We conclude that **1** and **2** reversibly isomerize through the intermediacy of E by single alkyne rotation. Although we cannot rule out D as being kinetically accessible, if formed it cannot be planar and has to be configurationally stable, since planarization would interconvert **1d** and **2e** and **1e** and **2d**.

Acknowledgment. This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division, of the U.S. Department of Energy under Contract No. W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, PA, and in part by NSF (CHE 79-03954). We are grateful for the astute comments of the referees.

---

(20) This system is in fact "hexalabeled" (two chiral, two silyl, two ^{13}C labels). **1d**: $J_{^{13}C-^{13}C} = 24.1$ Hz; $J_{^{13}C-^{13}CH} = 5.5$ Hz; $J_{^{13}C-H} = 177$ Hz. **2d**: $J_{^{13}C-^{13}C} = 2$ Hz; $J_{^{13}C-^{13}CH} = 9$ Hz; $J_{^{13}C-H} = 190$ Hz; as expected. Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980. Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: Philadelphia, 1978.

A New Geometrical Form of Silicon. Synthesis and Structure of Tetraethylammonium Bis(1,2-benzenediolato)fluorosilicate(IV)

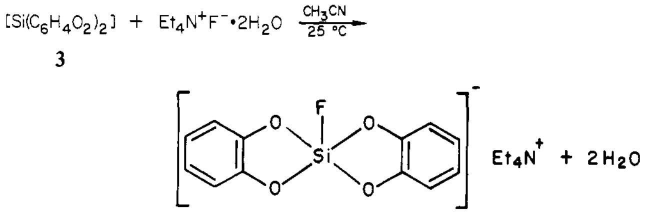
John J. Harland, Roberta O. Day, Jean F. Vollano,
Arjun C. Sau, and Robert R. Holmes*

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

Received May 4, 1981
Revised Manuscript Received June 29, 1981

Anionic pentacoordinated silicon compounds,[1] isoelectronic with phosphoranes, are extremely rare. Of those synthesized, X-ray structural characterization of a spirocyclic derivative $[(C_6H_4O_2)_2SiPh]^-Me_4N^+$ (**1**) has been reported[2] and reveals a trigonal-bipyramidal form displaced about one-third the way toward a square pyramid.

We report here the preparation and X-ray crystal structure of the first pentacoordinated Si(IV) compound having a square-pyramidal conformation. The compound, tetraethylammonium bis(1,2-benzenediolato)fluorosilicate(IV) (**2**), mp 208–210 °C,



3

2

was prepared by the reaction of bis(catecholato)silicon(IV) (**3**)[3] with $Et_4N^+F^-{\cdot}2H_2O$ in methyl cyanide at room temperature. Crystals suitable for X-ray diffraction analysis were grown from a 1:2 mixture of methyl cyanide–diethyl ether at 0 °C. Anal. Calcd for $C_{20}H_{28}O_4NFSi$: C, 61.04; H, 7.17; N, 3.55. Found: C, 60.79; H, 7.15; N, 3.49.

Crystal Data for $C_{20}H_{28}O_4NFSi$ (**2**): Space group $C2/c$ (C_{2h}^6, No. 15),[4] with $a = 28.091$ (4), $b = 11.213$ (1), $c = 33.582$ (8) Å; $\beta = 128.76$ (1)°; $Z = 16$. Independent reflections (4711) were measured on an Enraf–Nonius CAD4 automated diffractometer, using graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode, to a maximum $2\theta_{MoK\bar{\alpha}}$ of 43°. The structure was solved by using direct methods (MULTAN). Full-matrix least-squares refinement[5] (54 independent nonhydrogen atoms, anisotropic, varied; 32 independent hydrogen atoms, excluding methyl hydrogen atoms, isotropic, fixed) led to a conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.064 for the 2705 independent reflections having $I \geq 2\sigma(I)$.

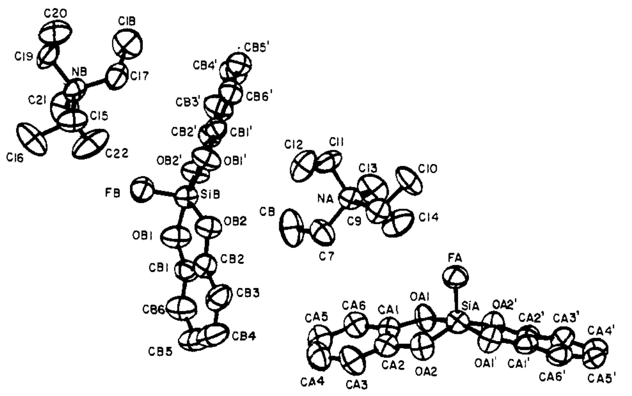


Figure 1. ORTEP plot of $[(C_6H_4O_2)_2SiF]^-Et_4N^+$ (**2**), with thermal ellipsoids shown at the 50% probability level. Bond parameters for anion A (those for anion B are in parentheses), lengths (Å): Si–F = 1.607 (4) (1.599 (4)), Si–O1 = 1.742 (5) (1.741 (5)), Si–O1′ = 1.736 (5) (1.738 (5)), Si–O2 = 1.704 (5) (1.699 (5)), Si–O2′ = 1.706 (5) (1.701 (5)). Angles (deg): O1–Si–O1′ = 164.0 (2) (168.4 (3)), O2–Si–O2′ = 145.5 (3) (140.7 (3)).

