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Editorial
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Preface to *The Journal of Organic Chemistry*'s Special Issue "50 Years and Counting: The Woodward–Hoffmann Rules in the 21st Century"

It was a singular event. It was in the air. Both. Something important clearly happened 51 to 46 years ago, at the meeting ground of organic and theoretical chemistry. Not in one fell swoop, but in stages—from the first three *JACS* Communications in 1965 to the full paper in *Angewandte Chemie* in 1969 took four years. It was my fortune to take part in the work of those wonderful days. My partner (for sure, that is not how I thought of R. B. Woodward in those days) is sadly not with us. It nevertheless gives me great pleasure to introduce this special issue celebrating 50 years of orbital symmetry control of organic reactions, and looking to the future.

■ IT WAS IN THE AIR

The orbitals of polyenes, phases and all, were by 1964 familiar to physical and theoretical chemists. But it took the pedagogically effective, strikingly so, books of Jack Roberts and Andy Streitwieser to familiarize the organic community with molecular orbital theory. The (delayed) success of Hückel's rules in the 1950s, with the synthesis of cyclopropenyl and cycloheptatrienyl cations and cyclopentadienyl anions, certainly sensitized everyone in the organic community to the utility of orbitals. Even the nonclassical ion kerfuffle served a purpose—it made organikers aware of the necessity of thinking about out-of-the-safe-aromatic-plane orbital interactions. The sophistication of physical organic chemistry grew, marked by sharp thermodynamic and kinetic reasoning. So some very smart people here and there gleaned a reaction path from the stereochemical dance that molecules had to go through to reach a product.

■ AND A SINGULARITY

One crafted of inward streaks: First, by RBW, ever the synthetic adventurer, perceiving in his part of the B_{12} synthesis the stereochemically rich choices offered up by what came to be called an electrocyclic reaction. And RBW, abstracting from vitamin D photochemistry, and from "no mechanism" reactions, the simple underlying essence of a family of electrocyclic processes. RBW again, bringing to me, the calculator, the frontier orbital argument for what was known of the way butadiene and hexatriene behaved. And, if that were not enough, in one elegant conceptual swing, putting the cyclopropyl to allyl cation opening (then a piece of another game in town, that of solvolysis) into play.

I am the lesser part to begin with, just a calculator. Albeit one very, very interested in organic chemistry. Here's the luck, mine and RBW's: I'm prepared. With the extended Hückel method in hand, I am the only one (for just a short period of 2–3 years, before Hartree–Fock SCF methods and CNDO overtake me) to be able to study computationally the distinction between con- and disrotatory motions. I *can* do it, I *do* do it.

■ THE CONSEQUENCES TO THE COMMUNITY

The impact of the five communications and the long paper were substantive. Molecular orbital theory became part of the necessary education of our graduate students. The essence of Kenichi Fukui's brilliant idea, a perturbation-theory-based frontier orbital theory, was in time understood. And, in fact, became as teachable as arrow-pushing and Lewis structures. We began to trust computational chemistry, propelled by Paul Schleyer's advocacy. And slowly, as this *JOC* special issue will show, we are beginning to develop ways of thinking of trajectories of molecules traversing a surface.

■ AND WHAT IT MEANT TO ME

I did not know the problem (of pericyclic reactions) was important, not for a year; Jeff Seeman documents this in his article. I saw that it was fun, for sure. Through this work I was drawn into the organic literature, in this following my inclinations, helped by conversations with E. J. Corey and others, also by a course on small ring compounds taught by Doug Applequist, then visiting Harvard, and by organic seminars I had begun to attend. I fell deeper in love with stereochemistry and the denumerable infinity of organic structures.

I also learned from RBW the power of simple explanations. So in the five years of our work together, I was totally transformed from being a calculator to an explainer. The extended Hückel calculations occasionally failed, and other, so-called *ab initio,* as well as semiempirical methods quickly made extended Hückel the method to which all other methods were superior. Well, that just made me work harder to *understand.* I knew perturbation theory, of course—as equations, lovely sums—from quantum mechanics courses. Now I rediscovered it for myself, in a diagrammatic fashion, as the natural language of orbitals interacting. Orbital pictures grew on me; I was again helped by the fact that those reams of extended Hückel theory computer output did *not* provide orbital representations. I had to draw them.

In the end, a chance event. One that brought the world's greatest synthetic organic chemist of his time, a man with incredible insight, together with a young theoretical chemist. Who in turn was open to organic complexity, not too intimidated by authority, and who would (and could, at the drop of a punched card) calculate any molecule under the sun. Out of that grew a nexus of theory and organic chemistry that remains alive, and teaches us. And will continue to do so, as you can see in this special issue.

Roald Hoffmann

■ AUTHOR INFORMATION

Notes

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