Contribution ID : **62** Type : **Poster Presentation**

Collective Bonding

Cina Foroutan-Nejad Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland cina.foroutan-nejad@icho.edu.pl A century after G. N. Lewis introduced his foundational model of chemical bonding, its core principles remain central to our understanding of molecular structure. Traditionally, neighboring atoms in a Lewis structure are assumed to share stabilizing interactions. However, this assumption begins to falter at the boundary between covalent and noncovalent bonding. Our work reveals that, in certain molecules with the general formula MAX_3—where M is a metal, A a nonmetal, and X an electron-rich or electron-withdrawing group—the interaction between adjacent M and A atoms can be destabilizing, Figure 1. Remarkably, the overall structure is preserved due to strong interactions between electron-deficient metals and the X groups.[1–6] This phenomenon gives rise to unconventional structures, such as the inverted $LiCF_3$, where lithium interacts preferentially with fluorine atoms over the central carbon in the gas phase. These collective interactions extend beyond organometallic compounds and offer insight into anomalous bond dissociation energies and stability trends across a wide range of molecules—from perhaloalkanes to the elusive cyclic C_6O_6. Our computational studies highlight the broad relevance of this concept in modern chemical bonding theory.

Figure 1. (a) The general Lewis structure of the molecules prone to collective bonding, and (b) the stabilizing/destabilizing nature of interactions in MAX3 clusters. While the 1,2 interactions in a Lewis structure are destabilizing or merely weakly stabilizing, the 1,3 interactions proved to be strongly stabilizing. Panels (c) and (d) provide schematic representations of the pyramidal and inverted MAX3. The inverted structures are distinguishable by their negative $\Delta\angle$M–A–X values defined as the difference between the $\angle$M–A–X angle and a rectangle (shown as a grey dashed line perpendicular to the M–A bond).

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Primary author(s) : FOROUTAN-NEJAD, Cina (Institute of Organic Chemistry, Polish Academy of Sciences)

Presenter(s) : FOROUTAN-NEJAD, Cina (Institute of Organic Chemistry, Polish Academy of Sciences)