On the nature and extent of chalcogen ···π interactions

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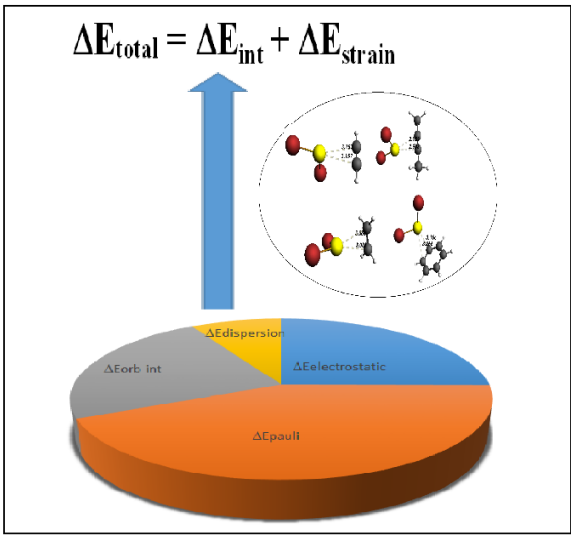
Weak non-covalent interactions have gained paramount importance in chemistry. They play a crucial role in different phenomena, among which the self-assembly of large molecules, biological pattern recognition and crystal packing. Chalcogen···π interactions, which are the focus of the present study, were found in biological active compounds like cysteine, selenocysteine, selenomethionine.[1-2]

In our analysis, calculations were performed to predict, characterize and quantify chalcogen···π interactions between X_2Y (X = F, Cl, Br, I and Y = S, Se, Te) and an unsaturated substrate (ethyne, 2-butyne, ethylene and benzene). The density functional BLYP in combination with TZ2P basis set was used and scalar relativistic effects were accounted for through zeroth-order regular approximation (ZORA).[3] MP2/aug-cc-PVTZ (PP) results were included for selected cases. A fragment-based approach (Activation Strain Analysis, ASA) [4] was employed to gain insight on the nature of the interaction established between the chalcogen center and the π system, which behave like a Lewis acid-base couple. Trends are shown and discussed and in perspective will be extended to biological sites to investigate chalcogen based redox active enzymes and supramolecular aggregated architectures.

Keywords: Activation Strain Analysis, (ASA), chalcogen….π interactions, DFT calculations, ZORA, chalcogen centers



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