

Carbonyl...Carbonyl Interactions are Structurally Ubiquitous and Important

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Recent years have seen an increasing interest in intermolecular interactions that are *not* mediated by hydrogen. An early analysis [1] of the Cambridge Structural Database (CSD) identified the isosteric nature of nitro and carbonyl groups in molecular design applications. This prompted further work on dipolar carbonyl-carbonyl interactions that will be reviewed and extended in this talk. In *small organic molecules* it has been shown that CO groups in simple ketones and trans-amides form three main interaction motifs, and that the most frequent sheared-antiparallel arrangement has an attractive interaction energy of ca. -22kJ mol^{-1} , competitive with medium-strength H-bonds. In *proteins*, PDB analyses show that CO...CO interactions stabilise α -helices, β -sheets and β -strands, including the stabilization of the partially allowed Ramachandran conformations of asparagine and aspartic acid. In *organometallics*, we are now studying CO...CO interactions using the CSD. Although compromised by steric hindrance, very significant numbers of CO...CO interactions are observed in M-C=O systems. The antiparallel motif again predominates, and C...O distances are usually shorter than in organic systems, indicative of the stronger dipole in the M-C=O case. Preliminary DFT calculations indicate attractive energies of -20 to -30 kJ mol^{-1} for the predominant motif, similar to or stronger than the attractive energies in organic systems.

[1] Taylor R., Mullaley A., Mullier G.W., *Pestic. Sci.*, 1990, **29**, 197-213.

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