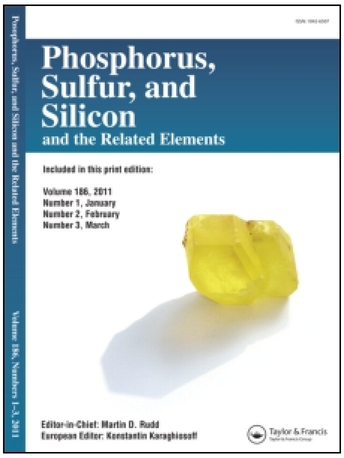

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Peter, Lyle and Loi, Giang(1988) 'THE NATURE OF THE HOMONUCLEAR BOND IN ORGANIC AND INORGANIC DICHALCOGENIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 40: 3, 129 — 134
To link to this Article: DOI: 10.1080/03086648808072904
URL: http://dx.doi.org/10.1080/03086648808072904

Phosphorus and Sulfur, 1988, Vol. 40, pp. 129–134
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THE NATURE OF THE HOMONUCLEAR BOND IN ORGANIC AND INORGANIC DICHALCOGENIDES

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(Received March 29, 1988; in final form March 29, 1988)

The electronic structures of a number of disulfide R_2S_2, and peroxide, R_2O_2, compounds are theoretically investigated or reinvestigated, and the results are compared and contrasted with each other as well as with experimental data. The results show that the enormous bond length variations in these compounds cannot be explained on the basis of the simple electronegativity difference model, but rather one must take into consideration terminal group atomic orbital contributions to the predominately homonuclear bonding molecular orbitals. The qualitative aspects of the bonding parameters of a large number of disulfide and peroxide compounds are explained.

Key words: Dichalcogenides; disulfides; peroxides; sulfur–sulfur bond; oxygen–oxygen bond; molecular orbitals.

INTRODUCTION

One of the many interesting aspects of the chemistry of sulfur is the enormous range of internuclear distances ascribed to intramolecular linkages which could be called sulfur–sulfur single bonds. The range extends from 189 pm in disulfur difluoride,[1] S_2F_2, to 239 pm in the dithionite ion,[2] $S_2O_4^{2-}$. If we narrow our discussion to homonuclear bonds involving only dicoordinate sulfur, the range closes somewhat at the top end,[3] but there is still considerable variation. This study focuses further on a class of compounds of general formula R_2S_2, where R is hydrogen, a halogen, an alkyl group, or any other group capable of forming a single covalent bond to a sulfur atom. The structures of these molecules are chain-like, RSSR, generally have C_2 symmetries, have $\angle$RSS's ranging from 90° to 120°, and have median dihedral angles of about 85°. A "normal" sulfur–sulfur single bond has a length[3] of 205 ± 3 pm. For example, elemental sulfur,[4] H_2S_2,[5] and the organic disulfides have S—S bond lengths in this range.[3] On the other hand, the S—S bonds in the disulfur dihalides are much shorter, 198 pm[6] in S_2Br_2, 194 pm[7] in S_2Cl_2, and 189 pm[1] in S_2F_2. The oxygen system is analogous, with H_2O_2 and the organic peroxides having oxygen–oxygen bond distances[8] of about 148 pm, but the O—O bond in O_2F_2 is only 122 pm long,[9] a dramatic difference.

Although many of the molecules mentioned above have been investigated theoretically,[10–16] these investigations usually focussed on one species, to the near exclusion of the others, and no real agreement has been reached as to the nature of these flexible homonuclear bonds. We decided to reinvestigate these molecules, comparing the calculated electronic properties of not only the experimentally determined most stable structures, but also of a number of structures in which the bond lengths were varied systematically.

RESULTS AND DISCUSSION

Disulfane, H_2S_2, is the simplest RSSR type molecule, and it has bond length parameters in accord with expectation. The S—S bond length is about the same as that found in elemental sulfur,[3,4] and the H—S bonds are the same as those found in H_2S and the mercaptans.[3b] The valence molecular orbital scheme of disulfane can be considered a perturbation of that of the S_2 molecule. Figure 1(a) is our calculated MO scheme for S_2 and Figure 1(b) is for H_2S_2. In terms of sulfur–sulfur bonding, molecular orbitals **1a** and **1b** are σ-bonding and antibonding respectively, and primarily have sulfur s-orbital character. Likewise, the bonding **2a** and **2b** orbitals are countered by the antibonding **3b** and **4a** orbitals. These four are π-type with respect to the S—S bond. Hence, the bonding comes primarily through the σ-bonding **3a** orbital, which has no filled antibonding counterpart. The H—S bonds have contributions from **1a**, **1b**, **2a**, and **2b**. The oxygen system is completely analogous. Figure 2(a) is the valence molecular orbital energy diagram for O_2, and Figure 2(c) is that for H_2O_2, using

