Bond-Stretch Isomers and Spin-State Isomers: A Comment on the Article "Bond-Stretch Isomers: Fact not Fiction"[1]

Gerard Parkin* and Roald Hoffmann

Molecules which differ only in the length of one or several bonds have been termed bond-stretch isomers. The first reports of this phenomenon, both theoretical[2] and experimental,[3] date back to the early 1970s, while the first comprehensive article was published in 1988 by Jean, Lledos, Burdett, and Hoffmann.[4] The 1988 article summarized the phenomenon and provided a theoretical rationalization, and thereby stimulated considerable interest in the subject.

However, in 1991 it was discovered that the original example of bond-stretch isomerism in transition metal complexes was an artifact due to crystallographic disorder[5, 6] Thus, it was demonstrated that the green "isomer" of *cis-mer*-[$MoOCl_2(PMe_2Ph)_3$] was in fact a solid solution of blue *cis-mer*-[$MoOCl_2(PMe_2Ph)_3$] and yellow *mer*-[$MoCl_3(PMe_2Ph)_3$], and that the crystallographic disorder between an oxygen atom and a chlorine atom was manifested by an *apparent* increase in the Mo=O bond length. Indeed, it is presently recognized that impurities may commonly serve to modify apparent bond lengths.[7] There is therefore no longer a well-characterized example of bond-stretch isomerism for which it can be stated with certainty that the observed bond-length changes are not an artifact. Nevertheless, it is still possible that one day the phenomenon of bond-stretch isomerism will be experimentally verified.

It was, therefore, of great interest to read an article in this journal titled "Bond-Stretch Isomers: Fact not Fiction".[1] By its title, the article implies that examples of bond-stretch isomers have been discovered. However, the content of the article is not related to the concept of bond-stretch isomerism in the spirit in which it was originally discussed,[4] but rather is concerned with the well-established, valuable, and interesting phenomenon of *spin-state* isomerism, in which changes in bond length are associated with changes in spin-state.

Three review articles on bond-stretch isomerism[7–9] have indeed discussed the phenomenon of spin-state isomerism, and also related effects such as "deformational isomerism".[10, 11] However, bond-stretch isomerism was a concept that was introduced for isomers of the same spin-state, on the same potential energy curve, for which there was no obvious explanation. It may have been a failing of the original papers not to have excluded spin-state isomerism from the definition, but a reading of those papers and a general sense of the community make it clear that the interest of the bond-stretch isomerism phenomenon resides in those cases where the isomers belong to the same spin state. As interesting as they are, there is no special intrigue associated with the observed changes in bond lengths for spin-state isomers.

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[*] Prof. Dr. G. Parkin
Department of Chemistry, Columbia University
New York, NY 10027 (USA)

Prof. R. Hoffmann
Department of Chemistry
Cornell University
Ithaca, NY 14853 (USA)

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