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ROLE OF SULFUR d ORBITALS IN THE S···N BOND STABILITY OF AMMONIOALKYLSULFURANES

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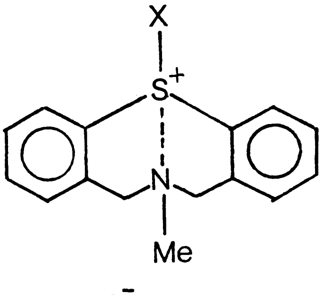
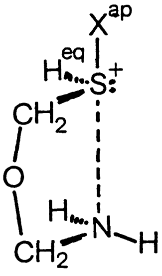
Using $H_2NCH_2OCH_2SHX^+$ (X=H and Cl) as model compounds, we examined the role of sulfur d orbitals on the stability of S···N bonded cyclic ammonioalkylsulfuranes. The ab initio Hartree-Fock calculation with sulfur d orbitals gives a cyclic structure, while the calculation without d causes breaking of the S···N bond.

Akiba et al.1) have recently prepared and determined the molecular structure of σ-ammonioalkylsulfuranes of the general form **1**.



1 : X = O^-, Me, OMe



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2a : X=H
2b : X=Cl

The short S···N distance found, 2.2-2.6 Å, clearly indicates the existence of direct interaction between the amino and the sulfonio group. One also notes that the geometry around the sulfur is essentially trigonal bipyramidal.

The origin of this S···N bond is the topics of the present paper. We will adopt **2** as the model compound and show that d orbitals on the sulfur atom are essential in stabilizing the S···N bond. Using the energy gradient in the ab initio Hartree-Fock method2) with the 4-31G basis set augmented with a set of Gaussian d functions on both S (exponent α=0.6) and N (α=0.8) (called the basis set A), we fully optimized the geometry of **2a**. The result, shown in Fig. 1, has a cyclic structure with an S•••N distance of 2.89_5 Å and the sulfur atom nearly trigonal bipyramidal. The S•••N distance changes little to 2.90_2 Å if the nitrogen d orbitals are removed (Set B). When the sulfur d orbitals are omitted as well (Set C), the geometry reoptimization starting from the structure of Fig. 1 causes the S•••N bond to break; after 10 iterations the S•••N distance is 4.0 Å, still falling apart. In order to test whether this difference is really due to d orbitals but not to the insufficiency of basis functions, the same reoptimization was carried out with an extended sp basis set on S((12s9p) /[7s5p]) and on N((10s6p)/[5s4p]). This also led to the dissociation of the S•••N bond. These results indicate that the sulfur d orbitals play the critical role in the stabilization of the S•••N bond in ammonioalkylsulfuranes.

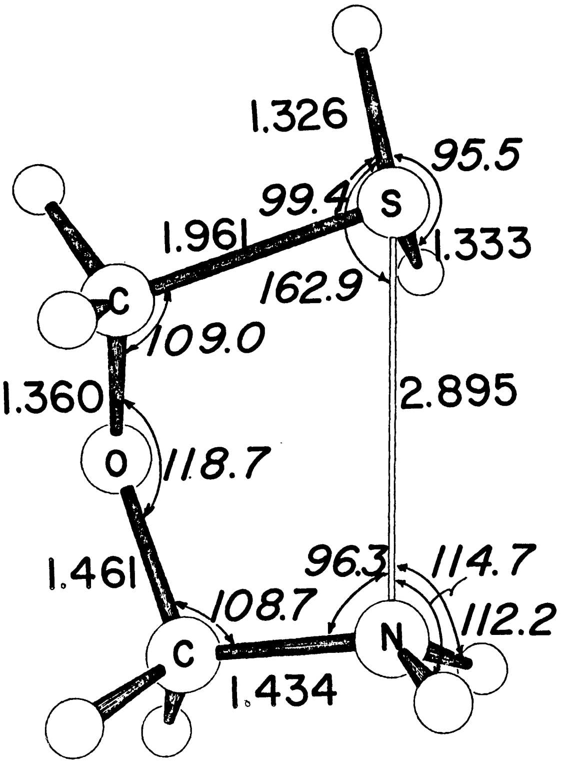


Fig. 1. The geometry of **2a**, optimized with d orbitals (the basis set A), with bond distances in Å and angles in degrees.

