

# Bond stretch isomerism. Did this idea first surface 100 years ago?

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# Bond stretch isomerism. Did this idea first surface 100 years ago?

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The phenomenon of *bond stretch isomerism*, two isomers of a compound differing predominantly in just one bond length, is one of those chemical concepts that wax and occasionally wane. Here I explore such isomerism for the elements Ge, Sn and Pb.

In [one earlier post](#), I noted a form of bond stretch isomerism that can arise from a Jahn-Teller distortion ending in two different geometries in which one or more pairs of bonds swap short/long lengths. Examples include substituted cyclo-octatetraenes and octahedral  $d^9$ -Cu(II) complexes. A more interesting seminal possibility was implied by [G. N. Lewis](#) a century ago when discussing the arrangement of electrons in a (carbon-carbon) triple bond.

The triple bond represents the highest possible degree of union between two atoms.\* Like a double bond it may break one bond, producing two *odd* carbon atoms, but it may also break in a way in which the double bond cannot, to leave a single bond and two carbon atoms (bivalent), each of which has a pair of electrons which is not bound to any other atom. The three tautomeric forms may be represented in the case of

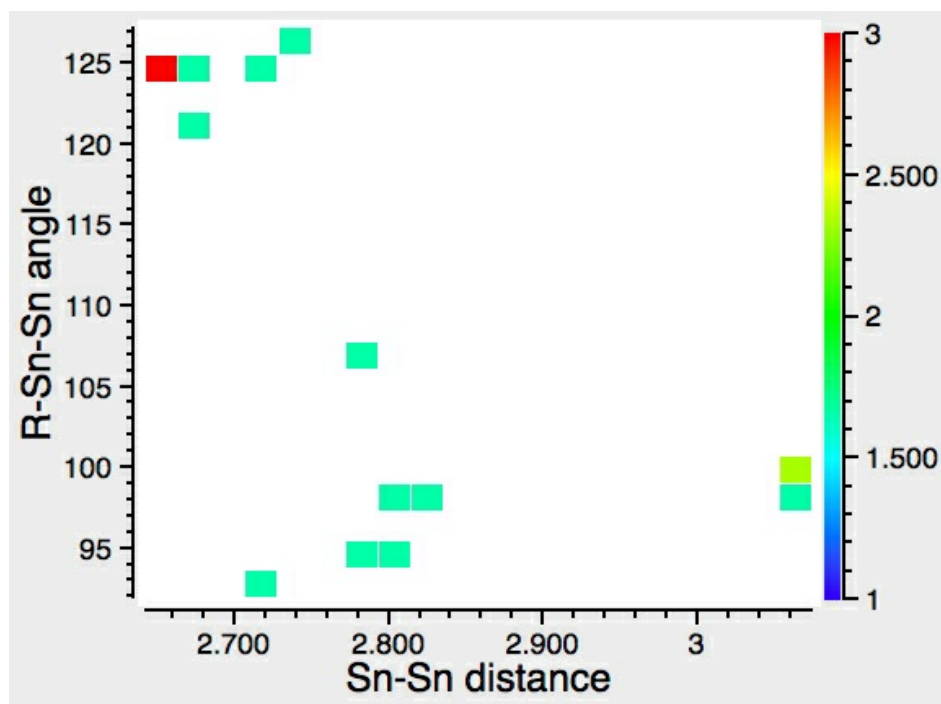
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acetylene by  $H:C:::C:H$ ,  $H:\dot{C}::\dot{C}:H$ , and  $H:\ddot{C}:\ddot{C}:H$ . In addition we have a form corresponding to Nef's acetylidene and such forms as may exist in highly polar media, such as the acetylide ion  $:C:::C:H$ .

\*It took ~50 years to prove this assertion wrong[5]

