Phosphorus complexes of *N*-fused porphyrin and its reduced derivatives: new isomers of porphyrin stabilized via coordination.

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Streszczenie

N-fused isophlorin **3** and its tautomeric phlorin forms **4** and **5**, the new constitutional isomers of porphyrin which preserve the basic skeleton of their maternal *N*-fused porphyrin, have been identified in the course of investigation of phosphorus insertion into *N*-fused porphyrin **2**. *N*-fused porphyrin reacts with PCl_3 in toluene yielding phosphorus(V) *N*-fused isophlorin **3**-P wherein the macrocycle acts as a trianionic tridentate ligand. The identical product has been formed in the reaction of *N*-confused porphyrin **1** and $POCl_3$ or PCl_3. The coordinating environment of phosphorus(V) in **3**-P as determined by X-ray crystallography resembles a distorted trigonal pyramid with the nitrogen atoms occupying equatorial positions with the oxygen atom lying at the unique apex. Phosphorus(V) is significantly displaced by 0.732(1) Å from the N_3 plane. The P−N distances are as follows P−N(22) 1.664(2), P−N(23) 1.645(2), and P−N(24) 1.672(2). All P−N(pyrrolic) bond lengths are markedly shorter than the P−N distances in phosphorus porphyrins. **3**-P is susceptible to proton addition at the inner C(9) carbon atom, yielding aromatic **4**-P. The modified macrocycle acts as a dianionic ligand and allows the efficient 18 π-electron delocalization pathway. Two stereoisomers affording the *syn* (**4**-P_{syn}) and *anti* (**4**-P_{anti}) location of the H(9) atom with respect to the oxygen atom of the PO unit have been identified by ^1H NMR. A regioselective reduction of free base *N*-fused porphyrin **2** with $NaBH_4$ yielded a nonaromatic isomer of **4**, that is, *N*-fused phlorin **5** due to an addition of a hydride to the C(15) carbon and a proton to one of the pyrrolic nitrogens. The isomer **5** reacts with PCl_3 yielding phosphorus(V) fused isophlorin **3**-P. Density functional theory has been applied to model the molecular and electronic structure of porphyrin isomers **3**, **4**, and **5** and their phosphorus(V) complexes.

Słowa kluczowe

Aromatic compounds, Macrocycles, Molecular structure, Phosphorus, Pyrroles

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