Geometry and tautomerism of sapphyrin - DFT studies.

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Streszczenie

The structure and total energy have been investigated, applying the density functional theory (DFT), for idealized sapphyrin derivatives, created by replacements of *meso*-phenyl groups of 5,10,15,20-tetraphenylsapphyrin or *β*-alkyl groups of decaalkylsapphyrin with hydrogens or two methyl groups, respectively. The following species have been considered: the dication of plain sapphyrin ($SapH_5^{2+}$) 12,13-dimethylsapphyrin (12,13-$DMSapH_3$), 12,13-dimethylsapphyrin dication (12,13-$DMSapH_5^{2+}$), and the 10,15-dimethylsapphyrin dication (10,15-$DMSapH_5^{2+}$). To address the issue of tautomerization the calculations have been carried out for the six feasible distribution patterns of NH protons among the five nitrogen centers of the planar sapphyrin **P***0*$_i$ (*i*=1–6). The B3LYP/6-31G optimized bond lengths and angles of sapphyrin or (dimethylated sapphyrin) skeletons are in satisfactory agreement with X-ray crystallographic values determined for decaalkylsapphyrin dications. The calculated total energies, using the B3LYP/6-31G**//3-21G approach demonstrate that the plain sapphyrin and 12,13-dimethylsapphyrin dications favor the planar geometry of the macrocycle. Localization of the methyl groups at the 10,15-*meso* positions of sapphyrin reversed the order of stability leading to the energy preference for the inverted structure. Thus, this steric factor related to the *meso* substitution seems to be instrumental in the*C* pyrrolic ring inversion. The DFT calculation also provided the relative stability frame for the complex tautomeric equilibria of $SapH_3$ which involve six different forms. Their relative stability decreases in the range: {25-NH, 26-N, 27-NH, 28-NH, 29-N} **P***0*$_3$>({25-NH, 26-N, 27-NH, 28-N, 29-NH}**P***0*$_1$>{25-NH, 26-NH, 27-N, 28-NH, 29-N} **P***0*$_5$>{25-N, 26-NH, 27-NH, 28-NH, 29-N} **P***0*$_2$>{25-NH, 26-N, 27-N, 28-NH, 29-NH}**P***0*$_6$>{25-N, 26-N, 27-NH, 28-NH, 29-NH} **P***0*$_4$. The stability order can be qualitatively related to the number and the nature of the *cis* NH interactions present in the sapphyrin core.

Słowa kluczowe

Sapphyrin, Tautomerism, density functional theory

Adres publiczny

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