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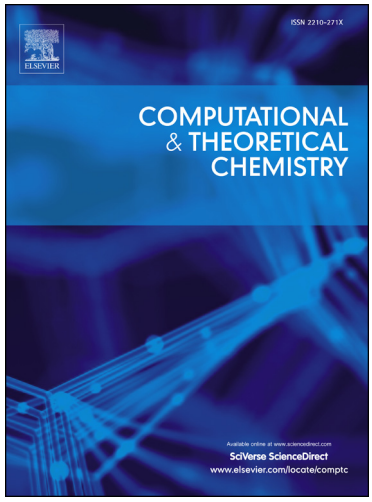

Scrutinizing ion-π and ion-σ interactions using the noncovalent index and energy decomposition analysis

Mercedes Alonso, Balazs Pinter, Tatiana Woller, Paul Geerlings, Frank De Proft

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Scrutinizing ion-π and ion-σ interactions using the noncovalent index and energy decomposition analysis

Mercedes Alonso, Balazs Pinter, Tatiana Woller, Paul Geerlings and Frank De Proft*

Research Group General Chemistry (ALGC), Member of the QCMM VUB-UGent Alliance Research Group, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels (Belgium); Fax: (+32)(0)26293317

E-mail: malonsog@vub.ac.be

Abstract

The nature and origin of ion-π and ion-σ interactions has been systematically investigated using dispersion-corrected density functional theory and the recently developed noncovalent interaction (NCI) method. A detailed analysis of these interactions is performed with the aim to identify the requirements that have to be fulfilled by the molecular system for strong ion···ligand interactions. Interestingly, our results indicate that aliphatic systems, such as cyclohexane, can interact as strong as aromatic ones with both cations and anions, despite of having a negligible quadrupole moment. In fact, cyclohexane binds anions stronger than benzene itself but slightly weaker that hexafluorobenzene. The NCI method reveals that the interaction between the ions and three C-H bonds of the saturated fragment are responsible for the surprisingly strong ion/σ interaction. A weakening of the ion/σ interactions is observed in the order: $Li^+ > F^- > Na^+ > Cl^- > Br^- \approx K^+$. In addition, a complete Ziegler-Rauk type energy decomposition analysis has been carried out in order to reveal the origins of the thermodynamic driving force for complex formations. The electron density deformation upon complex formation has been scrutinized with a complementary NOCV analysis allowing the identification of molecular orbital interaction contributions to the stabilization. Based on these analysis, it is shown that the formally anion-π interaction is rather an anion-σ* interaction.

Keywords
noncovalent interactions • ion/π • ion/σ • density functional theory • aromaticity • NCI method

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