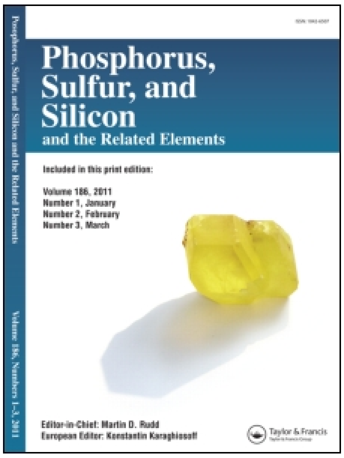


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactivities, Conformational Properties, and Molecular Structures of σ-Bonded Cyclic Selenurane Dications

Tsukasa Nakahodo; Ohgi Takahashi; Ernst Horn; Naomichi Furukawa

To cite this Article Nakahodo, Tsukasa , Takahashi, Ohgi , Horn, Ernst and Furukawa, Naomichi(1998) 'Reactivities, Conformational Properties, and Molecular Structures of σ-Bonded Cyclic Selenurane Dications', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 565 — 568

To link to this Article: DOI: 10.1080/10426509808545997

URL: http://dx.doi.org/10.1080/10426509808545997

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 565–568
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIVITIES, CONFORMATIONAL PROPERTIES, AND MOLECULAR STRUCTURES OF σ-BONDED CYCLIC SELENURANE DICATIONS

TSUKASA NAKAHODO, OHGI TAKAHASHI, ERNST HORN,
and NAOMICHI FURUKAWA
Department of Chemistry and Tsukuba Advanced Research Alliance Center, University of Tsukuba, Tsukuba, Ibaraki 305, Japan.

Abstruct: The synthesis of σ-selenurane dication salts *via* transannular interactions and the reactivities of these dication salts are described. The X-ray crystallographic analyses of the dication salts show that the dications have selenium atoms in a trigonal-bipyramidal bonding environment. *Ab initio* calculations carried out for the dication revealed that the selenium atoms exclusively carry the positive charge. The interesting conformational properties of these dications are also described.

Keywords: transannular interaction;, selenurane; dication; X-ray crystallographic analysis; three-center four-electron bond

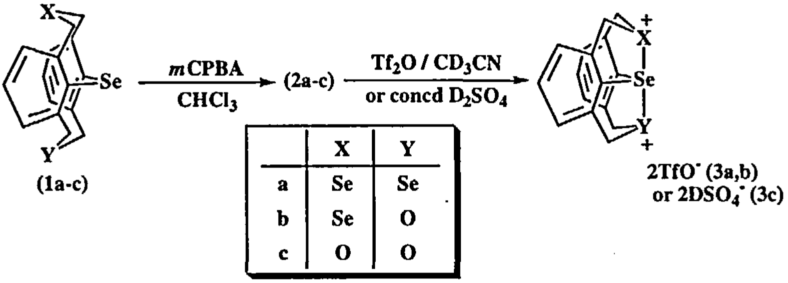
INTRODUCTION

Although it has been shown that the transannular interaction among three heteroatoms (Se-Se-Se or N-Se-N) of selenium heterocycles produces the dicationic σ-selenuranes,[1,2] similar behavior involving oxygen and chalcogen atoms has received less attention.[3] Recently, we have succeeded in the synthesis of oxygen- or selenium-bridged metacyclophane compounds (1a-c), analogous to 1,11-(methanoselenomethano)-*5H,7H*-dibenzo[*b,g*][1,5]-diselenocin.[4,5] The transannular interaction among three chalcogen atoms (O, Se) was investigated using the reaction of these selenide (1a-c) with oxidizing agent.

RESULTS AND DISCUSSION

The oxidation of these compounds (1a-c) with *m*CPBA afforded the corresponding mono-selenoxides (2a-c). When the mono-selenoxides (2a-c) were treated with trifluoromethanesulfonic anhydride in anhydrous CD_3CN or concentrated D_2SO_4 at room temperature, the transannular bond formation was observed by ^1H, ^{13}C, and ^{77}Se NMR spectra (Scheme 1).

SCHEME 1



	X	Y
a	Se	Se
b	Se	O
c	O	O

Especially, the oxidative reaction of chalcogenide (2c) provided a new type of σ-selenurane dication salt (3c) with two apical oxonio ligands. Fortunately, these new type of σ-selenurane dication salts (3a,b) were stable, and the suitable single-crystals of (3a) and (3b) for X-ray crystallographic analyses could be obtained by recrystallization from the CH_3CN solutions, respectively. In contrast to stable dicationic salts (3a,b), the dicationic salt having two apical oxonio ligands (3c) is too unstable to isolate. Therefore, the single-crystal of (3c) for X-ray crystallographic analysis could not be obtained. The crystal structure of dicationic salts (3a) and (3b) determined by X-ray crystallographic analyses showed that the dications have distorted boat-boat forms fixed by the three-center bond among the three chalcogen atoms. The central selenium atom shows a trigonal-bipyramidal bonding (Figure 1).

