Theoret. Chim. Acta (Berl.) 33, 227—238 (1974)

A Molecular Orbital Description for Sulfur Compounds of Valences 2, 4 and 6

Vlasta Bonačić Koutecký* and Jeremy I. Musher
Belfer Graduate School of Science, Yeshiva University, New York, N.Y. 10033

Received September 24, 1973

The qualitative picture of the bonding involved in sulfur compounds with valences 2, 4 and 6 is discussed. Molecular orbital CNDO/2 calculations are used to describe the covalent and hypervalent bonds in the three simplest hydrides and fluorides half of which are hypothetical. The results with and without *d*-orbitals on the sulfur atom are compared and bonding can be understood without *d*-orbitals. Possible structures of a sulfurane dimer and sulfurane oxides which are likely intermediates or stable compounds in this chemistry are considered briefly.

Key words: Sulfur compounds, CNDO/2 calculations of ~ – Sufuranes – Persulfuranes

1. Introduction

The organic chemistry of tetracoordinate and hexacoordinate sulfur has until recently been essentially restricted to polyfluoro derivatives of the type RSF_3 [1–3], RSF_5 [3–6] and nitrogen substituted derivatives with the first non-halogen-containing compounds reported in 1968–9 by Allen *et al.* [8], Owsley *et al.* [9], and Johnson [10]. Recently a series of "sulfuranes" [sulfurane (IV) compounds] has been prepared by Martin [11–14], Kálmán [15], Sheppard [16], and Denney [17] and their coworkers, and it is anticipated that more "persulfuranes" [sulfur (VI) compounds] will be prepared before long. A non-halogen-containing sulfurane oxide, analogous to SF_4O and the nitrogen-fluoro compounds of Glemser [7], has been recently prepared by Martin [18] all of which bodes well for an extensive chemistry of hypervalent organosulfur compounds. Curiously enough the first such selenium compound was prepared in 1914 [19] with no successor in the literature until very recently with the work of Agenas and Lindgren [20, 21], Reich [22] and Okamoto [23].

The chemistry of such sulfur compounds had been predicted theoretically by one of us with qualitative arguments based on both valence bond [24, 25] and molecular orbital theory [26]. The qualitative descriptions emphasize the theoretical difference between the sulfuranes which utilize essentially pure *p* hypervalent-I bonds and persulfuranes which utilize *sp*-hybridized hypervalent-II bonds. The first theoretical discussion of SF_4 is that of Willett in 1964 [27] and calculations have been carried out by Santry and Segal [28, 29], Brown [30], van Wazer [31–33], Gianturco *et al.* [34, 35], Roos [26] and Companion [36].

---

* Present address: Institut für Physikalische Chemie, Freie Universität, Berlin

The present article carries out the first calculations for the four real and the two as yet hypothetical sulfur hydrides and fluorides, SX_2, SX_4 and SX_6 with $X = H$ and F, and goes on to give a qualitative picture of the several isomers of a solfurane oxide as well as an analysis of some possible dimeric structures for SF_4. These calculations are carried out in the spirit of the three recent phosphorane calculations [37–39], in which each group used a different MO approximation technique – both with models and with calculational procedures – to obtain results of interest. The present calculations utilize the CNDO/2 procedure [40, 41], not because it is the best of all worlds, but merely because it gives us the series of results desired yet involves no great difficulty in computation. This enables us to show in a semi-empirical way the types of bonding involved in sulfur-containing compounds and the energetics to be expected. Throughout the paper *d*-orbitals are only utilized when explicit reference is made to them which is consistent both with Rundle's [42, 43] and one of the present author's ideas [44] as exemplified by Willett [27] for SF_4. The well-known weakness of the CNDO/2 technicue for predicting geometries should not be forgotten, however, and a particularly dramatic demonstration of this occurs in the work of Deb and Coulson [45] where interhalogen AB_5 compounds are calculated to have a minimum for a trigonal bipyramid geometry rather than for the observed square pyramid geometry.

2. Molecular Orbital Description

An analysis of the bonding in the three hydrides (two of which are hypothetical) and the three fluorides (one of which has not been isolated) of sulfur can be obtained from MO calculations using the CNDO/2 method. These calculations are carried out for the experimental bond distances and bond angles of SH_2, SF_4 and SF_6 where the corresponding values for SF_2, SH_4 and SH_6 are arbitrarily assumed to be the same. The values utilized are 1.328 Å and 92.2° for SX_2 [46], 1.545 Å, 1.648 Å and 101.5°, 87.8° for the two bond lengths and angles in SX_4 [47], and 1.58 Å and 90° for SX_6 [48][1]. Pictures of the occupied orbitals of interest for all three hydrides and for SF_4, an illustrative example of the more complex fluorides, are given in Figs. 1–4.

