MOLECULAR STRUCTURE AND ENERGETICS

Volume 1

Chemical Bonding Models

Edited by
Joel F. Liebman
and
Arthur Greenberg

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VCH

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SERIES FOREWORD

Molecular structure and energetics are two of the most ubiquitous, fundamental and, therefore, important concepts in chemistry. The concept of molecular structure arises as soon as even two atoms are said to be bound together since one naturally thinks of the binding in terms of bond length and interatomic separation. The addition of a third atom introduces the concept of bond angles. These concepts of bond length and bond angle remain useful in describing molecular phenomena in more complex species, whether it be the degree of pyramidality of a nitrogen in a hydrazine, the twisting of an olefin, the planarity of a benzene ring, or the orientation of a bioactive substance when binding to an enzyme. The concept of energetics arises as soon as one considers nuclei and electrons and their assemblages, atoms and molecules. Indeed, knowledge of some of the simplest processes, e.g. the loss of an electron or the gain of a proton, has proven useful for the understanding of atomic and molecular hydrogen, of amino acids in solution, and of the activation of aromatic hydrocarbons on airborne particulates.

Molecular structure and energetics have been studied by a variety of methods ranging from rigorous theory to precise experiment, from intuitive models to casual observation. Some theorists and experimentalists will talk about bond distances measured to an accuracy of 0.001 Å, bond angles to 0.1°, and energies to 0.1 kcal/mol and will emphasize the necessity of such precision for their understanding. Yet other theorists and experimentalists will make equally active and valid use of such seemingly ill-defined sources of information as relative yields of products, vapor pressures, and toxicity. The various chapters in this book series use as their theme "Molecular Structure and Energetics" and it has been the individual authors' choice as to the mix of theory and of experiment, of rigor and of intuition that they have wished to combine.

As editors, we have asked the authors to explain not only "what" they know but "how" they know it and explicitly encouraged a thorough blending of data and of concepts in each chapter. Many of the authors have told us that writing their chapters have provided them with a useful and enjoyable (re)education. The chapters have had much the same effect on us and we trust readers will share our enthusiasm. Each chapter stands autonomously as a combined review and tutorial of a major research area. Yet clearly there are interrelations between them and to emphasize this coherence we have tried to have a single theme in each volume. Indeed the first four volumes of this series were written in parallel, and so for these there is an even higher degree of unity. It is this underlying unity of molecular structure and energetics with all of chemistry that marks the series and our efforts.

Another underlying unity we wish to emphasize is that of the emotions and of the intellect. We thus enthusiastically thank Alan Marchand for the opportunity to write a volume for his book series which grew first to multiple volumes and then became the current, autonomous series for which this essay is the foreword. We likewise thank Marie Stilkind of VCH Publishers for her versatility, cooperation and humor. We also wish to emphasize the support, the counsel, the tolerance and the encouragement we have long received from our respective parents, Murray and Lucille, Murray and Bella; spouses, Deborah and Susan; parents-in-law, Jo and Van, Wilbert and Rena; and children, David and Rachel. Indeed, it is this latter unity, that of the intellect and of emotions, that provides the motivation for the dedication for this series:

"To Life, to Love, and to Learning".

Joel F. Liebman
Baltimore, Maryland

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Newark, New Jersey

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PREFACE

The present volume examines nine topics in the fundamental, conceptual and theoretical framework of molecular structure and energetics. All the essays explicitly compare and interweave findings from experiment and from both calculational and qualitative theory.

Chapter 1, by Pauling and Herman, commences with a discussion of the complementary roles of experiment and qualitative and quantitative theory in chemical understanding. Proceeding from Pauling's earlier pioneering work, they give a brief commentary on atoms, bonds, molecules, structure and energetics in terms of electronegativity and atomic charges. While application is generally made to small inorganic molecules, the reader is shown how these concepts are also useful in the understanding of "larger" species and the solid state.

