Effects of Dihedral Angle and Substitution on S — S Bond Lengths. A CNDO/2 Molecular Orbital Study of Simple Disulfides

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The relationship between dihedral angle and bond length in HSSH has been studied by the CNDO/2 molecular orbital method. The results are in better qualitative agreement with experimental data when sulfur $3d$ orbitals are included in the basis set. Calculations on simple disulfides, XSSX, where $X = H$, CH_3, Cl, and F show that relative changes in S — S bond lengths are fairly well reproduced.

From a survey of experimental bond lengths between divalent sulfur atoms, Hordvik[1] suggested that the sulfur-sulfur bond length varies with the dihedral angle.

Dihedral angle = 0°   Dihedral angle = 90°

In non-cyclic and saturated cyclic compounds the smallest S — S bond lengths were found for dihedral angles of about 90° while smaller dihedral angles gave longer bond lengths. A more recent investigation[2] supports this contention, but the relationship is not obvious in other cases.[3]

The purpose of this paper is to study the above mentioned relationship from a theoretical point of view. To the author's knowledge this has not been done before, although the barriers to internal rotation in disulfides have been investigated in great detail by numerous workers.[4] The semiempirical CNDO/2 method[5] is used in the calculations presented here. The HSSH molecule was chosen as the geometrical model for a general disulfide. The reason for this choice is that in the accurately determined

molecular structure, the S — S bond length (2.055 Å) is comparable with those in a number of organic disulfides.[1−3] Furthermore, the molecule has no bulky substituents that may cause sterical hindrance problems in twisted configurations (as is the case, e.g., with the methyl groups in CH_3SSCH_3).

Experimental data indicate that the S — S bond length also depends on the electronegativities of the disulfide substituents.[6] This dependence is demonstrated for the molecules HSSH, CH_3SSCH_3, ClSSCl, and FSSF, where the sulfur-sulfur bond lengths are found to decrease with increasing electronegativity of the substituents. The S — S bond lengths for these molecules have therefore been calculated and the optimized values compared in order to evaluate how well the CNDO/2 method can reproduce the experimentally observed trends.

The calculations were done both with and without sulfur and chlorine $3d$ orbitals in the basis set. The program CNINDO distributed by the Quantum Chemistry Program Exchange[7] was used.

RESULT AND DISCUSSION

I. *Calculations on HSSH.* The CNDO/2 total energy[8] was calculated for HSSH as a function of the S — S bond length for dihedral angles between (and including) 0 and 180°. The S — H bond length and S — S — H bond angle were held fixed at the experimental values.[9]

Fig. 1 shows the S — S bond length corresponding to minimum energy as a function of dihedral angle. The results are compared with Hordvik's empirical curve,[1] which is also
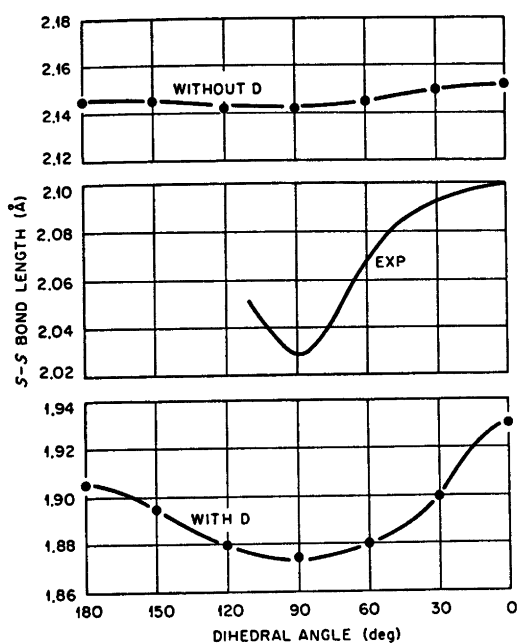
Fig. 1. Calculated S – S bond length as a function of dihedral angle compared with the experimental curve derived by Hordvik (*cf.* Ref. 1). The calculations are performed both with and without sulfur 3*d* orbitals.

shown in Fig. 1. As can be seen from the figure, the calculated S – S bond length decreases when the dihedral angle is varied from 180 to 90°, and increases to a maximum value for 0°. The same qualitative trends are obtained both with and without sulfur 3*d* orbitals. However, the results are in better qualitative agreement with the experimental curve when *d* orbitals are included in the basis set (*spd* approximation). The dependence is far less pronounced when *d* orbitals are excluded (*sp* approximation).

