Parallel π–π Stacking Interactions: Substituent Effects at Different Displacement

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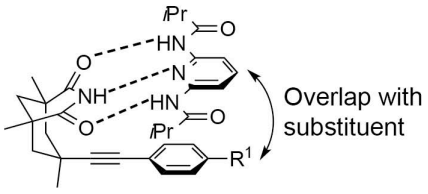
Parallel-displaced π–π stacking interactions were investigated experimentally using two different host–guest model systems with Rebek imide-type receptors **1** or **2** and 2,6-di(isobutyramido)pyridine ligand **3** (Figure 1).[1,2]

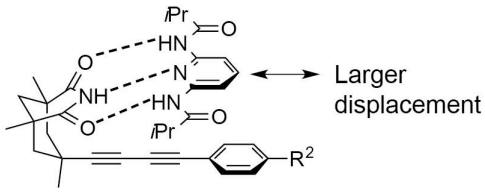
Guest **3** forms a triple H-bonding array to the imide moieties of receptors **1** or **2**. This allows for a parallel stacking geometry between the pyridine ring in **3** and the aromatic platform of **1** or **2** at different displacement, as confirmed by comprehensive structural analysis in solution and in solid state. In complex **1·3**, partial overlap between the pyridine core of **3** and the *para*-substituent R^1 is generated by a short ethyne-1,2-diyl spacer and enables direct, through space interactions. Any substituent had a stabilizing effect on the stacking interaction, independent of its electronic nature. In complex **2·3**, the elongated buta-1,3-diyne-1,4-diyl spacer prevents local, direct interactions between guest **3** and *para*-substituent R^2. Here, the electronic influence of the substituent on the aromatic platform affected the stacking strength crucially.

Changing the distance between substituent and intermolecularly interacting aromatic ring results in a fundamentally different substituent effect on parallel π–π stacking interactions.



1·3

R^1 = NO_2, CF_3, Br, F, H, Me, OMe, NMe_2



2·3

R^2 = NO_2, CN, CF_3, CHO, Br, F, H, Me, OMe, NMe_2

[1] Michael Harder, Marjorie A. Carnero Corrales, Nils Trapp, Bernd Kuhn, François Diederich, *Chem. Eur. J.* **2015**, *21*, 8455–8463. [2] Leslie-Joana Riwar, Nils Trapp, Bernd Kuhn, François Diederich, *Angew. Chem. Int. Ed.* **2017**, in press.