Chemists identify a rare case of isomerism in which a cagelike macromolecule turns itself inside out

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INSIDE AND OUT Gladysz and coworkers' dibridgehead diphosphine molecule exists as three in/out isomers based on the orientation of each phosphorous atom's lone pair of electrons.

In chemistry that contortionists can relate to, a research team led by Michael Stollenz and John A. Gladysz of Texas A&M University has identified a rare case of isomerism in which a macromolecule turns itself inside out (Angew. Chem. Int. Ed., DOI: 10.1002/anie.201100893). By careful study of $^{31}$P NMR spectra, the researchers discovered that the alkyl chains of a cagelike bicyclic diphosphine, made up of two phosphorus atoms linked by three (CH$_2$)$_4$ chains, can reversibly slide between one another to invert the molecule, flipping over the phosphorus atoms and interconverting three configurational isomers. The researchers designate these isomers as in/in, out/out, and in/out, depending on whether each phosphorus atom's lone pair of electrons is facing into or out of the molecular cage. This type of isomerization might be a general mechanism for encapsulating atoms or molecules that has been overlooked, Gladysz says. It could be useful for controlled sequestration, transport, and delivery of guest molecules that bind to the phosphorus lone pairs, he suggests.

MOLECULAR CONTORTIONIST In this schematic representation, a dibridgehead diphosphorus molecule transitions through different configurations as the molecule turns itself inside out.

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