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Air- and Moisture-Stable *p*-Monothiobenzoquinones Incorporated in an Octaalkyl-*s*-hydrindacene Skeleton

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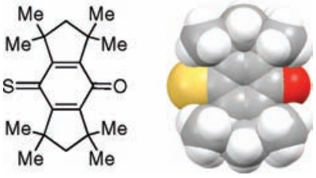
ABSTRACT



***p*-Monothiobenzoquinones incorporated in a fused-ring octaalkyl-*s*-hydrindacene skeleton have been synthesized as air- and moisture-stable reddish orange crystals by the oxidation of mercaptophenol derivatives with DDQ, which have been characterized by X-ray crystallography to show a planar quinoid framework.**

There have been extensive efforts to investigate the various functions of the *p*-benzoquinone derivatives as a hydrogen acceptor and oxidant in organic synthesis as well as bioactive molecules in photosynthesis and metabolism.[1] In contrast, the sulfur analogues, monothio- and dithiobenzoquinones, have rarely been explored (Figure 1).[2–4] The parent molecules (**3** and **4**) were initially generated by the thermal decomposition of 1,4-di(heteroallyl)benzenes in the gas phase and spectroscopically characterized at cryogenic temperatures in an argon matrix.[3] Additional experimental work has been devoted to the synthesis of benzoquinone sulfur congeners,[4] but their high reactivity always makes it difficult to isolate them in a pure form, thus producing the dimer or polymers through the formation of disulfide bonds concurrent with the gaining of the benzene aromatic stabilization energy. Such intermolecular reactions would be suppressed by taking advantage of the steric protection with bulky substituents on the carbon atoms of the benzoquinone skeleton. A labile but isolable 2,6-di-*tert*-butyl-4-thio-1,4-benzoquinone **5** was reported by Oda et al. in 2000 as a greenish yellow solid around room temperature.[5] The two *tert*-butyl groups are not bulky enough for steric protection, and compound **5** was still sensitive to moisture and other protic substrates; thus, its boat form was only predicted by a semiempirical theoretical calculation. Transition-metal complexes of the otherwise reactive dithio- and diselenobenzoquinones through the η^4-coordination of the four diene carbons have recently been synthesized by Amouri et al.[6]

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(1) Patai, S.; Rappoport, Z. In *The Chemistry of the Quinonoid Compounds*, 2nd ed.; Wiley: New York, 1988.

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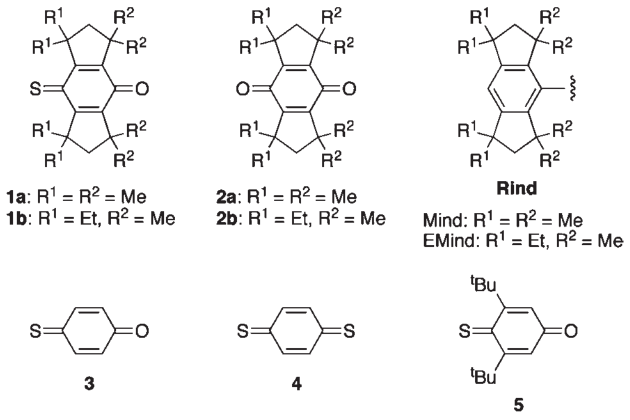


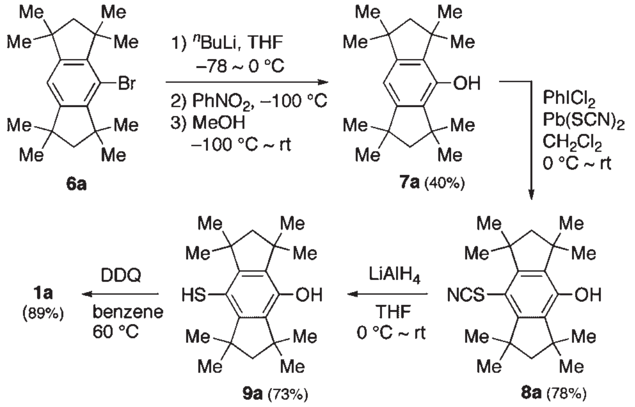
Figure 1. *p*-Monothiobenzoquinones and Rind Groups.

