Supporting Information

Content

1. Reference T-shape interaction

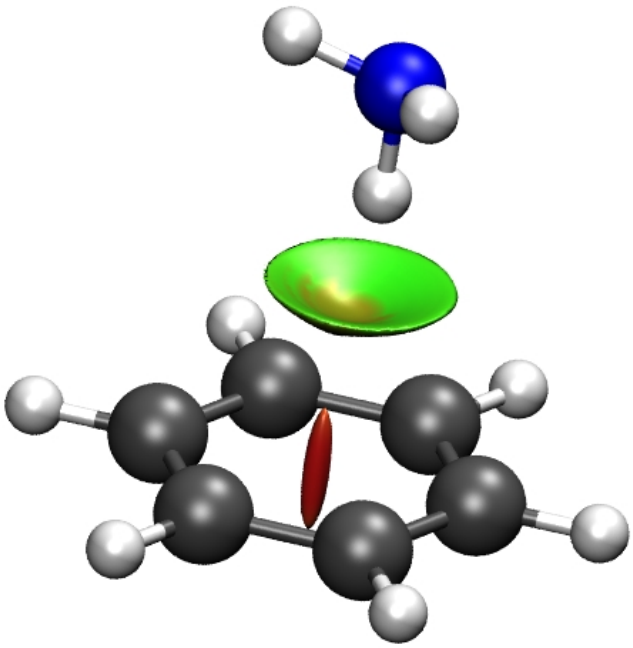

Figure S1. T-shape interaction between ammonia and Benzene

2. NCI Integrations

Density properties can be integrated within the NCI region to obtain the volume (V_{NCI}) of the isosurface and the charge (q_{NCI}) enclosed within it.[i]

$$V_{\mathrm{NCI}} = \int_{\Omega_{\mathrm{NCI}}} \mathrm{d}\,\vec{r} \qquad (1)$$

$$q_{\mathrm{NCI}} = \int_{\Omega_{\mathrm{NCI}}} \rho(\vec{r})\mathrm{d}\,\vec{r} \quad (2)$$

To perform such integrations, it is necessary to establish a unique definition of the NCI region, for which a reference is taken. The lower edge of the reference *s(ρ)* curve is splined and all the points of the dimer *s(ρ)* plot lying below the splined curve are localized in real space. In practice, these integrations are performed numerically, by summation over a cubic grid with 0.1 a.u. increments.

Integrations have been performed for all the diastereoisomers with benzaldehyde as reference and a density cutoff of 0.1 a.u. These integrations are compared to the D3 correction in Figure S2. It can be seen that two trends are obtained: one for *anti*, *ent-anti* and *ent-syn*, and another one for the *syn* conformers (indeed, the latter are the ones with the greater D3 correction). This can be interpreted as an indirect proof of the different nature of the stabilization in these two classes of conformers. Whereas the dispersion coming from the O-N region is crucial for explaining the dispersion interactions in most of the conformers, the additional dispersive stabilization of the *syn* conformers requires taking the T-shape interaction into account. Indeed, the *syn* confomers are the ones which present the greatest D3 correction, and not the *anti* ones as could have been expected. Looking at the NCI surfaces this is not surprising: the main non-covalent interaction in the *anti* conformers is of electrostatic nature, and hence it is well recovered by the functional itself, there is no need to resort to the dispersion correction. Still, in the case of the most stable conformer, the planarity of the electrostatic region gives rise to dispersion also in that region, which explains the relevance of the D3 term in this case.

Although the different scaling of these interactions does not allow us to take one step further and compare the *syn* and the *anti* conformers, it allows us to confirm and identify the role of non-covalent interactions in the outcome of the reaction.

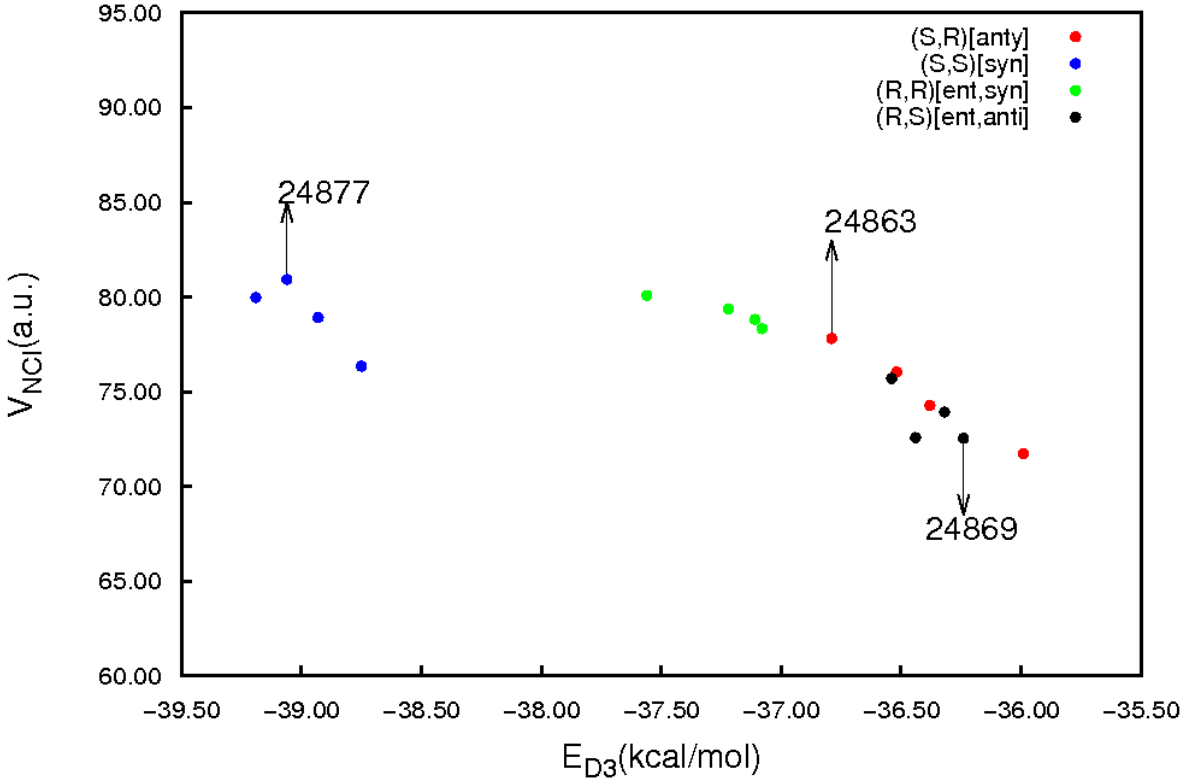

Figure S2. NCI volume vs D3 correction for the conformers. Again, a clear separation between anti and the rest of the conformers appears. In the syn case there is an extra region of dispersion, the stacking part, which outscales the other conformers, where the main interaction is the carbonyl-amine region.