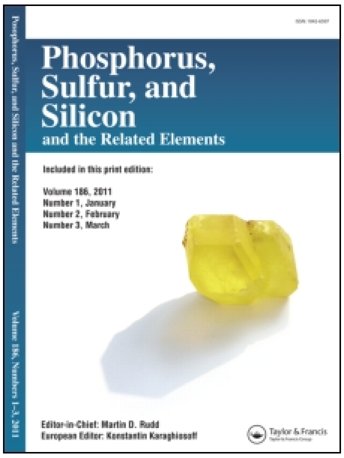

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STRUCTURE OF OXIDIZED DISULFIDE BONDS AS CALCULATED BY THE CNDO/2 METHOD

T. Gillbro[a]
[a] The Swedisch Research Counsil's Laboratory, Studsvik, Nyköping, Sweden

To cite this Article Gillbro, T.(1978) 'STRUCTURE OF OXIDIZED DISULFIDE BONDS AS CALCULATED BY THE CNDO/2 METHOD', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 2, 133 — 135
To link to this Article: DOI: 10.1080/03086647808076555
URL: http://dx.doi.org/10.1080/03086647808076555

Phosphorus and Sulfur
1978, Vol. 4, pp. 133-135

STRUCTURE OF OXIDIZED DISULFIDE BONDS AS CALCULATED BY THE CNDO/2 METHOD

T. GILLBRO

The Swedisch Research Counsil's Laboratory, Studsvik, S-61101 Nyköping, Sweden

(Received March 24, 1977)

CNDO/2 calculations indicate that disulfide cation radicals, e.g. $HSSH^+$ and $CH_3SSCH_3^+$, have a trans-planar structure in contrast to the twisted structure of the parent molecule. The main reason for this difference is the removal of an electron from the sulfur lone-pair orbitals. The bond energy in the disulfide cation radical is much lower than in the parent molecule, which makes the reaction $CH_3SSCH_3^+ \rightarrow CH_3S\cdot + CH_3S^+$ allowed, as observed previously in radiolysis of CH_3SSCH_3 single crystals.

Several studies of disulfide structures have been reported in the literature.[1] One important conclusion from these studies is that the neutral molecule is twisted in the ground state with a dihedral angle (β) of approximately 90° in most dialkyl disulfides. This twisted structure is mainly the result of the mutual repulsive force exerted by the lone-pair electrons on each sulfur atom. It has also been shown that the activation energy for rotation around the S–S bond is high,[2] i.e. roughly 10 kcal/mol for the cis- and 5 kcal/mol for the trans-barrier.[3] The CNDO method has previously been used with good results in calculations of the change in optical spectra and optical activity with dihedral angle in disulfides.[1,4] Extended Hückel MO calculations of ionization potentials on some disulfides have also been performed by Bock and coworkers[5] and show good agreement with photoelectron spectra.

In an ESR investigation on γ-irradiated CH_3SSCH_3 single crystals[6] we reported that both anion and cation radicals are formed. The experimental results also indicated that the cation radical, in contrast to the neutral molecule, has a planar structure. There is also a significant difference in the optical spectra of disulfide cations that possess bulky alkyl groups if they are studied in the solid as opposed to the liquid state. In di-t-butyl disulfide λ_{max} shifts from ~780 nm[7] to 410 nm[8] on comparing a glass with a liquid solution. This shift might be produced by a change of structure.

In Figure 1 the total energy is plotted as a function of the dihedral angle for HSSH, $HSSH^-$ and $HSSH^+$. The structural parameters used in these calculations are $r_{S-S} = 2.04$ Å, $r_{S-H} = 1.33$ Å and $\angle SSH = 95°$. They differ slightly from the experimental values[2] which are reported to be $r_{S-S} = 2.055$ Å, $r_{S-H} = 1.327$ Å and $\angle SSH = 91.32°$. The parameters above have been chosen for present purposes since the experimental values had previously been used in a CNDO/2 calculation relating to the neutral HSSH molecule[1] and it was of interest to see how a small reduction of the S–S bond might influence the total energy and the activation energy for the trans/cis rotation.

The calculations of the HSSH indicated the occurrence of an energy minimum at $\beta = 85°$ and two energy maxima at $\beta = 0$ and 180° (Figure 1). The activation energy for rotation through the cis-barrier is 13.1 kcal/mol and that for the trans-barrier is 7.3 kcal/mol. These values are to be compared to 10.4 and 3.2 kcal/mol derived from measured structural parameters (see circles in Figure 1). It is noteworthy that the structure chosen in this work affords a lower total energy for the HSSH molecule for all dihedral angles than does the experimentally derived structure. The rotation barriers also seem to be in better agreement with experimental observation.[2]

