

Advances in
HETEROCYCLIC
CHEMISTRY

A. R. KATRITZKY

A. J. BOULTON

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HETEROCYCLIC CHEMISTRY

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Preface

The fifth volume of *Advances in Heterocyclic Chemistry* surveys the chemistry of four well-defined groups of compounds: pyrrolizidines (N. K. Kochetkov and A. M. Likhoshesterov), aromatic quinolizines (B. S. Thyagarajan), 1,2,4-thiadiazoles (F. Kurzer), and the amino-chrome pigments (R. A. Heacock).

The other two chapters deal with the application of molecular orbital theory to heterocyclic chemistry. The groups surveyed are (a) sulfur heterocycles and (b) azines. The chapters, which are authored by R. Zahradnik and J. Koutecky, discuss the relevance of theoretical calculation to reactivity, electronic structure, and other physico-chemical properties of the compounds. The new techniques of theoretical chemistry have been applied with great success to carbocyclic compounds; their significance in heterocyclic chemistry will surely increase.

Suggestions are welcome for contributions to further volumes; they should be in the form of a short synopsis.

Thanks are due to the Editorial Board, the publishers, and the authors for their cooperation. I am especially grateful to the assistant editors, Dr. A. J. Boulton and Dr. J. M. Lagowski, for all their help.

A. R. KATRITZKY

Norwich, England
August, 1965

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Electronic Structure of Heterocyclic Sulfur Compounds

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I. Introduction

A. SCOPE

The objective of the present review is to give a critical and, as far as possible, synthetic survey of those problems of the chemistry of σ -bivalent sulfur that have been studied by quantum-chemical methods. For various reasons, this limitation had to be disregarded in several places; this applies above all to the compounds mentioned in Section II, E. Sulfoxides and sulfones are not included, but references

are given to papers in which models of these compounds were studied theoretically. Similarly treated are compounds containing sulfur outside the ring as well as acyclic compounds. In view of this selection it is apparent that numerous important studies of sulfur compounds have been omitted; experimental studies are mentioned only to the extent necessary for checking the validity of theoretical predictions. Special attention is paid to chemical reactivity and electronic spectra. The review contains molecular diagrams of only a few compounds which were not available in the literature at the time this manuscript was written. On the other hand, energy characteristics are summarized as completely as possible, along with the corresponding data for the parent hydrocarbons.

B. METHODS OF THEORETICAL TREATMENT

1. *A Note on Theoretical Methods*

More than 95 percent of the theoretical studies of heterocyclic sulfur compounds have been performed by the simple molecular orbital (MO) method. The basic concepts underlying this method and the course of numerical computations for models of various compounds have been described in numerous monographs,¹⁻⁴ that by Streitwieser⁴ being particularly suitable for chemists. Here it will be sufficient to remind the reader (cf. ref. 5) that the wave functions of delocalized π -molecular orbitals, ψ_i , are represented by linear combinations of atomic functions, φ_j , which describe the state of p_z atomic orbitals having a nodal plane in the plane of the σ -bond skeleton of a conjugated planar molecule and directed along the axes that pass through atom nuclei and are perpendicular to the plane of the σ -skeleton:

$$\psi_i = \sum_{j=1}^n c_{ij} \varphi_j \quad (i = 1, 2, \dots, n) \quad (1)$$

¹ C. A. Coulson, "Valence." Oxford Univ. Press, London, 1952.

² R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry." Interscience, New York, 1959.

³ B. Pullman and A. Pullman, "Les théories électroniques de la chimie organique." Masson, Paris, 1952.

⁴ A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists." Wiley, New York, 1961.

⁵ J. H. Ridd, in "Physical Methods in Heterocyclic Chemistry" (A. R. Katritzky, ed.), Vol. I, p. 109. Academic Press, New York, 1963.