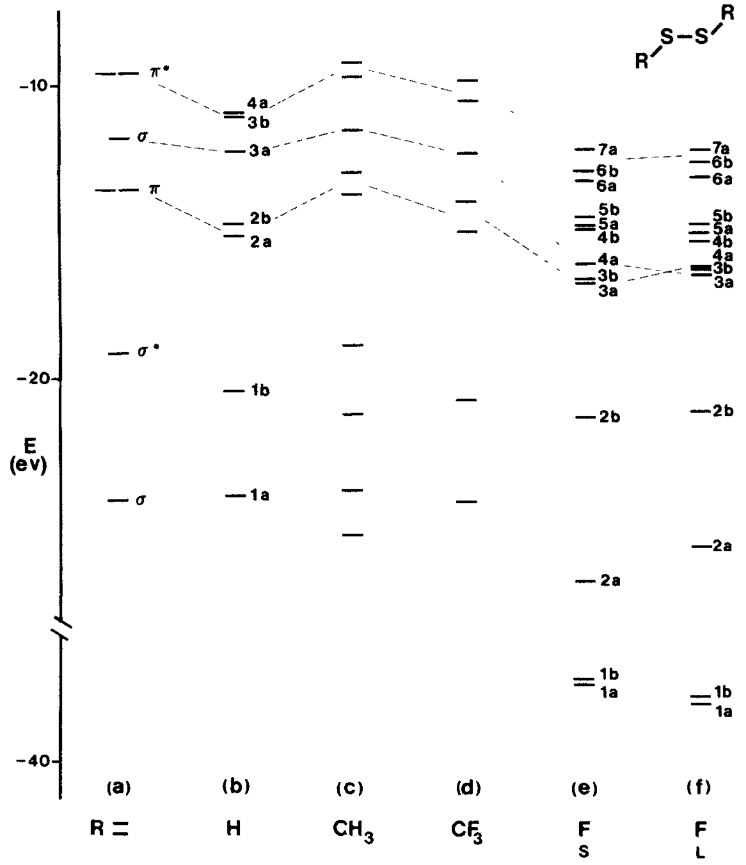


FIGURE 1 Filled Valence Molecular Orbital Energy Diagram for R_2S_2 Molecules. (a) S_2, (b) H_2S_2, (c) $(CH_3)_2S_2$, (d) $(CF_3)_2S_2$, (e) S_2F_2, short S—S, (f) S_2F_2, long S—S.