Chapter 2, by Bent, introduces isoelectronic reasoning and applies it to a variety of well-defined series of molecules and ions characterized by a given number of heavy (non-hydrogen) atoms and valence electrons. The simple, fundamental, and diverse topics of acidity and basicity, the octet rule and coordination number, covalent, metallic and ionic bonding arise naturally. Likewise, applications to inorganic and organic compounds alike, to compounds in the gas phase, solution and as solids, all occur in this conceptually unified chapter.

Chapter 3, by Liebman and Simons, discusses the structure, energetics and spin states of carbenes and related reactive species. The underlying principles of many quantitative calculational approaches, hitherto discussed almost solely in the quantum chemical literature, are presented. The results of these methods are compared with each other and with the admittedly sparse experimental literature. Likewise, various qualitative rules and regularities are discussed and used to interrelate carbenes with isolable, conventional and thus better understood, organic and inorganic compounds.

Chapter 4, by Gordon, discusses theoretical aspects of the new field of compounds that have multiple bonded silicon. Although carbon and oxygen (and silicon itself) are the customary partners for silicon in these species, theory has matched experiment in the diversity of the wide variety of other elements also investigated. Indeed, given the sparse degree of quantitation in the experimental literature, quantum mechanical calculations have been nearly the sole source of data employed to derive patterns of understanding.

Chapter 5, by King, examines topological relationships in structure and energetics. From both chemical precedent and mathematical theorems, he makes the strong case that knowing merely the number of electrons in the molecular framework and number of nearest neighbors to each atom allows one to understand much of the observed diversity that characterizes chemical phenomena. Applications range from simple hydrocarbons to polyhedral inorganic cages and clusters.

Chapter 6, by Fehlner and Housecroft, examines boranes and heteroboranes wherein "hetero" is taken here to include carbon, as well as numerous metals and nonmetals. Results from crystallography, diverse spectroscopic techniques, serendipitous syntheses, thermochemistry, and quantum mechanical calculations are combined to present a coherent understanding. Indeed, simple relations between the number of the skeletal electrons and the derived polyhedral geometry are also used to explain the dazzling diversity of structural types for these species of surprising stoichiometry.

Chapter 7, by Burdett, examines the relationships of structure and energetics as found in the solid state. The chapter employs group theory, simple Hückel Molecular Orbital theory, and principles, theorems and results from the physics and mathematics literature. By doing so, the idiosyncracies of the three-dimensional structure of numerous elements and binary compounds is not only seen to be self-consistent, but also found to relate to the strain and resonance energies of simple hydrocarbons and their substituted derivatives.

Chapter 8, by Schaad and Hess, presents a detailed, generally mathematically complete and rigorous, derivation of the Schrödinger equation. Most chemists accept this equation unaware and unconcerned by either the assumptions in its formulation and/or its use in modern computational science. This chapter provides the reader with many of the principles and theorems needed for a better understanding of the fundamental equation that underlies chemical phenomena.

Chapter 9, by Del Bene, discusses the numerous and generally implicit assumptions made when reaction enthalpies derived from quantum mechanical calculations are equated with those from experimental measurements. Explicit correction terms, both their magnitude and functional form, are presented along with their rigorous source in thermodynamics, statistical mechanics and quantum chemistry. Application is made to reactions as diverse as cation binding, hydrogenolysis, and the isomerization of heterocycles.

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CHAPTER 1

The Nature of the Chemical Bond Fifty Years Later: The Relative Electronegativity of Atoms Seen in Perspective

Linus Pauling* and Zelek S. Herman

Linus Pauling Institute of Science and Medicine, Palo Alto, California

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MOLECULAR STRUCTURE AND ENERGETICS, Vol. 1

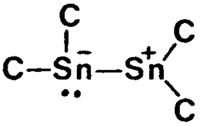
1. INTRODUCTION

Some 50 years have now passed since the publication of a series of papers bearing the title "The Nature of the Chemical Bond."[1-7] These papers have provided chemists, physicists, biologists, and mineralogists with the conceptual framework, based on simple valence bond theory and the theory of hybrid bond orbitals, required to investigate a myriad of problems involving the nature of the bonding exhibited in molecules and solids. The ideas contained in these papers were subsequently elaborated on in *The Nature of the Chemical Bond,*[8] which is probably the most often-cited book in the scientific literature.[9]

