

Anion Recognition by Heterocalixarenes: Understanding the Physical Nature of the Interaction

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Abstract:

Non-covalent interactions are the main forces involved in the recognition, transport and regulation of virtually all events in biological systems [1]. Although the chemical relevance of anionic molecules is very defined, the chemistry of anion receptors is still a growing area [2]. Host molecules which can interact with anionic species through non-covalent interactions have some advantages due to intrinsic characteristics of the anions, such as size, polarizability and coordination number [3].

Recently, Wang and co-workers [4] prepared a family of heterocalixarenes containing rings of 1,3,5-triazine, bridged by either oxygen or nitrogen atoms. Using the Wang's compound *bis*-cloro-tetraoxacalix[2]arene[2]triazine as a reference model compound, we carefully addressed the nature and the magnitude of the anion- π interactions with the anionic guests Cl⁻, Br⁻, I⁻, BF₄⁻, CH₃CO₂⁻, H₂PO₄⁻, HSO₄⁻, NCS⁻, NO₃⁻, PF₆⁻, and SO₄²⁻ [5]. The role of the bridging heteroatoms (N(H)-, O-, and S-) were also studied. The magnitude and the physical nature of the interaction in these hostguest complexes were analyzed through the energy decomposition analysis (EDA) [6], natural bond orbitals (NBO) [7] and the non-covalent index (NCI) [8] as fundamental tools.

The most stable situation in the host-guest systems was observed when the anions are disposed between the triazine rings, leading to different sorts of non-covalent interactions, as well as hydrogen bond formation (Fig. 1a). Anions containing hydrogen atoms also acts as weak hydrogen bond donors to the nitrogen atoms of the triazine units. Non-covalent regions due dispersion interactions are observed between the anions and the triazine unities, specially for the sulfur-bridged heterocalixarene, Fig 1c. The



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EDA results reveal stabilizing interactions in all host-guest complexes. The electrostatic interaction plays a fundamental role in oxygen-bridged complexes, whereas the orbital term is the most significant contribution in sulfur- and nitrogen-bridged heterocalixarene complexes. Since in all complexes the Pauli repulsion and the electrostatic term are very similar in magnitude, they cancel each other to a large extent, which suggests that is the orbital interactions the driven forces to the host-guest complex formation.

Two different orbital contributions to the host-guest interaction was found in the NBO analysis: (a) the donation from lone pairs of the anion to the σ^* antibonding orbital of C-H bonds, which is related to the hydrogen bonds and (b) the donation from the anion lone pair to the triazine C-N π^* antibonding orbital, which is the orbital part of the anion- π interaction, Fig. 1b.



Figure 1: (a) Minima structure with selected geometrical parameters; (b) NBO donor-acceptor interactions with their respective energy; and the (c) Perspective and superior view of NCI analysis for the host-guest complex of oxygen-bridged heterocalixarene with chloride.

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