The CNDO/2 calculations are carried out utilizing the 3*s* and 3*p* sulfur electrons and the 1*s* hydrogen or the 2*s* and 2*p* fluorine electrons as appropriate although the energies for the 2*s* fluorine electrons is not discussed explicitly.

The molecules SX_2 and SX_4 utilize mostly *p*-bonding on the sulfur atom and SX_4 is said to involve hypervalent-I bonding. The SX_6 molecule, however, utilizes a significant amount of *s*-bonding as occurs in all hypervalent-II bonds since there are an insufficient number of *p*-electrons to provide one electron for each of the bonds without recourse to the *s*-electrons. This simplified qualitative picture is that illustrated in the series of Figs. 1–4. Of

---

[1] The microwave spectrum of SF_2 [49] gives the S – F bond length as 1.589 Å and the F–S–F bond angles as 98.3°. It would have been preferable to use these values in the SF_2 calculations, and also to have used the H_2S bond length in the SH_4 and SH_6 calculations. These, however, were unfortunately not done. The mass spectrum of SF_2 has also been reported [50, 51].

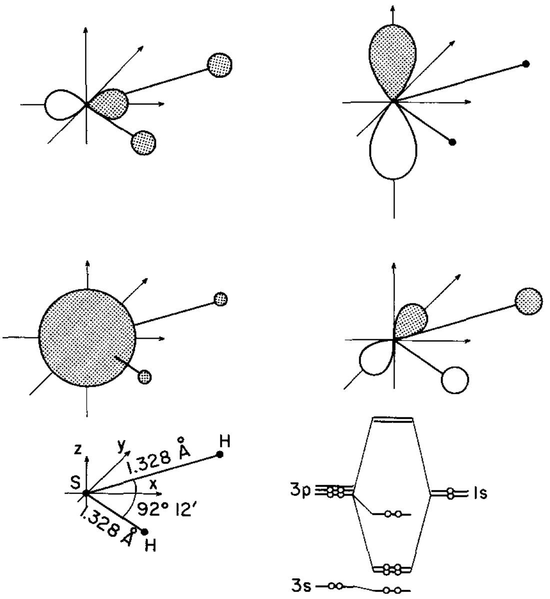


Fig. 1. The geometry, MO description and occupied orbitals of SH_2. The *a* and *b* orbitals are on the left and right side respectively

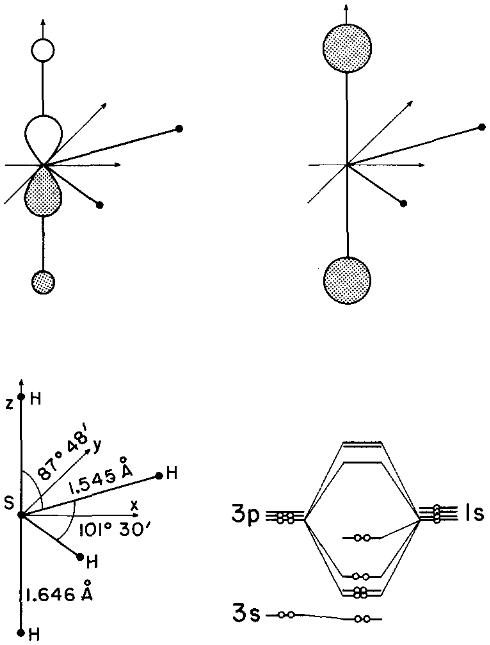


Fig. 2. The geometry, MO description and occupied orbitals different from those of SH_2 for SH_4. These orbitals are bonding and non-bonding MO's which give rise to the hypervalent-I bond

