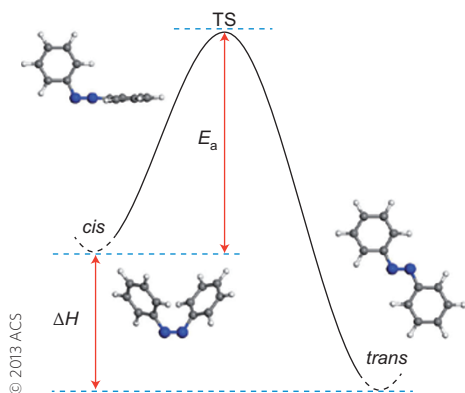


ENERGY STORAGE

Solar-thermal enters the ring

J. Phys. Chem. Lett. **4**, 854–860 (2013)



Harnessing energy directly from the Sun is key to meeting our increasing energy demands. Most research is focused on photovoltaics or photocatalysis, but another option is to store the energy directly in the bonds of molecules that undergo photoisomerization. In this scenario, light

'charges' the molecule, switching it to a higher energy — but still relatively stable — isomer. An external trigger can then switch the molecule back to its original form, accompanied by the release of heat. The development of practical 'solar-thermal' materials has, however, been hampered by their instability and low energy density. Now E. Durgun and Jeffrey Grossman from MIT have used density functional theory to show that these properties can be improved by incorporating photoswitchable molecules into strained molecular rings.

They exploit the photoisomerization of stable *trans*-azobenzene to its less stable, higher energy, *cis* isomer, a reaction that is found to have a ΔH value — a measure of how much energy the molecule can store — of 0.6 eV. The ΔH value is calculated for the all-*trans* to all-*cis* reactions of molecular rings formed from multiple (two to six) azobenzene groups connected by CH_2 groups. It was found that the dimer stores less energy than monomeric azobenzene, the trimer stores about the same energy and the tetramer can store around 65% more, with ΔH calculated to be ~ 1 eV.

The differences in ΔH arise from steric effects caused by the imposed ring geometry with the *cis*- and *trans*-isomers destabilized to different degrees with respect to isolated azobenzene. If the *trans* form is destabilized less than the *cis* form, then this leads to an increase in ΔH . Substituting the CH_2 linkers for N_2 groups or adding stabilizing OH groups to each benzene ring were also seen to alter ΔH . The molecules with larger ΔH values for the isomerization reaction, and thus greater energy-storage capacity, also showed an increase in the stability of the high-energy isomer, leading to a longer 'shelf life' of the charged form. GA

HETEROMETALLIC COMPLEXES

Meeting of the metals

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Multiple bonds between metal atoms are still a rarity, which lends them an air of mystery and a loyal following of researchers determined to make new examples. Among the rarest of the metal–metal bonds are those involving first-row transition metals.

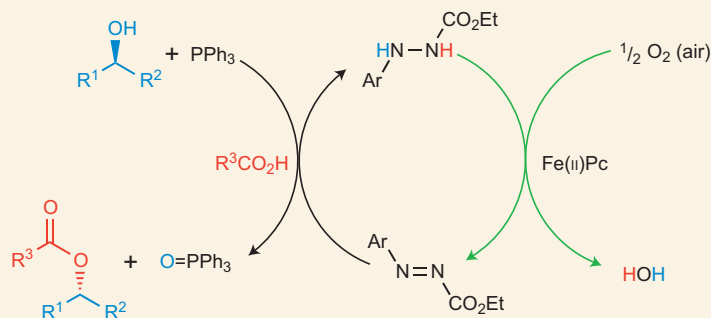
GREEN CHEMISTRY

Mitsunobu minus waste

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First reported in 1967, the Mitsunobu reaction is a methodology widely used to activate alcohols towards reaction with nucleophiles. In its original incarnation, it is used to form esters from the reaction of alcohols and carboxylic acids, but similar conditions can be used to react alcohols with a variety of nucleophiles including azides, imides, phenols and sulfonamides. Activation of the alcohol is achieved through reaction with a stoichiometric combination of an azodicarboxylate and a phosphine, which, at the end of the reaction, produce waste in the form of a hydrazine dicarboxylate and a phosphine oxide. Even putting aside the environmental issue posed by such waste, these by-products can be difficult to separate from the desired reaction products.

Now, Tsuyoshi Taniguchi and co-workers from Kanazawa University, Japan, have developed conditions under which the hydrazine component of this waste can be recycled so that it may be used catalytically. The research team had previously reported the use of an



iron(II) phthalocyanine catalyst for aerobic oxidation of a hydrazine monocarboxylate, and wondered if this reaction might be applied in the context of a Mitsunobu reaction. Hydrazine dicarboxylate had to be replaced with arylhydrazine carboxylate for an effective aerobic oxidation, and the team then showed that this could be applied in a modified Mitsunobu setting. Recent work from other research groups has described phosphine oxides that can be recycled for application in the Wittig reaction — it remains to be seen whether the two procedures could be combined to effect

a Mitsunobu reaction that is catalytic in all the necessary components.

An inversion of stereochemistry in the reaction of chiral alcohols is a key piece of evidence that the reaction occurs by a Mitsunobu-type mechanism. Taniguchi and co-workers have also previously described alcohol–acid condensations catalysed by an iron(II) phthalocyanine alone. These reactions, however, occurred with retention of configuration, and this raises the intriguing possibility that the hydrazine somehow inhibits that reaction while promoting the Mitsunobu pathway. SD