rotational relationships observed in the crystals of **1** and **2** correspond to an idealized symmetry of D_2. With this structure[5] our calculations (taking the Z axis as the Hf–Hf axis) show that the HOMO and SHOMO are nearly degenerate and are formed by donation of metal d_{xy} and $d_{x^2-y^2}$ electron density into the slightly split components of the empty arene $e_2\pi^*$ orbitals (see Figure 3). The next 16 molecular orbitals below the SHOMO are 8 I lone-pair, 4 M–I σ-bonding, and 4 M–P σ-bonding orbitals, after which we have the filled arene $e_1\pi$ orbitals that donate moderately to and split (by 0.4 eV) the metal d_{xz} and d_{yz} orbitals. The nondegenerate arene π orbital is essentially unperturbed by its surroundings and the metal d_{z^2} orbitals interact with each other only weakly to form a nearly degenerate pair of LUMOs. The bonding is thus understandable in terms of arene frontier orbitals donating to and accepting from metal d orbitals.

With this picture of the bonding it seems likely that rotation of the central arene about the M–M axis will have little electronic hindrance. There is also a clear indication that the dinuclear character is not essential and that $MI_2(PR_3)_2$(arene) species may be capable of existence. These and other ideas are under active study.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant A494.

Supplementary Material Available: Tables of crystallographic parameters, atomic positions, thermal displacements, and bond lengths and angles (16 pages); table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

---

[5] To make the calculation tractable we have also replaced Hf by Zr and PMe_2Ph by PH_3.

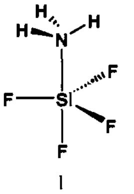
Ab Initio Study of the Structure and Infrared Spectrum of the 1:1 Adduct of SiF_4 and NH_3

Jiani Hu, L. J. Schaad,* and B. Andes Hess, Jr.*

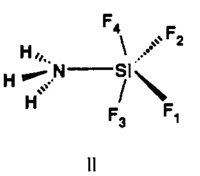
Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235

Received April 11, 1990

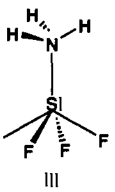
Ault has reported the matrix isolation of a 1:1 adduct of SiF_4 and NH_3.[1-3] On the basis of its infrared spectrum, he proposed that this adduct has a trigonal-bipyramidal arrangement about the central silicon with the NH_3 group in an axial position (I). Subsequent ab initio calculations by Marsden[4] located three stationary points (I–III) on the potential surface and gave theoretical support to Ault's original proposal that I is the structure of the 1:1 adduct. However, no theoretical vibrational analyses were done on these structures, and therefore there is no certainty that any of these are truly minima on the potential surface since some symmetry constraints were imposed in the geometry optimizations. We therefore undertook the vibrational analysis of I–III both to determine which if any are minima and also to obtain the calculated infrared spectra of those that might prove to be minima for comparison with the reported spectrum of the adduct.



I



II



III

Table I. Computed IR Frequencies and Intensities (Given in Parentheses) of I[a]

symmetry	$SiF_4{\cdot}NH_3$	$SiF_4{\cdot}{}^{15}NH_3$	$SiF_4{\cdot}ND_3$
A_1	164 (0.00)	164 (0.00)	117 (0.00)
E	177 (16.39)	176 (15.68)	170 (13.44)
A_1	221 (61.93)	217 (58.87)	209 (51.27)
E	309 (0.82)	308 (0.64)	284 (0.02)
E	421 (63.13)	421 (62.60)	420 (60.61)
A_1	473 (120.35)	471 (122.94)	466 (135.71)
E	764 (54.43)	759 (56.74)	608 (38.93)
A_1	788 (0.22)	788 (0.24)	787 (0.03)
A_1	957 (343.15)	957 (343.08)	957 (348.94)
E	1064 (588.83)	1064 (588.62)	1060 (544.87)
A_1	1439 (249.70)	1431 (246.32)	1097 (140.64)
E	1831 (71.94)	1828 (71.56)	1327 (39.56)
A_1	3696 (19.56)	3692 (18.77)	2643 (16.20)
E	3826 (77.13)	3815 (75.80)	2820 (48.72)

[a] Frequencies in cm^{-1} and intensities in km/mol.

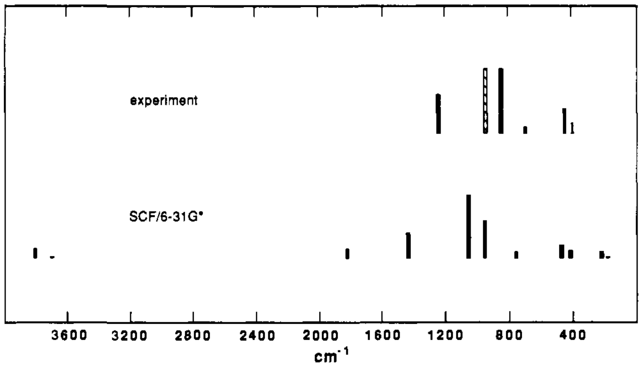


Figure 1. Experimental and theoretical spectra of I. Ault did not report a relative intensity for the open bar shown in the experimental spectrum.