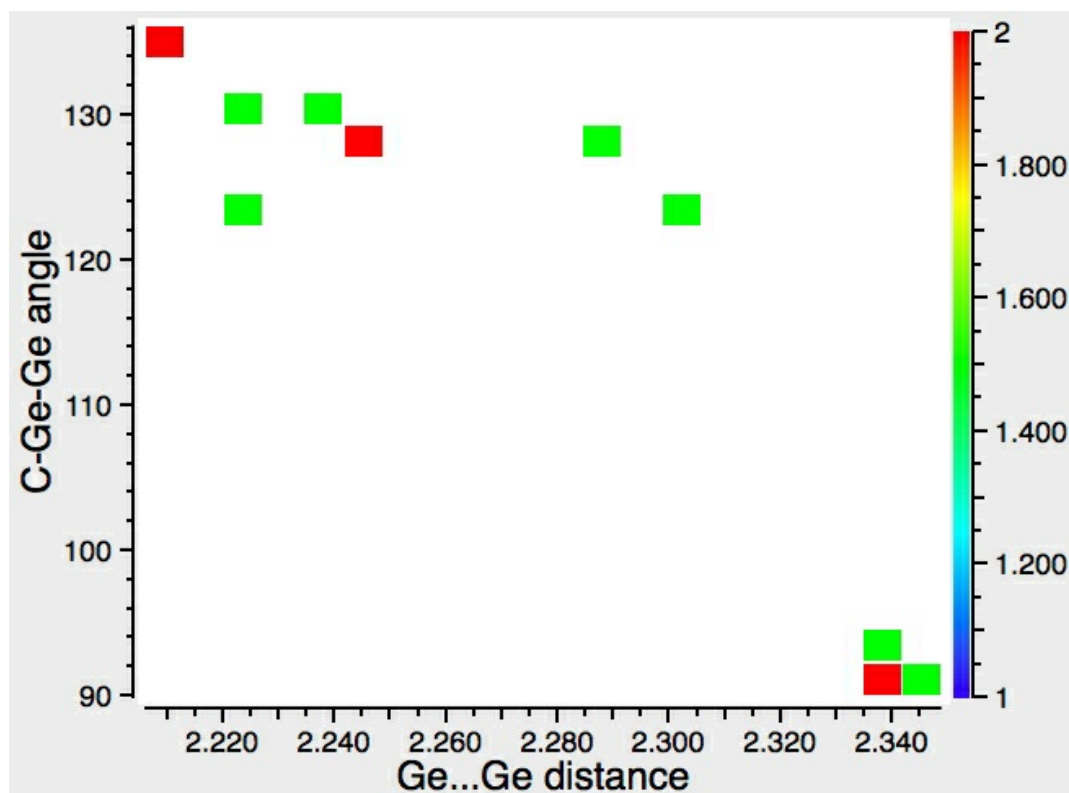
In a [commentary](#), I reported the results of a search of the crystal structure database for the geometries associated with  $RX\equiv XR$  systems ( $X = C, Si, Ge, Sn, Pb$ ). Here I focus the search specifically for  $X=Sn, Ge$ ; this version of bond stretch isomerism also allows angles to change (= rehybridisation at atoms) in order to provide a mechanism for a barrier separating the two forms.



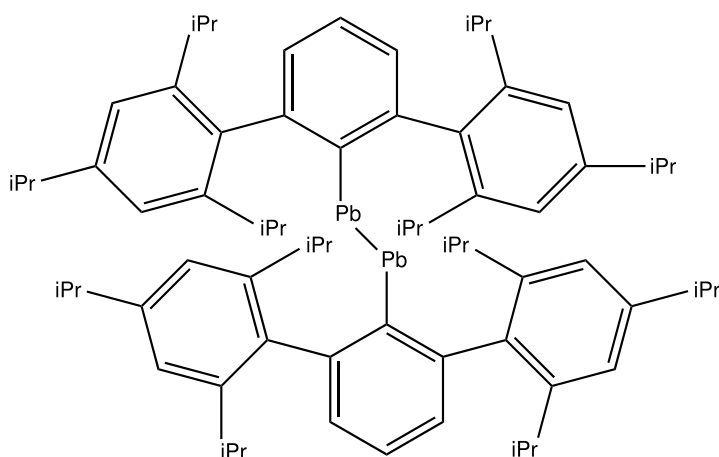
For X=Sn, note the presence of up to three clusters, although the relatively low number of hits makes the statistics less certain.

1. The hotspot cluster centered around angles of 125° and a Sn-Sn distance of ~2.6Å.
2. Another with angles of <100° and Sn-Sn distances of ~3.3Å.
3. A third with angles of <100° and Sn-Sn distances of 2.8Å, which may or may not be a genuine unique form of bonding.

