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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## First Isolation and Molecular Structure of Sulfuranyl Dication Compounds $[8-S-4(C4)]^{2+}$

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Sulfuranyl dication species  $(R_4S^{2+}) \cdot 2X^-$  belong to the isoelectronic molecules of the silanes  $(R_4Si)$  and phosphonium salts  $(R_4P^+)X^-$ , but only a few studies have been presented to date. If the central sulfur atom of these compounds obeyed the Lewis octet rule, such as  $[8-S-4]^{2+}$ , they should have tetrahedral structures with  $sp^3$  hybridization of the sulfur atom.

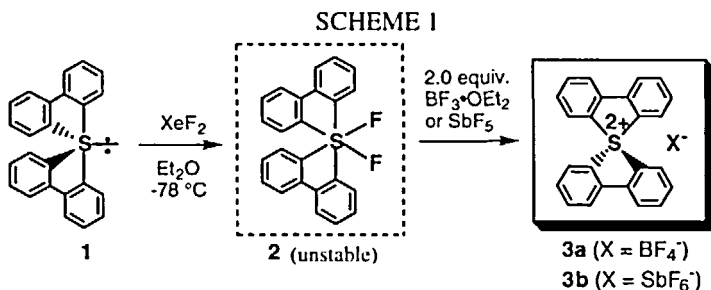
**Keywords:** sulfurane; persulfurane; sulfuranyl dication; hexavalent; X-ray crystallographic analysis; *ab initio* calculation

### Bis(2,2'-biphenylene)sulfuranyl Dication Compounds $[8-S-4]^{2+}$

Bis(2,2'-biphenylene)sulfurane **1** was reacted with 1 molar equiv. of xenon difluoride in the presence of  $BF_3 \cdot OEt_2$  or  $SbF_5$  in dry  $CH_3CN$  at  $-40^\circ C$  to give bis(2,2'-biphenylene)sulfurane bis(tetrafluoroborate) (**3a**) or bis(hexafluoroantimonate) (**3b**) as a stable moisture-insensitive yellow powder, respectively. The products **3a** and **3b** were identified by  $^1H$ ,  $^{13}C$ , and  $^{19}F$  NMR, mass spectroscopy and elemental analysis.

Examination of the  $^1H$  and  $^{13}C$  NMR spectra of the compounds **3a** and **3b** reveals that the two phenyl rings of the biphenylene groups are in

equivalent states. All of the  $^1\text{H}$  NMR chemical shifts appear at a unusually low field compared with those of the corresponding sulfurane **1**. Both of the respective  $^{11}\text{B}$  and/or  $^{19}\text{F}$  NMR spectra of **3a** and **3b** show only a single peak for the fluoro anions,  $\text{BF}_4^-$  or  $\text{SbF}_6^-$ . These results indicate that both **3a** and **3b** have a symmetrical structure and contain  $\text{BF}_4^-$  or  $\text{SbF}_6^-$  as a counter anion. Persulfurane **2** was detected as an unstable intermediate for the reaction of sulfurane **1** with  $\text{XeF}_2$  in a NMR tube during low temperature.



Furthermore, we have succeeded in determining the structure of the products **3a** and **3b** by X-ray crystallographic analysis. The central sulfur atom of each dication has a distorted tetrahedral bonding geometry with the two biphenylene groups. The least-square planes of two biphenylene groups in compounds **3a** and **3b** are perpendicular to each other. The average of S–C bond distance of **3a** is 1.753 Å and the bond angles range from 94.9(3) to 118.3(3)°.

#### Acknowledgment:

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