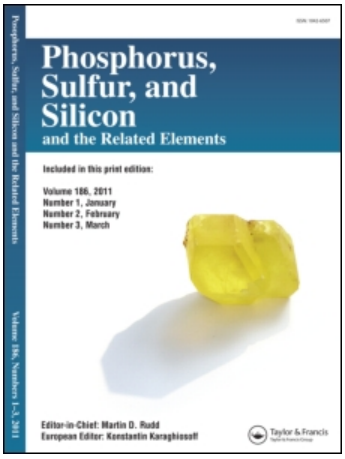


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Structures of Tetrasilsesquisulfides: Tetrakis(*tert*-butyl-silsesquisulfide) and Tetrakis((1,1,2-trimethylpropyl)silsesquisulfide)

Masafumi Unno; Hiroaki Shioyama; Hideyuki Matsumoto

To cite this Article Unno, Masafumi , Shioyama, Hiroaki and Matsumoto, Hideyuki(1997) 'Synthesis and Structures of Tetrasilsesquisulfides: Tetrakis(*tert*-butyl-silsesquisulfide) and Tetrakis((1,1,2-trimethylpropyl)silsesquisulfide)', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 377 — 378
To link to this Article: DOI: 10.1080/10426509708545556
URL: http://dx.doi.org/10.1080/10426509708545556

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 377–378
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Structures of Tetrasilsesquisulfides: Tetrakis(*tert*-butylsilsesquisulfide) and Tetrakis((1,1,2-trimethylpropyl)silsesquisulfide)

MASAFUMI UNNO, HIROAKI SHIOYAMA, AND HIDEYUKI MATSUMOTO*
Department of Applied Chemistry, Faculty of Engineering,
Gunma University, Kiryu, Gunma 376, JAPAN

Two tetra(alkylsilsesquisulfides) ($R_4Si_4S_6$, R = *t*-Bu, 1,1,2-trimethylpropyl) were synthesized. The structures were determined by X-ray crystallography and novel "double decker"-type structure was revealed for tetrakis((1,1,2-trimethylpropyl)-silsesquisulfide).

INTRODUCTION

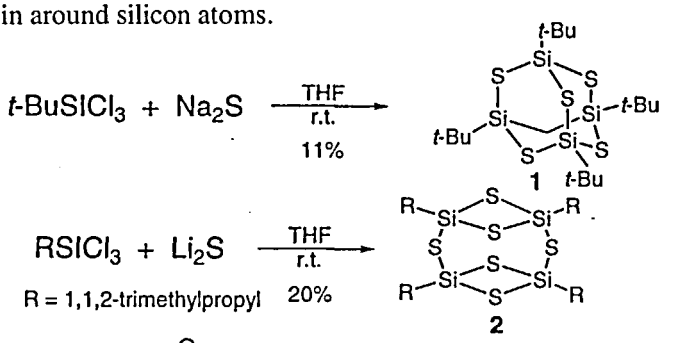
Cage silsesquioxanes are basically stable and various compounds with different sizes ($R_6Si_6O_9$, $R_8Si_8O_{12}$, $R_{10}Si_{10}O_{15}$) and with different substituents (H, alkyl, aryl, alkoxy) have been synthesized and characterized.[1] However, the chemistry of silicon-sulfur cage compounds are relatively much less known due to their susceptibility to hydrolysis. By introducing bulky groups, we have synthesized octasilacubane and related compounds and studied their unique reactions.[2] Here we report the synthesis and structures of silicon-sulfur cage compounds, tetrasilsesquisulfides.

RESULTS AND DISCUSSION

Until now, some tetrasilathianes were reported ($R_4Si_4S_6$, R = H, Me, Et, Ph, *t*-Bu) and all are known to possess adamantane-type structure.[3,4b] On the other hand, two structures are known in $R_4Ge_4S_6$. When R is methyl or mesityl, the structure is adamantane-type, but when R is *tert*-butyl, the structure is "double decker"-type.[4] For organic tetrasilathianes, no "double decker"-type structure has been reported.[5] In this paper, synthesis and structures of tetra(alkylsesquisulfides), ($R_4Si_4S_6$, **1**: R = *t*-Bu, **2**: R = 1,1,2-trimethylpropyl) are described.