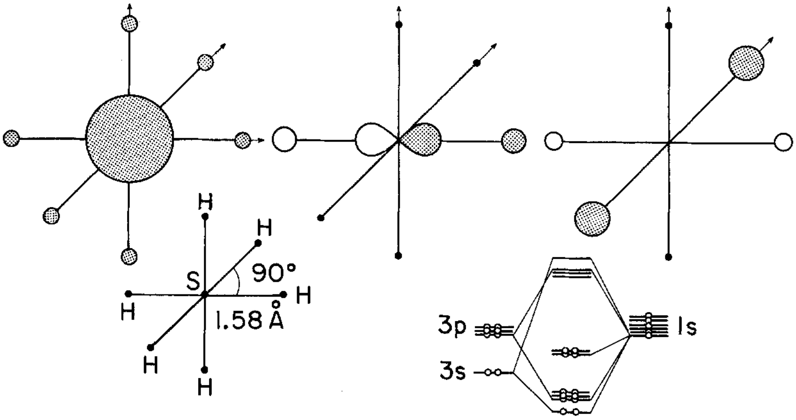


Fig. 3. The geometry, MO description and occupied orbitals of SH_6. These MO's are $1a_{1g}$, one of the $1t_{1u}$ and one of the $1e_{1g}$ orbitals

course, all calculations given in the tables utilize the experimental bond lenths and bond angles for the known molecules.

The three hydrides, whose MO pictures are shown in Figs. 1–3 are easily described theoretically. The molecular orbitals for SH_2 contain two bonding orbitals $1b_1$ and $2a_1$ antisymmetric and symmetric respectively about the plane bisecting the two bonds, and the nearly pure 3*s* and the pure 3*p* orbitals $1a_1$ and $1b_2$. The energies of these orbitals are given in Table 1. The two bonds in this molecule can also be imagined as a pair of non-canonical localized orbitals constructed from linear combinations of the two bonding MO's although this has no consequential effect on any result.

The hypothetical molecule SH_4 contains two covalent bonds, differing somewhat but not significantly from those of SH_2 as can be seen in Tables 2 and 3. The two lone-pair p_z electrons of SH_2 are now replaced by a pair of electrons in a three-center bonding orbital and a pair of non-bonding electrons essentially localized on the two nearly colinear hydrogens which are added to make the molecule SH_4. This combination of a three-center bonding orbital and a purely ligand non-bonding orbital gives rise to the hypervalent bond. The three-center bond provides net bonding when electron density is transferred from the sulfur atom to the ligand. This is not expected to occur for the electropositive hydrogen as it should for the fluorides discussed below even though our CNDO/2 calculations show there to be bonding. Once again the 3*s* sulfur orbital provides a small contribution to the bonding. Just as the MO's in SH_2 can be added and subtracted to give non-canonical localized bonding orbitals the three-center bond in SH_4 can be envisaged as two degenerate non-canonical localized bonds pointing towards the two hypervalent ligands. Thus the three-center bonding MO and the non-bonding symmetric purely ligand orbital can be added and subtracted to give rise to two apparent bonding orbitals. As always, it must be remembered that such orbitals are only a construct sometimes useful for visualizing the results, but caution must be

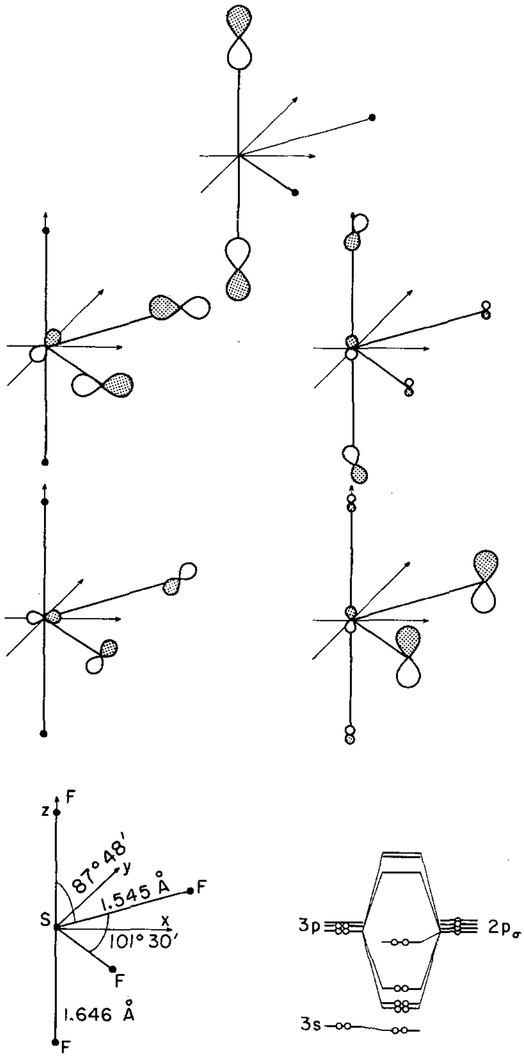


Fig. 4. The geometry, MO description and key occupied orbitals of SF_4. Reading from left to right and from bottom to top the first and third MO's are $4a_1$ and $2b_1$ describing covelent bonds, the second MO is $2b_2$ and describes a π-bond, and the last two MO's are $6a_1$ and $9a_1$ describing a hypervalent-I bond with the two axial ligands

exerted before automatically assuming that the valence-bond analogue, to which this is extremely close, can be actually applied. As usual with valence-bond structures one has to be able to show that the canonical structure does actually provide bonding.