In Eq. (1), c_{ij} represents the expansion coefficient at the j -th atomic orbital (φ_j) in the i -th π -molecular orbital (ψ_i). The coefficients c_{ij} ($j = 1, 2, \dots n$) fully describe the wave function ψ_i ; their numerical values are obtained by solving the system of equations (2).

$$\sum_{j=1}^n (H_{jk} - S_{jk} E) c_{ij} = 0 \quad (i = 1, 2, \dots n) \quad (2)$$

In the simple version of the MO LCAO (linear combination of atomic orbitals) theory, the quantities H_{jk} and S_{jk} , defined by Eqs. (3-5), are treated as empirical parameters, thus there is no need for detailed information concerning the character of the atomic functions φ_j .

$$H_{jk} = \beta_{jk} = \int \varphi_j \mathbf{H}' \varphi_k d\tau \quad (\text{resonance integral}) \quad (3)$$

$$H_{jj} = \alpha_j = \int \varphi_j \mathbf{H}' \varphi_j d\tau \quad (\text{Coulomb integral}) \quad (4)$$

$$S_{jk} = \int \varphi_j \varphi_k d\tau \quad (\text{overlap integral}) \quad (5)$$

In Eqs. (3) and (4), \mathbf{H}' stands for the effective one-electron Hamiltonian; the integration is over the whole space. In the simple method, a number of simplifying assumptions about the values of the integrals β_{jk} , α_j , and S_{jk} are introduced; in the case of molecules containing no heteroatoms these are known as the Hückel approximations. It seems useful to use this designation also for molecules with heteroatoms, and in the present review this method will be referred to as the Hückel molecular orbital (HMO) method according to Streitwieser's suggestion.⁴

Physically meaningful solutions of the system of equations (2) are obtained only for certain values of molecular orbital energies, E_i , which follow from the determinantal equation

$$|H_{jk} - S_{jk} E| = 0 \quad (6)$$

It only remains to be added that the Coulomb integral of the carbon $2p_z$ orbital (α_C) is conventionally set equal to zero (the origin of the energy scale in the HMO method) and that the resonance integral of the C—C π -bond (β_{CC}) is equal to one (the energy unit in the HMO method). The values of Coulomb integrals of p_z orbitals of heteroatoms are in general different from α_C and are usually given in the form (for a $2p_z$ orbital of atom X):

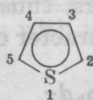
$$\alpha_X = \alpha_C + \delta_X \beta_{CC}, \quad (7)$$

where constant δ_X , roughly speaking, is a measure of the electronegativity of the relevant orbital. In a similar way, resonance integrals of π -bonds other than C—C are usually given in β_{CC} units. For a C—X π -bond:

$$\beta_{CX} = \rho_{CX} \beta_{CC}, \quad (8)$$

where ρ_{CX} is a constant roughly expressing the strength of the π -bond.

As an example, starting assumptions and the result of an HMO treatment of a model of the thiophene molecule are presented:



Starting assumptions:

$$\alpha_S = \alpha_C + 0.5\beta_{CC}; \quad \alpha_{C_1} = \alpha_{C_2} = \alpha_{C_3} = \alpha_{C_4} = \alpha_C$$

$$\beta_{CS} = 0.6\beta_{CC}; \quad \beta_{C_1C_2} = \beta_{C_2C_3} = \beta_{C_3C_4} = \beta_{CC}$$

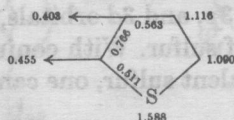
$$S_{ij} = 0 (i \neq j); \quad S_{jj} = 1.$$

Solving a determinantal equation of the type (6) (orbital energies) and systems of equations of the type (2) (expansion coefficients) gives the results shown in the following tabulation.

i	E_i	ψ_i
1	$\alpha_C + 1.8013\beta_{CC}$	$0.3776\varphi_1 + 0.4094\varphi_2 + 0.5110\varphi_3 + 0.5110\varphi_4 + 0.4094\varphi_5$
2	$\alpha_C + 0.6860\beta_{CC}$	$0.8070\varphi_1 + 0.1251\varphi_2 - 0.3984\varphi_3 - 0.3984\varphi_4 + 0.1251\varphi_5$
3	$\alpha_C + 0.6180\beta_{CC}$	$0.6015\varphi_2 + 0.3718\varphi_3 - 0.3718\varphi_4 - 0.6015\varphi_5$
4	$\alpha_C - 0.9873\beta_{CC}$	$-0.4541\varphi_1 + 0.5628\varphi_2 - 0.2832\varphi_3 - 0.2832\varphi_4 + 0.5628\varphi_5$
5	$\alpha_C - 1.6180\beta_{CC}$	$0.3718\varphi_2 - 0.6015\varphi_3 + 0.6015\varphi_4 - 0.3718\varphi_5$

