Redox Behaviour of Pyrazolyl-Substituted 1,4-Dihydroxyarenes: Formation of the Corresponding Semiquinones, Quinhydrones and Quinones

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Z. Naturforsch. **61b,** 252 – 264 (2006); received November 25, 2005

Pyrazolyl-substituted 1,4-dihydroxybenzene and 1,4-dihydroxynaphthene derivatives have been synthesized by reaction of 1,4-benzoquinone and 1,4-naphthoquinone, respectively, with pyrazole. Cyclovoltammetric measurements have shown that 1,4-benzoquinone possesses the potential to oxidize 2-(pyrazol-1-yl)- and 2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene. The 2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene reacts with air to give quantitatively black insoluble 2,5-bis(pyrazol-1-yl)-1,4-quinhydrone. Black crystals of 2,5-bis(pyrazol-1-yl)-1,4-quinhydrone suitable for X-ray diffraction were grown from methanol at ambient temperature (monoclinic $C2/c$). The poor yields of pyrazolyl-substituted 1,4-dihydroxybenzene and 1,4-dihydroxynaphthene derivatives can be explained by the formation of insoluble black quinhydrons in the reaction of benzoquinone and naphthoquinone with pyrazole. The dianions of 2-(pyrazol-1-yl)- and 2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene react with oxygen to give the corresponding semiquinone anions. 2,5-Bis(pyrazol-1-yl)-1,4-benzoquinone shows two reversible one-electron reduction processes in cyclovoltammetric measurements, whereas pyrazolyl-substituted 1,4-dihdroxybenzene and -naphthene derivatives undergo irreversibile electron-transfer processes.

Key words: Quinhydrone, Semiquinone, Hydroquinone, Redoxactive Ligands, Crystal Structure