Extended Hückel Calculations on Two Heterocyclic Systems Containing 2.41- and 2.64-Å Sulfur–Oxygen Distances[1,2]

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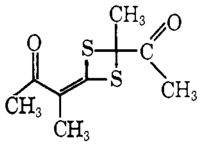
Abstract: The extended Hückel molecular orbital method has been used to probe for sulfur–oxygen bonding interactions in two heterocyclic systems known through X-ray crystallographic structure determinations to have short (2.41- and 2.64-Å) S–O distances. In both cases, a 2-acetylmethylene-1,3-dithiacyclobutane cycloadduct from 3-diazobutanone and carbon disulfide, and a 3-acetylmethylene-1,2-dithiole, the calculated S–O overlaps are close to zero, indicating that covalent bonding between sulfur and oxygen is negligibly weak.

Structure **1** has been determined for the cycloadduct from 3-diazobutanone and carbon disulfide by single-crystal X-ray diffraction techniques.[5] The molecule possesses several interesting structural features, including a 2.64-Å S–O distance notably shorter than the combined van der Waals radii of sulfur and oxygen (3.25 Å).[6]



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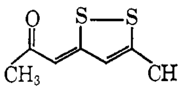
The structure of **1**,[5] in which the four-membered ring and the five atoms of the α,β-unsaturated carbonyl system are coplanar (mean deviation 0.04 Å), is consistent with the notion that the molecule adopts the *s-cis* orientation of the conjugated carbonyl group in response to some electronic preference for this geometry, such as a substantial bonding interaction across the short S–O distance.

Several other compounds (**2**, **3**, **4**) whose structures have been determined by X-ray crystallography show similar short S–O distances.



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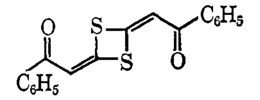

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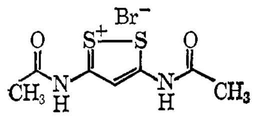

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In the planar 3-acetylmethylene-1,2-dithiole (**2**), the close S–O proximity (2.41 Å) was said to be due less to S–O overlap than to a reluctance to distort bond angles.[7] On the basis of van der Waals radii and bond distances, the authors[7] ascribed about 55% single bond character to the S–O bond.

The heterocyclic **3** has an S–O distance (2.64 Å) and angular distortions similar to those observed in the dithiacyclobutane **1**.[8] The geometry was considered suggestive of a sulfur–oxygen attraction.

In structure **4**, σ-bond orders of 0.44 and 0.47 have been estimated for the two S–O bonds 2.52- and 2.57-Å long.[9] Other examples of short S–O contact distances have been summarized and discussed.[5,10]

We now report on a series of extended Hückel molecular orbital calculations carried out in an attempt to clarify the nature and significance of sulfur–oxygen interaction in heterocyclic systems **1** and **2**.

The Method

The extended Hückel program of Hoffmann,[11,12] as modified in these laboratories by Van Der Voorn and Dugre,[13] was utilized. With this program, no preconceived notions of atomic hybridization or of which atoms are joined by bonds are specified. The overlap integrals are calculated from the Cartesian coordinates of the atoms and the orbital exponents of the single Slater functions in a manner similar to that described by Mulliken.[14] The exponents employed were calculated from the recipe of Burns[15] and are summarized in Table I; these exponents are held[15] to

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(5) J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *Tetrahedron Letters*, 5307 (1967); *J. Am. Chem. Soc.*, 90, 5800 (1968).

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(7) M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, *Nature*, **192**, 1282 (1961).

(8) T. R. Lynch, I. P. Mellor, S. C. Nyburg, and P. Yates, *Tetrahedron Letters*, 373 (1967).

(9) A. Hordvik and H. M. Kjøge, *Acta Chem. Scand.*, 20, 1923 (1966).

(10) See also W. H. Schmidt and A. Tulinsky, *Tetrahedron Letters*, 5311 (1967), and P. Yates and L. I. Williams, *ibid.*, 1205 (1968), for a case where different conclusions concerning the significance of the S–O interaction were based on the same crystallographic data.

(11) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

(12) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(13) P. C. Van Der Voorn, Ph.D. Thesis, University of Illinois, 1965; D. H. Dugre, Ph.D. Thesis, University of Illinois, 1968; see also M. F. Rettig, Ph.D. Thesis, University of Illinois, 1967.

