Non-Aufbau Electronic Structure: Influence on Hydrogen Atom Transfer Reactions

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Abstract

Radicals are highly reactive chemical species that have widespread applications. Recent reports indicate that certain persistent organic radical systems having electronic structures that apparently do not obey the Aufbau Principle. For example, Bredas et al. characterized a series of donor–acceptor organic radical systems that possess non-aufbau electronic structures and high photostability. Coote and coworkers reported some highly stable radical anions with non-aufbau character, including 4-carboxy-TEMPO. Radical systems of these types display electronic structures wherein their singly-occupied molecular orbitals (SOMOs) are lower in energy than their highest-occupied molecular orbitals (HOMOs), thereby exhibiting SOMO-HOMO inversion (SHI). The studies of systems displaying SHI suggest a tantalizing connection between radical stability/persistence and non-aufbau electronic structure.

I will provide brief overview of some recent studies in which non-aufbau radical systems have been studied. I will then share some examples from our recent work in which a strong connection between non-aufbau character and radical reactivity found. Implications for Nature's use of SHI in the control of the reactivity and selectivity in radical enzymes will be discussed.

Biography

Gino DiLabio received his BSc and MSc degrees from Carleton University (Ottawa, Canada) and his PhD from Clarkson University (USA). He is a full professor in the Department of Chemistry at The University of British Columbia's Okanagan campus, which he joined in 2014. In addition to non-Aufbau behaviour in radical enzymes and radical chemistry in general, his research interests include computational chemistry methods development and electric field catalysis at water interfaces. Prior to joining UBC, he was a senior staff scientist at Canada's National Institute for Nanotechnology (now the Nanotechnology Research Centre) where he worked on the development of novel quantum cellular automata and hybrid organic-silicon systems. He has published more than 160 papers, patents, and book chapters.