Initially I–III were optimized by using the SCF/3-21G basis set with the following symmetry constraints: I with C_s symmetry (it converged to a C_{3v} structure); II with the F_1–Si–F_2 plane (this plane also contains the nitrogen atom) held perpendicular to the F_3–Si–F_4 plane; III with C_{4v} symmetry of the SiF_4 skeleton. Vibrational analyses gave all real frequencies for I, but a single imaginary frequency was found for both II (67*i*) and III (151*i*), which indicates that I is a minimum and II and III are transition structures on the potential surface. Examination of the normal mode of the imaginary frequency in both II and III indicates that these transition structures may involve fluorine scrambling.

Therefore further calculations were carried out on I to determine if it corresponds to the structure isolated by Ault. An SCF/6-31G* geometry optimization (energy of the optimized structure = −743.148 408 au) was performed for I with a C_{3v} symmetry constraint (the hydrogens attached to nitrogen were staggered with respect to those bound to silicon; $R_{\text{Si–F(axial)}} = 1.591$ Å, $R_{\text{Si–F(equal)}} = 1.584$ Å, $R_{\text{Si–N}} = 2.146$ Å, $R_{\text{N–H}} = 1.004$ Å, $\angle_{\text{Si–N–H}} = 111.0°$, $\angle_{\text{N–Si–F(equal)}} = 81.9°$, $\angle_{\text{F(equal)–Si–F(equat)}} = 118.0°$, $\angle_{\text{H–N–H}} = 107.9°$), and a subsequent vibrational analysis with the same basis set again gave all real frequencies. The computed frequencies and IR intensities for I are given in Table I along with their symmetries. In Figure 1 are plotted the computed infrared spectrum of I (those bands with a relative intensity >0.00) and the experimental spectrum reported by Ault for the 1:1 adduct of ammonia and silane. It is immediately seen that there is a very good correspondence between the computed and observed spectra[3] (Ault reported the spectrum only in the region of 380–1260 cm^{-1}). This is strong evidence that the structure of the adduct is indeed I as suggested. Furthermore Ault's symmetry assignments of the observed bands are in agreement with those calculated.[5]

Also given in Table I are the computed frequencies and intensities of the isotopomers $SiF_4{\cdot}{}^{15}NH_3$ and $SiF_4{\cdot}ND_3$. Comparison with the frequencies reported by Ault for these isotopomers

---

[1] Ault, B. S. *Inorg. Chem.* **1981**, *20*, 2817.
[2] Lorenz, T. J.; Ault, B. S. *Inorg. Chem.* **1982**, *21*, 1758.
[3] Ault, B. S. *Rev. Chem. Intermed.* **1988**, *9*, 233.
[4] Marsden, C. J. *Inorg. Chem.* **1983**, *22*, 3177.

[5] The 456-cm^{-1} absorption should have been assigned in ref 1 as an A_1 rather than an E mode (Ault, B. S., private communication).

0002-7863/91/1513-1463$02.50/0

gives even stronger support to his structural assignment of I. He finds that for the ^{15}N isotopomer only two bands are significantly shifted to lower frequency. The band at 1253 cm^{-1} is shifted by 6 wavenumbers and that at 706 cm^{-1} by 5 wavenumbers. The corresponding computed bands predict a shift of 8 and 5 wavenumbers. For the deuterated case only one band is reported to be shifted significantly (that in the parent compound at 1253 cm^{-1} by 300 cm^{-1}), and this agrees qualitatively with our computed shift for this band (340 cm^{-1}).

Finally the frequency of the Si-N stretch is of interest. It was predicted by Marsden to be located at about 200 cm^{-1}. In agreement with this we calculate (SCF/6-31G*) a frequency of 221 cm^{-1} and predict the transition to be of relatively weak intensity.

In conclusion we have found that I does correspond to a minimum on the potential surface, and the comparison of its computed IR spectra to the experimental spectra reported by Ault gives strong support for the assignment of structure I to Ault's 1:1 adduct.

Acknowledgment. We thank the National Science Foundation for support through research Grant CHE 8605951 as well as for an instrument grant (CHE 8808018) that allowed the purchase of the Scientific Computer Systems computer.

The First Nonconjugated Mononuclear Benzene Dianion. Isolation and Characterization of Bis[(tetrahydrofuran)lithium(I)] