

ORGANIC CHEMISTRY OF SULFUR

Edited by S. Oae

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Preface

In recent years organic sulfur chemistry has been growing at an even faster pace than the very rapid development in other fields of chemistry. This phenomenal growth is undoubtedly a reflection of industrial and public demands: not only was sulfur recently in overall surplus for the first time in the history of the chemical industry but it has now become a principal environmental hazard in the form of sulfur dioxide, sulfuric acid and hydrogen sulfide. Another reason, discernible in the last fifteen years, has been the desire, on the part of individual chemists and all types of research managers, to move away from the established chemistry of carbon into the less well understood and sometimes virgin chemistries of the other elements which form covalent bonds.

As a result of this movement the last decade has seen the development of sulfur chemistry into a well-organized and now much better understood branch of organic chemistry. Enough of the detail has become clear to see mechanistic interrelationships between previously unconnected reactions and with this clarification the whole subject has in turn become systematized and subdivided. The divalent sulfur chemistry of thiols, monosulfides, disulfides and polysulfides is a large area in itself, much of it devoted to oxidation-reduction and the breakage and formation of sulfur-sulfur bonds, although interesting discoveries are now being made about the reactivity of certain sulfur-carbon bonds. Of course, this area has its own massive biochemical branch involving enzymes and proteins.

The chemistry of sulfur in higher oxidation states evolved at first in an analogous way around sulfur-oxygen compounds — sulfoxides, sulfones, and sulfur oxyacids and their thiol esters. There has since been an expansion into sulfur compounds containing other hetero atoms and into the recently characterized tetravalent sulfuranes. A third area with many ramifications is that of sulfur heterocycles. Much of the recent interest here has been engendered by pseudoaromatic ring systems and structures exhibiting "no bond" resonance, such as the thiathiophthens.

A number of guide books have appeared for this fast-advancing frontier of chemistry. Professor Charles C. Price and I wrote one of the pioneering books more than ten years ago and I wrote another in Japanese six years ago. However, the growth of the subject in recent years has been so rapid that when I was asked to consider the preparation of a new guide book I readily agreed. However, the subject is now so broad that I felt I should

not assume sole authorship but rather enlist the help of intimate colleagues, the top experts in their respective fields. Thus this book was born.

The text offers a comprehensive survey of most of the basic aspects of organosulfur chemistry. Since it is intended to be used primarily as a textbook for graduate courses, the subjects of each of the twelve chapters, written by a well-known authority, are carefully chosen and are explained in the light of the most modern concepts in physical organic chemistry. Therefore, I hope that not only students but also many of those actively engaged in industrial and biological chemistry, agriculture and medicine will find this book useful and stimulating.

As readers will realize, this book is a synthesis of international cooperation. There are one German, two British, four Japanese and five American authors. Although the cooperation has been harmonious and genuine, readers will note considerable differences in the styles of the chapters. This was to some extent inevitable in any case but, as editor, I have taken the view that each individual author will have chosen the wording he considers best for expression and to revise that wording was to risk destroying the nuances of meaning and flavors of the sentences. I have therefore preserved the authors' wording as much as possible.

It is a pleasure to acknowledge the real cooperation of all the authors who have willingly devoted their time in the pursuit of this international undertaking. In addition, I wish to thank many young colleagues in our laboratories at Osaka City University who have rendered assistance in various ways, among them Drs. T. Numata, A. Nakanishi, K. Fujimori, T. Aida and F. Yamamoto. Of course, I alone am responsible for all errors.

Shigeru Oae

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Chapter 1

SULFUR BONDING

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1.1 INTRODUCTION

1.1.1 The *d*-Orbital Problem

Does sulfur use *d* orbitals? That has been the central issue in theoretical studies of bonds to sulfur ¹⁻⁴ — and other second-row elements ^{5,6} — from the time Pauling employed, in qualitative descriptions of octahedrally co-ordinated atoms, sp^3d^2 hybrid orbitals ^{7,8}.