We now report the synthesis of air- and moisture-stable *p*-monothiobenzoquinones **1** incorporated in the bulky octa-R-substituted *s*-hydrindacene (Rind) skeleton and their full characterization including the first X-ray molecular structures, in comparison to the dioxygen counterparts, the *p*-benzoquinones **2** (Figure 1).

We recently set out to investigate novel π-conjugated compounds containing multiple bonds of the heavier main group elements by the introduction of the fused-ring bulky Rind groups.[7,8] A variety of Rind derivatives, as represented by Mind ($R^1 = R^2 =$ Me) and EMind ($R^1 =$ Et, $R^2 =$ Me), can be prepared by the intramolecular Friedel–Crafts double-cyclization reaction with some modification of the method reported for the octamethyl prototype Mind.[9] These Rind groups have several advantages, such as a high chemical stability, tunability of solubility by the peripheral R^1 substituents, and size-controllability of the steric bulkiness by the proximal R^2 substituents. Another unique feature of the bulky Rind groups resides in the fact that the *para* position is not occupied in the skeleton, which provides the potential candidates to act as *p*-phenylene types of difunctional compounds. Thus, we designed and synthesized two Rind-based monothiobenzoquinones (**1a** and **1b**).

The synthetic route to the Mind-based **1a** starting from (Mind)Br (**6a**) is outlined in Scheme 1. A bulky phenol derivative, (Mind)OH (**7a**), was prepared by the reaction of (Mind)Li with $PhNO_2$.[10] The treatment of **7a** with a mixture of $PhICl_2$ and $Pb(SCN)_2$[11] in CH_2Cl_2 led to the formation of *p*-thiocyanated phenol, NCS(Mind)OH (**8a**), despite its steric bulkiness. The subsequent reduction of the thiocyanate group of **8a** with $LiAlH_4$ afforded mercaptophenol, HS(Mind)OH (**9a**), as colorless crystals. Finally, the monothiobenzoquinone **1a** was synthesized by oxidative treatment of **9a** with excess dichlorodicyano-*p*-benzoquinone (DDQ) in benzene at 60 °C and isolated as an orange solid in 89% yield by silica gel column chromatography in air using dry hexane and Et_2O as the eluent. Recrystallization from hexane afforded the reddish orange crystals of **1a**. The EMind-based **1b** was also prepared as a deep orange solid by a similar synthetic procedure.[12] As reference compounds, the hydrindacenequinones[13] (**2a** and **2b**) were obtained by the reaction of (Rind)Li with CuBr[14] and then their overoxidation upon exposure to O_2 gas.[12]

Scheme 1. Synthesis of *p*-Monothiobenzoquinone **1a**



The formation of **1** has been clearly confirmed by the spectroscopic methods. In the ^{13}C NMR spectrum of **1a**, two characteristic signals due to the thiocarbonyl (C=S) and carbonyl (C=O) groups appear at 224.2 and 188.9 ppm. The IR spectrum of **1a** shows an intense carbonyl absorption at 1618 cm^{-1} and a weak thiocarbonyl absorption at 1160 cm^{-1}, which are comparable to those previously reported for **5** (1639 and 1141 cm^{-1}).[5] It is noteworthy that the resulting monothiobenzoquinones are quite air- and moisture-stable for more than half of a year in the solid state with no detectable change found in the ^1H NMR spectra and for a few days in a dilute hexane solution (ca. 10^{-5} mol/L) as confirmed by their UV–vis spectra, which indicates the efficient protection ability of the bulky Rind system.

The molecular structures of **1** were studied by X-ray crystallography as shown in Figure 2. A slightly *cis*-bent geometry was found for the monothiobenzoquinone skeleton of the Mind-based **1a** as represented by the angles of

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(7) Reviews: (a) Matsuo, T.; Kobayashi, M.; Tamao, K. *Dalton Trans.* **2010**, *39*, 9203. (b) Matsuo, T.; Li, B.; Tamao, K. *C. R. Chim.* **2010**, *13*, 1104.