Two discrete molecules of **2** are present in the unit cell shown in the ORTEP plot of Figure 1. The bond angle data given in the legend indicate that the structure of the molecule labeled A is more square pyramidal than the B molecule. On the basis of the dihedral angle data, as applied to cyclic phosphoranes,[6,7] the geometry about the silicon atom for molecule A is displaced by 70.5% (68.7% using unit vectors) from the trigonal bipyramid toward the square-pyramidal configuration. The structure of the B molecule is displaced 54.6% (52.8%) toward the square pyramid. Both molecules follow the local C_{2v} constraint of the coordinate connecting the trigonal bipyramid to the rectangular pyramid. Each molecule has approximate 2-fold symmetry with the 2-fold axis coincident with the Si–F bond. Following the trend observed for cyclic phosphoranes,[6-8] the "axial" Si–O bonds are longer than the "equatorial" Si–O bonds, averaging 0.03 Å longer for each independent molecule.

Although crystal packing effects exert some influence on the structural form obtained for **2**, the recent discovery of the rectangular pyramidal geometry for related pentacoordinated Ge(IV)[9] and Sn(IV)[10] species suggests the operation of substituent effects as the principal structural determinant.

For each of these pentacoordinated derivatives, the structures obtained follow the factors deemed important in forming the rectangular pyramidal geometry for phosphoranes.[7,8]

The placement of the structures for **1** and **2** on the ligand exchange coordinate connecting the trigonal bipyramid and square pyramid suggests that fluxional behavior, common for phospho-

---

(1) Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 3170.

(2) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 6973.

(3) Allcock, H. R.; Nugent, T. A.; Smeltz, L. A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 97.

(4) *Int. Tables* X-ray *Crystallogr.* **1969**, *1*, 101.

(5) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_1$. Mean atomic scattering factors were taken from: *Int. Tables X-ray Crystallogr.* **1974**, *4*, 72–98 Real and imaginary dispersion corrections for Si, F, and O were taken from the same source, pp 149–150.

(6) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(7) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(8) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175.*

(9) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972.

(10) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.

0002-7863/81/1503-5269$01.25/0

ranes,[8,11,12] should be an observable characteristic of pentacoordinated silicon.

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Supplementary Material Available: Atomic coordinates (Table I) and anisotropic thermal parameters (Table II) (4 pages). Ordering information is given on any current masthead page.

---

(11) Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433.
(12) Holmes, R. R. *Acc. Chem. Res.* **1972**, *5*, 296.

Book Reviews *

Advances in Heterocyclic Chemistry. Volume 27. Edited by A. R. Katritzky and A. J. Boulton. Academic Press, New York. 1981. ix + 331 pp. $49.50.

There are four contributed chapters in this volume; two of them are reviews of recent advances in subjects reviewed in this series some time ago. 1-Azabicyclo[3.1.0]hexanes and Analogs, by Black and Doyle, treats the ring system in which an aziridine and a pyrrolidine or pyrroline ring share an edge and a nitrogen atom. Heteroaromatic Radicals, Part II, by Hanson continues the subject begun in Vol. 25. This section includes radicals from oxygen, sulfur, and selenium heterocycles and those with combinations of two or more different heteroactoms from groups 5 and 6. The 1,2- and 1,3-Dithiolium Ions, by Lozac'h and Stavaux, reviews the last 15 years of a subject previously reviewed in Vol. 7. Advances in Imidazole Chemistry, by Grimmett, deals with the last 10 years of the subject, which previously appeared in Vol. 12. The reviews are well-done and nicely illustrated, and it is a pleasure to find the references at the foot of the pages on which they are first cited. The volume concludes with a cumulative index of titles, but a subject index to the present volume is nowhere to be found.

Lecture Notes in Chemistry. Volume 16. Ab Initio Calculations; Methods and Applications in Chemistry. By P. Čársky (Czechoslovak Academy of Science, Prague) and M. Urban (Comenius University, Bratislava). Springer-Verlag, New York. 1980. vi + 247 pp. $21.00, softcover.

This is an excellent general review of the current status of ab initio computational techniques for atoms and molecules. It is intended as a practical handbook, replete with recipes for basis sets and data handling in large-scale computations. The first third of the book describes SCF methods. By now, Hartree–Fock procedures based on contracted Gaussians plus polarization functions are quite standardized. By contrast, the region beyond Hartree–Fock is still a frightening jungle (especially for chemists!). The reader is introduced to some of the more popular methods for correlation energy including configuration interaction, cluster expansions, many-body perturbation theory and the various electron-pair approximations. The authors are themselves active contributors to this area.

