Tetraamidosulfurane and its Decomposition Products — an ab initio MO Study[‡]

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Ab initio MO calculations at the G3(MP2) level of theory show that sulfur tetraamide $S(NH_2)_4$ is a local minimum energy structure but thermodynamically unstable with respect to both sulfur diamide $S(NH_2)_2$ plus hydrazine and sulfurimidediamide $S(NH)(NH_2)_2$ plus ammonia. The activation enthalpy of the latter reaction is 63 kJ·mol^{-1} at 298 K.
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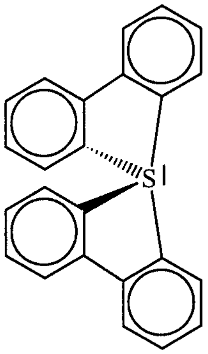
Introduction

The hypercoordinate compounds of sulfur — also termed as hypervalent — have attracted much attention owing to their unusual bonding situation with formal violation of the octet rule. In particular, sulfur hexafluoride has been investigated theoretically many times. It is now generally accepted that the covalent bonds in this species can be understood on the basis of multi-center interactions of the 3s and 3p atomic orbitals of sulfur with the 2p orbitals of the fluorine atoms, while the high-energy sulfur 3d valence orbitals play a minor role and, to a first approximation, can be neglected, although d and f functions serve as polarization functions in the basis sets used.[1] Compounds of this type are, however, thermodynamically stable only with highly electronegative substituents. The same holds for sulfuranes of the type SX_4, of which many derivatives have been prepared. Examples are SF_4,[2] $SClF_3$,[3] SCl_2F_2,[3] SCl_3F[3] and a large number of tetraoxosulfuranes with bidentate ligands.[4] Tetrachlorosulfurane (SCl_4) is thermodynamically unstable with respect to SCl_2 and Cl_2.[2] Therefore, SCl_4 is still unknown and the same holds for SMe_4,[5] $S(SH)_4$ [6] and SH_4.[7] However, in favorable cases, sulfuranes with substituents of low electronegativity can be prepared, as the successful synthesis of bis(2,2′-biphenylylene)sulfurane has demonstrated.[8]



If there is a high enough barrier for the decomposition of SX_4 to the corresponding sulfane (SX_2) and X_2 the molecule SX_4 should be accessible experimentally even if unstable in a thermodynamic sense.

The missing sulfuranes with four identical first-row atoms attached to sulfur are the tetraamidosulfurane $S(NH_2)_4$ and substituted organic derivatives thereof. The electronegativity of nitrogen is slightly higher than that of chlorine on the scales published by Allred[9] and by Allen[10] and should sufficiently stabilize such a structure. Therefore, we have explored for the first time the structure and stability of $S(NH_2)_4$ which represents one of the most basic structures in the very rich chemistry of sulfur-nitrogen compounds.[11] In this context we have also studied the related imidodiamide $S(NH)(NH_2)_2$ and the diamide $S(NH_2)_2$, which are both hypothetical compounds but probable decomposition products of $S(NH_2)_4$. So far, only the sulfurdiamide has been studied by theoretical methods: Leroy et al. reported calculations at the MP2(full)/6-31G(d,p) level of theory resulting in a C_{2v} symmetry for $S(NH_2)_2$, although they did not publish any geometrical details.[12] Kontopoulos and Sigalas[13] optimized the geometry of $S(NH_2)_2$

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at the MP2/3-21+G(d,p) level and reported two bond lengths and three bond angles but neither the molecular symmetry nor any torsion angles were published. It seems that the latter authors either assumed or obtained the molecular symmetry C_{2v} but the exact geometry remains unknown since two conformations of this symmetry are possible (see below). Partly and fully organyl-substituted derivatives of **1** are known.[11]