The question as to whether or not sulfur atoms use *d* orbitals arises chiefly with regard to bonds to sulfur –

- 1) From such atoms as oxygen, nitrogen, and carbon (in carbanions) that have; at least nominally, unshared valence-shell electrons; and
- 2) In such molecules as SF_6 , where the classical valence of sulfur – less the overall charge (if any) on the sulfur-containing species (+1 for sulfonium compounds, Chapter 9; –1 for RS^- ; –2 for S^{2-}) – is greater than 2. (No compounds with a sulfur-valence-less-ionic-charge number less than 2 are discussed in this volume.)

Some investigators have asserted that sulfur's *3d* orbitals are *too diffuse* to be used effectively in chemical bonds ⁶. In atomic sulfur, e.g., the excited state configuration $3s^2 3p^3 3d$ lies, in energy, over eighty percent of the way up from ground state S to ground state S^+ plus an electron in the most diffuse of all orbitals, the *continuum* ⁹.

Other investigators have stressed that in the intense field of the positively charged kernel of a highly electronegative ligand, such as F (in SF_6), the *effective* orbital exponent α of a Slater-type sulfur *3d* orbital, $\text{Nr}^2 \exp(-\alpha r)$, is significantly *increased* over its value in atomic sulfur, leading to a marked *contraction* of the sulfur *3d* orbital, whose maximum probability for the radial function occurs at $r = 3/\alpha$ ^{1,10,11}.

Still other investigators have stressed, however, that, in molecular orbital theory, to rationalize the existence of such compounds as SF_6 (rare gas halides, polyhalides and, generally, "hypervalent" compounds), it is not necessary to use any *d* orbitals at all ¹²⁻¹⁴. An explicit, if qualitative, set of low-lying molecular orbitals adequate in number to accommodate all valence-shell electrons can be set down solely in terms of ligand orbitals and sulfur *p* orbitals. In these applications of molecular orbital theory, as in the earliest orbital theories of valence, an attempt is made to account for the broad features of molecular geometry – bond angles, particularly – purely with *p* orbitals.

1.1.2 Importance of the Exclusion Principle

If sulfur can form a hexafluoride without the use of *d* orbitals, one might wonder, why cannot oxygen? Why, essentially, is sulfur so different, physically and chemically, from oxygen?

Insight into this sulfur/oxygen, second-row/third-row, *p*-only/contracted-*d* orbital question can be achieved by examining a model of electronic structure that exhibits *directly*, in visualizable, physical terms, the outcome of the operation in chemical systems of the fundamental principles of electron physics.

To understand the distinctive chemistries of the elements, a model is needed that will enable one to sense intuitively what the outcome will be,

in complex systems, of the joint operation of three physical factors: coulombic forces, the wave-like character of electrons, and the Exclusion Principle.

Coulombic forces have long been recognized as important in chemistry. Berzelius's early models of polar attractions have been steadily refined, most notably, for homopolar compounds, by Gilbert N. Lewis^{15,16}, in the shared-electron-pair bond, and, for heteropolar compounds, by Born¹⁷, Bragg¹⁸, Goldschmidt¹⁹, and Pauling⁸, in the ion-packing model of crystals.

During the last half-century, most work in theoretical chemistry has been focused on the problem of examining the implications for chemistry of the wave-like character of electrons. The perceived problem has been to find analytical expressions, or numerical values, for a wave function Ψ that is an eigenfunction of Schrödinger's electrostatic Hamiltonian. Relatively little work has been expended on examining directly the role of the Exclusion Principle in chemistry.

Yet, as Lennard-Jones emphasized in 1954, *the effect of the Exclusion Principle is most powerful, much more powerful than electrostatic forces*. "It does more to determine the shapes and properties of molecules," wrote Lennard-Jones, "than any other single factor. It is the Exclusion Principle which plays the dominant role in chemistry"²⁰.

How important the Exclusion Principle is can be seen in the simplest case: the ionization potentials of the first three elements, hydrogen, helium, and lithium. The ionization potential (in ev) of hydrogen is 13.6; of He^+ $2^2 \times 13.6 = 54.4$; of He, only 24.6, owing to electrostatic repulsion — or "screening of the nucleus" — of one electron for — or by — the other. From those numbers, one might suppose, correctly, that, without any significant modification in procedure, a direct application of Schrödinger's equation to lithium would yield for lithium's first ionization potential 30-50 ev. In fact, to a zeroth approximation, the ionization potential of lithium is almost zero; it is only 5.39 ev. The effective positive field seen by the most easily removed electron of lithium is remarkably small. It is smaller than the field seen by either electron in a helium atom. It is smaller, even, than the positive field seen by the single electron in an hydrogen atom, a most remarkable conclusion. Two electrons in lithium somehow screen the third electron from the field of the nucleus more effectively than they would were they localized entirely within the atom's nucleus. The effect of the Exclusion Principle is indeed most powerful, much more powerful than electrostatic forces.