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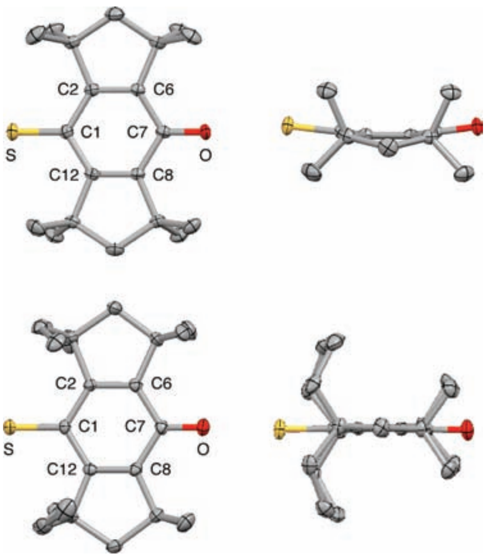

Figure 2. Molecular structures of **1a** (top) and **1b** (bottom); top view (left) and side view (right). Hydrogen atoms are omitted for clarity.

S−C1···C7 = 173.27(8) and O−C7···C1 = 172.3(2)°, but it is difficult to determine the precise positions of the sulfur and oxygen atoms because of their mutual disorder in the crystal.[12] Alternatively, the molecular structure of the EMind-based **1b** has been characterized by no crystallographic disorder, showing a highly planar monothiobenzoquinone framework with the bent angles of S−C1···C7 = 178.58(9) and O−C7···C1 = 179.08(12)°. Thus, the rigid fused-ring Rind system makes a planar quinoid π-electron system, which is in sharp contrast to the boat form predicted for **5**. The C=S bond length of **1b** [1.6496(15) Å] is much shorter than the C−S single bond length of HS(Mind)OH **9a** [1.7861(17) Å][12] and in the range of those for the alkyl- or aryl-substituted thioketones (1.57−1.74 Å).[15] The C=O bond length of 1.2362(18) Å is comparable to those found in *p*-benzoquinone **2b** [1.2230(15) and 1.2292(15) Å].[12] The C−C distances around the quinone ring of **1b** and **2b** are also similar to each other; the short C2−C6 and C8−C12 bonds [1.352(2) (**1b**) and 1.3424(17) and 1.3437(17) Å (**2b**)] and the long C1−C2, C6−C7, C7−C8, and C1−C12 bonds [1.471(2)−1.480(2) (**1b**) and 1.4819(17)−1.4893(17) Å (**2b**)] are indicative of a closed-shell quinoid structure.

The UV−vis spectrum of **1a** in hexane exhibits a strong absorption peak at 341 nm (ε = 26800) along with a weak absorption at 422 nm (ε = 500). The former strong band is assignable to the π−π^* transition, which is red-shifted by 60 nm relative to that of **2a** [281 nm (ε = 12900)]. The latter weak band is responsible for the orange color of **1a**; the maximum wavelength absorption is much different from that of the green-colored **5** [758 nm (ε = 32)], which was assigned to the n−π^* transition of the thiocarbonyl group.[5] Thus, the electronic absorption properties of these monothiobenzoquinones (**1** and **5**) are quite different from each other, which may depend on their molecular structures.

We have also examined the electrochemical properties of **1a** and **2a**. The reversible reduction waves were observed at −0.97 V for **1a** and −1.38 V for **2a** by cyclic voltammetry. This observation suggests that the introduction of a sulfur atom into the quinone skeleton causes the lowering of the LUMO energy level.

To elucidate the electronic nature of the monothiobenzoquinone, DFT calculations were carried out for **1a** at the B3LYP/6-311+G** level using the Gaussian 03 program package.[16] Two optimized structures, a slightly *cis*-bent form (C_s symmetry) and a planar form (C_2 symmetry) have been found to have nearly the same energies; the relative energies are 0.00 (C_s) and 0.78 (C_2) kcal mol^{-1}, which reproduce the X-ray molecular structures of **1a** and **1b**, respectively.[12] These conformational differences may be associated with the ring-puckering of the two five-membered rings linked by the C=S and C=O moieties.