In the meantime there have occurred many novel experimental findings, and advances in theoretical methodology and computer technology have been so extensive that computer calculations of certain molecular and solid state properties rival or sometimes even exceed experimental results in accuracy.[10] Indeed, sophisticated computer programs have now become one of the pieces of laboratory equipment of many experimental scientists. Nevertheless, there remains a critical need for the simple conceptual models, which are firmly rooted in quantum mechanics, contained in *The Nature of the Chemical Bond* and the work of such investigators as Roald Hoffmann,[11] to assist in providing a systematization and rationalization of the ever-increasing profusion of established experimental facts and to understand the results of sophisticated computer calculations.[12] It must not be forgotten that computational quantum chemistry employs algorithms that always are subject to breakdown in a way that is not obvious to a nontheoretician (eg, the incorrect diagonalization of certain spurious matrices), and there remains a multitude of possible problems, including linear dependence of the basis set employed, symmetry breaking, nonconvergence, the use of minimal sets, and the effect of configuration interaction on specific properties. Thus the computer cannot be viewed as a black box any more than any other piece of laboratory equipment can be so regarded. The chapters in this series manifest the successful interaction of simple bonding concepts, sophisticated theoretical investigations, and recent experimental results.

There exists yet another aspect of the importance of the concepts of simple valence bond theory and the theory of hybrid bond orbitals, namely, their usefulness in leading to the discovery of novel ideas. We shall cite as examples a number of recent discoveries in our own laboratory. First, the concepts of simple valence bond theory and the theory of hybrid bond orbitals have been employed to elucidate the unusual bonding angles and structures often displayed by compounds containing transition metals or elements of the lanthanide or actinide series.[13-29] Just as the tetrahedral bond angle 109.47° is characteristic of sp^3 hybrid bond orbitals, it was found that the bond angles 73.15° and 133.62° are characteristic of sp^3d^5 hybrid bond orbitals and the bond angles 54.88°, 100.43°, and 145.37° are characteristic of sp^{3}d^{5}f^7 hybrid bond orbitals. The implications of this discovery have been explored in detail in the aforementioned papers.

Second, the theory of hybrid bond orbitals was utilized recently to discover a new type of chemical bond involving the resonating unshared electron pair.[30,31] For example, bis(bistrimethylsilylmethyl) tin(II), $\{(CH_3)_3Si\}_2HCSnCH\{Si(CH_3)_3\}_2$, forms dimers in the solid state having a tin–tin bond characterized by resonance of an unshared electron pair or



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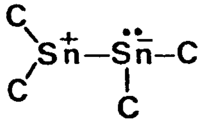
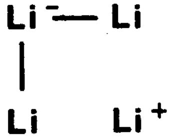


When there is electronic resonance, the bond lengths, bond angles, and nuclear positions are intermediate between those corresponding to the individual resonance structures, as found in the crystal structure of the tin dimer.[32] This type of bond, that is, a single bond plus a resonating unshared electron pair, was subsequently found to occur on the {100} surfaces of silicon.[33]

Finally, the use of simple valence bond theory has led recently to a significant discovery concerning the nature of metals. Many years ago one of us noticed, based on an analysis of the experimental values of the saturation ferromagnetic moment per atom of the metals of the iron group and their alloys, that for a substance to have metallic properties, 0.72 orbital per atom, the "metallic orbital," must be available to permit the unsynchronized resonance that confers metallic properties on a substance.[34–38] Using lithium as an example, unsynchronized resonance refers to such structures as follows.



Successive pivoting resonances of a covalent bond allows for electrical conduction to occur, as shown in Figure 1-1. A test of this theory was provided by gray and white tin. Gray tin is not metallic because all its valence orbitals are used for bonding and there is no metallic orbital available. White tin, on the other hand, has the metallic orbital available and therefore has metallic properties.