The disulfide anion radical, $HSSH^-$, has two energy minima at $\beta = 0$ and 125° (Figure 1) respectively. The rotation barriers are lower than in the neutral molecule with a maximum activation energy of 4.7 kcal/mol. This means that rotation around the S–S bond might be allowed in the anion radical in contrast to the neutral molecule. The total bond energy is raised by 18.1 kcal/mol at $\beta = 90°$ in going from the neutral molecule to the anion radical. This is rather small compared to the calculated total bond energy of 436 kcal/mol in HSSH. The disulfide anion radical is thus expected to be stable, as has been found by several workers.[6,9-11]

The change in the total energy of the $HSSH^+$ cation radical with dihedral angle exhibits an altogether dif-

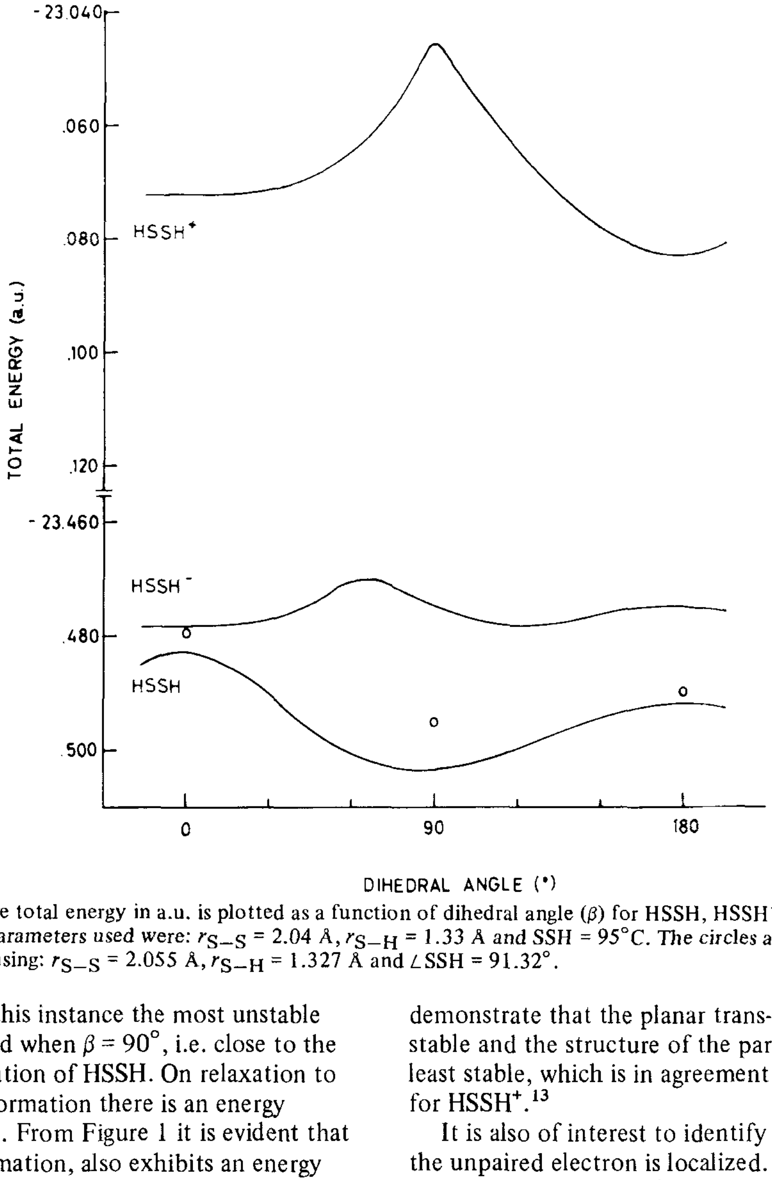

FIGURE 1 The total energy in a.u. is plotted as a function of dihedral angle (β) for HSSH, HSSH$^-$ and HSSH$^+$. *The structural parameters used were:* $r_{S-S} = 2.04$ *Å,* $r_{S-H} = 1.33$ *Å and SSH = 95°C. The circles are from calculations on HSSH using:* $r_{S-S} = 2.055$ Å, $r_{S-H} = 1.327$ Å and ∠SSH = 91.32°.

ferent behaviour. In this instance the most unstable conformation is found when $\beta = 90°$, i.e. close to the most stable conformation of HSSH. On relaxation to the trans-planar conformation there is an energy gain of 23.0 kcal/mol. From Figure 1 it is evident that the cis-planar conformation, also exhibits an energy minimum. The cis-form is not as stable as the transform, however, as a result of the repulsive force that is set up between the hydrogen atoms. The total bond energy is far lower in HSSH$^+$ (trans) than in HSSH (twisted), namely 171 *vs.* 436 kcal/mol (calculated). This result seems to support the earlier conclusion[6] that $\cdot SCH_3$ radicals are in fact formed from activated cation radicals during γ-irradiation of CH_3SSCH_3.[6]

CNDO/2 calculations were also performed for $CH_3SSCH_3^{+}$ with $r_{S-S} = 2.022$ Å, $r_{S-C} = 1.806$ Å, $r_{C-H} = 1.09$ Å and ∠SSC = 104.1°[12] for values of $\beta = 0$, 90, 180° and gave the relative energies −9.0, 0 and −21.4 kcal/mol, respectively. These results demonstrate that the planar trans-form is the most stable and the structure of the parent molecule the least stable, which is in agreement with the results for HSSH$^+$.[13]