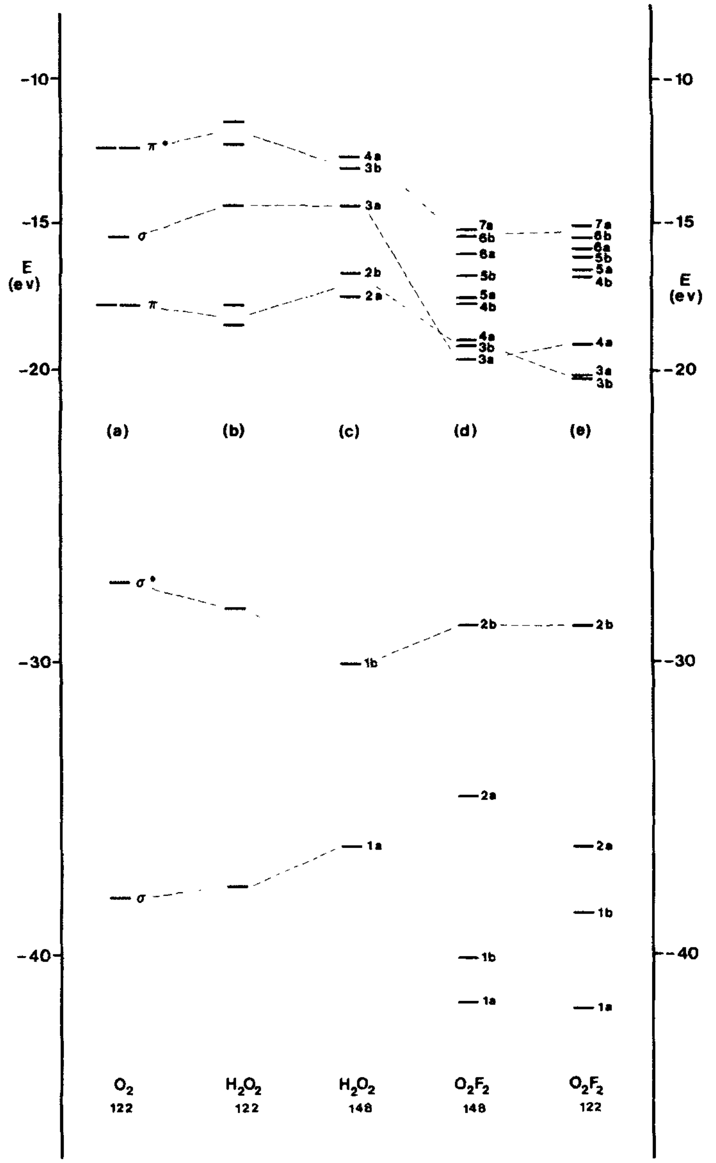
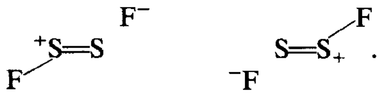


FIGURE 2 Filled Valence Molecular Orbital Energy Diagram for R_2O_2 Molecules. (a) O_2, (b) H_2O_2, short O—O, (c) H_2O_2, long O—O, (d) O_2F_2, long O—O, (e) O_2F_2, short O—O.

experimental bonding parameters. Shortening the S—S bond in H_2S_2 or the O—O bond in H_2O_2 tends to stabilize **1a**, **2a**, and **2b**, further destabilize **1b**, **3b**, and **4a**, and has little effect on **3a**. This is illustrated in Figure 2(b), in which the MO energies were calculated for H_2O_2 with an short O—O bond distance of 122 pm. Because the increased stabilization of MO's **1a**, **2a**, and **2b** is countered by the destabilization of their antibonding counterparts, the net result is no improvement in the S—S or O—O bonding, and a slight weakening of the H—S or H—O bonds; our model does not even take into account the increased intramolecular van der Waals repulsions that would occur with bond shortening. Figures 1(c) and 1(d) show the MO schemes of $(CH_3)_2S_2$ and $(CF_3)_2S_2$, but for clarity, minus the MO's that are primarily C—H or C—F bonding and F nonbonding. The S—S bonding in these two are quite similar to that of H_2S_2, and experimentally have similar S—S bond lengths.[3] The predominately S—S bonding and antibonding MO's experience similar changes when the homonuclear bond is shortened. That is, there is no net gain in bonding to counter the expected increase in van der Waals repulsion.

The S_2F_2 and the O_2F_2 situations are quite different. The experimental S—S bond length is 16 pm shorter than one would expect for a single bond, and the S—F bonds are about 5 pm longer. Figures 1(e) and 1(f) are MO diagrams for FSSF with the experimental lengths[1] (S—S, 189 pm; S—F, 164 pm), and with "normal" bond lengths (S—S, 206 pm; S—F, 159 pm), respectively. Orbitals **1a** and **1b** are nonbonding fluorine orbitals. Orbitals **2a** and **2b** are S—S σ-bonding and antibonding. Orbitals **3a** and **3b** in Figure 1(e) and **3b** and **4a** in Figure 1(f) are mostly S—S π-bonding, orbitals **4a** in 1(e) and **3a** in 1(f) are S—S σ-bonding, orbitals **4b**, **5a**, **5b**, and **6a** are fluorine nonbonding, orbitals **6b** and **7a** are S—S π-antibonding, but only weakly so as they also have considerable fluorine character. In comparing Figures 1(e) and 1(f), we see that the **2a** σ-bonding orbital and the S—S π-bonding orbitals are relatively stabilized in Figure 1(e), without the destabilization of the corresponding antibonding orbitals. The effects of homonuclear bond shortening are even better illustrated in the analogous oxygen system. Figures 2(d) and 2(e) have the filled MO's for O_2F_2 with "normal" single bond lengths (O—O, 148 pm; O—F, 142 pm), and at the unusual experimental[9] bond lengths (O—O, 122 pm; O—F, 158 pm), respectively. Notice the substantial stabilization of the O—O π-bonding orbitals, **3b** and **3a** in Figure 2(e) in comparison to 2(d), with little destabilization of the O—O π-antibonding, **6b** and **7a**. In addition, the **2a** orbital, which is primarily O—O σ-bonding derived from s-type atomic orbitals, is stabilized in Figure 2(e) in comparison with Figure 2(d), while the antibonding **2b** orbital remains essentially unchanged. Indeed, a closer examination of the substituent atomic orbital coefficients indicates that the most stable MO, **1a**, becomes increasingly important in the O—O bond.

