

How the electron-deficient cavity of heterocalixarenes recognizes anions: Insights from computation

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We have quantum chemically analyzed the bonding mechanism behind the affinity of various heterocalixarenes for anions with a range of geometries and net charges, using modern dispersion-corrected density functional theory (DFT-D3BJ). The purpose is to better understand the physical factors that are responsible for the computed affinities and thus to develop principles for a more rational design of anion receptors. Our model systems comprise heterocalixarenes 1-4 as hosts, which are characterized by different bridging heteroatoms (O, N, S) as well as the anionic guests Cl⁻, Br⁻, I⁻, BF₄⁻, CH₃CO₂⁻, H₂PO₄⁻, HSO₄⁻, NCS⁻, NO₃⁻, PF₆⁻, and SO₄²⁻. We use various analysis schemes (EDA, NCI, and NBO) to elucidate the interactions between the calixarene cavity and the anions to probe the importance of the different bonding modes (anion-?, lone-pair electron-?, ?-complexes, hydrogen bonds, and others) of the interactions. Electrostatic interactions appear to be dominant for heterocalixarenes with oxygen bridges whereas orbital interactions prevail in the case of nitrogen and sulfur bridges. Dispersion interactions are however in all cases non-negligible. © 2017 the Owner Societies.