On the other hand, the calculated S – S bond lengths at 90° are far from the experimental value (2.055 Å) with both basis sets. However, the CNDO/2 method seems to be able to reproduce the relative changes reasonably well. The difference between the calculated S – S bond lengths for HSSH at 0 and 90° is 0.055 Å in the *spd* approximation. Adding this value to the experimental value for HSSH (2.055 Å), one obtains 2.110 Å which is close to the S – S single bond length (2.10 Å) suggested by

Hordvik for a *cis* planar disulfide group.[1]

The present study for HSSH indicates that 3*d* orbitals may be important for the description of the geometry of disulfides, at least within the CNDO/2 framework. The importance of *d* orbital participation to the bonding in HSSH may be understood from an analysis of the electron density-bond order matrix, $P_{\mu\nu} = 2\sum_{i}^{occ} C_{\mu i} C_{\nu i}$, where $C_{\mu i}$ are LCAO coefficients and the summation being over all occupied molecular orbitals. Since the sign of the bond-order matrix elements are defined according to the coordinate system, it was decided to multiply all bond-orders, $P_{\mu\nu}$, with the *sign* of the corresponding overlap integral, $S_{\mu\nu}$. In this way bonding and antibonding interactions are given positive and negative values, respectively.[10]

The atomic orbitals and dihedral angle θ are defined according to the coordinate system in Fig. 2. The redistribution of electron density is discussed by inspecting the atomic orbitals (AOs) on H^A and S^A. The two sulfur atoms (S^A and S^B) are, of course, identical, and have the same electron densities. However, since the atoms H^A and S^A are stationary when the dihedral angle is varied, the AO's on these atoms will not change their nature, *e.g.*, the sulfur p_z AO on atom A (Sp_z^A) will remain perpendicular to the $H_A - S_A - S_B$ plane. At $\theta = 90°$ this orbital will be equivalent to Sp_y^B. Similarly Sd_{xy}^A is equivalent to Sd_{xz}^B at $\theta = 90°$, and these orbitals as well as the Sp orbitals mentioned have π symmetry with respect to the $S^A - S^B$ axis.
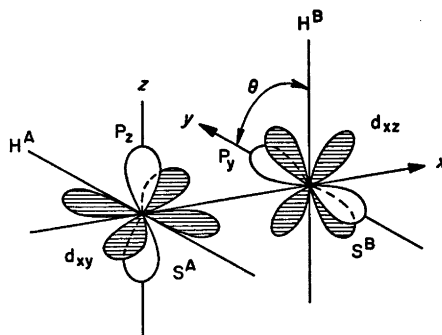

Fig. 2. Definition of the coordinate system axes.

One finds the greatest changes of the electron densities with dihedral angle for Sp_z^A and Sd_{xy}^A, cf. Table 1. The electron densities of the other $3d$ orbitals are small and do not change much with θ. The minimum value for Sp_z^A at about 90° corresponds to a maximum value for Sd_{xy}^A. The variation of bond orders with θ are all relatively small except for those involving the AO's mentioned above. Table 1 shows that the $Sp_x^A - Sp_x^B$ bond order is slightly antibonding at 0 and 180° but becomes fairly bonding at 90°. More important is the strong increase in bond order for $Sd_{xy}^A - Sp_y^B$ with a maximum value at about 90°. This strong increase in bond character is also reflected in the "bond index", $W(A-B) = \sum_\mu^A \sum_\nu^B P_{\mu\nu}^2$, indroduced by Wiberg [11] as a measure of the bond strength between atoms A and B.

The interaction between S and H on the other hand, do not change very much. Both the $Sp_y^A - Hs^A$ bond order and the $W(S^A - H^A)$ bond index remain almost constant. This is also true for the Hs^A electron density, which has a small maximum at 90°. The net charge on the S atom will, of course, follow the opposite trend, being $-0.03e$ and $-0.04e$, respectively, at 0 and 180°, and $0.01e$ only at 90°. The net charges on the atoms at 90° are therefore close to zero. This is in agreement with a recent *ab initio* calculation [12] on HSSH.