Silsesquisulfides **1** or **2** was prepared by the reaction of trichlorosilane with Na_2S or Li_2S. The compounds are both remarkably stable and no decomposition was observed in the air at room temperature. The structures of **1** and **2** were determined by X-ray crystallography (Figure 1). The result revealed that **2** possesses novel "double decker"-type structure. The formation of this unique structure is thought to be due to

the bulkiness of the 1,1,2-trimethylpropyl groups, which makes smaller ring more favorable. Also unsymmetrical structure of the substituents may give contribution to the generation of **2**. Average Si-S bond lengths were similar for both structures (2.132 Å for **1** and 2.133 Å for **2**), and interestingly, the distance of two silicon atoms of the four-membered ring in **2** was 2.82 Å. This unusual short distance can be a result of the relief of the strain around silicon atoms.



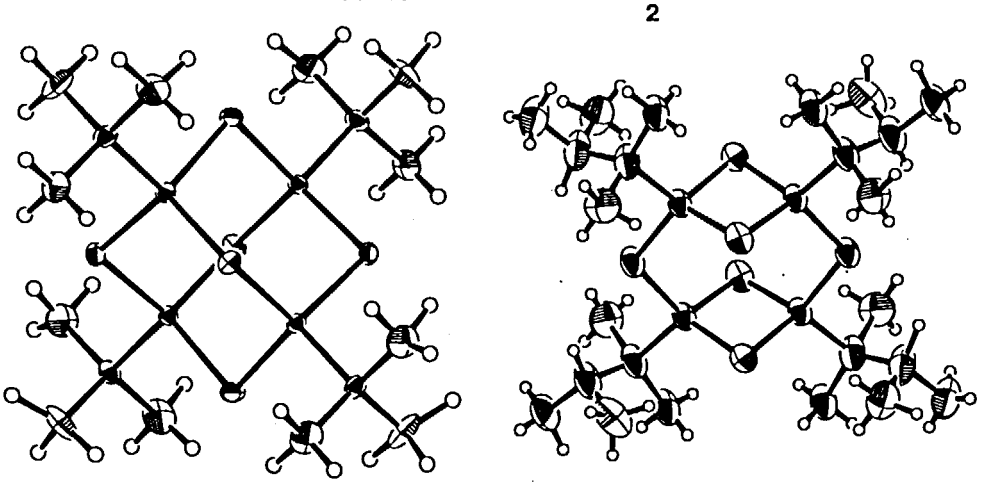


FIGURE 1 Thermal ellipsoids are drawn at the 30% probability level.

REFERENCES and NOTES

1. (a) U. Dittmar, B.J. Hendan, U. Floerke, and H.C. Marsmann, *J. Organomet. Chem.*, **489**, 185, (1995) and references cited therein. (b) M. Unno, S.B. Alias, H. Saito, and H. Matsumoto, *Organometallics*, **15**, 2413 (1996).
2. (a) M. Unno, K. Higuchi, M. Ida, H. Shioyama, S. Kyushin, H. Matsumoto, M. Goto, *Organometallics*, **13**, 4633 (1994). (b) M. Unno, H. Shioyama, M. Ida, and H. Matsumoto, *Organometallics*, **14**, 4004 (1995). (c) M. Unno, T. Yokota, and H. Matsumoto, *J. Organomet. Chem., in press* (1996).
3. J.C.J. Bart and J.J. Daly, *J. Chem. Soc., Dalton Trans.*, 2063 (1975), and references cited therein.
4. (a) W. Ando, T. Kadowaki, Y. Kabe, and M. Ishii, *Angew. Chem. Int. Ed. Engl.*, **31**, 59 (1992). (b) W. Ando, T. Kadowaki, A. Watanabe, N. Choi, Y. Kabe, T. Erata, and M. Ishii, *Nippon Kagaku Kaishi*, 223 (1994). Compound **1** is reported in this paper, however no structural information was given.
5. K. Merzweiler quoted the double-decker structure for iron-substituted tetrasilathiane, $\{Cp'(CO)_2Fe\}_4Si_4S_6$. K. Merzweiler, in *Organosilicon Chemistry II*, edited by N. Auner and J. Weis, (VCH, Weinheim, 1995), pp. 536-537.