Calculations

Standard ab initio MO calculations were performed using the Gaussian 98[14] series of programs. The energies of various equilibrium structures and transition states were examined at the G3(MP2) level of theory.[15] In brief, the G3(MP2) method is a composite procedure which provides an accurate approximation to the high level of theory at QCISD(T)/GTMP2LARGE//MP2(full)/6-31G(d), with the incorporation of zero-point energy [calculated from HF/6-31G(d) vibrational wavenumbers, scaled by 0.8929] and higher level corrections. This level of theory is usually accurate to within 6 kJ·mol^{-1} of experimental values.[15] A charge density analysis, at the MP2(full)/6-31G* level, was performed using the natural bond orbital (NBO) approach.[16] Unless otherwise noted, all relative energies reported in this publication are given as $\Delta H°_{298}$ and correspond to the G3(MP2) level, while structural parameters were obtained at the MP2(full)/6-31G* level. The harmonic vibrational wavenumbers of $S(NH_2)_2$, $S(NH)(NH_2)_2$ and $S(NH_2)_4$ were calculated at the same level.

Results and Discussion

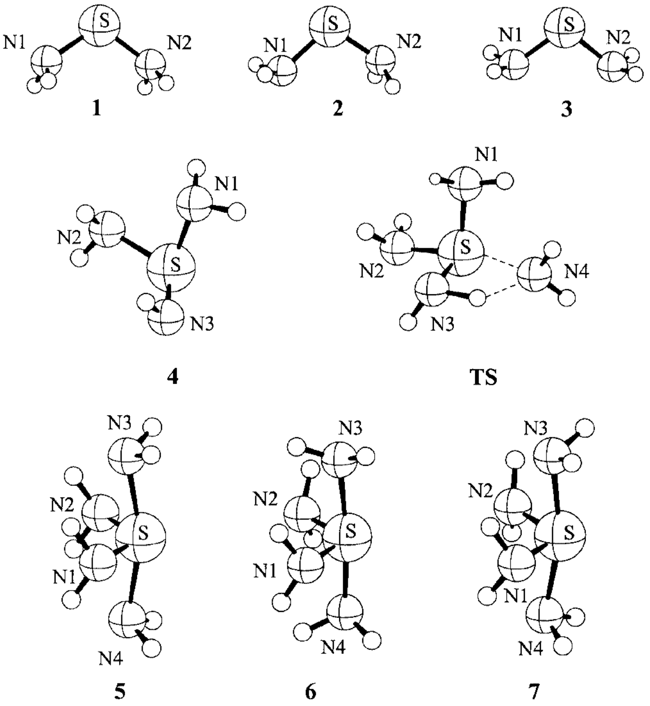

Figure 1. Structures of various rotamers of $S(NH_2)_2$ (**1**−**3**) and $S(NH_2)_4$ (**5**−**7**) as well as structure as $S(NH)(NH_2)_2$ (**4**) and of the transition state **TS** for the formation of **4** from **5**, calculated at the MP2(full)/6-31G* level

The structures of $S(NH_2)_2$, $S(NH)(NH_2)_2$ and $S(NH_2)_4$ are shown in Figure 1; selected geometrical parameters are given in Table 1. At the global minimum the diamide has C_{2v} symmetry (**1**), although two rotational isomers **2** (C_s) and **3** (C_{2v}) also exist. While **1** and **2** are almost degenerate ($\Delta H°_{298}$ = 1 kJ·mol^{-1}), isomer **3** is less stable than **1** by 9 kJ·mol^{-1} (Table 2), probably as the result of the repulsion between the nitrogen lone pairs which are directed towards each other. In all three conformers the nitrogen lone pairs are orthogonal to the sulfur 3p lone pair, which is expected to occupy the HOMO of these molecules. In the most stable isomer **1** the NBO atomic charges on sulfur, nitrogen and hydrogen are +0.61, −1.03 and +0.36, respectively. The geometrical parameters all have normal values.