The hypothetical molecule SH_6 assumed to be of octahedral symmetry is the first molecule we discuss that requires a significant amount of 3*s* sulfur bonding. The 3*s* electron of the sulfur atom lies in a totally symmetric orbital

Table 1. Energies, ε, of occupied MO's without d-orbitals and energy increments, Δ, with addition of d-orbitals (a.u.)

SH_2			SF_4			SF_6		
	ε	Δ		ε	Δ		ε	Δ
$1b_2$	−0.483	−0.008	$9a_1$	−0.476	−0.263	$2e_{1g}$	−0.603	−0.148
$2a_1$	−0.578	−0.012	$8a_1$	−0.643	0.011	$3t_{1u}$	−0.762	−0.042
$1b_1$	−0.609	−0.031	$4b_1$	−0.661	−0.092	$2t_{2g}$	−0.810	0.005
$1a_1$	−0.992	−0.008	$7a_1$	−0.677	−0.140	$1t_{2u}$	−0.835	0.010
			$2a_2$	−0.682	−0.057	$1t_{2g}$	−0.872	−0.118
			$6a_1$	−0.737	0.014	$2t_{1u}$	−0.992	0.028
			$5a_1$	−0.774	−0.041	$2a_{1g}$	−1.108	0.041
			$3b_1$	−0.796	0.006	$1e_{1g}$	−1.582	−0.135
			$1a_2$	−0.853	−0.056	$1t_{1u}$	−1.747	0.024
			$2b_2$	−0.901	0.010	$1a_{1g}$	−1.917	0.043
			$2b_1$	−0.915	−0.017			
			$4a_1$	−0.915	−0.002			
			$3a_1$	−1.048	0.011			
			$2a_1$	−1.497	−0.140			
			$1b_2$	−1.583	−0.064			
			$1b_1$	−1.684	−0.049			
			$1b_1$	−1.808	0.021			

Table 2. Total charges[a]

	SH_2	SH_4	SH_6	SF_2	SF_4	SF_6
S	6.081	5.466	5.069	5.544	4.631	3.954
X_1, X_2	0.960	0.927	1.155	7.228	7.224	7.341
X_3, X_4		1.340	1.155		7.461	7.341
X_5, X_6			1.155			7.341

[a] X = H or F as appropriate. X_3 and X_4 refer to the nearly colinear bonds in SH_4 and SF_4.

Table 3. Change in the net charge of 3s- and 3p-orbitals on sulfur

	SH_2	SH_4	SH_6	SF_2	SF_4	SF_6
ΔS_s	−0.165	−0.181	−0.491	−0.151	−0.229	−0.671
$\Delta S_{p(\mathrm{CV})}$	0.246	0.413		−0.305	−0.049	
$\Delta S_{p(\mathrm{LP})}$	0.000			0.000		
$\Delta S_{p(\mathrm{HV-I})}$		−0.766			−1.091	
$\Delta S_{p(\mathrm{HV-II})}$			−0.440			−1.375

ΔS_s and $\Delta S_{p(\mathrm{LP})}$ is the change in net charge of the sulfur 3s-orbital and 3p-orbital describing the lone pair electrons, respectively. $\Delta S_{p(\mathrm{CV})}$, $\Delta S_{p(\mathrm{HV-I})}$, $\Delta S_{p(\mathrm{HV-II})}$ are the changes in net charge of 3p orbitals in covalent, hypervalent-I and hypervalent-II types of bonds, respectively.

