

Geometry and tautomerism of 26,28-dioxasapphyrin and 26,28-dithiasapphyrin: DFT studies.

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The density functional theory (DFT) calculations have been carried out on 26,28-dioxasapphyrin (O₂SapH) and 26,28-dithiasapphyrin (S₂SapH) including all likely geometrical isomers and NH tautomers. The peculiar skeleton of sapphyrin with an inverted pyrrole ring lying opposite to the bipyrrrolic unit (**I**) and the regular planar arrangement (**P**) of the macrocycle with three nitrogens and two heteroatoms pointing to the center of the macrocycle were considered. Consequently, a total of eight structures resulting from the feasible geometrical isomerism and NH tautomerism of diheterosapphyrins were studied. The optimized bond distances and angles of 26,28-diheterosapphyrins compare favorably with the relevant X-ray structures of sapphyrins and heterosapphyrin. The pyrrole bond distances decrease in the series: C_α-C_β > C_α-C_{meso} > C_α-N > C_β-C_β, reproducing the pattern of the regular porphyrin or dicationic sapphyrins. There is an appreciable effect from the aromatic character of the macrocycle on the furan or thiophene moieties. These C_α-C_β distances are longer and the C_β-C_β distances are shorter than those in free furan or thiophene. The relative stability of the postulated tautomeric forms decreases in the order of {25-NH, 27-N, 29-N} **P**₂₅ > {25-NH, 27-N, 29-N} **I**₂₅ > {25-N, 27-NH, 29-N} **P**₂₇ > {25-N, 27-NH, 29-N} **I**₂₇ for O₂SapH and {25-NH, 27-N, 29-N} **P**₂₅ > {25-N, 27-NH, 29-N} **P**₂₇ >> {25-NH, 27-N, 29-N} **I**₂₅ > {25-N, 27-NH, 29-N} **I**₂₇ for S₂SapH. The formation of the inverted 26,28-dithiasapphyrin structure is strongly energetically disfavored (ca. 30 kcal/mol). Both extreme geometries **P** and **I** are energetically accessible for 26,28-dioxasapphyrin. The localization of the NH proton on the bipyrrrolic fragment is evidently preferred in each investigated case.

Słowa kluczowe

Chemical structure, Energy, Mathematical methods, Molecular structure, pyrrols

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