It is also of interest to identify the MO to which the unpaired electron is localized. In the trans-planar structure of $CH_3SSCH_3^{+}$ the spin density (ρ) is mainly in the $3p_z$ orbital of each sulfur atom with $\rho = 0.52$. There is also a small contribution from the d orbitals of each sulfur atom ($\rho(d_{xz} + d_{yz}) = -0.036$). The remaining spin density is found in the 1*s* orbitals of the hydrogen atoms ($\rho = 0.007$). The latter spin density leads to a calculated isotropic coupling constant of $a_H = 3.7$ G. The experimental value from ref. 6 is 9.1 G.

In HSSH$^+$ ($\beta = 180°$ and $r_{S-S} = 2.04$ Å) the unpaired electron is confined to the $3p_z$ and $3d_{xz}$ sulfur orbitals with $\rho = 0.53$ and -0.03 respectively. This situation is in sharp contrast to the conformation $\beta = 90°$, where the unpaired electron is localized to the lone-pair orbital on each sulfur ($\rho = 0.44$) and with $\rho = 0.07$ in each of the hydrogen 1*s* orbitals. It should, therefore, be fairly easy to distinguish between these conformations in an ESR experiment performed on $HSSH^+$.

The highest occupied (HO) MO in HSSH varies with β between 4*a* and 3*b*, using the notations in Ref. 1. At $\beta = 90.6°$ 4*a* and 3*b* have about the same energy. Both orbitals have lone-pair character, however, largely owing to the out-of-plane 3*p* atomic orbitals of each sulfur. When the cation is formed, by removing one electron from these orbitals, the mutual repulsion decreases and a rotation is permitted around the S–S bond to the trans-planar conformation.[14] The same is true for other dialkyl disulfides since the HOMO is always a lone-pair orbital independent of the dihedral angle.[1]

Disulfide bonds often play an important rôle in the formation of complicated biomolecule structure such as those of enzymes. It therefore seems reasonable to expect that an oxidation of the disulfide bonds by biochemical or radiation chemical agencies can lead to an appreciable structural change in these molecules.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Ove Edlund for adapting the CNINDO program[16] with the CDC Cyber 172 computer at Studsvik. Professor Jan Linderberg is acknowledged for several valuable comments on the manuscript.

REFERENCES AND NOTES

1. D. B. Boyd, *J. Phys. Chem.* **78**, 1554 (1974), and references therein.
2. G. Winnewisser, M. Winnewisser and W. Gordy, *J. Chem. Phys.* **49**, 5465 (1968).
3. D. B. Boyd, *Theoret. Chim. Acta (Berl.)* **30**, 137 (1973) and references therein.
4. J. Linderberg and J. Michl, *J. Amer. Chem. Soc.* **92**, 2619 (1970); J. Webb, R. W. Strickland and F. S. Richardson, *J. Amer. Chem. Soc.* **95**, 4775 (1973).
5. G. Wagner and H. Bock, *Chem. Ber.* **107**, 68 (1974); B. Solouki and H. Bock, *Inorg. Chem.* **16**, 665 (1977).
6. T. Gillbro, *Chem. Phys.* **4**, 476 (1974).
7. T. Shida, *J. Phys. Chem.* **74**, 3055 (1970).
8. M. Bonifacic, K. Schäfer, H. Möckel and K.-D. Asmus, *J. Phys. Chem.* **79**, 1496 (1975).
9. J. H. Hadley, Jr. and W. Gordy, *Proc. Nat. Acad. Sci. USA* **71**, 4409 (1974).
10. K. Akasaka, S. Onishi, T. Suita and I. Nitta, *J. Chem. Phys.* **40**, 3110 (1964).
11. H. C. Box and H. G. Freund, *J. Chem. Phys.* **41**, 2571 (1964).
12. B. Beagley and K. T. McAloon, *Trans. Faraday Soc.* **67**, 3216 (1971).
13. Calculations of the optimum S–S bond length in HSSH (twisted) and $HSSH^+$ (trans-planar) gave $r_{S-S} = 1.87$ Å in both instances. Although this is different from the experimental bond length (2.055 Å) for HSSH one can conclude that the S–S bond length does not change much when oxidized, which is expected as the electron is removed from a non-bonding lone-pair orbital.
14. In the LCAO treatment of the disulfide bond by Bergson[15] it has been found that when excited the most stable conformation of the disulfide bond is obtained when $\beta = 0$ or 180°. The cation disulfide radical and the excited disulfide bond thus seem to have the same structure.
15. G. Bergson, *Arkiv Kemi* **12**, 233 (1958).
16. CNINDO program by Pople, Beveridge and Dobosh from Quantum Chemistry Program Exchange, Bloomington, Indiana.