(14) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(15) G. Burns, *ibid.*, **41**, 1521 (1964).

Table I. Orbital Exponents for Neutral Atoms[a]

Atom	Orbital	Exponent
H	1s	1.20[b]
C	2s	1.55
C	2p	1.325
O	2s	2.20
O	2p	1.975
S	3s	1.966
S	3p	1.517
S	3d	0.833

[a] Computed according to Burns.[15] [b] From SCF calculations.[17]

Table II. Valence-State Ionization Potentials (VSIP's) and Charge Correction Terms[a]

Atom	Orbital	$-\mathrm{VSIP}^0$, eV	A, eV	B, eV	C, eV
H	1s	13.6	27.2	13.6	0
C	2s	21.2	11.9	0	1.70
C	2p	11.4	11.9	0	1.50
O	2s	34.1	15.2	0	2.10
O	2p	17.6	15.2	0	2.30
S	3s	23.72	9.7	0	2.43
S	3p	12.50	9.7	0	1.12
S	3d	2.007	5.66	1.11	0

[a] The values listed are from ref 25 (H), 20 (C, O), 21 (S 3s and 3p), and 26 (S 3d).

reproduce the outer portions of wave functions better than the exponents calculated according to Clementi and Raimondi.[16] The value of 1.2 for the exponent in the hydrogen wave function was taken from SCF MO calculations.[17]

It has been argued that a single Slater-type orbital inadequately represents the atomic orbital at distances very near or far from the nucleus.[18] Calculations for C–C bonds have shown that the SCF overlaps exhibit a more gradual decrease at large internuclear distances than do the Slater functions; the overlaps differ by as much as 300% in some cases.[14] Because a major purpose of this work was to examine the nature of some S–O interactions outside of normal bonding distances, comparisons of π-type S–O overlaps as a function of internuclear distance computed both with SCF atomic orbitals[18] and with single Slater functions were made. The results obtained showed that, over the internuclear range in question, the differences in calculated overlaps are small, the largest being about 10%. Slater-type orbitals were therefore used in all subsequent calculations.

The Coulomb integrals (H_{ii}) were approximated by the valence state ionization potentials (VSIP's)[19–26] according to eq 1;[25,27,28] q is the charge on the atom, θ

$$\mathrm{VSIP}^q = \mathrm{VSIP}^0 - Aq - Bq^2 + C\theta \qquad (1)$$

is the orbital population minus 1 and is included only when $\theta > 0$, and the values for VSIP^0, A, B, and C are listed in Table II. The VSIPs were adjusted for charge and new charges calculated. Iteration proceeded until the difference between each initial and calculated charge was within 0.04; eq 2[21,27,28] was used to introduce a damping factor λ ($\lambda = 6.0$ or 7.0) at each iteration. In equation 2, q_i^n is the input charge for the nth iteration cycle, and q_0^n is the output charge calculated from the nth cycle.

$$q_i^{n+1} = (\lambda q_i^n + q_0^n)/(1 + \lambda) \qquad (2)$$

The resonance integrals (H_{ij}) were calculated by using the Wolfsberg–Helmholz approximation (eq 3),[29] with $K = 1.75$.[12]

$$\mathrm{H}_{ij} = KS_{ij}(\mathrm{H}_{ii} + \mathrm{H}_{jj})/2 \qquad (3)$$

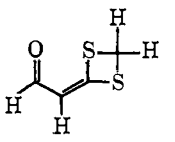
Expression 4 derived by Pople and advocated by Dewar[30] as decisively superior to the EH approximation for H_{ii} corrects for charge in much the same fashion as eq 1. In eq 4, q_i is the Hückel charge density, c_i is the core charge of atom i, and γ_{ij} is an electron–electron repulsion term between orbitals i and j. When there is little net charge on atom i, $q_i \cong c_i$, the last term in eq 4 becomes insignificant, and the expression

$$H_{ii} = \mathrm{VSIP}_i + {}^1\!/_2 q_i\gamma_{ii} + \sum_{j\neq i}[(q_j - c_j)\gamma_{ij}] \qquad (4)$$

for H_{ii} becomes a truncated version of eq 1 with more disposable parameters. When there is an appreciable net charge on an atom, the charge correction terms in eq 1 and 4 make similar modifications on the VSIP. For orbitals on the same atom, $^1/_2\, q_i\gamma_{ii}$ is independent of atomic environment; for orbitals on different atoms, the correction falls off with distance and, when charges are not large, becomes the product of two small numbers.