constructed from a linear combination of the six ligand orbitals with the sulfur *s*-orbital. The presence of this important *s*-bonding causes us to refer to this type of bonding as hypervalent-II bonding to distinguish it from the purely *p*-bonding hypervalent-I bonding as in SH_4. In addition to the *s*-bonding orbital there are three three-center bonding orbitals similar to the single such orbital which occurs in SH_4. There are also two non-bonding orbitals which contain contributions only from the ligand orbitals, although obviously, when *d*-orbitals are included these orbital energies can be significantly low [26]. Pictures of the orbitals are shown in Fig. 3. The important difference between SH_4 and SH_6 arise from the (obvious) fact that no typical covalent bonds appear in SH_6, and the bonding arises not only from three three-center bonds but also from the still lower-lying *s*-bonding orbital. A more realistic description via an *ab initio* calculation would only modify the electron density on the atoms which would presumably account for the instability of SH_4 and SH_6 (if such is indeed the case). Once again the six occupied orbitals could be combined into six equivalent linear combinations each of which is degenerate and looks like an SH bonding orbital pointed in the appropriate direction. The weakness of such a picture, unless it is used as the basis for a real VB calculation, is that all orbitals appear to be degenerate whereas in fact they are non-canonical linear combinations of one a_1, a triply-degenerate t_{2g} and a doubly-degenerate e_g orbital.

The molecular orbitals of the three fluorides SF_2, SF_4 and SF_6 can be described in an exactly analogous manner and the orbital energies for SF_4 and SF_6 are given in Table 1. The non-bonding nature of the $9a_1$ orbital is easily seen, as it lies 0.2 a.u. higher than the three-center bonding $2a_2$ orbital. The fluorides all have the added complication of mixing the fluorine π-electrons with the σ-electrons which makes for some quantitative contribution to the bonding but has little effect on the qualitative description. For illustrative purposes the orbitals in SF_4 are shown in Fig. 4. The energy dependence on axial bond length and equatorial bond angle is shown in Fig. 5. Calculations with *d*-orbitals exhibit a minimum for the axial bond length 1.600 Å close to the experimental 1.646 Å. Minima for the bond angle dependence are very flat and, as is well-known, the geometric predictions from CNDO/2 calculations are not very reliable.

The MO energies without inclusion of *d*-orbitals for the three stable molecules SH_2, SF_4 and SF_6 are presented in Table 1 along with the changes in orbital energies, Δ, when *d*-orbitals are included. In Tables 2 and 3 are given the total charges and the change in net charge from that on an isolated sulfur atom for the six molecules. The total energies for SH_2, SH_4, SH_6, SF_2, SF_4 and SF_6 are -12.249 (-12.331), -13.476 (-13.767), -14.665 (-15.234), -65.819 (-66.387), -120.709 (-121.940) and -175.463 (-177.385), and the binding energies are -0.206 (-0.288), -0.155 (-0.446), -0.066 (-0.633), 0.045 (-0.523), 0.253 (-0.978) and 0.598 (-1.324) where the results in parentheses come from the calculations which include the *d*-orbitals. These numbers are given for completeness only since we consider such CNDO/2 numbers to be of little significance. Despite this limitation we feel, as do many others, that much can be learned from these calculations despite their limitations. As can be seen

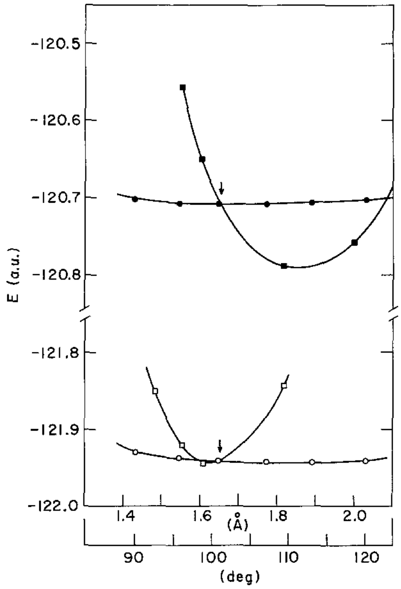


Fig. 5. Energy dependence of axial SF bond length (☐, ■) and diequatorial FSF bond angle (○, ●) where white and black refer to calculations with and without *d*-orbitals

the calculations do not always provide bonding until *d*-orbitals are included, and when *d*-orbitals are included they *always* provide bonding, which clearly shows the absurdity of drawing any conclusions thereby. The changes in the orbital energies themselves with the addition of *d*-orbitals as indicated by the Δ's show the shift in orbital energy to be either positive *or* negative. This demonstrates that the *d*-orbitals have negligible effect and only modify the first-order Coulomb and exchange energies. Notice also that the lowering of the t_{2g} and e_g levels occur because only with *d*-orbitals is mixing with sulfur electrons permitted for orbitals with these symmetries. A similar conclusion in which the addition of *d*-orbitals raises the energy of almost all the orbitals can be drawn [26] from the extremely accurate studies of Roos on SF_6 [34, 35] and van Wazer on phosphoranes [31–34] using large contracted gaussian bases[2]. Of course, more angular dependent properties such as dipole moments and spin-spin interactions require that less angularly limited basis sets be used in calculations.

