure 2. UV/Vis absorption and fluorescence spectra recorded in CH_2Cl_2.

The reactivity of the subporphyrin *B*-peroxides was briefly examined (Scheme 3). Subporphyrin *B*-hydroperoxide **2** smoothly oxidized triphenylphosphine to triphenylphosphine oxide in good yields with concurrent formation of **5**. However, **2** could not oxidize phenyldodecylsulfide or dodesylmethylsulfide, thus indicating its weak oxidation ability compared to *tert*-butylhydroperoxide and 3-chloroperoxybenzoic acid. The other *B*-peroxides **4**, **7**, and **8** could not oxidize triphenylphosphine. Finally, it was found that the reaction of **7** with $Ph_3C[B(C_6F_5)_4]$ produced triphenylmethyl-*tert*-butylperoxide and the borenium cation in good yields.[11d]



Scheme 3. Reactions of subporphyrinatoboron(III) peroxides. [a] Yields were determined by ^1H NMR spectroscopy, using 1,1,2,2-tetrachloroethane as an internal standard.

In summary, the subporphyrin *B*-peroxides **2**, **7**, and **8** were synthesized effectively in good yields by nucleophilic substitution of the boron methoxide **3** with the corresponding hydroperoxides. Thermal dimerization of **2** provided peroxo-bridged subporphyrin dimer **4** quantitatively. Single-crystal X-ray diffraction analysis revealed the first solid-state structures of a boron hydroperoxide, an acyclic boron organylperoxide, and a neutral peroxo-bridged diboron. As the electron-donating ability of the peroxy substituents increases, the O−O bond length increases while the s-orbital character of the central boron atoms decreases. The electrochemical properties of the peroxides can be modulated by exchanging the substituent on the peroxy moiety, with the photophysical properties remaining almost unchanged. These *B*-peroxides show only poor oxidizing abilities, but study of the novel reactivity of subporphyrin *B*-peroxides is worthy of further investigation.

Acknowledgements

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[12] The reaction mechanism for the oxygenation of **1** is unclear, but plausibly occurs through hydrogen abstraction by molecular oxygen, which forms a boryl radical intermediate (see Scheme S3-1); see also a) J. A. Baban, B. P. Roberts, *J. Chem. Soc. Perkin Trans. 2* **1987**, 497; b) B. Roberts, *Chem. Soc. Rev.* **1999**, *28*, 25.

[13] Crystallographic data for **2**: $C_{33}H_{22}BN_3O_2$, $M_r = 503.35$, triclinic, space group $P\bar{1}$, $a = 7.452(2)$, $b = 12.8870(19)$, $c = 13.6805(15)$ Å, $\alpha = 67.55(2)$, $\beta = 82.21(4)$, $\gamma = 84.73(4)^\circ$, $V = 1201.9(4)$ Å^3, $\rho_{\text{cald}} = 1.391\ \text{g cm}^{-3}$, $Z = 4$, $R_1 = 0.0448$ $(I > 2.0\sigma(I))$, $wR_2 = 0.1200$ (all data), GOF = 1.042. **4**: $(C_{66}H_{42}B_2N_6O_2)_2 \cdot CH_3CN$, $M_r = 1013.73$, monoclinic, space group $P2_1/n$, $a = 17.558(3)$, $b = 13.547(3)$, $c = 21.786(4)$ Å, $\beta = 92.192(5)^\circ$, $V = 5178.4(16)$ Å^3, $\rho_{\text{cald}} = 1.300\ \text{g cm}^{-3}$, $Z = 4$, $R_1 = 0.0541$ $(I > 2.0\sigma(I))$, $wR_2 = 0.1465$ (all data), GOF = 1.03. CCDC 1436115 (**2**), 1436116 (**4**), 1436117 (**5**), 1436118 (**7**), 1436119 (**8**), and 1436120 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[14] The crystal structures of **2**, **4**, **7**, and **8** have not revealed the presence of a short contact between the subporphyrin moiety and peroxy substiuents. Therefore, the effect of steric interactions on the O-O bond length of subporphyrin *B*-peroxides is inferred to be negligible.

[15] Optimizations and single point calculations were performed using the Gaussian 09 package: Gaussian 09, Revision A.03. The full list of the authors is given in the Supporting Information.

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