A new breed of stable anti-aromatic compound

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By synthesizing a stable "antiaromatic" compound, as well as a never before seen intermediate version of that compound, chemists at The University of Texas at Austin have written an important new chapter in the story of modern chemistry.

The research was done in collaboration with an international roster of colleagues from Yonsei University in Korea, the University of Hyderbad in India, and Osaka University in Japan. The results were published this week in *Nature Chemistry*.

This particular story began in 1825, when English scientist Michael Faraday first isolated benzene from gas lights. Benzene would later be identified as one of a class of compounds known as aromatics, which have immense importance in both biological function and industrial production.

In humans, for instance, all five nucleotides that constitute DNA and RNA are aromatic. In industry, aromatics derived from oil and coal tar are precursors to, among other things, plastics, solvents, lubricants, rubber, dyes, herbicides, and textiles.

"Benzene is probably the most famous aromatic compound," said Jonathan Sessler, the Rowland Pettit Centennial Chair in Chemistry in the College of Natural Sciences. "But there are many other critically important aromatic species. The heme in hemoglobin, which is what gives blood its red color, is one of a group of aromatics known as

porphyrins. Without them we'd have either a very different or no existence."

Aromatic compounds have a ring-like structure that enables electrons to be shared amongst the different bonds between the atoms. This results, among other things, in an extraordinary degree of stability. They tend to persist in their structure under conditions that would cause other molecules to react.

"That's one of the reasons why they're so useful in industry," said Sessler. "It's also why they tend to be pro-carcinogenic. They're very hard for us to metabolize or catabolize, and the results of that are usually not benign. One of the first class of tumors ever observed was testicular cancer. It was highly prevalent among 18th century chimney sweeps, who were exposed to aromatic compounds found in coal tar."

Sessler made his name as a chemist synthesizing new classes of porphyrins, including Texaphyrin, a very large porphyrin, which is being developed as a key element in a potential new approach to treating cancer.

What he and his colleagues have now done is taken an already existing molecule, which was first synthesized by Sessler in 1992, and found a way to stabilize it in its so-called antiaromatic form. Antiaromatic systems are the evil twins of aromatics. Compounds that are antiaromatic have two additional or two fewer electrons than aromatic compounds.

"They don't want to exist in a planar form without giving up or adding the two electrons that distinguish them from their aromatic analogues," said Sessler, "so they tend to twist around, to a lower energy state. That destroys their antiaromaticity. The net result is that bona fide antiaromatic compounds are elusive. What we have done, by rational design, is put big buttressing groups around the compounds, basically

clamping them into place."

The resulting compounds are antiaromatic—with two electrons gone—and an intermediate something, with both aromatic and antiaromatic properties, that doesn't have a common name yet because it hasn't been seen before.

"When you have to struggle for the words to describe what's being done, you know that it's cutting edge," said Christian Brueckner, a fellow porphyrin chemist and a professor at The University of Connecticut. "Twenty years ago when I was a graduate student I was told simply that you can't make large antiaromatics like this. Later the idea was that you can make them but you can't do much with them. Now you can do it, and it can switch between states, and it can exist in the intermediate state. It's just a beautiful progression of scholarship, a beautiful example of how the ability of chemists to manipulate matter is advancing."

In their natural state antiaromatics are as unstable as aromatics are stable. As a result they have only been stabilized a few times in the history of the field. The antiaromatic that Sessler has made, working with colleagues in Korea, Japan, and India, is significant simply for joining this elite group. As significant is the synthesis of the intermediate state, a scientific first, as well as the capacity of the system to be toggled back and forth between the three different electron states.

"It's the first time you can really do a Coke vs. Pepsi taste test," said Sessler. "We've had very sophisticated theory for a long time, but you need positive and negative controls in science to reach a really robust conclusion. Now we finally have a detailed, controlled comparison of what aromaticity really does, how it changes interactions with light, how it affects color, what an excited state does to the lifetime, and so on."

Sessler's compounds also have potential implications in the field of

information storage.

"We are very good as humans at manipulating electrons," said Sessler, "and although this isn't my game at the moment, it's not hard to imagine how a system that has three different electron states, and is reversible, could provide an opportunity to store information in a way we couldn't previously. Binary gives us computers. Ternary could give us even more power."

Provided by University of Texas at Austin