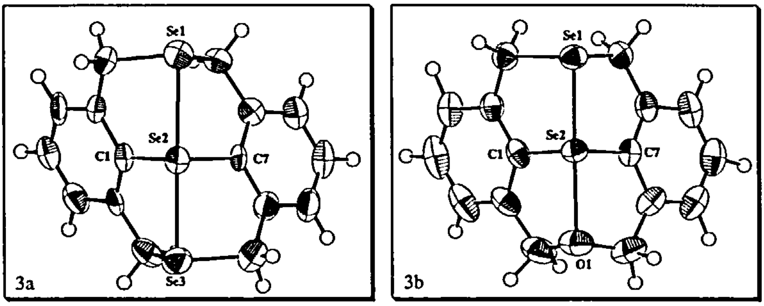
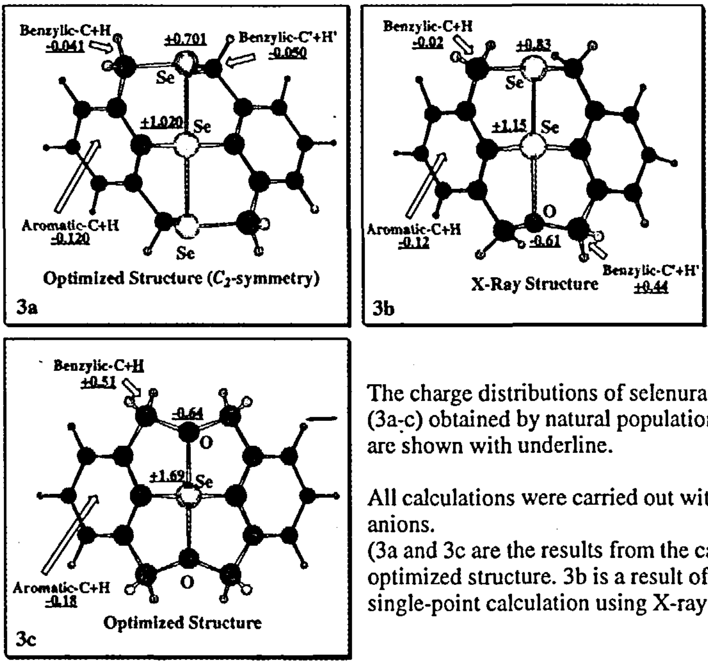


FIGURE 1. ORTEP view of 3a, and 3b.
(For clarity, the triflate anions are omitted.)

The respective Se-Se distances, 2.634(5) and 2.550(5) Å for Se1-Se2 and Se2-Se3 in (3a), are longer than the normal Se-Se single bond (2.34 Å) found in diselenides.[6] The bond length of Se1-Se2 in (3b) is 2.3857(7) Å which is only slightly longer than the nomal Se-Se single bond. The transannular O1-Se2 contact in (3b) is 2.426(3) Å which is remarkably shorter than the sum of van der Waals radii (3.4 Å) of the two elements. In order to understand the electronic structures of these dication salts, we carried out *ab initio* calculations using the 3-$21G^{(*)}$ basis set. The charge distribution obtained by natural population analysis is shown in Figure 2. Although the counterions were not included in the *ab initio* calculation, the calculated structure (3a) is in good agreement with the X-ray structure. We think that the electrostatic factor is dominant in the dication-counterions interaction. It should be noted that selenium atoms exclusively carry the positive charges in the absence of the counterions; a further accumulation of the positive charge induced by the counterions is not expected. The central selenium atom carries a more positive charge than the two apical selenium atoms in (3a), indicating that the two apical Se-Se bonds are highly polarized as in the neutral hypervalent molecules having a three-center four-electron (3c-4e) bond. Treatment of selenurane dication salts 3a and 3b with a reducing agent such as PhSH or SmI_2 generates the neutral state selenide 1a and 1b, respectively. Especially, the selenurane dication 3a undergoes a reversible two-electron reduction, which is a precedented reaction mode for selenuranes. Therefore, two-electron redox reaction of 3a is accompanied by conformational changes of the twin-chair and twinboat forms. This behavior may be suitable for novel systems with "molecular hysteresis", which could satisfactorily fulfil practical requirements,[7] and the dications 3b and 3c also may have such special features.



The charge distributions of selenurane dications (3a-c) obtained by natural population analyses are shown with underline.

All calculations were carried out without counter anions.
(3a and 3c are the results from the calculated optimized structure. 3b is a result of the single-point calculation using X-ray structure.)

FIGURE 2. The *ab initio* RHF calculations using 3-21G(*) basis set.

REFERENCES

[1.] H. Fujihara, H. Mima, T. Erata, and N. Furukawa, *J. Am. Chem. Soc.*, **114**, 3117 (1992).
[2.] H. Fujihara, H. Mima, T. Erata, and N. Furukawa, *J. Am. Chem. Soc.*, **115**, 9826 (1993).
[3.] H. Fujihara, T. Nakahodo, and N. Furukawa, *Tetrahedron Lett.*, **36**, 6275 (1995).
[4.] H. Fujihara, T. Nakahodo, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 311 (1996).
[5.] T. Nakahodo, O. Takahashi, E. Horn and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, 1767 (1997).
[6.] *The Chemistry of Organic Selenium and Tellurium Compounds*, vol. 1 and 2, ed. S. Patai and Z. Rappoport, Wiley, New York, 1986 and 1988.
[7.] M. Sano, H. Taube, *J. Am. Chem. Soc.*, **113**, 2327 (1991).