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EPR properties of free porphyrin bases

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Experiments have been carried out with free porphyrins bases belonging to two groups: (1) α, β, γ, δ *meso*-tetraphenylporphyrin (TPP) and (2) octaethylporphyrin (OEP). Group (1) included (TMPP) - meso-tetra(4methyl)phenylporphyrin, (TDPP) - *meso*-tetra(4-deutero)phenylporphyrin, (TMXPP) - *meso*-tetra(methoxy)phenylporphyrin, (T4H3MXPP) - *meso*-tetra(4-hydroxy-3-methoxy)phenylporphyrin, (TPIPP) - *meso*-tetra(piperonyl)phenylporphyrin while Group (2) was represented by (OEP) - 2,3,7,8,12,13,17,18- octaethylporphyrin. For synthesized compounds, electron paramagnetic resonance (EPR) spectra have been measured. Linewidths *ΔH, g*-factors and EPR amplitudes *(A)* in arbitrary units were calculated. Deuteration of phenyl groups in *para* position of TDPP increases *g*-factor to 2.0028 but linewidth change is negligible. *g*-factors all other porphyrins are in the range of 2.0024-2.0026. Linewidths of EPR spectra are between 0.39 mT and 0.67 mT. This indicates that unpaired electron is delocalized over more than one porphyrin ring. Partial deuteration (TDPP) of the porphyrin does not change the linewidth of the spectrum because deuterons are not localized close to the porphyrin ring. Methoxy and hydroxy peripheral substituents in porphyrins increase the intensity of EPR signal by one to two orders of magnitude in comparison to methyl, ethyl and piperonyl substituents.