In fact, the chalcogen homonuclear bonds in S_2F_2 and $O_2\ F_2$ are nearly of the same lengths[17] as the formal double bonds in S_2 and O_2. The bonding has been rationalized on the basis of terminal group electronegativities,[3b] or rather, chalcogen-terminal group electronegativitity differences.[18] The extreme case would be, in valence bond terms, a resonance hybrid of the two ionic canonical structures:



This description is inadequate. From electronegativity difference criteria alone, one would predict that the ionic forms like those above would make greater contributions to the molecular wavefunction of S_2F_2 than O_2F_2, but their bond lengths indicate that this is not the case. One would predict also that the S—S bond in $(CF_3)_2S_2$ would be significantly shorter than the one in $(CH_3)_2S_2$, when in reality it is a little bit longer.[3] Our calculations indicate that two factors need to be considered. To be sure, one factor is the electron withdrawing power of the terminal groups, but the other is the availability of terminal atom orbitals to interact with the chalcogen p-π orbitals. These orbital interactions must preserve substantially the homonuclear bonding character (orbitals **3a** and **3b** in Figure 1(e)), but minimize the homonuclear π-antibonding character (orbitals **6a** and **7a**) when the internuclear distances are shortened. The halogens in S_2X_2 compounds have both sufficient electronegativities and available orbitals to induce multiple bond character in the homonuclear bond. The terminal sulfur in S_4^{2-} ($^-SSSS^-$) have available orbitals, but not electron withdrawing ability, and hence, the central S—S bond is a normal single bond.[18] Perfluoro carbon groups have the electronegativities, but not available orbitals, and H_2S_2 and the organic disulfides have neither available orbitals nor high electronegativities. In all of our calculations, the two highest occupied molecular orbitals are the ones with chalcogen homonuclear π-antibonding character. When the terminal groups are H, CH_3, or CF_3, these orbitals have mostly chalcogen character, and when the homonuclear bond is shortened, they are destabilized, but when their terminal groups are halogens, these orbitals have substantial halogen character, and their energies are affected little when the homonuclear bonds are shortened. Indeed, the atomic orbital coefficients of the lowest *un*occupied MO's have considerable chalcogen π-antibonding character. The halogens, especially fluorine, seem to be able to "push" some of the chalcogen π-antibonding character out to the unoccupied orbitals, thus allowing multiple bonding in the homonuclear bond.

In conclusion, we have qualitatively rationalized the bonding in the R_2S_2 and R_2O_2 type molecules, but neither the best semiempirical[11] nor sophisticated *ab initio*[13] calculations have been able to calculate satisfactory quantitative results. We suggest that these are excellent test species for any new quantitative quantum mechanical model for molecules.

METHOD

We used the Extended Hückel Molecular Orbital model and programs of Hoffmann,[19] most of the time using Method 2, which involves an iterative procedure around atomic charge self consistency. The extended Hückel parameters used are listed in Table I.

TABLE I

Extended Hückel parameters

Element	Orbital	Exponent	H_{ii}(e.v.)
H	1s	1.3	−13.6
C	2s	1.55	−19.42
	2p	1.325	−10.64
O	2s	2.2	−32.34
	2p	1.975	−15.8
F	2s	2.525	−40.12
	2p	2.3	−18.65
S	3s	1.967	−20.67
	3p	1.517	−11.58
	3d	1.0	−2.5

ACKNOWLEDGEMENTS

This work was made possible by a grant by the Faculty Research Committee of Seattle Pacific University and the use of the facilities of the Academic Computer Center of the University of Washington. The authors want to especially thank D. Russell for his encouragement.

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