

# Enolate Chemistry with Anion- $\pi$ Interactions

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## Editorial

On the surface of  $\pi$ -acidic aromatic planes with positive quadrupole moments, anion- $\pi$  interactions occur. Their ability to aid in the binding and transport of anions has recently been demonstrated. Their ability to stabilise anionic reactive intermediates and transition states, on the other hand, has largely gone unexplored. This situation contradicts the widely acknowledged importance of complementary cation- $\pi$  interactions in catalysing the most important reactions in biology and chemistry. We present direct experimental evidence that single unoptimized anion- $\pi$  interactions can stabilise enolates by nearly two pKa units. These anion-stabilized reactive enolate intermediates are added to enones and nitro olefins with transition-state stabilizations of up to 11 kJ mol, and anionic cascade reactions accelerate on  $\pi$ -acidic surfaces.

It is critical to increase the number of tools available to create molecular functional systems. The basic set of interactions between and within molecules includes hydrogen bonds, ion pairing, and hydrophobic,  $\pi$ - $\pi$ , and cation- $\pi$  interactions. Recent advances in ion-pairing catalysis show how the clever use of already moderately novel interactions can rapidly change a field to an entirely unexpected extent. Anion- $\pi$  interactions and halogen bonds have been identified as promising candidates to contribute to the acceleration of transformations with anionic transition states in relevant anion transport experiments. Because complementary cation- $\pi$  interactions are essential in biocatalysis and are increasingly used in organocatalysis, anion- $\pi$  interactions are particularly intriguing. In contrast, anion- $\pi$  interactions in catalysis are largely unexplored. This makes sense given that standard aromatic rings have negative quadrupole moments and are thus  $\pi$ -basic. Their electron-rich surfaces are the result of a delocalized  $\pi$ -cloud of electrons beneath and above the plane. They can, of course, attract cations. The negative quadrupole moment of  $\pi$ -basic aromatics must be inverted in order to attract anions. This is possible by using strongly electron-withdrawing substituents. Hexafluorobenzene and 2, 4, 6-trinitrotoluene are two common examples. Because their intrinsic quadrupole moment is very high, naphthalenediimides (NDIs) have been identified as privileged platforms for investigating anion- $\pi$  interactions, and the introduction of withdrawing substituents provides access to the strongest organic  $\pi$ -acids known today. Since about a decade, theorists and crystal engineers have been fascinated by the ability of  $\pi$ -acidic aromatics to bind anions on

their surfaces. However, confirming their functional relevance in solution was difficult. It has been particularly difficult to distinguish anion- $\pi$  interactions from other phenomena, that is, interactions of anions with electron-deficient  $\pi$ -orbitals on  $\pi$ -acidic aromatic planes with positive quadrupole moment. However, once transmembrane transport with anion- $\pi$  interactions was confirmed, it was obvious that they should also be capable of stabilising anionic transition states. All polyketide, terpenoid, and steroid natural products are derived from enolate chemistry using malonates or acetoacetates as substrates. They are favoured substrates because their conjugate bases, enolates, are stabilised by resonance with two proximal carbonyl groups. In NMR titrations with 1,1,3,3-tetramethylguanidine (TMG), the resonance of the bridged syn-atropisomer 5's malonyl hydrogens vanished with much less TMG than those of the diethyl malonate.

The importance of anion- $\pi$  interactions in the stabilisation of enolate 6 for enolate chemistry was first assessed with the Michael addition to enone 7, a classical reaction of general interest in the community. NMR spectroscopy was used to determine the reaction kinetics of a 50 mM solution of 5 and 7 in CD<sub>3</sub>CN/CDCl<sub>3</sub> 1:1 in the presence of 5 mM DBU (1,8-diazabicycloundec-7-ene). Diethyl malonate 1 was used as a control in the absence of the  $\pi$ -acidic auxiliary. Coumarins, which are abundant in plants, are shikimate natural products with the distinctive sweet odour of freshly mown hay. Coumarins are best known in chemistry as fluorescent probes and laser dyes. Given that catalysis in its broadest sense is defined as transition-state stabilisation, the use of anion- $\pi$  interactions in covalent auxiliaries was used to provide direct experimental evidence with maximum precision and least ambiguity based on <sup>1</sup>H NMR spectra.