The major effect of changing the dihedral angle from 0 to 90° is therefore an internal redistribution of electron density from the lone-pair $p\pi$ orbital and into the $3d\pi$ orbital. This back donation of electrons is mainly accomplished by the interaction between the $p\pi$ lone pair on one sulfur atom with the corresponding $3d\pi$ orbital on the other. At 90° two such π bonds are established ($Sd_{xy}^A - Sp_y^B$ and $Sp_z^A - Sd_{zz}^B$). The difference in S–S bond lengths at 0 and 90° can therefore be explained (according to the CNDO/2 results), to be partly due to lone pair repulsion at 0°, and partly due to π bonding which is most pronounced at 90°.

The discussion so far has been confined to the spd approximation, mainly because this basis set gave best agreement with experimental data. In the sp approximation there are only small changes in the electron density-bond order matrix when the dihedral angle is varied. The $Sp_x^A - Sp_x^B$ bond order is essentially independent of the dihedral angle (as in the spd approximation). There is a small π bond order (0.08) between Sp_z^A and Sp_z^B at 90°, while the corresponding bond order is zero at 0 and 180°. The increase in π bond-order is, however, (according to CNDO) too small to affect the S–S bond length.

II. *The S–S bond length in simple disulfides*, XSSX. The results in Fig. 1 show that the S–S

Table 1. Electron densities, bond-orders,[a] and bond indices[b] for HSSH as a function of dihedral angle at optimum S–S bond lengths. Sulfur $3d$-orbitals are included.

Dihedral angle (°)	0	30	60	90	120	150	180
Electron densities							
Sp_x^A	1.87	1.78	1.70	1.68	1.71	1.79	1.86
Sd_{xy}^A	0.06	0.13	0.19	0.21	0.19	0.12	0.07
Hs^A	0.97	0.99	1.00	1.01	1.00	0.98	0.96
Bond orders [a]							
$Sp_z^A - Sp_z^B$	-0.4	0.07	0.16	0.20	0.17	0.04	$-.05$
$Sd_{xy}^A - Sp_y^B$	0.25	0.38	0.53	0.60	0.53	0.37	0.26
$Sp_y^A - Hs^A$	0.88	0.87	0.86	0.86	0.86	0.86	0.86
Bond indices [b]							
$W(S^A - S^B)$	1.66	1.82	1.97	2.03	1.96	1.83	1.75
$W(S^A - H^A)$	0.94	0.94	0.94	0.93	0.93	0.92	0.92

[a] Defined as the product of the bond order matrix element, $P_{\mu\nu}$, and the *sign* of the corresponding overlap integral, $S_{\mu\nu}$. [b] Bond indices according to Wiberg (Ref. 11), $W(A-B) = \sum_\mu^A \sum_\nu^B P_{\mu\nu}^2$.

Table 2. Calculated S — S bond lengths in simple disulfides compared with experimental results. All values are given in Å.

Molecule	Exp	With D^a Calc	Diff	Without D^a Calc	Diff
HSSH	2.055 [b]	1.875	0.18	2.14	− 0.085
CH_3SSCH_3	2.022 [c]	1.84	0.18	2.14	− 0.12
ClSSCl	1.931 [d]	1.80	0.13	2.13	− 0.20
FSSF	1.888 [e]	1.79	0.10	2.12	− 0.23

[a] Calculations were performed both with and without sulfur and chlorine 3d-orbitals. [b] Ref. 9. [c] Ref. 13. [d] Ref. 6. [e] Ref. 14.

bond length for HSSH is too short in the *spd* approximation and too long in the *sp* approximation. The differences between observed and calculated values at 90° are 0.18 and − 0.09 Å, respectively. However, we have shown above that the CNDO/2 method is able to reproduce relative bond length differences. In order to test this assumption further, the S — S bond lengths of the molecules CH_3SSCH_3, ClSSCl, and FSSF were optimized in the CNDO/2 scheme. In each case the remaining bonds and angles were fixed at the experimental values (Refs. 13, 6, and 14, respectively). The S — S bond lengths determined in this way are compared with the observed values in Table 2.

The experimental S — S bond lengths in Table 2 are seen to vary considerably with the disulfide substituents. Both basis sets are, however, able to reproduce the relative change in bond lengths fairly well, as is seen from the differences between observed and calculated values.

Kiers and Vos [15] have performed similar calculations in the *sp* approximation both for disulfides and oxy-disulfides. Although no specific compound is mentioned, the calculated bonds are found to be 0.10 to 0.13 Å longer than the observed values, in agreement with the results presented here.

