Phenanthrene cyclocarbonylation – core post-synthetic modification of phenanthriporphyrin

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Streszczenie

The unique [$Fe(CO)_5$]-induced cyclocarbonylation of the phenanthriporphyrin core is an intriguing example of a post-synthetic core modification of the macrocycle. The reaction involves the activation of C(22)–H and C(25)–H bonds, located in the bay region of the phenanthrene fragment. The transformation is induced by iron coordination and leads to the incorporation of a CO molecule into the hydrocarbon fragment. By introducing the carbonyl moiety into the macrocycle core, thus, creating cyclopenta[*def*]phenanthrene-4-one, the molecule adopts a highly bent conformation, as confirmed by X-ray diffraction. The reversible protonation occurring at the central *meso* carbon atom stabilizes its constitutional isomer,*i.e.*, the C_s-symmetric isoketophenanthriporphyrin in its dicationic form. The protonation of the *meso* position causes a significant change in the spectral properties of the macrocycle. Initially misleading, “quasi-aromatic” relocations of ^{1}H NMR signals detected for the macrocyclic dications were accounted for by the carbocation-natured mesomers contributing to the electronic structure of the molecule.

Adres publiczny

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