Interactions between methyl groups in homodimers in the light of quantum chemical analyses

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The interaction between methyl groups is quite unique and hard to establish. However, based on the Cambridge Structural Database a few crystal geometries where the C···C distances of methyl groups were shorter than the sum of the van der Waals radii have been selected. Among these structural motifs, two dimers being parts of the crystal structures were taken into further consideration. Interaction energy calculations for these crystalline solids (without any additional pre-optimization) showed interesting results. For one of them the interaction energy was negative (NAWYES02 refcode) suggesting attractive interaction between subunits while for the second one (RIZMIW refcode) the value of E_{int} was positive what implied the presence of the repulsion rather than attraction.

The commonly utilized quantum chemical analyses such as the QTAIM, NBO and NCI ones depicted the same picture for both compounds, namely quite similar magnitude of an attractive interaction between subunits. For the former (NAWYES02), the detailed QTAIM and NCI analyses revealed that as the subunits get closer together by the interval of 0.2 Å for the C···C distance, the descriptors derived from these analyses indicate an increasingly strong attractive interaction while interaction energy was more and more positive (until +22.6 kcal/mol) signifying the opposite trend.

Thus, the results of these analyses should be interpreted with caution. A similar case was observed in our previous works on the interactions between some CSD-derived anionic subunits. The aforementioned analyses for such systems indicated the existence of an attractive interaction despite the overall strong repulsion between subsystems embodied in highly positive values of the interaction energies.