For X=Cl, **2b**, the Set B optimization gives the S•••N distance of 2.53 Å. This is consistent with the experimental trend that the bond becomes shorter as the electron withdrawing effect of X increases.$^{1)}$

In order to clarify the origin of the S•••N interaction, we consider a model complex $H_3N{\cdots}SH_3^+$. When the geometry of the complex is optimized with d orbitals (Basis set A), as shown in Fig. 2, the NH_3 lone pair approaches the sulfur from the direction nearly opposite to one of the S-H bonds. Apparently

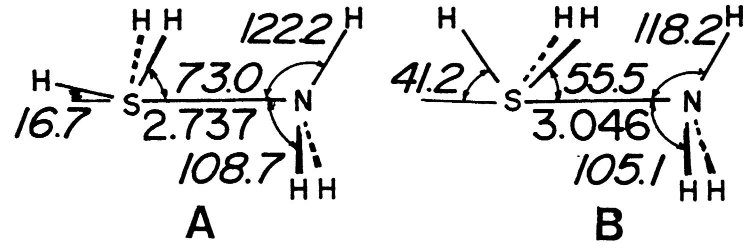


Fig. 2. Optimized geometries of $H_3S^+\cdots NH_3$ complex (I) with d orbitals and (II) without. Bond distances in Å and angles in degrees.

the role of the connecting chain CH_2OCH_2 is to clamp both ends so that the nitrogen lone pair can approach the sulfur from a favorable direction. Actual compounds 1 studied experimentally have two connecting chains, a more rigid and favorable situation. One notes in Fig. 2 that the optimization without d orbitals (Basis set C) leads to a much longer S···N bond and a non-linear H-S···N.

The energy component analysis$^{3)}$ for the $H_3S^+\cdots NH_3$ complex, given in Table 1, indicates that the S···N binding energy (e.g. -22 kcal/mol at 2.7 Å) originates mainly from the electrostatic + exchange interaction and the charge transfer interaction. The difference in the S···N bond stability (e.g. -4.9 kcal/mol) between calculations with and without d orbitals also comes similarly from the electrostatic + exchange and the charge transfer interaction Though the Mulliken population indicates that the contribution of the charge transfer configuration $H_3S-N^+H_3$ is only about 5% at 2.7 Å, it is enough to create substantial binding. Without d orbitals, the trigonal bipyramidal sulfur atom essentially has sp^2-hybridized σ orbitals in the trigonal plane and a pure p_z orbital perpendicular to it. When d orbitals are available, the d_{z^2} orbital mixes with the p_z orbital to form two pd hybrids. With one of them the $S-X^{ap}$ σ

Table 1. Energy Decomposition Analysis for $H_3S^+\cdots NH_3$ at R_{SN}=2.7 Å(kcal/mol)

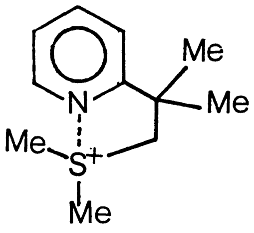
Basis set	4-31G with/without d on S		
	with	without	Δ
ΔE	-22.1	-17.2	-4.9
ES	-26.7	-24.4	-2.3
EX	+13.6	+14.0	-0.4
CT	-6.2	-4.7	-1.5
PL	-2.9	-2.5	-0.4
MIX	+0.1	+0.4	-0.3

bond becomes more localized in the S-X region than with the pure p_z, exposing the sulfur positive charge and making the electrostatic interaction with the nitrogen lone pair more favorable. The other pd hybrid is used as the acceptor orbital for charge transfer from the nitrogen lone pair. The sulfur d_{z^2} Mulliken population for **2a** is 0.06e, suggesting that the d participation is not very large but, nontheless, is significant enough to cause a drastic geometry change.

The present situation is quite different from the well-known case of SH_4. Ab initio calculations have shown that d orbitals shorten the S-H distance (C_{4v} geometry) by only 0.05 Å.4) Resembling the present example more closely is SH_5^+. The geometry optimization with d orbitals (Set B) gives an equilibrium geometry of trigonal bipyramidal structure with the $S\text{-}H^{ap}$ and $S\text{-}H^{eq}$ distance of 1.38_9 and 1.35_2 Å, respectively. Without d orbitals the $S\text{-}H^{eq}$ distance increases to 1.50_3 Å, while the $S\text{-}H^{ap}$ distance changes little to 1.40_0 Å.

The present calculations suggest that for N···S interactions to take place, the ring structure containing S and N atoms as in **1** is not indispensable, since the open chain model compound **2** is calculated to make an N···S bond. A very recent experiment by Akiba et al. suggests that in an open chain compound **3** N and S are in fact located nearby in the crystal. One also notes that a similar S···N interaction has been found in the X-ray study of $CH_3C(=O)NHCH_2C(=S)SC_2H_5$.6)

Numerical calculations were carried out at the IMS Computer Center.



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