1.1.3 Pauli Mechanics

At the present time, it would appear that any fundamental model of

electronic structure should emphasize explicitly the prominent, even dominant role played by the Exclusion Principle in any close confederation of particles that contains more than two electrons.

Indeed, for centuries chemists have been articulating, slowly but surely, and most explicitly, in the classical structural model of homopolar compounds, in the ionic model of heteropolar compounds, in the doctrine of co-ordination, and in such concepts as directed valence, steric effects, electron sharing, inner-shell electrons, unshared valence-shell electrons, and hybrid orbitals, a practical, working mechanics of the Exclusion Principle as it applies to complex, chemical systems^{21,22}.

Unlike classical mechanics, unlike even pure quantum mechanics without the Exclusion Principle, this chemical mechanics — this *Pauli Mechanics* — has the peculiar, but to chemists familiar feature that it produces stable, *complexly articulated structures*. The salient features of these Pauli mechanical structures can be usefully, if not yet perfectly described with simple packing models that incorporate and display perspicuously nearly all the accumulated insights into chemical bonding of classical structural theory²².

1.1.4 Representation-Independent Terms

One of the principal functions of a model is to supply a terminology. Physical models are said to be useful if they account for a large number of facts in simple ways and if (consequently) they suggest terms and a nomenclature eventually deemed essential for a proper description of the phenomena²³. Such functions are achieved, emphasized Schrödinger, through the *deliberate suppression of quantitative details*²⁴.

Suppression of details, continues Schrödinger, may yield results more interesting than a full treatment. Most importantly, it may suggest new concepts. Pure quantum mechanics alone, in all its detail, cannot supply a definition of, e.g., an acid or a base, or a double bond²⁵.

Unlike conventional valence-bond and molecular orbital models, Pauli mechanical packing models supply concepts and terms that, through a deliberate suppression of quantitative details, are, appropriately, largely representation-independent²⁵. Hence, they permit one to see, as will be shown, that the bonding in, e.g., SF_6 can be described without the use of sulfur 3d or sulfur 3p orbitals. They permit one to see, also, that the p-only and contracted-d orbital models are merely different ways of describing, qualitatively, the same thing: the potential energy space about the kernel of a medium-sized atom. Most importantly, perhaps, Pauli packing models permit one to see, at a glance, how operation of the Exclusion Principle conjointly with coulombic forces and the wave-like

character of electrons makes the chemistry of sulfur, so amply illustrated in this volume, so different from that of its Group VI congener oxygen.

1.2 BONDING IN SF₆

1.2.1 Conventional Molecular Orbital Model

Symmetry-determined combinations of fluorine 2*p* orbitals for construction of molecular orbitals for SF₆, assumed octahedral, are given in Table 1.1, following Mitchell¹. Orbital axes are shown in Fig. 1.1.

The atomic core of sulfur has been taken to be S⁶⁺ (1*s*²2*s*²2*p*⁶), that of a fluorine atom F⁵⁺ (1*s*²2*s*²), leaving 36 electrons, 6 from sulfur, 5 from each of 6 fluorine ligands, to be placed in valence-shell molecular orbitals.

Following Rundle¹², one ignores, initially, participation by sulfur 3*d* orbitals — and additional sulfur orbitals of still higher energies with representations *t*_{1*g*} and *t*_{2*u*}. The *e_g* and *t*_{2*g*} molecular orbitals, like the *t*_{1*g*} and *t*_{2*u*} orbitals, are then completely determined by symmetry; together, the 11 orbitals can accommodate 22 electrons. Three relatively weak “back-bonding type” molecular orbitals of *t*_{1*u*} symmetry formed between sulfur 3*p* orbitals and *π*-type combinations of fluorine 2*p* orbitals can accommodate 6 more electrons, leaving 8 electrons for the four strongly bonding *a*_{1*g*} and *t*_{1*u*} molecular orbitals¹.