The development during the past year of a statistical theory of unsynchronized resonance of covalent bonds in a metal, with atoms restricted by the electroneutrality principle to forming bonds only in number $\upsilon - 1$, υ, and $\upsilon + 1$, with υ the metallic valence, has led directly to the value 0.70 ± 0.02 for the number of metallic orbitals per atom.[39] This theory also has led to the conclusions that stability of a metal or alloy increases with increase in the ligancy and that for a given value of the ligancy, stability is a maxi-

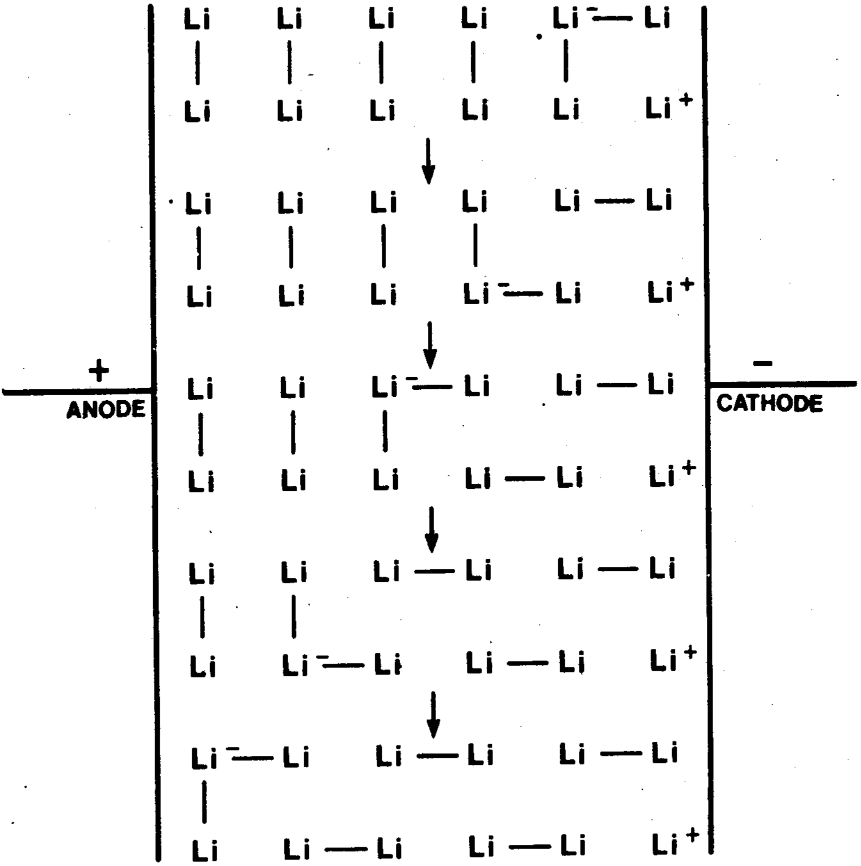

+
ANODE
−
CATHODE
Li Li Li Li Li⁻— Li
Li Li Li Li Li Li+
Li Li Li Li Li — Li
Li Li Li Li⁻— Li Li+
Li Li Li⁻— Li Li — Li
Li Li Li Li — Li Li+
Li Li Li — Li Li — Li
Li Li⁻— Li Li — Li Li+
Li⁻— Li Li — Li Li — Li
Li Li — Li Li — Li Li+

Figure 1-1. Motion of an electron from the cathode to the anode by successive pivoting resonances of a covalent bond.

mum for valence equal to half the ligancy. These results, along with consideration of the repulsion of unshared electron pairs on adjacent atoms, go far toward explaining the selection of different structures by different elemental metals and intermetallic compounds. This theory has just been applied to comprehend the anomalous behavior of vanadium sesquioxide (V_2O_3) in the solid state.[40]

One of the most pervasive ideas to emerge from the series of papers entitled "The Nature of the Chemical Bond" is the concept of the relative electronegativity of atoms. The sections that follow examine some of the consequences of this concept.

2. THE RELATIVE ELECTRONEGATIVITY OF ATOMS

The original table of values of the electronegativity of elements[4,41] was developed on the basis of quantum mechanical argument about the differences in

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