On The Aromaticity of Porphin

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We have undertaken a study of the bromination of porphin. We have learned contrary to literature reports, that bromine (in chloroform) attacks porphin preferentially at the meso position and that bromination of this meso monobromoporphin produces a single dibromo product, namely 5, 15-dibromoporphin. Our results are interpreted in terms of the aromaticity of the different peripheral carbon atoms.

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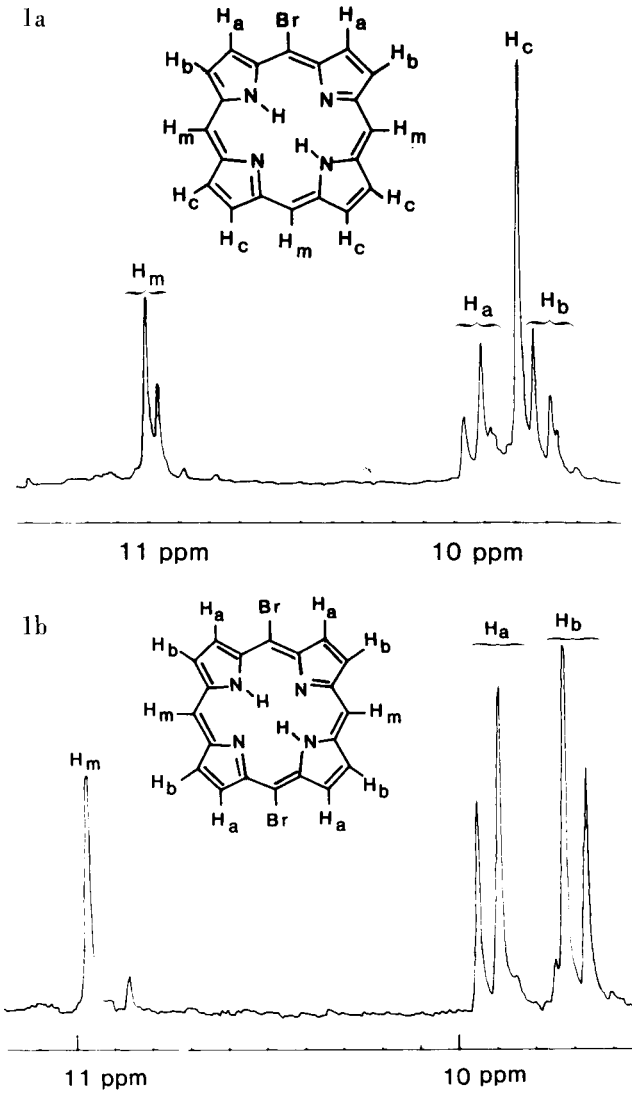
The bromination of porphin and other porphyrins has been studied by several groups (1-5). All these workers report that attachment of bromine occurs at the pyrryl positions. For instance, Caughey, Alben, Fujimoto, and York (1) studied the bromination of the dimethyl ester of deuteroporphyrin IX and found that substitution occurs at the pyrryl positions, producing the 3,8-dibromo derivative. Samuels, Shuttleworth, and Stevens (2) report that the bromination of porphin by reaction of bromine in chloroform or *N*-bromosuccinimide in carbon tetrachloride yields a single product, β-monobromoporphin. Schlozer and Fuhrhop (3) confirmed the report of Samuels *et al.* Bonnett, Gale, and Stephenson (4) have reported that direct bromination of octaethylporphin fails. Hence, all



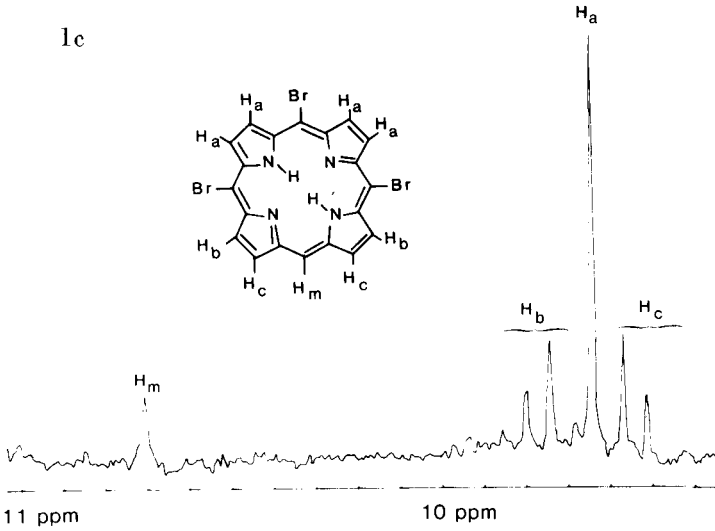


Figure 1. NMR Spectra. The spectra shown were taken on solutions made up by dissolving ~2 mg of porphyrin in 0.6 ml of solution containing 50% by volume mixture of deuteriochloroform and deuteriotrifluoroacetic acid with a trace of TMS. a. 5-Monobromoporphin. The ratio of the area under the β peaks to the area under the meso peaks ($A\beta/A_m$) is (2.7 ±0.1):1; theoretical: 2.67:1. b. 5,15-Dibromoporphin. $A\beta/A_m$ = (4.0 ±0.2):1; theoretical 4:1. c. 5,10,15-Tribromoporphin. $A\beta/A_m$ = (9.0 ±1.8):1; theoretical 8:1.

reports in the literature indicate that bromination of the pyrryl position is favored over the meso position. This work is significant in terms of the aromaticity of the porphyrin nucleus.

On the basis of our earlier results on the nitration of porphin (6) we joined the school which holds that the inner cycle of 16 atoms and 18π electrons is the aromatic part of the porphyrin molecule and that the β-β bonds in the residues are more olefinic in nature. The reported bromination at the pyrryl position would not be inconsistent with our point of view provided the bromination proceed *via* addition-elimination. Our experiments, which were designed to test this hypothesis, all failed. We did not obtain β-monobromoporphin when we treated porphin with bromine in chloroform or in acetic acid. The chloroform reaction yielded at least three products (I, II, III); the acetic acid reaction yielded at least six products, only three of which were produced in appreciable amounts. The three major products of the acetic acid preparation are identical with the three bromoporphins obtained in the chloroform preparation.

All porphyrins were separated and purified by repeated chromatography on dry, acidic alumina. They were then re-crystallized from 50v:50v hexane-benzene solutions. Compound I has a visible spectrum identical to that reported by Samuels, *et al.* for the product which they identified as β-monobromoporphin. The mass spectra (Finnegan 4021 GS/MS/DS System) of compounds I, II, and III showed that they were a mono-, a di-, and a tribromoporphin, respectively. The nmr (Joel FX 90Q/EM/LPCS) spectra showed that I is 5-monobromoporphin, II is 5,15-dibromoporphin, and III is 5,10,15-tribromoporphin. (See Figures 1a, b and c.) These results strongly suggest that the bromination of porphin is electrophilic, that a bromine substituent on a porphin nucleus has a very strong and predictable directing effect (since only a single dibromo structure was formed in any appreciable amount), and that only the methine bridge positions are chemically benzene-like, *i.e.*, aromatic.

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