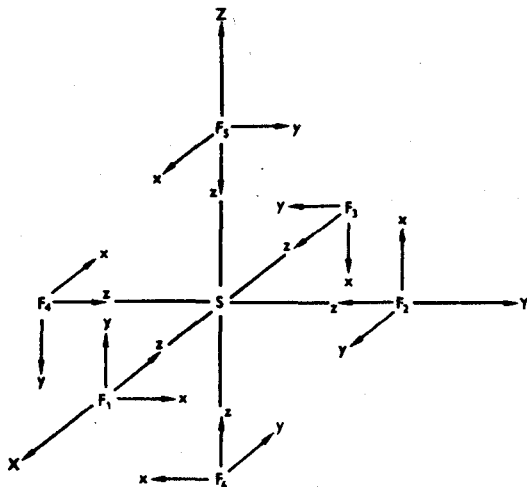


Fig. 1.1. Axes used in the description, Table 1.1, of the symmetry orbitals for octahedral SF₆.

From the molecular orbital description of SF_6 given above (and from similar m.o. descriptions of other hypervalent compounds), it is often said to follow that "the stability of SF_6 [and hypervalent compounds, generally] can be interpreted without recourse to 3d-orbital participation"¹ [emphasis added].

TABLE 1.1
Symmetry Orbitals for Octahedral SF_6

Representation	Sulfur orbital	Fluorine orbitals	
		σ	π
a_{1g}	3s	$z_1 + z_2 + z_3 +$ $z_4 + z_5 + z_6$	
t_{1u}	3p _x	$z_1 - z_3$	$y_2 + x_5 - x_4 - y_6$
	3p _y	$z_2 - z_4$	$x_1 + y_5 - y_3 - x_6$
	3p _z	$z_5 - z_6$	$y_1 + x_2 - x_3 - y_4$
e_g	3d _{x²-y²}	$z_1 - z_2 + z_3 - z_4$	
	3d _{z²}	$2z_5 + 2z_6 - z_1 -$ $z_2 - z_3 - z_4$	
t_{2g}	3d _{xy}		$x_1 + y_2 + y_3 + x_4$
	3d _{xz}		$y_1 + x_5 + x_3 + y_6$
	3d _{yz}		$x_2 + y_5 + y_4 + x_6$
t_{1g}			$x_1 - y_2 + y_3 - x_4$
			$y_1 - x_5 + x_3 - y_6$
			$x_2 - y_5 + y_4 - x_6$
t_{2u}			$y_2 - x_5 - x_4 + y_6$
			$x_1 - y_5 - y_3 + x_6$
			$y_1 - x_2 - x_3 + y_4$

It is well known, however, that simple m.o. theory suggests stability for molecular species that have not so far been synthesized. Change, for example, the principal quantum number for the sulfur orbitals in Table 1.1 from 3 to 2, and the m.o. description given above for SF_6 applies, *mutatis mutandis*, to octahedral oxygen hexafluoride.

It is possible to give a "satisfactory", qualitative molecular orbital description for OF_6 — and NF_5 . From reasoning based on the *p*-only molecular orbital model, Rundle was, indeed, led to suppose that it should be possible to synthesize a compound in which a nitrogen atom has a ligancy of five^{1,2}.

Rundle's *p*-orbital model can, in fact, be taken a step further. The *p*-orbitals themselves can be omitted. The valence-shell electrons of SF_6 can be described, qualitatively, solely in terms of ligand orbitals. One can omit completely explicit reference to all sulfur extra-kernel orbitals, 3d and 3p.

For the essential physical feature of qualitative molecular orbital descriptions of SF_6 lies in the assignment of a relatively low potential energy for electrons in the region of space immediately surrounding the sulfur kernel (the "bonding region"), into which project, separately and collectively, the ligand's sigma orbitals. It is recognition of the field of the kernel S^{6+} — together (see later) with unstated assumptions regarding stable occupancy of that region by electrons — that leads one to assert that the a_{1g} and three t_{1u} molecular orbitals (Table 1.1) are "strongly bonding". It is the existence of the field of S^{6+} , not some representation-dependent expression of that field (local or non-local) in terms of spherical harmonics (s, p, d, \dots), spherical gaussians, or whatever, that lies at the basis of all interpretations of the stability of SF_6 . Since, however, the field about an O^{6+} kernel is even greater than the field about an S^{6+} kernel, the conventional molecular orbital theory summarized in Table 1.1 leaves unanswered the previous question: If SF_6 is stable, why is not OF_6 stable?