The results obtained may now be discussed with reference to the calculated electronic properties. The electron density-bond order matrix for the molecules HSSH, CH_3SSCH_3, ClSSCl, and FSSF have been analysed and some relevant elements are given in Table 3. The dihedral angle is 90° for all compounds in order to facilitate comparison, and in each case the

data refer to the optimized S — S bonds in Table 2.

For the *spd* approximation it is seen that when X gets increasingly more electronegative there is a pronounced decrease of electron density

Table 3. Bonding properties in simple disulfides at their optimum S — S bond length. Dihedral angle is 90°.

	HSSH	CH_3SSCH_3	ClSSCl	FSSF
With D				
Electron densities				
Sp_z^A	1.68	1.52	1.28	1.13
Sd_{xy}^A	0.21	0.33	0.42	0.43
S_{tot}^A	5.99	6.04	5.91	5.78
Bond orders [a]				
$Sp_z^A - Sp_z^B$	0.83	0.80	0.79	0.79
$Sp_z^A - Sp_z^B$	0.20	0.29	0.42	0.56
$Sd_{xy}^A - Sp_y^B$	0.60	0.64	0.64	0.59
Bond indices [a]				
$W(S^A - S^B)$	2.03	2.25	2.49	2.76
$W(S^A - X^A)$	0.93	1.07	1.33	1.17
Without D				
Electron densities				
Sp_z^A	1.99	1.98	1.98	1.97
S_{tot}^A	6.03	6.04	5.90	5.78
Bond orders [a]				
$Sp_z^A - Sp_z^B$	0.92	0.90	0.89	0.88
$Sp_z^A - Sp_z^B$	0.08	0.07	0.13	0.16
Bond indices [a]				
$W(S^A - S^B)$	1.01	0.99	1.01	1.03
$W(S^A - X^A)$	0.99	1.01	0.98	0.94

[a] Bond orders and bond indices are defined as in Table 1.

in the $Sp_x{}^A$ "lone-pair" orbital (see Fig. 2). The electron density is partly back donated into the $Sd_{xy}{}^A$ orbital and partly transferred to the substituents. This is accompanied by a net increase in $Sp_x{}^A - Sp_z{}^B$ bond order. The $Sd_{xy}{}^A - Sp_y{}^B$ bond order is substantial, but does not change much with substituents. The same is noted for the $Sp_x{}^A - Sp_x{}^B$ bond order. Thus the shortening of the $S-S$ bond length in these molecules (according to CNDO/2) may be explained almost entirely in terms of a net increase in $p-p$ π bonding due to delocalization of the lone-pair electrons.

In the sp approximation the decrease of the $Sp_x{}^A$ orbital is less pronounced. There is, however, an increase in $Sp_x{}^A - Sp_z{}^B$ bond order, and this seems to be responsible for the decrease in bond lengths. In both basis sets the increase in π bonding is reflected in the $W(S^A - S^B)$ bond index.

The discrepancies between observed and calculated bond lengths in Table 2, may in part be due to the choice of $3d$ orbital exponents given to the Slater-type orbitals used here. The CNDO treatment depends markedly on the values assigned to overlap integrals, and hence on the orbital exponents.[16] In the spd approximation the $3d$ orbital exponents are taken to be identical to those of $3s$ and $3p$ orbitals and regarded as being maximally contracted. The sp approximation is equivalent to setting the exponents to zero. Thus the importance of $3d$ orbitals are most probably over-emphasized in these calculations. The results in Table 1, for example, indicate quite substantial $3d$ orbital contribution in HSSH, while large basis set *ab initio* calculations show only modest occupation of sulfur $3d$ orbitals.[12]

CONCLUSIONS

CNDO/2 calculations on the dihedral angle/bond length dependence in HSSH give results in better qualitative agreement with experimental data when sulfur $3d$ orbitals are included in the basis set. This is mainly because of $p-d$ π bonding which is most pronounced when the dihedral angle is 90°.

Calculations on simple disulphides, XSSX, where $X = H$, CH_3, Cl, and F, show that the relative decrease in $S-S$ bond length is reproduced fairly well. The shortening observed

in these molecules is explained to be due to increasing $p-p$ π bonding. The bond lengths are, however, calculated to be too short when $3d$ orbitals are used and too long when they are omitted. Sulfur $3d$ orbitals may, therefore, be important for the description of the geometry of disulfides, but they are most probably overemphasized in the conventional CNDO/2 parametrization.

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