The imidodiamide **4** has no symmetry at all (C_1). The S=N bond length of 155.0 pm is considerably shorter than the two formal S−N single bonds of length 173.4 and 174.5 pm. The orientation of the two amido groups seems to be influenced by weak N−H···N hydrogen bonds between N1 and a hydrogen on N2 (250.2 pm) and between N2 and a

Table 1. Selected geometrical parameters of the most stable isomers of $S(NH_2)_2$, $S(NH)(NH_2)_2$ and $S(NH_2)_4$ and of the transition state **TS** for the ammonia extrusion reaction (bond lengths in pm, bond angles and torsion angles in degree); for numbering of atoms see Figure 1

	$S(NH_2)_2$ **1** (C_{2v})	$S(NH)(NH_2)_2$ **4** (C_1)	$S(NH_2)_4$ **5** (C_{2v})	**TS** (C_1)
S−N1	169.6	174.5	169.8	169.6
S−N2	169.6	173.4	169.8	172.3
S−N3		155.0	191.4	166.9
S−N4			191.4	234.9
N−H	101.6	102.1−102.9	102.0(eq)/102.6(ax)	102.0−102.6
N1−S−N2	110.5	87.9	116.9	98.4
N1−S−N3		118.7	85.5	105.5
N1−S−N4			85.5	87.6
N2−S−N3		106.4	85.5	94.3
H−N−H	111.4	109.1±0.2	103.9(ax)/111.4(eq)	
S−N−H	115.0	112.3(S=NH)		108.9(S=NH)

Table 2. Relative energies and enthalpies (kJ·mol^{-1}) of $S(NH_2)_2$ and $S(NH_2)_4$; the absolute energies of **1** and **5** are −509.47982 and −621.15958 hartree, respectively

G3(MP2)	ΔE^o_0	ΔH°_{298}	ΔG°_{298}
$S(NH_2)_2$ **1**	0	0	0
$S(NH_2)_2$ **2**	1	1	1
$S(NH_2)_2$ **3**	8	9	8
$S(NH_2)_4$ **5**	0	0	0
$S(NH_2)_4$ **6**	12	12	11
$S(NH_2)_4$ **7**	14	15	13

hydrogen on N1 (249.4 pm); the N···H bond lengths given in parentheses are slightly shorter than the sum of the van der Waals radii (270 pm). The NBO atomic charges are +1.52 on sulfur, −1.14 on the amido nitrogens and −1.22 on the imido nitrogen. The four amido hydrogen atoms (+0.40) are slightly more positive than the imido hydrogen (+0.36). Salts containing the anion $S(NR)_3{}^{2-}$ — formally the substituted dianion of **4** — have been prepared recently.[17]

The tetraamide exists as three conformers: the most stable one is of C_{2v} symmetry (**5**) while the other two are of C_s symmetry (**6** and **7**). Their structures are in agreement with the expectations from VSEPR theory placing the lone pair at sulfur in an equatorial position of the trigonal bipyramids. The two axial substituents are bent towards the equatorial ones with $N_{ax}-S-N_{ax}$ bond angles of 162.7° (**5**), 165.4° (**7**) and 171.1° (**6**). The most symmetrical structure **5** seems to be stabilized by four N···H hydrogen bonds of length 215.8 pm between the axial nitrogens and the hydrogen atoms of the equatorial amido groups. However, since these bridges are bent by 94.4° and not aligned with the axes of the lone pair orbitals on the nitrogen atoms the hydrogen bonds will be weak. Interestingly, the two equatorial amido groups together with the sulfur atom have the same conformation as the most stable conformer of $S(NH_2)_2$ **1**. There are no indications for hydrogen bonds in rotational isomer **6**; however, four short N···H contacts of 216 pm (two) and 227 pm (two) can be recognized in **7**. However, for these interactions the same geometrical restrictions hold true as mentioned above in the case of isomer **5**. The absolute and relative energies of the di- and tetraamides are given in Table 2.

Table 3. Reaction energies and enthalpies (kJ·mol^{-1}) for the decomposition of $S(NH_2)_4$ **5**. The absolute energies of **TS**, $S(NH)(NH_2)_2$, N_2H_4 and NH_3 are −621.13591, −564.72321, −111.69962, and −56.47014 hartree, respectively

G3(MP2):	ΔE^o_0	ΔH°_{298}	ΔG°_{298}
$S(NH_2)_4 \rightarrow S(NH_2)_2$ **1** + N_2H_4	−52	−48	−102
$S(NH_2)_4 \rightarrow$ **TS**	62	63	62
$S(NH_2)_4 \rightarrow S(NH)(NH_2)_2 + NH_3$	−87	−83	−134

The data presented in Table 3 demonstrate that tetraamidosulfurane is thermodynamically unstable with respect to a decomposition both to the diamide plus hydrazine and to the imidodiamide plus ammonia. The latter reaction is clearly favored with a reaction enthalpy of −83 kJ·mol^{-1} compared to only −48 kJ·mol^{-1} for the hydrazine extrusion.

