

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

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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 BBr_3 and oxidation with PbO_2 . 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.

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