Within the HMO framework, simple arithmetic leads from the values of orbital energies to the values of total π -electronic energy (W), delocalization energy (DE), excitation energy of the $N \rightarrow V_1$ transition [$E(N \rightarrow V_1)$], and other quantities.¹⁻⁴ In our case, these values are: $W = 6\alpha_C + 6.2107\beta_{CC}$; $DE = 1.2107\beta_{CC}$; and $E(N \rightarrow V_1) = 1.6053\beta_{CC}$. It is a frequent practice to lead discussions in terms of the factors k_i which appear in the expressions for orbital energies, $E_i = \alpha_C + k_i\beta_{CC}$.

The sum of all these factors for a specific problem is equal to the trace of the matrix of the corresponding characteristic problem⁴; the sum of their squares equals the sum of the squares of all matrix elements of the corresponding characteristic problem.^{5a} These relations are useful for checking the values of orbital energies. By an equally simple procedure¹⁻⁴ the values of expansion coefficients yield the values of π -electron densities (q), bond orders (p), and free valences (F); these quantities are usually presented in the form of a molecular diagram:



Somewhat more involved is the computation of further reactivity indices: Wheland's atom localization energy, A^6 ; exact superdelocalizability, S^7 ; various polarizabilities, π^8 ; Brown's factor, Z^9 ; Dewar's reactivity number, A_D^{10} and the approximate superdelocalizability, S'^7 .

The values of q , p ,¹¹ and S may be checked by use of the relations shown in Eqs. (9-11).

$$\sum_{j=1}^m q_j = l \quad (9)$$

$$W = \sum_{j=1}^m q_j \alpha_j + 2 \sum_{k < j} p_{kj} \beta_{kj} \quad (10)$$

$$\sum_{j=1}^m S_{j,e} = 2 \sum_{i=1}^n 1/k_j \quad (11)$$

In Eqs. (9-11), l means the total number of π -electrons in the molecule, m is the total number of orbitals in conjugation, n is the number of

^{5a} J. Koutecký, J. Čížek, and J. Paldus, personal communication (1960).

⁶ G. W. Wheland, *J. Am. Chem. Soc.* **64**, 900 (1942).

⁷ K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan* **27**, 423 (1954).

⁸ C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **192A**, 16 (1947).

⁹ R. D. Brown, *J. Chem. Soc.* 2232 (1959).

¹⁰ M. J. S. Dewar, *J. Am. Chem. Soc.* **74**, 3357 (1952).

¹¹ C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **191A**, 39 (1947).

occupied π -molecular orbitals, k and j are the indices of atomic orbitals (positions), and the subscript e means electrophilic substitution; similar relations hold for $S_{j,n}$ and $S_{j,r}$ (n means nucleophilic and r radical substitution).

2. Models of Sulfur Atom Orbitals

In its ground state, the sulfur atom has the electron configuration $(1s)^2(2s)^2(2p_x)^2(2p_y)^2(2p_z)^2(3s)^2(3p)^4$ and, in addition, disposes of five $3d$ orbitals exploitable for bonding. We shall restrict our further considerations to the $3s$, $3p$, and $3d$ orbitals, which are important for the bonding capability of sulfur. With conjugated heterocyclic compounds containing σ -bivalent sulfur, one can imagine, in the simplest

