Magnetic circular dichroism of 5,10,15,20-tetraphenylsapphyrin.

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Streszczenie

Magnetic circular dichroism (MCD) spectra were obtained for the inverted and "normal" forms of doubly protonated 5,10,15,20-tetraphenylsapphyrin and for the inverted neutral form. In all these species, the same pattern of the signs of Faraday B terms, {+,−,+, −}, is revealed for the four lowest singlet electronic transitions. This sequence is opposite to that observed in sapphyrins that are unsubstituted at the meso *positions. The results can be accounted for by the reversed patterns of the orbital energy splittings in the two highest occupied π orbitals (ΔHOMO) and the two lowest unoccupied π orbitals (ΔLUMO). Indeed, the application of the perimeter model leads to the prediction that in the parent sapphyrin, ΔHOMO<ΔLUMO, whereas the opposite becomes true after fourfold phenyl substitution at the* meso *positions. These predictions are corroborated by the results of quantum-chemical calculations. The calculated values of ΔHOMO−ΔLUMO are quite small, which places sapphyrin close to the case of the so-called "soft chromophore", for which ΔHOMO=ΔLUMO. Titration of solutions containing the neutral chromophore with bases and acids leads to parallel changes in the electronic absorption and MCD spectra that indicate presence of the anionic and singly protonated species.*

Adres publiczny

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