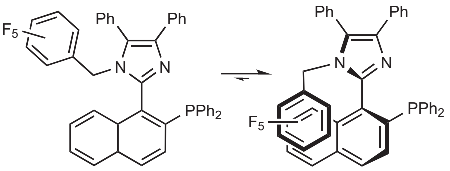
ASYMMETRIC CATALYSIS

Restricting rotation

J. Am. Chem. Soc. **135,** 14548–14551 (2013)



Ever since the Nobel-prize-winning work of Noyori, synthetic chemists have taken advantage of the defined steric environment of axially chiral compounds, and their excellent chiral discrimination at metal centres, to create numerous highly efficient catalysts. Axial chirality is maintained by avoiding rotation around a central axis — typically between two biaryl units — and traditionally this has been prevented using steric interactions to destabilize the planar transition state. Now, Aaron Aponick and co-workers at the University of Florida have developed a different strategy — stopping rotation by stabilizing the ground-state conformation of the molecule.

To achieve this they designed a structure containing one biaryl unit linked to a substituted imidazole. The reduced steric demand of the five-membered imidazole ring means that rotation around the central axis would be expected to be facile; however, the presence of a pentafluorobenzyl group on N1 stabilized the chiral ground-state conformations. They obtained the enantiopure compound using a deracemization approach, which involved coordination of the racemate to a chiral palladium complex and subsequent heating in the presence of KPF$_6$. This was then treated with 1,2-bis(diphenylphosphino)ethane, which regenerated the free ligand with an enantiomeric excess of 98%. This compound proved to be configurationally stable over a period of months, and this stability was attributed to π-stacking between the pentafluorophenyl ring and the biaryl unit. This claim was supported by X-ray crystallographic studies — showing π-stacking in the solid state — and by comparison with a sterically similar non-fluorinated analogue. This analogue showed a significantly decreased barrier to rotation and had a half-life of a mere 22 minutes at 75 °C, as opposed to 8.7 hours for the original compound.

Aponick and co-workers used the ligand to asymmetrically catalyse an A^3-coupling reaction. The results were highly impressive, with enantioselectivities up to 97% and yields up to 95% across a range of substrates. The reaction worked for both aromatic and aliphatic aldehydes, and the selectivity was reasonably insensitive to the presence of electron-donating or withdrawing groups. *EB*

HETEROGENEOUS ORGANOCATALYSIS

Catalytic cloth

Science **341,** 1225–1229 (2013)

Organocatalysis, the use of small organic molecules to catalyse chemical reactions,

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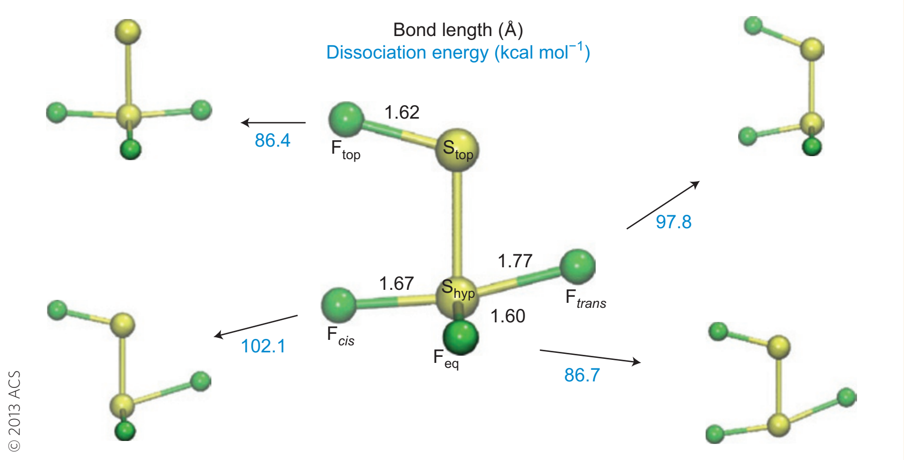
BONDING ANALYSIS

United they are strong

J. Phys. Chem. Lett. **4,** 3139–3143 (2013)

The most interesting chemical phenomena arise when common rules of thumb break down. One such rule is the relationship between bond length and bond strength. From infrared spectroscopy to organic synthesis, chemists usually assume an inverse correlation between the length of a bond and its dissociation energy and force constant. But as with every rule, there are exceptions: in various molecules with electronegative ligands such as fluorine, a longer bond can be a stronger bond.

The product of SF$_2$ dimerization, FSSF$_3$, is a particularly insightful representative of this class of compound, and has now been analysed theoretically by Beth Lindquist and Thom Dunning from the University of Illinois. FSSF$_3$ possesses four inequivalent fluorine atoms with four different sulfur–fluorine bond lengths (pictured). Removal of each fluorine atom yields a distinct structure that is a local minimum on the potential energy surface, facilitating the analysis of the bond length–bond dissociation energy relationship enormously. Surprisingly, the two longest S–F bonds, which are between the axial fluorine (F$_{cis}$ and F$_{trans}$) and the hypervalent sulfur atoms, have the largest dissociation energies.



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Dunning and Lindquist explain this puzzle using generalized valence bond theory, with which they find substantial repulsive overlap between the two axial S–F bond orbitals (SF$_{cis}$ and SF$_{trans}$). However, when one of these bonds is broken, the associated sulfur bonding orbital localizes on the hypervalent sulfur atom, which increases the repulsive overlap in the product. In other words, the axial S–F bonds are stabilized because two sulfur bonding orbitals get pulled away from each other, but this can only occur when both fluorine atoms are present. The authors rationalize this finding with the concept of a ‘recoupled bond dyad’. This bonding model is closely related to the three-centre, four-electron bond, with the major difference being that the bonds in a recoupled bond dyad are highly ionic and localized. A number of other hypervalent compounds with electronegative ligands abide by the same united-they-are-strong rule, and we can expect more surprises from analysing their bonding situations in the future. *LM*