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COMMENTARY

Relationship of Bonding to Electronic Spectra

Over years of attending conferences and reading papers on silicon compounds, I have repeatedly come across what I consider misconceptions concerning the relation between chemical bonding and electronic spectra. After gentle arm-twisting by our esteemed Editor, I now comment on the issues in this forum, in part because the validity of the comments is not limited to compounds of silicon.

It is an experimental fact, reproduced by high-quality ab initio calculations, that the singlet $\sigma \rightarrow \sigma^*$ excitation energy is much lower for the Si–Si bond than for the C–C bond.[1] In an attempt to rationalize it in simple terms, the difference has been attributed at times to the "weak-bond effect": the splitting of the σ_{SiSi} and $\overset{*}{\sigma}_{SiSi}$ orbitals is said to be smaller, since Si–Si is the weaker bond.

This is not a valid explanation, since in fact the Si–Si and C–C bond strengths are quite similar. For instance, the Si–Si bond strength in $(CH_3)_3Si{-}Si(CH_3)_3$ is 80 kcal/mol,[2] the central C–C bond strength in $(CH_3)_3C{-}C(CH_3)_3$ is 70 kcal/mol,[3] and yet the singlet $\sigma_{SiSi} \rightarrow \overset{*}{\sigma}_{SiSi}$ excitation in the former lies at least 30 kcal/mol below the corresponding excitation in the latter, and possibly much more (it is not easy to identify the energy of the $\sigma_{CC} \rightarrow \overset{*}{\sigma}_{CC}$ configuration from the spectrum).[1] True, the central CC bond in hexamethylethane is particularly weak because of steric crowding, but by the above argument, this should just shift its $\sigma \rightarrow \sigma^*$ excitation to particularly low energies.

Actually, it is the triplet $\sigma \rightarrow \sigma^*$ excitation energy that is linked to the covalent-bond strength, i.e., to the energy needed for homolytic dissociation. The singlet $\sigma \rightarrow \sigma^*$ excitation energy is related to the energy needed for heterolytic dissociation, i.e., to the sum of the ordinary (homolytic) bond strength and the energy needed to remove an electron from the sp^3 valence orbital of one of the partners, minus the energy gained by placing it into the sp^3 valence orbital of the other (the "hardness" of the dissociating bond). Since silicon has a lower ionization potential and a higher electron affinity than carbon, the singlet $\sigma_{SiSi} \rightarrow \overset{*}{\sigma}_{SiSi}$ excitation energy is lower than $\sigma_{CC} \rightarrow \overset{*}{\sigma}_{CC}$ even though the bond energies are roughly the same (the Si–Si bond is "softer").

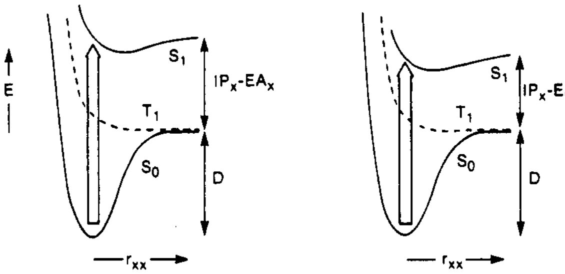

Figure 1. Schematic representation of the dissociation of bonds between two C sp^3 orbitals (left) and between two Si sp^3 orbitals (right) in their S_0, T_1, and S_1 states. Reprinted with permission from ref 4. Copyright 1989 American Chemical Society.

The reasons for the qualitative association of the $\sigma \rightarrow \sigma^*$ excitation energy with the homolytic bond strength for the triplet and with the heterolytic bond strength for the singlet are apparent in the simplest valence-bond description of the ground state, $R_3Si{\uparrow}{\downarrow}SiR_3$, the triplet $\sigma\sigma^*$ state, $R_3Si{\uparrow}{\uparrow}SiR_3$, and the singlet $\sigma\sigma^*$ state, $R_3Si^{+}\,{}^{-}SiR_3 \leftrightarrow R_3Si^{-}\,{}^{+}SiR_3$. This description becomes excellent in the dissociation limit as shown in Figure 1 (in which Rydberg states have been omitted as irrelevant in the first approximation).