This pattern was commented on in 2010 by Power, whose group synthesized most of the examples in the hits above. † A plot of compounds with Ge-Ge bonds reveals both similarity with (two, possibly three clusters) and difference from (the clusters are closely spaced in terms of the Ge-Ge bond length, but separated in terms of angle) Sn. †



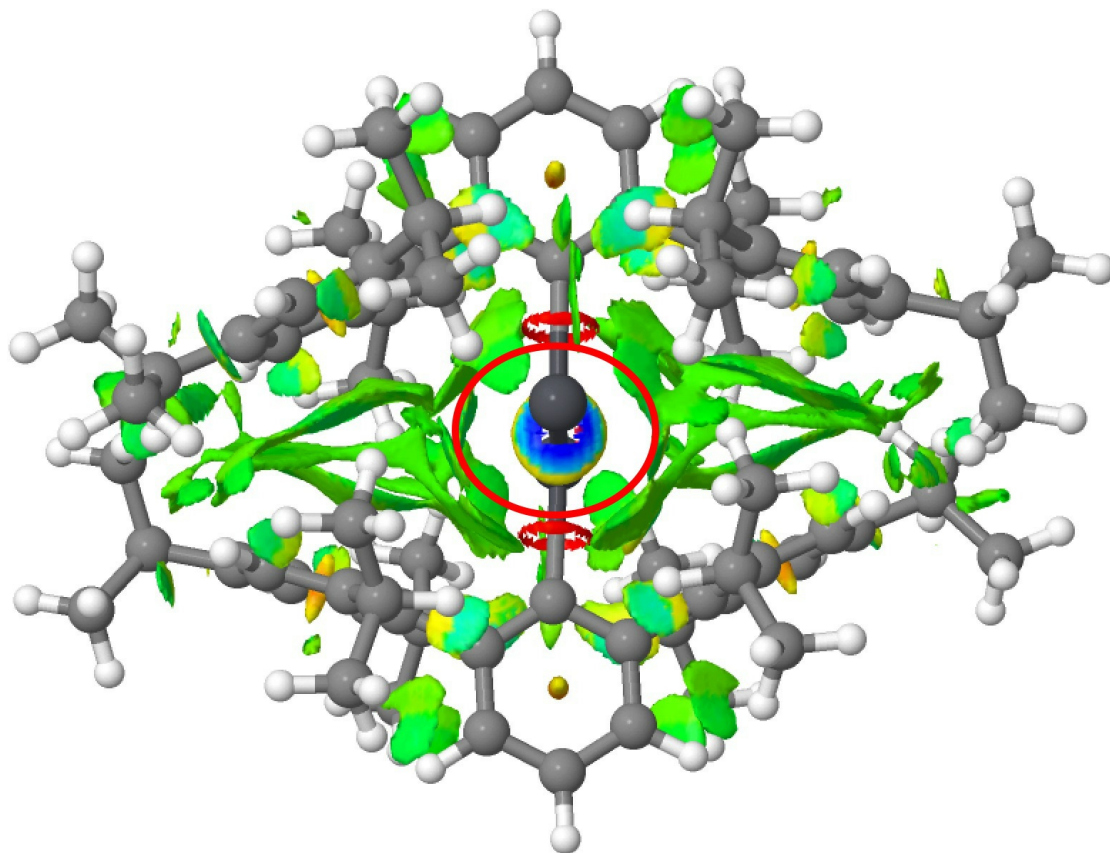
Time for some computations (which at least will remove random errors in the geometry). I selected the only known example of an  $\text{RPb-PbR}$  compound as a seed and put it through a B3LYP+D3/Def2-TZVPP calculation (with 172 atoms and 2920 basis functions, this is a relatively large calculation!), which reproduces the known structure pretty well (table).

