

Understanding the fundamental role of π/π , σ/σ and σ/π dispersion interactions in shaping carbon-based materials

Julia Contreras-García,^a M. Alonso,^b T. Woller,^b F. J. Martín-Martínez,^b
P. Geerlings,^b F. De Proft^b

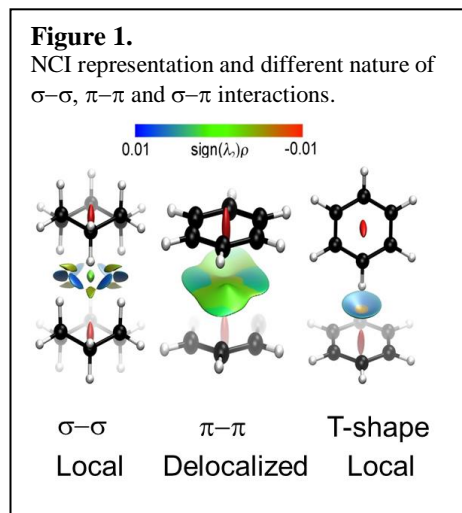
^aLaboratoire de Chimie Théorique, Université Pierre et Marie Curie, Paris (France).

^bEenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels (Belgium)

contrera@lct.jussieu.fr

Noncovalent interactions involving aromatic rings, such as π -stacking and CH/ π interactions, are central to many areas of modern chemistry. However, recent studies proved that aromaticity is not required for stacking interactions since similar interaction energies were computed for several aromatic and aliphatic dimers [1].

Herein, the nature and origin of π/π , σ/σ and σ/π dispersion interactions has been investigated using dispersion-corrected density functional theory, energy decomposition analysis and the recently developed non-covalent interaction (NCI) method [2]. NCI allows identification of interactions in real space, based on the peaks that appear in the reduced density gradient at low densities. This method is capable of distinguishing between hydrogen bonds, van der Waals interactions and repulsive steric clashes and it is also applicable to large systems such as DNA or proteins.



Our analysis [3] shows that π/π and σ/σ stacking interactions are equally important for the benzene and cyclohexane dimers, explaining why both compounds have similar boiling points. Also, similar dispersion forces are found in the benzene...methane and cyclohexane...methane complexes. However, for systems larger than naphthalene, there are enhanced stacking interactions in the aromatic dimers adopting a parallel-displaced configuration compared to the analogous saturated systems. Although dispersion plays a decisive role in stabilizing all the complexes, the origin of the π/π , σ/σ and σ/π interactions is different.

NCI reveals that the dispersion interactions between the hydrogen atoms are responsible for the surprisingly strong aliphatic interactions. Moreover, whereas σ/σ and σ/π interactions are

local, the π/π stacking are inherently delocalized (Figure 1), which give rise to a non-additive effect. These new types of dispersion interactions between saturated groups can be exploited in the rational design of novel carbon materials.

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