The results of Table 2 show the expected transfer of electrons from the sulfur to the fluorine in all cases this is believed to give rise to the bonding. The same polarization, however, occurs also for the hydrides and this serves to illustrate once again the anticipated weakness in the CNDO/2 method. The results of Table 3 exhibit a similar weakness. This can be seen, for example, by noting the identical average polarization for SF_4 and SF_6 both of which are *greater* than the polarization in the (shorter) SF_2.

---

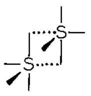
[2] The inclusion of *d*-orbitals in *ab initio* calculations has been most recently treated as a perturbation by Nakatsuji and Musher [52]. It is shown that when first-order results are dominant the orbital energies all increase and the total energy change is second order. The results presented here, therefore, point to an inadequacy of the CNDO/2 method.

3. Discussion

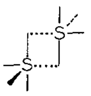
The bonding in sulfuranes has now been discussed so that several related problems of interest to the chemist can now be considered.

Recent experiments [53, 54] have shown that SF_4 exchanges its axial and equatorial fluorine atoms intramolecularly via an $aa \rightleftarrows ee$ rearrangement at about $-60°$ C. This might occur via a unimolecular rearrangement or via the formation of a non-symmetric dimer as postulated for PF_5 [55, 56]. There is also spectroscopic evidence for the existence of dimeric structures [57] as well as much speculation [24, 58, 59, 60] concerning their structure.

We carried out CNDO/2 calculations with *d*-orbitals for the energies of two possible dimers with the two SF_3 groups coplanar and the remaining two fluorines cis- and trans- as in *1* and *2*. When the S···F distance is 1.545 Å as for equatorial bonds, then the energies are -244.102 a.u. and -244.104 a.u. for *1* and *2* respectively, while when the S···F distance is 1.646 as in the longer axial bond, then the energies are -244.180 a.u. and -244.183. All of these energies are slightly *lower* than the -243.820 a.u. calculated for two monomers. This could lend credence to the possibility that SF_4 has a non-symmetrical dimer for its ground-state in matrix-isolation spectra. Of course, CNDO/2 energies are not necessarily reliable for such differences.

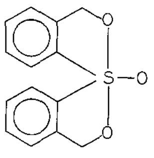


1

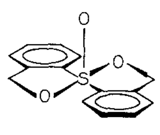


2

The first sulfurane oxide [18] was prepared recently and is presumably of structure *3*. The related compound *4* is also possible. However as it involves four monofunctional substituents which are essentially coplanar it is presumably not preparable from the sulfurane itself. There are of course several other geometrical isomers related to *3* and *4* with different orientations of the SC bonds. A similar analysis also applies to the related compound, R_2NSF_3O, prepared by Glemser [7]. It is worth noting that the equatorial-equatorial bond angle in SF_4 is 104°, far from the 120° expected from the pure VSEPR theory [61] referred to by many authors. The equatorial-equatorial bond angle in SF_4O is 123° and this is also consistent with the theory presented here, since the addition of the oxygen requires the utilization of the sulfur *s*-orbitals in the bonding. The *sp* "hybridization" which was not necessary in SF_4 allows the



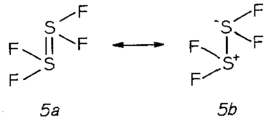
3



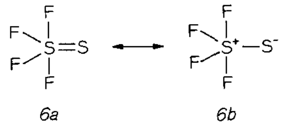
4

molecule to become more "symmetrical" while decreasing its energy. A similar result is shown in going from a sulfurane with C–S–C bond angle near 105° to a sulfurane oxide with C–S(O)–C bond angle of 117° [61a]. The situation is exactly analogous to what occurs in xenon chemistry where the OXeO bond is *opened* and the molecule stabilized in going from XeO_3 to XeO_4 [24].