The last part of the book reviews applications of ab initio methods to molecular properties other than energy, including molecular geometries, potential curves, force constants, ionization potentials and intermolecular forces.

The reliability of various levels of theory for such properties is enumerated. An appendix describes briefly some of the widely used ab initio program packages, including POLYATOM and GAUSSIAN 70. An impressive bibliography contains 709 references, including some 1979 entries.

S. M. Blinder, *University of Michigan*

Lecture Notes in Chemistry. Volume 19. Computational Aspects for Large Chemical Systems. By E. Clementi (IBM, Poughkeepsie, N.Y.). Springer-Verlag, New York. 1980. 184 pp. $17.50, softcover.

This publication includes quantum chemical techniques, augmented by semiempirical and statistical methods applied mainly to RNA/DNA structure and interactions with water.

Theoretical Chemistry. Advances and Perspectives. Volume 5. Edited by H. Eyring and D. Henderson. Academic Press, New York. 1980. xiii + 267 pp. $35.00.

Four articles are included in this publication: Primitive Electrolytes in the Mean Spherical Approximation (L. Blum); Lattice Sums (M. L. Glasser and I. J. Zucker); Lattice Model of Quantum Fluid (D. D. Betts and D. Cuthiell); and Computational Aspects of Chemical Equilibrium in Complex Systems (W. R. Smith).

Symmetries in Science. Edited by B. Gruber and R. S. Millman. Plenum Press, Inc., New York. 1980. ix + 495 pp. $49.50.

The publication contains the proceedings of the Einstein Centennial Celebration Science Symposium held at Southern Illinois University, Carbondale, IL, February 23–March 2, 1979. This collection of 30 invited and contributed papers honors the 100th birthday of Albert Einstein, who exploited the idea that symmetries and invariance principles govern the laws of Nature. Introductory tributes to Einstein's work by P. A. M. Dirac and E. P. Wigner are followed by a diverse collection of papers covering symmetry and group theory applied to atomic, nuclear and elementary particle physics, relativity, cosmology, quantum mechanics, statistical physics, and biology. Three articles—by Gruber, Judd, and Matsen, respectively—are of potential interest to quantum chemists.

Progress in Drug Metabolism. Volume 5. Edited by J. W. Bridges (University of Surrey) and L. F. Chasseaud (Huntingdon Research Centre). John Wiley and Sons, New York. 1980. ix + 358 pp. $85.00.

This volume provides the reader with critical accounts of newer developments or progress in five comprehensively written chapters covering: (1) The Distribution and Role of Cytochrome P-450 in Extrahepatic Organs; (2) Species Variation in some Hepatic Microsomal Enzymes that Metabolize Xenobiotics; (3) Pharmacokinetics and Metabolism of Nonsteroidal Anti-inflammatory Agents; (4) Monitoring of Drug disposition by Immunoassay, and (5) Pharmacokinetics and Metabolism of Industrial Chemicals. In addition to being of interest to the specialist, scientists in the interdisciplinary fields of medicinal chemistry, pharmacology, and toxicology will welcome the opportunity to acquaint themselves with those areas pertinent to their fields of interest. The last chapter should be of value to the industrial hygienist and toxicologist in permitting an understanding of how pharmacokinetics is utilized to arrive at realistic risk estimates from animal studies. A subject index is included and also a listing of the contents of the four previous volumes.

V. H. Maddox, *Warner-Lambert/Parke Davis*

Catalysis in Chemistry and Biochemistry. Theory and Experiment. Edited by Bernard Pullman. D. Reidel Publishing Company, Boston. i + 390 pp. $85.00.

The proceedings of the Twelfth Jerusalem Symposium on Quantitative Chemistry and Biochemistry held in 1979 have been recorded in this volume. The 30 papers compiled here are the works of a truly international group of scientists. Their contributions range from the experimental to the highly theoretical. Their topics include factors contributing to enzyme catalysis, micellar catalysis, a variety of enzymes, charge relay systems, thiamin, flavins, catalysis by metals and metal ions, and a series of papers on catalytic reactions in organic chemistry.

The publisher claims that this book will be of importance to chemists, biochemists, physical chemists, and quantum chemists. While there may be something for everybody in this book, there is not a lot to interest any one reader. The title reflects the diffuse nature of the contents. While individual contributions are of quality, there is the lack of depth and focus one would hope to see in a published volume. The broad ranging subject matter and the book's cost will probably limit it to library shelves.

Dennis Piszkiewicz, *Duquesne University*

The Calculation of Molecular Orbitals. By J. C. Slater (formerly of MIT and University of Florida, now deceased). Wiley, New York. 1979. vi + 104 pp. $16.95.

This short monograph is based on a manuscript found among professor Slater's effects. It describes his statistical exchange correlation or Xα method for simplifying atomic self-consistent-field equations. Detailed numerical examples are given, along the lines of Herman and Skillman's 1963 atomic structure calculations. Molecules and solids are discussed in the latter part of the book, largely from the viewpoint of cellular (muffin tin) models and multiple scattering methods.

---

*Unsigned book reviews are by the Book Review Editor.