Applications of Extended Hückel Method

Great savings in computer time can be realized whenever portions of a structure may reasonably be expected to play an insignificant role in determining the calculated properties of interest, and thus be ignored. The two models **5** and **6** were used for calculations in place of **1**. For compound **2**, both the actual molecule and model **7** were employed.



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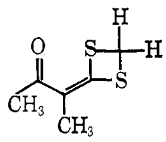

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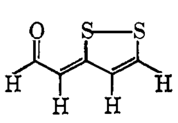

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(16) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(17) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966).

(18) E. Clementi, supplement to *IBM J. Res. Develop.*, **9**, 2 (1965).

(19) W. Moffitt, *Rept. Progr. Phys.*, 17, 173 (1954).

(20) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965).

(21) L. C. Cusachs, J. W. Reynolds, and D. Barnard, *ibid.*, **44**, 835 (1966).

(22) R. S. Mulliken, *ibid.*, **2**, 782 (1934).

(23) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(24) H. O. Pritchard and H. A. Skinner, *J. Chem. Phys.*, **22**, 1963 (1954).

(25) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta* (Berlin), **3**, 458 (1965).

(26) L. C. Cusachs and J. R. Linn, *J. Chem. Phys.*, **46**, 2919 (1967).

(27) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966).

(28) R. Rein, N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris, *ibid.*, **45**, 4743 (1966).

(29) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

(30) M. J. S. Dewar, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 186.

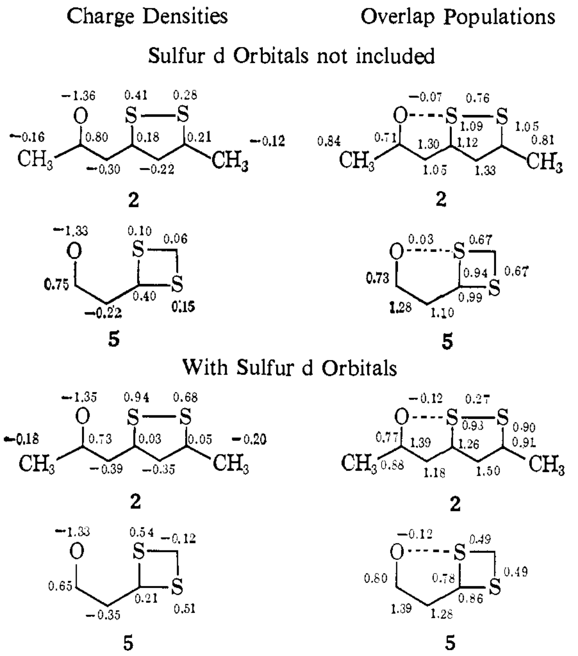

Figure 1. Calculated charge densities and overlap populations for the heterocyclic systems **2** and **5** without iteration to convergence of charge.

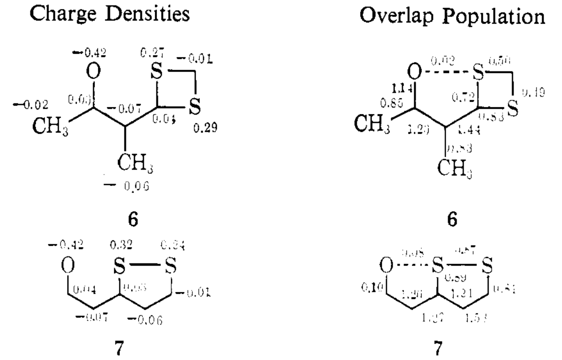

Figure 2. Calculated charge densities and overlap populations for the heterocyclic systems **6** and **7** with iteration to convergence of charge and including sulfur d orbitals.

Cartesian coordinates of the atoms were obtained from the published X-ray studies.[5,7] The C–H bond lengths were taken to be 1.10 Å except in the methylene group in **5** and **6**, where a value of 1.08 Å was employed.

Calculations without Charge Iteration, with and without Inclusion of Sulfur d Orbitals. For models **5** and **2**, calculations with neutral VSIP's and orbital exponents were carried out with and without inclusion of sulfur d orbitals. Figure 1 gives the reduced overlap populations and charge densities obtained. In all four cases, the S–O interaction is antibonding. Addition of the two methyl groups to model **5** to give **6** gave no significant changes.

