5,10,15-triaryl-21,23-dioxacorrole and its isomer with a protruding furan ring.

Autorzy

Miłosz Pawlicki

Lechosław Latos-Grażyński

Ludmiła Szterenberg

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Artykuł

An oxa-analogue of 5,10,15-triarylcorrole, i.e., 5,10,15-triaryl-21,23-dioxacorrole (21,23-O_2Cor)H, where two pyrrole rings are replaced by furan moieties, has been produced by condensation of 2,5-bis(arylhydroxymethyl)furan, 2-phenylhydroxymethylfuran, and pyrrole. 2-Phenylhydroxymethylfuran serves as the suitable synthone to introduce a furan ring with the ability create a direct pyrrole−furan α−α bond. The replacement of 2-phenylhydroxymethylfuran by 3-phenylhydroxymethylfuran led to a nonaromatic isomer of (21,23-O_2Cor)H, i.e., (iso-21,23-O_2Cor)H, which accommodates two furan rings. The protruding furan is built into the macrocycle via β and β‘ carbon atoms with the oxygen atom pointing outward. Crystal structures of the [(21,23-O_2Cor)H_2]$_2$[$ZnCl_4$] and [(iso-21,23-O_2Cor)H_2]Cl have been studied by X-ray crystallography. The complex $ZnCl_4^{2-}$ anion is located in a clam-shell-like cavity formed by two 21,23-dioxacorrole cations of the [(21,23-O_2Cor)H_2]$_2$[$ZnCl_4$] unit. The 21,23-dioxacorrole cation is only slightly distorted from planarity. In [(iso-21,23-O_2Cor)H_2]Cl, the macrocycle is strongly puckered as the internal ring is contracted by two carbon atoms when compared to regular porphyrin. The chloride anion is located over the center of the macrocycle and is involved in two intra (N)H···Cl and two intermolecular (C)H···Cl interactions to be classified as a tetrafurcate system. The (21,23-O_2Cor)H molecule preserves aromaticity of the parental corrole with characteristic downfield positions of furan and pyrrole resonances in ^{1}H NMR accompanied the NH resonance at the upfield position (−2.53 ppm). The temperature-dependent features detected in ^{1}H NMR spectra of (21,23-O_2Cor)H are consistent with the existence of a tautomeric equilibrium which involves two tautomers alternatively protonated on N(22) or N(24) nitrogen atoms. The density functional theory (DFT) has been applied to model the molecular and electronic structure of two tautomers of 21,23-dioxacorrole {22-N, 24-NH}, {22-NH, 24-N}. The total energies calculated using the B3LYP/6-31G**//B3LYP/6-31G* approach demonstrate a very small energy difference (1.4 kcal/mol) between tautomers suggesting their simultaneous presence in equilibrium. Insertion of nickel(II) into (21,23-O_2Cor)H yields five-coordinate (21,23-O_2Cor)Ni^{II}Clthe first high-spin nickel(II) in a corrole-like macrocyclic environment.

Słowa kluczowe

Anions, Aromatic compounds, Macrocycles, Molecular structure, Pyrroles

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