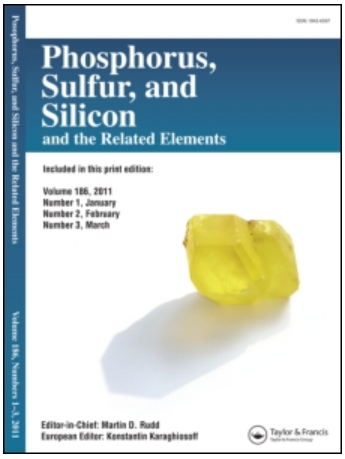


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Soichi Sato; Hitomi Ameta; Hironori Tsutsui; Kaoru Matsunaga; Ernst Horn; Naomichi Furukawa

To cite this Article Sato, Soichi , Ameta, Hitomi , Tsutsui, Hironori , Matsunaga, Kaoru , Horn, Ernst and Furukawa, Naomichi(1999) 'First Isolation and Molecular Structure of Sulfuranyl Dication Compounds $[8\text{-}S\text{-}4(C4)]^{2+}$', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 349 — 350
To link to this Article: DOI: 10.1080/10426509908546465
URL: http://dx.doi.org/10.1080/10426509908546465

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 349-350
Reprints available directly from the publisher
Photocopying permitted by license only

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

SOICHI SATO, HITOMI AMETA, HIRONORI TSUTSUI, KAORU MATSUNAGA, ERNST HORN and NAOMICHI FURUKAWA

Tsukuba Advanced Research Alliance Center and Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Sulfuranyl dication species (R_4S^{2+})•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.

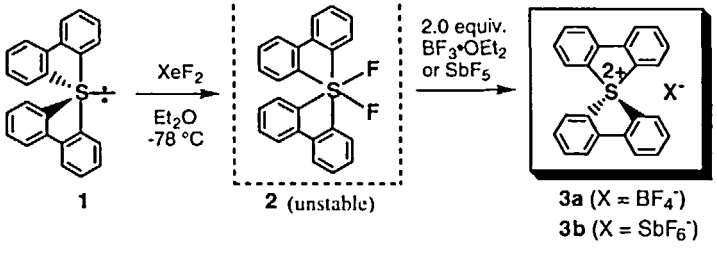
Keywords: sulfurane; persulfurane; sulfuranyl dication; hexavalent; X-ray crystallographic analysis; *ab initio* calculation

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

Bis(2,2'-biphenylylene)sulfurane **1** was reacted with 1 molar equiv. of xenon difluoride in the presence of BF_3•OEt_2 or SbF_5 in dry CH_3CN at –40 °C to give bis(2,2'-biphenylylene)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 biphenylylene groups are in

equivalent states. All of the ^{1}H NMR chemical shifts appear at a unusually low field compared with those of the corresponding sulfurane **1**. Both of the respective ^{11}B and /or ^{19}F NMR spectra of **3a** and **3b** show only a single peak for the fluoro anions, BF_4^- or SbF_6^-. These results indicate that both **3a** and **3b** have a symmetrical structure and contain BF_4^- or SbF_6^- as a counter anion. Persulfurane **2** was detected as an unstable intermediate for the reaction of sulfurane **1** with XeF_2 in a NMR tube during low temperature.

SCHEME 1



1 **2** (unstable) **3a** (X = BF_4^-) **3b** (X = SbF_6^-)

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 biphenylylene groups. The least-square planes of two biphenylylene 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:
This work was supported by the Ministry of Education, Science, Sports and Culture, Japan [Grant-in-Aid for Scientific Research on Priority area: Grant No. 09239104], the Fund of Tsukuba Advanced Research Alliance (TARA) project [University of Tsukuba] and Yamada Science Foundation for S. Sato.

References

Sato, S.; Ameta, H.; Horn, E.; Takahashi, O.; Furukawa, N. *J. Am. Chem. Soc.*, **119**, 12374 (1997).