
The Exceptional Stability of Azacalixphyrin and its Dianion

Gabriel Marchand*^{†1}, Adèle Laurent¹, and Denis Jacquemin^{2,1}

¹Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation (CEISAM) – CNRS : UMR6230, Université de Nantes – UFR des Sciences et des Techniques - 2 rue de la Houssinière BP 92208 - 44322 NANTES Cedex 3, France

²Institut Universitaire de France (IUF) – Ministère de l'Enseignement Supérieur et de la Recherche Scientifique – Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

Résumé

Azacalixphyrin (Fig.1, left) is the precursor of potentially highly versatile isostructural and isoelectronic "pyrrol-free" analogues to porphyrins (Fig.1, right) [1]. Like porphyrins, the molecular basis of azacalixphyrin is composed of a 16-membered ring containing 18 delocalized pi electrons, implying aromaticity according to the Hückel's rule. Surprisingly, this new macrocyclic compound is stable to such an extent that it could be exposed to air for months as a solid or for days in solution without detectable changes. This high stability is preserved even in the presence of water under air. However, no rationalization of this specific property has been established yet.

Here, we present a theoretical study on the stability of azacalixphyrin. In addition, since we find that azacalixphyrin has the ability to capture easily two electrons, we also discuss the results obtained with its dianion. We show that the aromaticity of azacalixphyrin is very close to that of highly aromatic compounds such as benzene. We also find that all reactions with water are extremely endergonic, especially for the dianion.

Chen, Z.; Giorgi, M.; Jacquemin, D.; Elhabiri, M.; Siri, O. *Angew. Chem. Int. Ed.* **2013**, *52*, 6250-6254

Mots-Clés: Azacalixphyrin macrocycle, porphyrin analogue, stability, dianion, density functional theory

*Intervenant

[†]Auteur correspondant: gabriel.marchand@univ-nantes.fr