It is interesting to speculate, at the suggestion of the referee, as to the possible existence of the SF_2 dimer, *5*. This compound is not actually as curious as it seems since the known F_2SS is an analogue of F_2SO in which the S(IV) S–O bond has a large amount of single-bonding character as in the sulfonium ylides [62] $R_2SC(R'R'')$. The structure of this compound is not obvious since 5b, being non-symmetrical, would have the $S^+S^-(F)F$ coplanar with probably the FS^-F group colinear, either in the FS^+F bisector or perpendicular to it. The structure might more likely be the average of the two as drawn here. There are known examples of SR_3^- ions, e.g. A. N. Nesmeyanov, Dokl. Akad. Nauk **133**, 602 (1960). A different structure isotopic with *5* is F_4SS, *6*, the analog to F_4SO, which could also be stable. As in *3* above, this compound could have another isomer with square-planar F's, analogous to *4*.

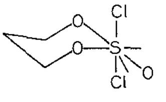


5a *5b*

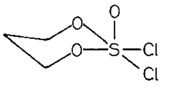


6a *6b*

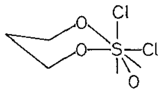
An example in which all isomers can be easily described occurs in the four possible intermediates of Klein [63], *ccct-trans*-S-dichloro-2, 6- dioxa-1-oxythiacyclohexane *7*, *eeee*-S-dichloro-2, 6-dioxa-1-oxythiacyclohexane *8*, *d-ccct-cis*-S-dichloro-2, 6-dioxa-1-oxythiacyclohexane *9* and its 2-isomer, where we have labeled the isomers following the notation for octahedral complexes [64]. The conversion of the sulfurane oxide *3* (or *4*) to a persulfurane is being attempted in our laboratory.



7



8



9

While we could discuss numerous further examples of interesting potential sulfuranes and persulfuranes and their rearrangements we feel it is premature to do so at the present time. The present discussion has shown that hypervalent bonding in sulfur is easily described theoretically, and it is hoped that awareness of its potentialities will lead to a varied new sulfur and chalcogen chemistry.

One of us (J.I.M.) is grateful to Professor Jozef Klein for valuable discussions. This work was supported by the ONR and the NSF.