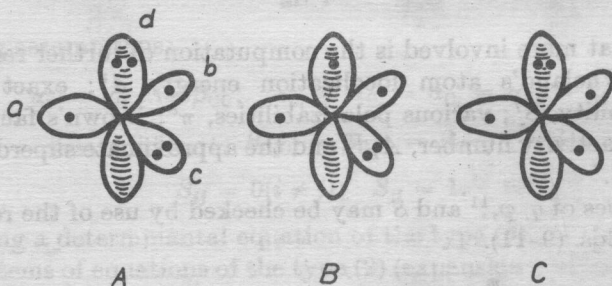


FIG. 1. Occupancy of the $3sp^2$ (a, b, c) and $3p_z$ (d) sulfur orbitals by electrons in various types of conjugated compounds. In cases A and B, c is a non-bonding atomic orbital (the orbitals are somewhat deformed for the sake of clarity).

approach, that three hybrid $3sp^2$ orbitals arise by combination of the $3s$, $3p_x$, and $3p_y$ orbitals, two of them being occupied by one electron and forming the C—S σ -bonds by overlap with carbon sp^2 orbitals while the third one, occupied by two electrons, is a non-bonding atomic orbital (Fig. 1A). The $3p_z$ orbital, occupied by two electrons, overlaps with neighboring p_z orbitals and participates in the formation of delocalized π -molecular orbitals. This model may be adopted when studying the electronic structure of compounds like thiophene (its most serious deficiency, in this case, being the fact that its hybrid $3sp^2$ orbitals lie at an angle of 120° while it is well known that the C—S—C angle in thiophene is only 91°) as well as of those of the thiapyrylium or cyclothiolium types (see Section II, E). With these systems, the positive charge results from the removal of one electron from the atomic orbitals when forming the molecule. In the case of thiapyrylium

the electron has been removed from the $3p_z$ orbital (Fig. 1B) and the resultant positive charge is therefore delocalized; on the other hand, in the case of σ -tervalent sulfur the electron has been removed from the non-bonding atomic orbital, hence the positive charge is localized at the sulfur atom (Fig. 1C).

Although d -orbital participation in the bonding of sulfur in conjugated compounds was first considered as early as 1939 by Schomaker

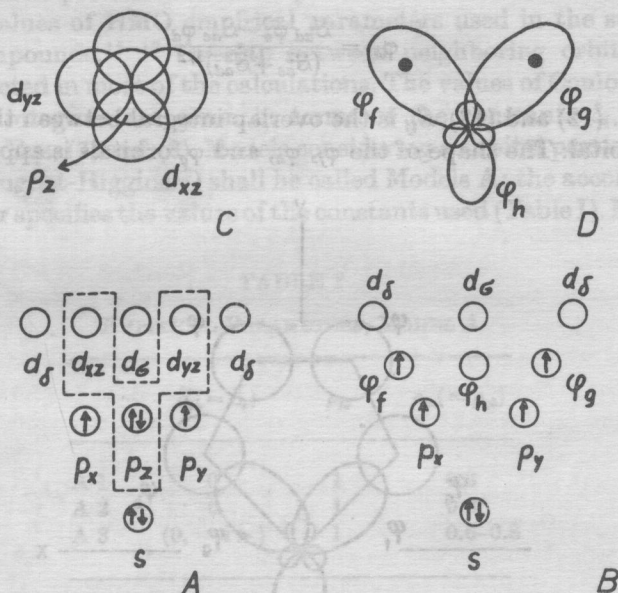


FIG. 2. Schematic representation of the formation of hybrid $3pd^2$ orbitals (B, D) from atomic orbitals (A, C). Figures A and B are taken from a paper by Metzger and Ruffler,¹⁴ C and D from one by Longuet-Higgins.¹³

and Pauling,¹² it was not until 1949 that Longuet-Higgins¹³ formulated the problem in terms of the MO theory. He studied the properties of orbitals resulting from hybridization of $3p$ and $3d$ orbitals, his starting point being the analogy between thiophene and benzene. According to Longuet-Higgins, the $2p_z$ atomic orbitals of carbon atoms adjacent to the sulfur atom are labeled ϕ_a and ϕ_b ; the $3p_z$, $3d_{yz}$, and $3d_{xz}$ orbitals of the sulfur atom are designated ϕ_c , ϕ_d , and ϕ_e , respectively. By linear

¹² V. Schomaker and L. Pauling, *J. Am. Chem. Soc.* **61**, 1769 (1939).

¹³ H. C. Longuet-Higgins, *Trans. Faraday Soc.* **45**, 173 (1949).

