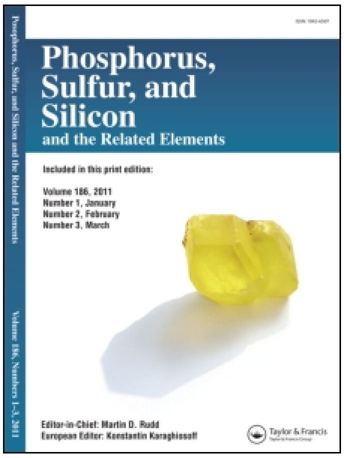

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Yana Drozdova; Ralf Steudel

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CYCLIC SULFUR IMIDES: WHEN AND WHY IS THE GEOMETRY AT NITROGEN PLANAR? – AN AB-INITIO STUDY[1]

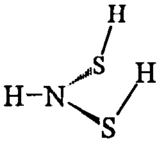
YANA DROZDOVA and RALF STEUDEL*
Institut für Anorganische und Analytische Chemie,
Technische Universität Berlin, D-10623 Germany

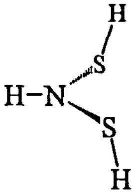
Negative hyperconjugation of the type $n_N \rightarrow \sigma^*$ is responsible for the planar or almost planar geometry at nitrogen in certain S–N compounds.

Keywords: Ab-initio MO calculations; S–N heterocycles

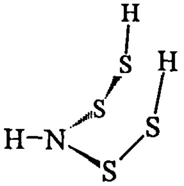
While most derivatives of ammonia are pyramidal at nitrogen certain sulfur imides show a planar or almost planar geometry at N (sum of bond angles $\Sigma\alpha > 350°$). Examples are the heterocycles S_7NH (357°)[2], S_9NH (357°)[3] and Cp_2TiS_7NMe (353°)[4]. Obviously, in these molecules the lone pair at N is partly delocalized into empty orbitals at neighboring atoms. To identify the nature of these empty orbitals the sulfenamide $HS{-}NH_2$ has previously been studied as a model compound. In the vapor phase $HSNH_2$ exists as *syn* ($\Sigma\alpha = 337°$) and *anti* (331°) conformers which both are of C_s symmetry[5]. The larger $\Sigma\alpha$ compared to NH_3 (323°) and the considerable torsional barrier of the S–N bond have been explained by a negative hyperconjugation of the nitrogen lone pair into the antibonding molecular orbital of the SH bond ($n_N \rightarrow \sigma^*_{SH}$).[6]

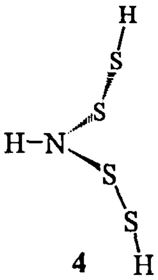
To further prove this hypothesis we have carried out ab-initio MO calculations at the MP2/6-311G**//MP2/6-311G** level of theory on several model compounds and obtained the following geometries and relative energies:





	1	**2**
$\Sigma\alpha$:	350°	360°
E_{rel}:	0	4 kJ mol^{-1}



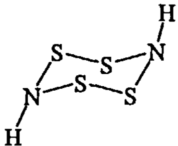


	3	**4**
$\Sigma\alpha$:	358°	360°
E_{rel}:	1	0 kJ mol^{-1}

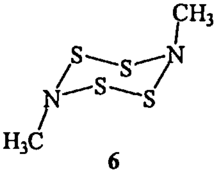
These structures may be interpreted as follows: In **2** the delocalization of the electrons from n_N is most efficient since the upper lobe of the lone-pair *p*-type orbital at N can overlap with the σ* orbital of one SH bond and the lower lobe with σ* of the other SH bond. In **1**, on the other hand, only one lobe of the lone pair orbital can interact with the two σ^*_{SH} orbitals. Therefore, $\Sigma\alpha$ is larger for **2** compared to **1**.

The geometry of **3** simulates the situation in S_7NH and S_9NH. In these cases a negative hyperconjugation of the type $n_N \rightarrow \sigma^*_{SS}$ is proposed. Since $\Sigma\alpha$ of **3** and **4** are 358° and 360° it has to be concluded that the MOs σ^*_{SS} of **3** and **4** are better acceptor orbitals than the σ^*_{SH} MOs of **1** and **2**. We have carried out natural bond orbital (NBO) analyses [7] of the species **1-4** which are in agreement with the idea of hyperconjugation: the occupancy of the nitrogen lone pair orbital decreases from 2.00 in NH_3 via 1.94 in **1** and **2** to 1.90 in **3** and **4**.

In small *cycles* like **5** the optimum geometry for $n_N \rightarrow \sigma^*_{SS}$ hyperconjugation may not always be available. Consequently, $\Sigma\alpha$ may deviate considerably from 360° as is in fact the case with the species **5-7**:



5



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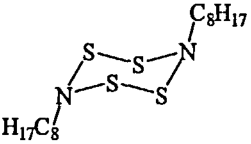

7

$\Sigma\alpha$: 346° 346° 344° (exp.)

The cycles **5** and **6** have been calculated at the level indicated above, while the *n*-octyl derivative **7** has been studied by an X-ray structural analysis [8]; in **5-7** the substituents are in axial positions. Calculated and experimental geometries agree very well.

Summarizing, it can be stated that the geometry at the nitrogen atoms of sulfur imides depends on the available acceptor orbitals for negative hyperconjugation as well as on the requirements for ring closure. Only in chain-like compounds and rings of size 8 and larger the optimum geometry can be achieved and consequently a naerly planar coordination at nitrogen atoms id observed.

Acknowledgment

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