References

1. Laur, P. H.: In: Senning, A. (Ed.): Sulfur in organic and inorganic chemistry, Vol. 3. New York: Marcel Dekker 1972
2. Demitras, G. C., MacDiarmid, A. G.: Inorg. Chem. **6**, 1903 (1969)
3. Sauer, D. T., Shreere, J. M.: Chem. Commun. 1679 (1970)
4. Hoover, F. W., Coffman, D. D.: J. Org. Chem. **29**, 3567 (1964)
5. Czerepinski, R., Cady, G. H.: J. Am. Chem. Soc. **90**, 3594 (1968)
6. Plase, R. D., Williamson, S. M.: J. Am. Chem. Soc. **90**, 2550 (1968)
7. Glemser, O., Mews, R.: Advan. Inorg. Chem. Radiochem. **14**, 333 (1972)
8. Allan, M., Janzen, A. F., Willis, C. Y.: Can. J. Chem. **46**, 3671 (1968)
9. Owsley, D. C., Helmkamp, G. H., Rettig, M. F.: J. Am. Chem. Soc. **91**, 5239 (1969)
10. Johnson, C. R., Rigau, J. J.: J. Am. Chem. Soc. **91**, 5398 (1969)
11. Martin, J. C., Arhart, R. J.: J. Am. Chem. Soc. **93**, 2341 (1971)
12. Arhart, R. J., Martin, J. C.: J. Am. Chem. Soc. **94**, 4997, 5003 (1972)
13. Paul, I. C., Martin, J. C., Perozzi, E. F.: J. Am. Chem. Soc. **94**, 5010 (1972)
14. Kaplan, L. J., Martin, J. C.: J. Am. Chem. Soc. **95**, 793 (1973)
15. Kapovits, I., Kálmán, A.: Chem. Commun. 646 (1971)
16. Sheppard, W. A.: J. Am. Chem. Soc. **93**, 5597 (1971)
17. Denney, D. B.: J. Am. Chem. Soc. (in press)
18. Perozzi, E. F., Martin, J. C.: J. Am. Chem. Soc. **94**, 5519 (1972)
19. Lesser, R., Weiss, R.: Ber. **47**, 2510 (1914)
20. Agenas, L., Lindgren, B.: Acta Chem. Scand. **24**, 3301 (1970)
21. Lindgren, B.: Acta Chem. Scand. **26**, 2560 (1972)
22. Reich, H. J.: J. Am. Chem. Soc. **95**, 964 (1973)
23. Okamoto, Y.: (to be published)
24. Musher, J. I.: Angew. Chem. Intern. Ed. Engl. **8**, 54 (1969)
25. Musher, J. I.: Sulfur research trends, Advan. Chem. **110**, 44 (1972)
26. Musher, J. I.: J. Am. Chem. Soc. **94**, 1370 (1972)
27. Willett, R. D.: Theoret. Chim. Acta (Berl.) **2**, 393 (1964)
28. Santry, D. P., Segal, G. A.: J. Chem. Phys. **47**, 158 (1967)
29. Santry, D. P.: J. Am. Chem. Soc. **90**, 3309 (1968)
30. Brown, R. P., Peel, J. B.: Australian J. Chem. **21**, 2589, 2605, 2617 (1968)
31. Absar, I., Van Wazer, J. R.: J. Am. Chem. Soc. **94**, 2382, 6294 (1972)
32. Robert, J. B., Marsmann, H., Schaad, L. J., Van Wazer, J. R.: Phosphorus **2**, 11 (1972)
33. Van Wazer, J. R., Absar, I.: Sulfur research trends 20 (1972)
34. Gianturco, F. A., Guidotti, C., Lamanna, V., Moccia, R.: Chem. Phys. Letters **10**, 269 (1971)
35. Gianturco, F. A.: Chem. Phys. Letters **17**, 127 (1972)
36. Companion, A. L.: Theoret. Chim. Acta (Berl.) **25**, 268 (1970)
37. Rauk, A., Allen, L. C., Mislow, K.: J. Am. Chem. Soc. **94**, 3035 (1972)
38. Florey, J. B., Cusachs, L. C.: J. Am. Chem. Soc. **94**, 3040 (1972)
39. Hoffmann, R., Howell, J. M., Muetterties, E. L.: J. Am. Chem. Soc. **94**, 3407 (1972)
40. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, 3289 (1966)
41. Dobosch, P. A.: QCPE 141, CNINDO: CNDO and INDO Molecular Orbital Program
42. Rundle, R. E.: Surr. Propr. Chem. **1**, 81 (1963)
43. Rundle, R. E.: J. Am. Chem. Soc. **85**, 112 (1963)
44. Musher, J. I.: Science (Washington) **141**, 736 (1963)
45. Deb, B. M., Coulson, C. A.: J. Chem. Soc. 958 (1971)
46. Burrus, C. A., Gordy, W.: Phys. Rev. **92**, 274 (1953)
47. Kimura, K., Bauer, S. H.: J. Chem. Phys. **39**, 3172 (1963)
48. Gaunt, J.: Trans. Faraday Soc. **49**, 1122 (1953)
49. Johnson, D. R., Powell, F. X.: Science **164**, 950 (1969)
50. Wanczek, K.-P.: Thesis, Saarbrücken 1970
51. Seel, F., Heinrich, E., Gombler, W., Buderz, R.: Chimia **23**, 73 (1969)
52. Nakatsuji, H., Musher, J. I.: Chem. Phys. Letters **24**, 77 (1974)
53. Klemperer, W. G., (personal communication)
54. Seel, F., (personal communication to R. Schmutzler)
55. Musher, J. I.: Tetrahedron Letters 1093 (1973)

56. Berry, R. S.: J. Chem. Phys. **32**, 933 (1960)
57. Frey, R. A., Redington, R. L., Khadir Aljibury, A. L.: J. Chem. Phys. **54**, 344 (1971)
58. Muetterties, E. L., Phillips, W. D.: J. Chem. Phys. **46**, 2861 (1967)
59. Redington, R. L., Barnay, C. V.: J. Chem. Phys. **46**, 2862 (1967)
60. Klemperer, W. G.: In: Cotton, F. A., Jackman, L. M. (Eds.): Dynamic nuclear magnetic resonance spectroscopy (in press)
61. Gillespie, R. J.: Angew. Chem. Intern. Ed. Engl. **6**, 749 (1967)
61a. Perozzi, E. L., Martin, J. C., Paul, I. C.: J. Am. Chem. Soc. **96**, 578 (1974)
62. Musher, J. I.: Tetrahedron (van't Hoff-Le Bel Memorial Issue, to be published)
63. Klein, J., Stollar, H.: J. Am. Chem. Soc. **95**, 743 (1973)
64. Musher, J. I.: Inorg. Chem. **11**, 2335 (1972)

Dr. Jeremy I. Musher
Belfer Graduate School of Science
Yeshiva University
New York, N.Y., 10033
USA