1.2.2 Orbitals and Wave Functions

1.2.2.1 Antisymmetrization and Spin-Exclusion

The key to understanding, from a quantum mechanical point of view, the extraordinary stability of SF_6 and the non-existence of OF_6 , lies in examining the relation between orbitals and wave functions.

In electronic interpretations of chemistry, the properties of a wave function are often assumed to be, in essence, the sum of the properties of the wave function's component orbitals. Orbital properties are assumed to carry over to the wave functions. Moreover, it is often assumed, implicitly, but incorrectly, that *all* chemically significant properties of a wave function are contained in, and adequately revealed by a study of, the properties of a set of delocalized molecular orbitals $\phi_1, \phi_2, \phi_3, \dots$.

A wave function constructed from delocalized molecular orbitals is not, however, merely a simple Hartree product $\phi_1(1)\phi_2(2)\phi_3(3)\dots$.

A wave function for a many-electron system has properties — for chemistry, enormously important properties — not possessed by delocalized molecular orbitals or a simple product formed therefrom.

From reasoning based on simple Hartree products, for example, one might suppose that, for a wave function constructed from a set of conventional, symmetry-adapted, mutually overlapping molecular orbitals, such as those exhibited in Table 1.1, the *configuration of maximum probability* occurs when each electron is assigned to the place in space when its orbital has a maximum absolute value. To illustrate with a simpler

case ²⁶, one might suppose, incorrectly, that the most probable location of two spin-paralleled electrons in an olefinic carbon-carbon double bond is for one electron, say 1, to be on the internuclear axis at the center of a σ orbital and for the other electron, 2, to be off the axis in one lobe of a π orbital, thereby maximizing the product

$$\alpha(1)\pi(2) \quad (1.1)$$

In fact, it is a fundamental postulate of electron physics that *electrons are indistinguishable*. A change in electron-labels should not change the absolute value of the wave function. Generally, however, scrambling the labels in a single Hartree product changes the absolute value of the product. In the present example, $\alpha(1)\pi(2) \neq \alpha(2)\pi(1) = 0$.

On physical grounds, a *Hartree product is a profoundly unsatisfactory wave function*. It does not satisfy a fundamental guiding principle that is applicable to all wave functions and that governs all reasoning about atomic and molecular systems ²⁷. This guiding principle was stated in 1926 by Heisenberg. It is a generalization of Pauli's initial statement of 1925 of the Exclusion Principle ²⁸. Curiously, Pauli's preliminary statement — that no more than two electrons may be placed in the same spatial orbital — is still cited more frequently in chemistry textbooks than is Heisenberg's more fundamental statement, that electronic wave functions must be antisymmetric.

Pauli's restricted statement of the Exclusion Principle cannot be applied to highly precise, many-electron wave functions — ones that, to allow for electron-electron repulsions, contain explicitly inter-electronic co-ordinates r_{ij} . Pauli's statement is restricted to wave functions that are expressed in terms of physically fictitious, if mathematically convenient electron orbitals. Heisenberg's statement, on the other hand, is applicable to *all* wave functions.

Heisenberg's statement rigorously excludes, as a simple Hartree-product function and Pauli's statement do not, configurations in which two electrons of parallel spin are at the same point in space at the same time ²⁹. *Electrons of like spin tend to avoid each other* ²⁰. The geometrical implications of this *spin-exclusion*, so manifest in a comparison of the ionization potentials of hydrogen, helium, and lithium, are not fully or adequately expressed by Pauli's statement of the Exclusion Principle. For, although Pauli's familiar statement requires that electrons of like spin be placed in different spatial orbitals, most single- and multi-centered orbitals are not spatially mutually exclusive. Most delocalized, valence-shell molecular orbitals, though perhaps mutually orthogonal, penetrate into similar, if not identical, regions of space.