¹⁴ J. Metzger and F. Ruffler, *J. Chim. Phys.* **51**, 52 (1954).

combination of the φ_c , φ_d , and φ_e orbitals, hybrid $3pd^2$ orbitals, φ_f , φ_g , and φ_h (Fig. 2), are introduced:

$$\varphi_x = \frac{S_{ac}S_{ae}\varphi_c + S_{ad}S_{ae}\varphi_d \pm (S_{ac}^2 + S_{ad}^2)\varphi_e}{[(S_{ac}^2 + S_{ad}^2)(S_{ac}^2 + S_{ad}^2 + S_{ae}^2)]^{1/2}} \quad (12)$$

In Eq. (12), the plus sign holds for $x = f$ and the minus sign for $x = g$.

$$\varphi_h = \frac{S_{ad}\varphi_c - S_{ac}\varphi_d}{(S_{ac}^2 + S_{ad}^2)^{1/2}} \quad (13)$$

In Eqs. (12) and (13), S_{ij} is the overlap integral between the i -th and j -th orbital. The shape of the φ_f , φ_h , and φ_g orbitals is apparent from

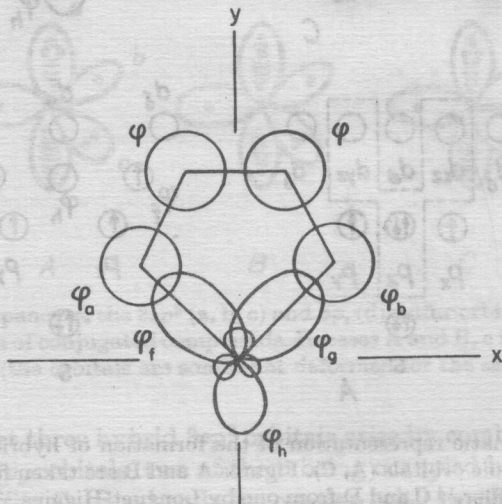


FIG. 3. Model of the atomic orbitals in thiophene (according to Longuet-Higgins¹³); φ 's indicate carbon $2p_z$ orbitals.

Fig. 2. The φ_h orbital does not interact with other atomic orbitals; for the sake of numerical calculations within the HMO framework, the φ_f and φ_g orbitals may simply be replaced by carbon $2p_z$ orbitals. The model of thiophene is presented in Fig. 3; the x and y axes are shown, the z -axis is perpendicular to the plane of the molecule.

Although this model is very attractive from the chemist's point of view, clearly reflecting analogies such as those between thiophene and

benzene, thiazole and pyridine, thialene and azulene, thiapyrylium and tropylium, which led to its rather frequent use, in the course of time some deficiencies have become apparent.

3. The Empirical Parameters of the HMO Method

This section presents a summary of data on the most frequently adopted values of HMO empirical parameters used in the study of sulfur compounds.¹⁵⁻¹⁷ Overlap between neighboring orbitals has been neglected in most of the calculations. The values of Coulomb and resonance integrals are given in terms of the constants δ_i and ρ_{ij} defined by Eqs. (7) and (8). Models considering d -orbital participation (due to Longuet-Higgins¹³) shall be called Models A: the accompanying number specifies the values of the constants used (Table I). Model B

TABLE I
EMPIRICAL PARAMETERS, MODEL A

	$\delta_i (= \delta_j)$	ρ_{10}	$\rho_{1a} (= \rho_{a0})$
A 1	0	1	0.6
A 2	0	1	0.8
A 3	(0, $-1 >$)	1	0.6-0.8

shall mean a model that does not consider d -orbital participation (Table II).

The δ and ρ values that are not given in the survey have the standard values of $\delta = 0$ and $\rho = 1$. In the case of compounds containing two sulfur atoms and/or other heteroatoms, the values given in Table III have also been used frequently. For the sake of brevity, we shall call this set of parameters Model C. It is easily seen that some of these values are not fully adequate, especially the parameters for oxygen.

¹⁵ R. Zahradník and J. Koutecký, *Collection Czech. Chem. Commun.* **28**, 1117 (1963).

