Stacking interactions of metal-chelate rings and hydrogen-bridged rings

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Stacking interactions are ubiquitous in many chemical and biological systems, and they are of great interest in the areas of crystal engineering and materials science. Stacking interactions are typically referred to as the interactions of aromatic molecules. However, there are moieties that frequently form stacking interactions that are stronger than stacking interactions of aromatic molecules. Two examples are metal-chelate rings [1] and hydrogen-bridged rings [2].

The searching of the Cambridge Structural Database (CSD) showed that metal-chelate rings can form both chelate-aryl and chelate-chelate stacking interactions [1]. The analysis of crystal structures also showed that C_6 aromatic rings prefer stacking with chelate ring than with other C_6 aromatic rings. Quantum chemical calculations explained this preference by showing that chelate-aryl stacking interactions (-6.39 kcal/mol) are stronger than stacking interactions between benzene molecules (-2.73 kcal/mol). Chelate-chelate stacking interactions are even stronger (-9.70 kcal/mol). It was shown that the nature of both chelate-benzene and chelate-chelate stacking depends on the metal [1,3].

The analysis of the CSD crystal structures showed that planar five-membered hydrogen-bridged rings frequently form stacking interactions, both with other hydrogen-bridged rings [2] and with C_6 aromatic rings [4]. Quantum chemical calculations showed that stacking interactions between hydrogen-bridged rings can be as strong as -4.89 kcal/mol, while stacking between benzene and hydrogen-bridged ring can be as strong as -4.38 kcal/mol.

References:
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Acknowledgement: This work was supported by an NPRP grant from the Qatar National Research Fund (a member of the Qatar Foundation) [grant number NPRP8-425-1-087].