In the σ - π description of a double bond, for example, Heisenberg's statement requires that the wave function for two spin-parallel electrons be written as this antisymmetric, linear combination of Hartree products:

$$\sigma(1)\pi(2) - \sigma(2)\pi(1) \quad (1.2)$$

The mathematical properties of the antisymmetric function (1.2) are profoundly different from those of the Hartree-product function (1.1). Unlike (1.1), expression (1.2) always changes its sign, but never its absolute value, when the labels on the electrons are interchanged. Consequently, whenever the co-ordinates of the two spin-parallel electrons are the same, expression (1.2), unlike (1.1), vanishes.

This spatial, spin-exclusion, which does more to determine the shapes and properties of molecules than any other single factor, is a property of the entire, properly antisymmetrized wave function. It is not a property of individual spectroscopic orbitals. Its implications for chemistry cannot be gleaned from an examination, however careful, of the properties of delocalized molecular orbitals.

Because the molecular orbital model is, in essence, an *independent-particle* model, *the most significant property of a wave function for chemistry is not contained in, or revealed by, a study of the properties of delocalized molecular orbitals.* Spin-exclusion, the physical basis — or explanation — for the existence of complexly articulated chemical structures is, in essence, a property of a *collective-particle* model.

Fortunately, the chief conceptual advantages of an orbital, independent-particle model can be largely retained — and, with regard to the transferability of structural parameters, greatly extended — in a simple, collective-particle model that captures for chemistry the essence of Heisenberg's statement of the Exclusion Principle. Owing to a mathematical property of antisymmetrized orbital products, it is possible to express in terms of mutually dependent, yet transferable orbitals — in vivid, visual, geometrical terms — the dominant role in structural chemistry of spin-exclusion ²².

1.2.2.2 Determinantal Wave Functions and Chemical Orbitals

In 1929 Slater pointed out that an antisymmetrized Hartree product, such as expression (1.2), can be written as a determinant ³⁰,

$$\begin{vmatrix} \sigma(1) \pi(1) \\ \sigma(2) \pi(2) \end{vmatrix} \quad (1.3)$$

Determinants have the property that columns can be added to each other without changing the value of the determinant. The expression

$$-\frac{1}{2} \begin{vmatrix} \sigma(1) + \pi(1) & \sigma(1) - \pi(1) \\ \sigma(2) + \pi(2) & \sigma(2) - \pi(2) \end{vmatrix} \quad (1.4)$$

yields identically, on expansion, expression (1.2), as does (1.3). Mathematically, the two expressions, (1.3) and (1.4), are equivalent.

It is convenient to introduce abbreviations for the functions $(\sigma + \pi)$ and $(\sigma - \pi)$ that appear in expression (1.4). Let

$$\eta_1 \equiv \frac{1}{\sqrt{2}} (\sigma - \pi) \quad (1.5)$$

$$\eta_2 \equiv \frac{1}{\sqrt{2}} (\sigma + \pi)$$

The "hybrid" orbitals η_1 and η_2 are called (in this instance) *equivalent orbitals*^{31,32}. Like, e.g., sp^3 hybrid orbitals, they are identical to each other except for their orientation in space: η_1 is concentrated below the molecular plane, η_2 above it. They correspond closely to the bent- or banana-bonds of classical structural theory. For that reason, they have been called *chemical orbitals*. Being relatively localized, spatially, they have been called, also, *localized molecular orbitals*³³. Substitution from (1.5) into (1.4) yields

$$\begin{vmatrix} \eta_1(1) & \eta_2(1) \\ \eta_1(2) & \eta_2(2) \end{vmatrix} \quad (1.6)$$

Mathematically, expressions (1.6) and (1.3) are equivalent, for all values of the electron co-ordinates. Physically, however, the two descriptions of a double bond — the σ - π description [expression (1.3)] and the bent- or banana-bond description [expression (1.6)] — do not, at first glance, look the same. The apparent difference between descriptions of bonding in terms of a chemist's localized orbitals and a physicist's delocalized orbitals has, in fact, been likened to the difference between day and night — or night and day.

Localized and delocalized orbital descriptions of bonding do lead to different mental pictures of electronic structure — when the working model one has of the link between orbitals and wave functions corresponds, perhaps unwittingly, to a simple Hartree product. Properly