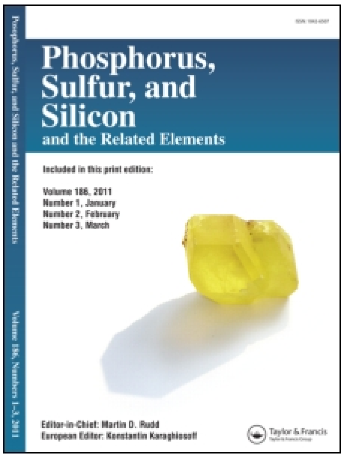
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Structural Variation Provided by Sulfur, Sulfinyl, and Sulfonyl Groups in Cyclic Silanes and Phosphoranes

Robert R. Holmes; A. Chandrasekaran; Roberta O. Day

To cite this Article Holmes, Robert R. , Chandrasekaran, A. and Day, Roberta O.(1997) 'Structural Variation Provided by Sulfur, Sulfinyl, and Sulfonyl Groups in Cyclic Silanes and Phosphoranes', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 431 — 432

To link to this Article: DOI: 10.1080/10426509708545583

URL: http://dx.doi.org/10.1080/10426509708545583

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

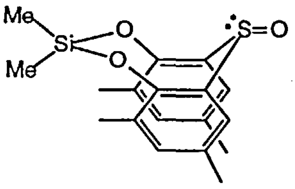
Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 431-432
Reprints available directly from the publisher
Photocopying permitted by license only

Structural Variation Provided by Sulfur, Sulfinyl, and Sulfonyl Groups in Cyclic Silanes and Phosphoranes

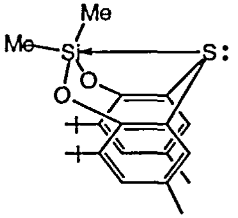
ROBERT R. HOLMES, A. CHANDRASEKARAN AND ROBERTA O. DAY

Department of Chemistry, Box 34510, University of Massachusetts, Amherst, MA 01003-4510 USA

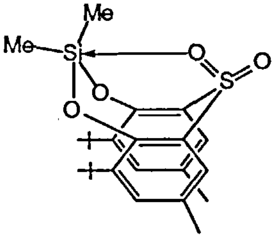
A series of new monocyclic diorganosilanes were prepared by condensation reactions of the appropriate diorganodichlorosilane with sulfur containing diols.[1-3] The eight-membered rings containing bridging sulfinyl groups[2] are positioned in *anti* chair-like conformations which precluded any additional coordination at silicon. This contrasts with silanes having sulfur[1] or sulfonyl[3] groups in place of sulfinyl in the ring system where Si–S or Si–O coordination was evident. In these molecules, X-ray studies showed[1,3] that the rings had *syn* boat-like conformations.



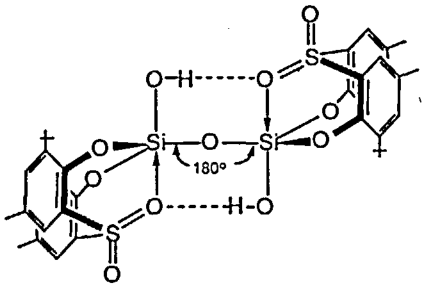
Si–S 3.615(1)Å



Si–S 3.074(1)Å



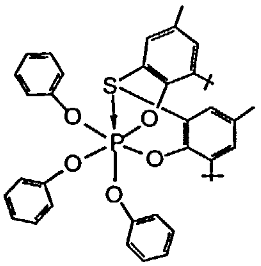
Si–O 2.841(2)Å



Si–O 2.898(3)Å

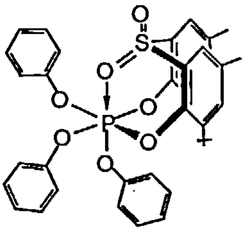
Likewise the cyclic disiloxane, $\{O_2S[(t\text{-Bu})MeC_6H_2O]_2Si(OH)\}_2O$, prepared as a hydrolysis product, possessed a similar pentacoordinate structure at each of the silicon centers.[3] The geometries are intermediate between a tetrahedron and a trigonal bipyramid.[1,3] Similar donor action is known with oxygen and nitrogen ligands in acyclic silanes.[4] In view of the reduced electronegativity of sulfur, the results suggest that the attainment of hypervalency through donor action may be a more common feature of silane chemistry than previously thought.[3]

In an analogous fashion, introduction of a sulfonyl group in a cyclic pentaoxyphosphorane leads to oxygen-phosphorus donor action with formation of octahedral phosphorus.[5] When these cyclic hexacoordinated phosphorus compounds that contain phenoxy ligands (*e.g.*, **2**) are reacted with catechols at 90°C, enhanced reactivity is observed compared to cyclic pentaoxyphosphoranes that contain trifluoroethoxy ligands (*e.g.*, **1**).[5] With a sulfur atom in place of a sulfonyl group (*e.g.*, **6**), reaction with catechols is even faster.[6] Investigation of the reaction process indicates an associative mechanism involving a seven-coordinated intermediate.[5]



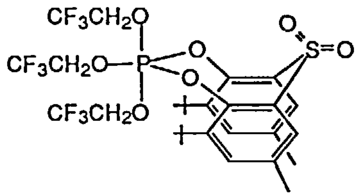
6

>



2

>>



1

Thus, introduction of either sulfur atoms or sulfonyl groups in ring components (that have *t*-butyl substituents) allows donor action that leads to increased coordination for both cyclic dioxysilanes and cyclic pentaoxyphosphoranes.

REFERENCES

1. N. V. Timosheva, T. K. Prakasha, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **35**, 3614 (1996).
2. A. Chandrasekaran, R. O. Day, and R. R. Holmes, "Structural Influence of a Sulfinyl Group in Eight-Membered Rings of Diorganosilanes," *Organometallics* **15**, July (1996).
3. A. Chandrasekaran, R. O. Day, and R. R. Holmes, "Structural Influence of a Sulfonyl Group in Eight-Membered Rings of Diorganosilanes," *Organometallics* **15**, July (1996).
4. R. R. Holmes, *Chem. Rev.*, **96**, 927 (1996), and references cited therein.
5. A. Chandrasekaran, R. O. Day, and R. R. Holmes, submitted for publication.
6. P. Sood, A. Chandrasekaran, R. O. Day, and R. R. Holmes, unpublished work.