Charge Iteration. All further calculations on systems **6** and **7** were carried out including d orbitals and with charge iteration. Orbital exponents were not adjusted as charge densities changed during the iterations; trial calculations indicated such adjustment had little influence on the results.

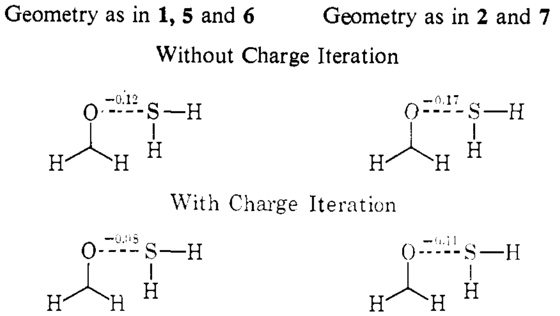

Figure 3. Calculated S–O overlap populations for the formaldehyde–hydrogen sulfide system with sulfur d orbitals included.

Bond orders and charges for models **6** and **7** are given in Figure 2. There is no substantial charge buildup on any atoms other than on the sulfurs and oxygen. The calculations with iterative adjustment of charge have changed the S–O interaction from antibonding to weakly bonding. The O–S d orbital antibonding interactions are reduced to about half their noncharge-iterated values while the overlap between the sulfur p and oxygen p and s orbitals goes from a net antibonding to a net bonding condition. In compound **7**, the O–S d orbital interactions after iteration of charge to convergence account for nearly half of the weak S–O bond. The sulfur d orbital interactions with orbitals on adjacent carbons remain antibonding.

Formaldehyde–Hydrogen Sulfide Model. Since the short S–O distance in the heterocyclic systems under consideration may well be within the repulsive region for a "normal" oxygen–sulfur interaction, might the calculated S–O overlap population of nearly zero be interpreted as the consequence of a relative partial bonding compensating for but not dominating the nonbonded repulsion? This question prompted calculations on the formaldehyde–hydrogen sulfide system oriented to be congruent with the relevant portions of adduct **1** (S–O distance 2.41 Å) or system **2** (S–O distance 2.64 Å). The calculated overlap populations are shown in Figure 3; the values obtained without charge iteration show slight antibonding between sulfur and oxygen, as do models **2** and **5** (Figure 1). The charge iteration scheme employed reduces the S–O antibonding in all cases, and in direct proportion to the size of the system. For the formaldehyde–hydrogen sulfide system, the change in S–O overlap with charge iteration is 0.04 and 0.06 for the two geometries considered: for adduct **5** it is 0.14; and for the still larger system **2**, 0.20.

Conformational Models. Charge iteration was not employed in testing the sensitivity of calculated parameters on molecular conformations. Charges on oxygen and sulfur were assumed equal to the calculated values in Figure 2 and the Slater exponents of these atoms were corrected for charge according to eq 5,[31] where μ^0 is the uncharged exponent, n is the effective principal quantum number, and q is the net charge on the atom.

$$\mu^q = \mu^0 + (0.350/n)q \qquad (5)$$

Lipscomb and coworkers[32] have used a similar

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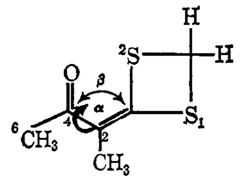
[31] *Cf.* J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[32] T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 846 (1963).

charge model technique in EH calculations on the nature of multiple bonding in sulfones, but without employing a charge iteration procedure to obtain charges for the model.



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Two different distortions in model **6** (**8**) have been simulated: rotation about the C(2)–C(4) bond through an angle α and variation in the angle β, keeping the O–C(4)–C(6) angle constant at 120.4°. (For the undistorted model, $\alpha = 0°$ and $\beta = 116.8°$; the overlaps calculated through this approach for the undistorted **6** were all within 0.03 unit of the respective values calculated from the iteration to convergence.) The energy differences of systems **8** as a function of α and β are summarized in Table III.