The transition state (**TS**) for the ammonia elimination has been located; its structure is shown in Figure 1. The reaction begins with a transformation of **5** into **7**. Then, one of the axial S−N bonds increases from 191.3 pm in the sulfurane **7** to 243.9 pm in **TS** while one hydrogen atom of an equatorial amido group forms a bridge to the leaving axial NH_2 group with N···H distances of 117.2 (to N3) and 145.6 pm (to N4). The angle N3−H−N4 is 133.6°. Thus, the formation of NH_3 can clearly be recognized in the structure of **TS**, which is of C_1 symmetry. Simultaneously, the other axial S−N bond decreases in length from 191.3 pm in **7** to 172.3 pm in **TS**. The activation enthalpy at 298 K with respect to the most stable conformer **5** is 63 kJ·mol^{-1}. Thus, it is surprising that $S(NH_2)_4$ has not been prepared yet.

Unexpectedly, the decomposition of **5** to hydrazine and sulfurdiamide is also strongly exothermic despite the weak N−N bond in hydrazine. Despite numerous attempts, at various levels of theory, we did not succeed in locating a transition state for this reaction on the potential energy hypersurface. Instead, the formation of ammonia was always the preferred reaction. If the NH distances were kept con-

Table 4. Calculated harmonic fundamental modes (cm^{-1}) of the most stable conformers of $S(NH_2)_2$, $S(NH)(NH_2)_2$ and $S(NH_2)_4$ [unscaled; MP2(full)/6-31G* level]; infrared intensities in parentheses (km mol^{-1})

$S(NH_2)_2$ **1** (C_{2v})	$S(NH)(NH_2)_2$ **4** (C_1)	$S(NH_2)_4$ **5** (C_{2v})
symm.: 3544(1), 3540(3), 1690(27), 1676(2), 921(86), 868(5), 640(30), 564(547), 330(1)	3616(16), 3604(17), 3496(16), 3474(10), 3438(2), 1652(13), 1645(96), 1224(19), 1167(41), 1087(30), 1067(200), 921(145), 905(103), 716(99), 712(123), 660(306), 461(14), 404(23), 389(23), 303(23), 276(1)	symm.: 3547(1), 3500(29), 3495(2), 3439(1), 1680(3), 1646(163), 1636(8), 1026(28), 1005(31), 972(93), 920(125), 769(448), 740(0), 475(1), 412(4), 372(38), 313(25), 234(0)
asymm.: 3666(0), 3660(28), 1123(6), 1118(0), 527(78), 451(0)		asymm.: 3622(89), 3621(0), 3546(0), 3440(9), 1667(39), 1239(67), 1175(0), 973(0), 925(230), 601(354), 522(0), 466(73), 404(10), 397(0), 273(0)

stant to suppress the NH_3 formation the only transition states found were those for the pyramidal inversion at the nitrogen atoms. Furthermore, the transition states for the decomposition of SF_4, SCl_4 and $S(SMe)_4$ were used to design the starting geometries for the wanted transition state,but these attempts also failed.

The thermodynamic instability of $S(NH_2)_4$ may be explained by the weakness of the two axial S−N bonds, which can be estimated from their rather long bond lengths (191.4 pm in **5**) compared to those of the equatorial bonds (169.8 pm) and to the S−N bonds in $S(NH_2)_2$ (169.6 pm in **1**). The gain in entropy also favors the two decomposition reactions.

To support future preparative work on these compounds the knowledge of the fundamental harmonic vibrational modes may be helpful. These data are given in Table 4.

Acknowledgments

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