¹⁶ R. Zahradník and C. Párkányi, *Collection Czech. Chem. Commun.* **30**, 195 (1965) (thiophenes) and *Collection Czech. Chem. Commun.*, in press (analogues of non-alternant hydrocarbons).

¹⁷ R. Zahradník, C. Párkányi, V. Horák, and J. Koutecký, *Collection Czech. Chem. Commun.* **28**, 776 (1963).

has been found many times, however, that this circumstance is relevant to qualitative reasoning. Moreover, it does not disturb quantitative correlations, e.g. of spectral data, provided that the set of

TABLE II
EMPIRICAL PARAMETERS, MODEL B

	δ_s	$\delta_{C(s)}$	ρ_{CS}
B 1	1	0.1	0.6
B 2	1	0	0.6
B 3	1	0.1	0.8

TABLE III
EMPIRICAL PARAMETERS, MODEL C

Atom	δ_i	Bond	ρ_{ij}
N, endocyclic (as in pyridine)	0.5	C-N	1.0
		S-N	0.6
N, nitrile	0.5	C=N	1.4
N, exocyclic	1.0	C-N	1.0
O, endocyclic	2.0	C-O	$\sqrt{2}$
O, exocyclic	2.0	C-O	$\sqrt{2}$
S	— ^a	S-S	0.5
		C-S	— ^a
Cl	2.0	C-Cl	0.4

^a Cf. Tables I and II.

compounds studied is sufficiently large. In the cases where other values of the parameters have been used, the relevant data are to be found at the corresponding place in the text.

C. SOME GENERAL REMARKS

During recent years it has become apparent that the HMO method is suitable not only for qualitative but—in a certain sense—also for quantitative studies of organic compounds. It should be realized, however, that it is only possible to obtain correct *relative* values of certain quantities. The reasonability of the conclusions reached by the theory is therefore best checked by examining the closeness of the

correlation between a sufficiently extensive set of experimental data and a series of corresponding theoretical quantities. If the correlation proves fairly close, it may be concluded that the physical model as well as the mathematical approximation are adequate. Now, the empirical relation thus obtained can, of course, be used for interpolations. As for the correlation itself, two facts must be kept in mind. In general, the regression lines need not go through the origin, and data for compounds of different structural types usually lie on separate straight lines. It further seems worth mentioning that the choice of HMO empirical parameters is a problem of secondary importance if a large set of structurally related compounds is studied.

The considerable arbitrariness in the nomenclature of organic compounds is somewhat puzzling. Moreover, none of the systems used is fully consistent and free of rather awkward names. The nomenclature used in this review is necessarily subject to these shortcomings; the rules given in the Second Edition of "The Ring Index" have been respected as far as possible. A note on the writing of structural formulas is included in Section I, D. The symbols α and β are used for α_C and β_{CC} , respectively. For the sake of brevity, expressions such as tropylia, dithiolia, etc. are used instead of tropylium ions, dithiolium ions, etc. in this review.

The reader's attention should be drawn to a recent review devoted to expansion of the sulfur outer shell.^{17a}

D. CLASSIFICATION OF COMPOUNDS STUDIED

To classify a conjugated heterocyclic sulfur compound containing one or more σ -bivalent sulfur atoms, all carbocyclic rings (usually benzene rings) attached to the heterocyclic system by one side only are disregarded (all compounds which yield the same parent skeleton by this procedure are further taken for benzo derivatives of this parent skeleton). In accordance with the Longuet-Higgins model, a $-\text{CH}=\text{CH}-$ group is then substituted for each sulfur atom and the isocyclic skeleton obtained is classified according to the number of rings and of carbon atoms in the rings (alternant and non-alternant) as follows¹⁸:

^{17a} G. Cilento, *Chem. Rev.* **60**, 147 (1960).

¹⁸ In principle, recently published¹⁹ rules for writing structural formulas have been adhered to in the present review with the one exception that a full circle in the cycle is used to denote not only a π -electron sextet but any number of π -electrons consistent with the Hückel rule in general.

¹⁹ W. Baker, *Proc. Chem. Soc. (London)* 75 (1959).