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Spotlights

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Spotlights on Recent *JACS* Publications

HIGH-SPEED PHOTOGRAPHY CAPTURES POPCORN-LIKE CRYSTALS

1,2,4,5-Tetrabromobenzene (TBB) is an uncommon material. Raise the temperature of this organic crystal to that of a very hot day, and it does not melt or burn—it jumps! Crystals of TBB are naturally twinned, meaning that they consist of two structurally different parts, bound together in the center. On the atomic scale, TBB looks like a series of carbon hexagons suspended at the corners by bromide bonds. Macroscopically it looks a little like a transparent number 2 pencil. The jumping phenomenon is known in only about a dozen materials, which may be why the purposes for these behaviors are not well-understood.

Panče Naumov and co-workers use high-speed photography and nanoindentation to probe how TBB's structure leads to such unusual behavior (DOI: 10.1021/ja4056323). The researchers discover that although TBB appears brittle on the human scale, microscopically the material is highly elastic. By heating and cooling over 200 TBB crystals and recording jumps, explosions, and other behavior in detail, the authors find that internal stresses build up within the crystal and then spontaneously release in a violent and complex kinematic process that includes six components.

The authors suggest that fast-actuating materials like TBB are needed to replace relatively sluggish polymer-based actuating materials, and they meet a growing need for ultrafast response times in electronic and optical devices. **Jenny Morber, Ph.D.**

NEW RECORD FOR SHORTEST NONBONDING H···H DISTANCE

In/*out* stereoisomerism commonly occurs in bridgehead atoms in multicyclic compounds, which can have interesting physical and chemical properties as a result. Robert A. Pascal, Jr., and co-workers prepare a macrobicylic *in*,*in*-bis(hydrosilane) with an unusually close H···H contact, which was predicted to be favored over its *in*,*out* counterpart by 6 kcal/mol, despite the great steric congestion (DOI: 10.1021/ja407398w).

The authors determine the configuration of this *in*,*in*-bis(hydrosilane) by the remarkable downfield shift of Si—H signals in ^{1}H NMR spectroscopy, a typical result of the steric deshielding effect. The higher IR frequency of the Si—H stretch, caused by steric compression, provides further corroboration.

The compound's crystal structure clearly confirms the *in*,*in*-geometry, in which the orientation of the two *in*-H atoms led to a "head-on collision". This highly congested environment, bracketed by two silicon atoms only 4.43 Å apart (X-ray), must contain two Si—H bonds and the close H···H contact. A normal Si—H bond distance is 1.48 Å, but due to steric compression in this molecule, the Si—H distances are calculated to be only 1.44—1.46 Å, leaving the H···H contact distance to be on the order of 1.56 Å, significantly shorter than the currently known minimum of 1.617(3) Å for nonbonding H···H contact. As these calculations overestimate the Si···Si distance, the authors believe that the actual H···H distance may in fact be even shorter, and they seek to confirm their observations by neutron diffraction experiments. **Xin Su**

REDEFINING RENALASE

Ever since its discovery in 2005, an enzyme called renalase has confounded researchers. When it is secreted by the kidney into the blood of a mammal, it lowers blood pressure and slows down the heart rate. But how renalase actually carries out these activities has been a source of confusion. Some researchers have suggested that the enzyme oxidizes molecules, like the hormone and neurotransmitter epinephrine, which leads to the observed physiological effects. Yet there has not been any substantial experimental evidence to support the hypothesis.

Now Graham Moran and colleagues demonstrate that renalase is an oxidase and an anomerase that acts on the coenzyme NAD(P)H (DOI: 10.1021/ja407384h). The enzyme oxidizes the central ring of the α form of the coenzyme by removing two electrons and also switches the configuration to the β form of NAD(P). The two electrons are transferred to a flavin cofactor in the enzyme, reducing the cofactor. To revert back to its oxidized form, the reduced cofactor transfers those two electrons to a molecule of oxygen to produce hydrogen peroxide.

From their data, the researchers surmise that the enzyme may have a more pervasive role in metabolism, in which renalase functions to salvage α-nicotinamides and return them to the β-nicotinamide pool such that they are available for normal redox cycling. **Rajendrani Mukhopadhyay, Ph.D.**

COMMON STRUCTURE IN DNA IMPROVES PERFORMANCE OF MOLECULAR ELECTRONICS

One version of artificial photosynthesis uses molecules to transform sunlight into fuel for transportation or electricity. Light-gathering molecules in such a system harness sunlight most efficiently when they contain a defined arrangement of electron-donating and electron-accepting groups to help molecules sustain and carry charge when excited by light.

Michael R. Wasielewski and his colleagues wondered if a common structure in nucleic acids could provide that defined structure for charge-carrying molecules (DOI: 10.1021/ja407648d). Guanine-rich stretches of DNA or RNA tend to assemble into G-quadraplexes, in which cations connect four guanine bases into flat sheets that stack on top of each other.

The researchers build a molecule containing an electron-donating guanine attached to an electron-accepting aromatic hydrocarbon. When placed in a solution of potassium ions, eight molecules gather into a two-layered G-quadruplex. In each layer, four guanines form a planar core with the aromatic hydrocarbons tilted around the center like arms of a propeller.

The ion-pair state of the quadruplex lasts about 1 ns, more than 100 times longer than one molecule by itself. Because it forms easily, G-quadraplexes could also be a useful scaffold for other molecular electronics like organic photovoltaics. **Melissae Fellet, Ph.D.**

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