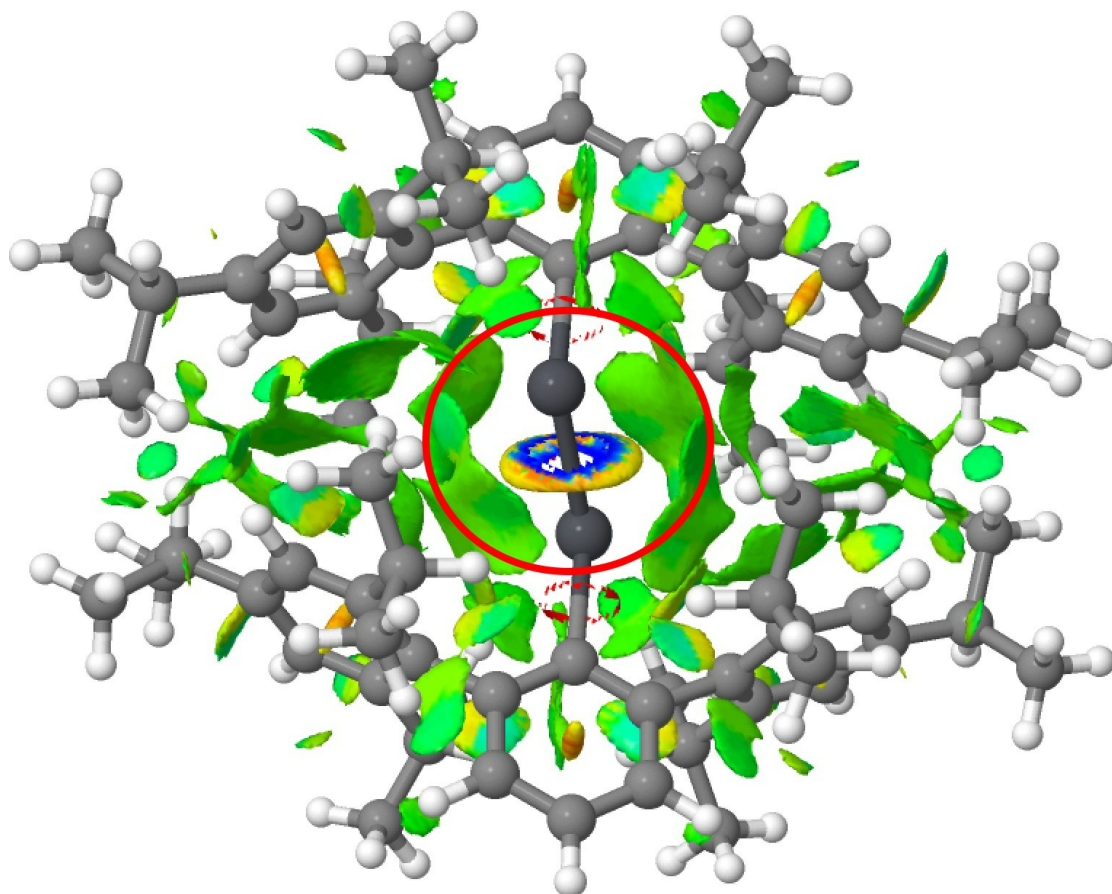


So what about another bond stretch isomers? The  $\text{Pb}=\text{Pb}$  variation is indeed a stable minimum around 28.0 kcal/mol above the known structure, which seems to put this form out of experimental reach (with this ligand/aryl group at least). With Sn for the same aryl ligand, the energy difference is smaller (~15.8 kcal/mol for this ligand; Powers reports other systems where the energy difference may be only ~5 kcal/mol). Judging by the distribution of the 13 hits recovered from the CSD search, both bond stretch isomers may be accessible experimentally. The calculations show that the GeGe bond isomers are much closer in energy than SnSn (for this ligand). For all three metals however, the calculated difference in the metal-metal length for the two isomers is ~0.45 - 0.52 Å. This strongly suggests that whereas the SnSn plot above is demonstrating bond length isomerism, the GeGe plot may not be; at least not of the same type that the calculations here are revealing ( *via* the Wiberg bond orders).

No doubt the particular bond length form is being facilitated by the nature of the ligand and the steric

interactions therein imparted, both repulsive AND attractive. These interactions can be visualised *via* NCI (non-covalent-interaction) plots (click on the image to obtain a rotatable 3D model). First Pb-Pb followed by Pb=Pb. Note how in both cases, the PbPb region is enclosed in regions of weak attractive dispersion interactions, which however avoid the "hemidirected" inert Pb lone pairs.





So in the end we have something of a mystery. There is evidence from crystal structures that at least two bond-stretch isomers of  $R\text{SnSn}R$  compounds can form, but the calculations indicate that the  $\text{Sn}=\text{Sn}$  form is significantly higher in energy (although not impossibly so for thermal accessibility). Conversely, the  $\text{Ge}=\text{Ge}$  equivalent is very similar in energy to a  $\text{Ge}-\text{Ge}$  form with a significantly longer bond length, but there seems no crystallographic evidence for such a big difference in bond lengths. Perhaps the answer lies with the ligands?

It seems particularly appropriate on the centenary of G. N. Lewis' famous paper in which he clearly notes the possibility of three isomeric forms for the *triple bond*, to pay tribute to the impact his suggestions continue to make to chemistry.

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