The actual vertical singlet $\sigma \rightarrow \sigma^*$ excitation energy can be expected to be somewhat lower than the heterolytic bond dissociation energy, because of Coulombic attraction in the ion pair, and the vertical triplet $\sigma \rightarrow \sigma^*$ excitation energy can be expected to be somewhat higher than the homolytic bond dissociation energy, because of the repulsive interaction in the triplet. Still, it is clear that trends in the energies of the heterolytic and homolytic dissociation limits will be reflected in the singlet and triplet excitation energies, respectively.

Similar considerations apply to the comparison of carbon–carbon bonds with those made by elements other than

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[1] Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: New York, 1974; Vol. 1, p 303.

[2] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. Davidson, I. M. T.; Hughes, K. J.; Ijadi-Maghsoodi, S. *Organometallics* **1987**, *6*, 639.

[3] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986; p 278. Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 77.

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silicon and to other types of bonds, such as $\pi \rightarrow \pi^*$. Of course, except in the case of metal–metal σ bonding [e.g., in $(OC)_5Mn{-}Mn(CO)_5$], the excitation energies of isolated σ bonds are usually too high for easy observation. This changes when several such bonds are linked in σ conjugation, and materials such as polysilanes actually absorb in the near-UV region. The electronic structure and spectra of these fascinating σ-conjugated systems are summarized elsewhere:[4] they are isoelectronic with π-conjugated polyenes with strong bond length alternation, yet their photophysical behavior is very different in some respects, since resonance integral alternation in a σ system is immutable to geometry changes: there are no nuclear motions that could dramatically stabilize bipolarons or solitons by modifying resonance integral alternation.

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Josef Michl

Center for Structure and Reactivity
Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712-1167

[4] Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

ARTICLES

Electrical Wiring of Redox Enzymes

ADAM HELLER

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

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Relaying of Electrons in Enzymes

This Account describes the chemical modification of regions of large biomolecules, transforming them from electrical insulators to electrical conductors. Redox enzymes are molecules of 40 000 Da (daltons) (e.g., galactose oxidase) to 850 000 Da (e.g., choline dehydrogenase) with one or more redox centers. Their average hydrodynamic diameters range from ~55 to ~150 Å. In the great majority of enzymes, the redox centers are located sufficiently far from the outermost surface (defined by protruding protein or glycoprotein domains) to be electrically inaccessible. Consequently, most enzymes do not exchange electrons with electrodes on which they are adsorbed, i.e., their redox centers are neither electrooxidized at positive potentials nor electroreduced at negative ones. Apparently, part of the protein or glycoprotein shell surrounding the redox centers is there to prevent indiscriminate electron exchange between the different redox macromolecules of living systems. Such exchange would, in the extreme case, lead to an equipotential system, which could not sustain life. Another function of this shell is to stabilize the structure of the enzyme. Because neither function is essential for catalysis, redox enzymes do function when part of the shell is stripped[1,2] or, as we shall see here, when the shell is chemically altered so as to make it electrically conductive.[3-5] Following such alteration, a redox center of an enzyme will directly transfer electrons to an electrode on which the enzyme is adsorbed.[3,4] We call the centers that increase the electron current flowing through their shells by accepting and transferring electrons "electron relays".

The distance dependence of the rate of electron transfer in proteins has been the subject of experimental[7-14] and theoretical[15-21] studies during the past

Adam Heller graduated from the Hebrew University in Jerusalem, where he received his Ph.D. degree in 1961. He joined the University of Texas at Austin in 1988, where he holds the Ernest Cockrell, Sr., Chair in Engineering. Earlier he headed the Electronic Materials Research Department of AT&T Bell Laboratories in Murray Hill, NJ. His accomplishments include construction of the first inorganic liquid laser, codevelopment of the lithium-thionyl chloride battery, demonstration of the first electrical power and hydrogen generating electrochemical solar cell of >10% efficiency, and the direct electrical communication between chemically modified redox enzymes and electrodes. He was elected to the National Academy of Engineering in 1987 and received the Vittorio De Nora Gold Medal of the Electrochemical Society for distinguished contributions to electrochemical technology in 1988.

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