Table III. Total Energy of System **8** as a Function of Angles α and β

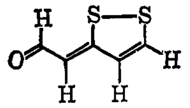
				S(2)–O(5)	
α, deg	β, deg	$-E$, kcal/mol	ΔE, kcal/mol	Distance, Å	Overlap population
0	116.8	20729.7	0.0	2.63	−0.002
65	116.8	20716.4	13.3	3.30	
180	116.8	20662.9	66.8	4.38	
0	112.0	20716.2	13.5	2.42	−0.002
0	120.0	20731.4	−1.7	2.73	−0.001
0	123.0	20730.3	−0.6	2.84	0.000
0	128.0	20721.4	8.3	3.02	0.000

Rotation through an angle α of 65° places the sulfur and oxygen 3.30 Å apart, just beyond the sum of their van der Waals radii (3.25 Å), and produces minimal variations in nonbonded interactions. The predominant factor causing a calculated increase in total energy of 13.3 kcal/mol would seem to be the partial breakdown of conjugation in the α,β-unsaturated carbonyl moiety: there is an increased overlap for C(1)–C(2) and C(4)–O and a decreased overlap in the C(2)–C(4), S(1)–C(1), and S(2)–C(1) bonds.

Increasing α to 180° raises the energy of the system to 66.8 kcal/mol above the model. Most of this increase is due to strong steric interactions between C(6) and S(2), which now lie 2.5 Å apart. Here a nonbonded interaction involving hydrogen becomes important: a hydrogen on C(6) coplanar with the four-membered ring shows an antibonding interaction with S(2) equal to some of the 1,3 C–C interactions.

Changing the angle β causes no systematic or significant variations in the bonding overlap populations, with the exception of the overlap of the C(4)–O bond, which decreases as β increases. There are only minor changes in S(2)–O interactions as the distance changes from 2.4 to 3.0 Å. This insensitivity of calculated overlap population on sulfur–oxygen distance (Table III) rebuts the commonplace correlations of internuclear distance with covalent bond strength: the calculations provide no justification for postulation of a substantial partial single bond between sulfur and oxygen in system **6**.

For model **7** and its geometrical isomer **9**, calculations with inclusion of d orbitals showed there was virtually no difference in energy between **7** and **9** (−17512.2 *vs.* −17512.1 kcal/mol), suggesting that the S–O covalent bonding plays an insignificant role in stabilizing or destabilizing the molecule.



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Discussion and Conclusions

The chemical implications from the variety of calculations detailed above are clear and consistent: covalent bonding between sulfur and oxygen is very weak or nonexistent in compounds like **1** and **2**, and presumably also in **3** and **4**, even though the S–O distance seems so short for nonbonded atoms. This result, we feel, places fresh uncertainty on any direct correlation of short interatomic distances between formally nonbonded atoms and partial single bonds or between preferred geometry and special types of bonding as in the thiothiophthenes.[33–35]

The changes in charge distributions resulting from iteration to convergence are significant for the neutral heterocyclic systems investigated. A comparison of the overlaps without and with iteration to convergence indicates that small effects, such as the S–O interactions, may be strongly influenced by the choice of H_{ii} and the charge correction scheme; through iteration, the small antibonding S–O overlap becomes slightly bonding in character.

Iteration to charge convergence for large molecules (*e.g.*, 54 orbitals in **6**) is a time-consuming process, even when good starting charges are employed. The use of a model corrected for charge but not iterated to convergence may be a good compromise for determining bond orders and relative energies in the absence of strong electrostatic effects.

Any presently feasible molecular orbital calculations for structures as extensive and complex as **1** and **2** are approximate but are nevertheless valuable as tests for possible interpretations of known data and as stimulating guides to fresh experimental work.[36] This molecular orbital examination of the S–O interactions in models for the heterocyclic compounds **1**–**4**, in which X-ray crystallographic data were used to fix atomic coordinates, unambiguously provides a result to be tested by other means: the covalent S–O bonding interaction across a gap of 2.4–2.7 Å in compounds like **1**–**4** has been grossly overestimated in earlier work and is of insignificant magnitude. It is not responsible for the observed geometry of the molecules.

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(33) E. Klingsberg, *J. Heterocyclic Chem.*, **3**, 243 (1966), and papers cited. The view that thiothiophthene systems are C_{2v} symmetric unless forced from this favored geometry by unsymmetrical substitution is still championed: E. Klingsberg, *J. Org. Chem.*, **33**, 2915 (1968).

(34) S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Commun.*, 1170 (1967).

(35) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(36) Compare J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 1072 (1968); J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).