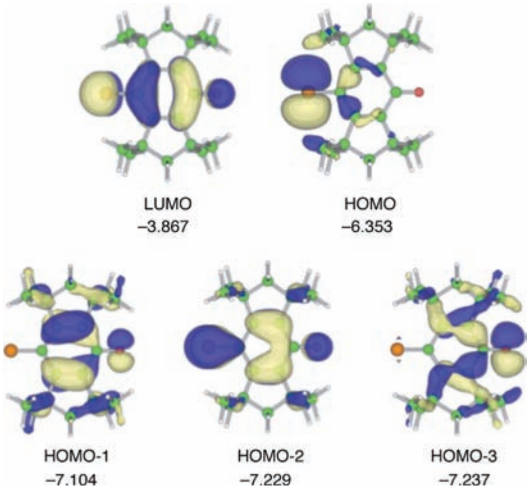

Figure 3. Selected molecular orbitals and their energy levels (eV) of **1a-C_s** (top view).

The selected molecular orbitals of **1a-C_s** are depicted in Figure 3. While the HOMO is mainly represented by the nonbonding pairs of electrons on the sulfur atom, the LUMO involves a substantial π^*-conjugation of 2p- and 3p-orbitals delocalized over the monothiobenzoquinone skeleton. The lower lying HOMO-1 and HOMO-2 are essentially represented by the π-type MOs, whereas the HOMO-3 involves the oxygen atom's nonbonding pairs. The HOMO level of **1a-C_s** (−6.353 eV) is much higher than that of **2a-C_{2v}** (−7.127 eV).[12] In addition, the LUMO level of **1a-C_s** (−3.867 eV) is lower than that of **2a-C_{2v}** (−3.426 eV), being in good agreement with the already mentioned

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(15) The Cambridge Structural Database, version 5.31 (Nov 2009). Allen, F. H. *Acta Crystallogr. Sect. B* 2002, *25*, 380.

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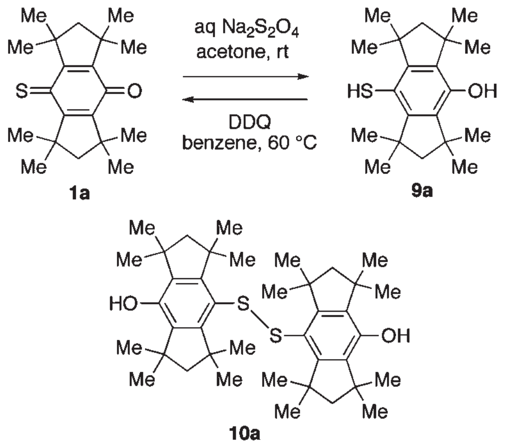
Scheme 2. Redox Transformation between **1a** and **9a**



electrochemical experimental results. Thus, the total HOMO−LUMO gap in **1a-*C*$_s$** (2.486 eV) is much smaller than that in **2a-*C*$_{2v}$** (3.701 eV).

The strong and weak absorption wavelengths were evaluated to be 357 and 507 nm on the basis of the TD-DFT calculations of **1a-*C*$_s$**. The former is mainly assigned to the HOMO-2→LUMO ($\pi-\pi^*$) transition. The latter is assignable to the mixed version of HOMO-3→LUMO ($n-\pi^*$) and HOMO-1→LUMO ($\pi-\pi^*$) transitions. The HOMO−LUMO transition is calculated to give a very weak absorption peak at 891 nm because of a forbidden transition.

In the context of the excellent electron-accepting ability of the monothiobenzoquinones, we have also investigated the chemical reduction of **1a** by the action of sodium dithionite ($Na_2S_2O_4$) (Scheme 2).[12] The treatment of an acetone solution of **1a** with an aqueous solution of $Na_2S_2O_4$ led to the stepwise formation of the half-reduced disulfide **10a** and the full-reduced mercaptophenol **9a**. The intermediate disulfide **10a** was isolated for structural characterization.[12] This compound was also observed in the ^1H NMR spectrum of the reaction mixture of **8a** with DDQ. Thus, we can now easily perform the redox transformation between the monothiobenzoquinone and mercaptophenol through the disulfide intermediate.

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Supporting Information Available. Experimental details, CIF for **1a**, **1b**, **2a**, **2b**, **9a**, and **10a**, DFT calculations, and complete listing for ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.