CC/NUMBER 37
SEPTEMBER 13, 1982

This Week's Citation Classic

Bent H A. An appraisal of valence-bond structures and hybridization in compounds of the first-row elements. *Chem. Rev.* 61:275-311, 1961.
[Sch. Chemistry, Inst. Technology, Univ. Minnesota, Minneapolis, MN]

A review of the effects of atom hybridization and electronegative substituents on molecular properties (bond angles, bond lengths, proton-C^{13} coupling constants, and inductive constants) suggested this rule: *atomic s-character concentrates in orbitals directed toward electropositive substituents.* **[The *SCI*® indicates that this paper has been cited in over 500 publications since 1961.]**

H.A. Bent
Department of Chemistry
North Carolina State University
Raleigh, NC 27650

June 23, 1982

"In 1955, as a research associate at the University of Minnesota, I was working on a post-World War II project concerning the infrared spectra of the flames of rocket propellants. One thing—a strong, unidentified absorption—led to another: low-temperature matrix isolation studies, discovery of a new dimer of N_2O_4 ('bent' $ONONO_2$), and a growing curiosity concerning the connection between molecular properties and molecular structure.

"Since Dalton, chemists have tried to express molecular properties in terms of a molecular 'structure.' After World War I, the implications for structural theory of metrical information from diffraction of X rays and electrons were summarized by L. Pauling in his classic book *The Nature of the Chemical Bond.*[1]

"Pauling popularized a relation between angles and hybridization. After World War II, peacetime uses of the microwave technology of radar made possible the determination of molecular shapes with increased precision. The results, it seemed to me in 1956, contradicted conventional molecular orbital theory. I marshaled evidence for the thesis that orbital hybridization has an effect not only on bond angles, but also on bond moments, inductive constants and coupling constants, bond force constants and dissociation energies, and bond lengths. Effects were summarized in the rule cited in the abstract, sometimes referred to as 'Bent's rule.' It has been widely cited, I think, chiefly for these reasons: It correlated a wide range of phenomena of current interest to many chemists. It built on well-received ideas, particularly those of G.N. Lewis and Pauling. It extended and refined the widely used concept of electronegativity. It created useful—and in retrospect obvious—distinctions. It explained numerous anomalies, some not previously noted. It employed extensively for the first time the now widely used term 's-character.' It was simply stated, easily remembered, and quickly applied. It lent itself to elementary, back-of-the-envelope calculations. It provided a physical explanation for a purely chemical phenomenon: the inductive effect. It had an air of novelty, even improbability. For several years my papers on the rule were rejected by *Journal of the American Chemical Society.* It had an air of respectability. A series of short papers and notes in foreign journals and *Journal of Chemical Physics* preceded the review. It was supported by a large body of data and a line of reasoning well seasoned from early, unsuccessful efforts at publication. It is cited in textbooks. It has about it an air of 'chemystery' conformable to the temperament of chemists, who have been described as being, from earliest times, either artisans or mystics.

"The rule created its own anomalies that, had they been known at the outset, would probably have overwhelmed the rule. The new anomalies fit a new rule complementary to its predecessor.[2] The new rule is more comprehensive than the s-character rule, but less in line with conventional thought and, to date, less cited.

"Eventually, I found a simple, nonmystical, physical explanation for the verbalism of the s-character rule.[3] It outrages conventional wisdom, however, even more than does the new rule cited above and, to my knowledge, has never been cited by other authors."

---

1. **Pauling L.** *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry.* Ithaca, NY: Cornell University Press, 1939. 429 p.
2. **Bent H A.** Structural chemistry and donor-acceptor interactions. *Chem. Rev.* **68**:587-648, 1968.
   [The *SCI* indicates that this paper has been cited in over 90 publications since 1968.]
3. ------------. Localized molecular orbitals and bonding in inorganic compounds. *Fortschr. Chem. Forsch.* **14**:1-48, 1970.
   [The *SCI* indicates that this paper has been cited in over 15 publications since 1970.]