Electron Donor-Acceptor Compounds. Synthesis and Structure of 5-(1,4-Benzquinone-2-yl)-10,15,20-trialkylporphyrins

Steffen Runge, Mathias O. Senge*

Institut für Organische Chemie (WE02), Fachbereich Chemie, Freie Universität Berlin, Takustraße 3, D-14195 Berlin, Germany

Z. Naturforsch. 53b, 1021–1030 (1998); received June 15, 1998

Porphyrians, Quinones, Electron Transfer Compounds, Crystal Structure, Conformation

A series of 5-(benzoquinone)-10,15,20-trialkylporphyrins was synthesized via cross condensation of the respective aldehydes, 2,5-dimethoxybenzaldehyde and pyrrole followed by demethylation with BBr₃ and oxidation with PbO₂. This method worked reasonably well for compounds bearing the benzoquinone substituent and butyl, isopropyl, 1-methylpropyl and 2-ethylpropyl residues (2a-d). The free base porphyrin quinones were converted into the zinc(II) complexes (3a-d) all of which showed remarkable stability for porphyrin quinones. The zinc(II) complex 3c bearing isopropyl residues was investigated by X-ray crystallography and showed a supramolecular structure consisting of polymeric chains facilitated by coordination of a benzoquinone oxygen to a neighboring zinc(II) center. Attempts to synthesize a 5-(benzoquinone)-10,15,20-tris(tert-butylporphyrin) resulted in the formation of a yellow porphomethene (4), which could not be oxidized further. A crystal structure analysis of 4, the first for a free base porphomethene, shows an extremely twisted conformation with syn-orientation of the three tert-butyl groups. The results indicate that new methods will have to be developed for the synthesis of nonplanar porphyrin quinones.

* Reprint requests to Prof. Dr. M. O. Senge. E-mail: mosenge@chemie.fu-berlin.de