

Oxophlorin and metallooxophlorin radicals - DFT studies.

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Streszczenie

*A flexible oxophlorin macrocycle, which allows the location of labile hydrogen atoms alternatively at the pyrrole nitrogen, oxygen, or meso-carbon atoms, has been studied by density functional theory (DFT). DFT calculations were carried out on oxophlorin **1**, 5-hydroxyporphyrin **2**, and two isomers of oxophlorin **3** and **4** (the proton added at the tetrahedral C(15) or the C(10) meso-carbon, respectively). The oxophlorin–hydroxyporphyrin structural changes are appropriately reflected by the significant changes of the meso carbon–oxygen bond lengths, which are in the limits of typical C–O and C=O distances. The rearrangement that creates the iso-oxophlorin macrocycle **3** (**4**) results in near tetrahedral geometry around the C(15) (C(10)) carbon atom, with the C(14)–C(15) and C(15)–C(16) (C(9)–C(10) and C(10)–C(11)) bond lengths corresponding to a single C–C bond. 5-Hydroxyporphyrin **2** is aromatic and has a bond pattern resembling that of regular porphyrin. In **1**, **3**, and **4**, a localization of single and double bonds was seen, which agrees with the nonaromatic nature of oxophlorin, or isooxophlorin. The relative stability decreases in the order: **2** (0) > **3** (4.85) > **1** (5.11) > **4** (10.04) > **3**-cis (12.89) (the number in parentheses is the relative energy, in kcal mol^{−1}). The energy difference between the NH-cis and NH-trans tautomers, which is 8.04 kcal mol^{−1} for **3**, results from a destabilizing NH–NH cis-interaction. DFT calculations were performed on the oxophlorin dianion radical (OP)^{2−} and a series of metallooxophlorin radicals ([(OP)Li^I][−], [(OP)Zn^{II}], [(OP)Ga^{III}]⁺, and (OP)Ga^{III}F, in order to assess their electronic structures. Typically, the largest atomic spin density was found at the C(10) (C(20)) and C(15) meso positions, with the spin density at C(15) being twice as large as that at C(10). The spin density at the C(5) atom is negligible. A large spin density was found at the O(5) oxygen atom. The amount of spin density at the meso positions decreased as the cationic charge increased. When considering the absolute values of the spin densities, the*

opposite trend was observed at the pyrrolic carbon atoms. The spin density at the nucleus (Fermi contact terms) has also been analyzed. The spin distributions of iron oxophlorins determined by NMR were attributed to an oxophlorin radical electronic structure. The calculated spin density maps accounted for the essential NMR spectroscopic features of important intermediates in the heme degradation process—iron oxophlorin complexes. The DFT calculations reproduced the following spectroscopic patterns: a) $|\delta H(15)| > |\delta H(10)| \gg |\delta(\beta-H)|$, b) a sign alternation of the contact shifts for identical substituents located on the same pyrrole ring.

Adres publiczny

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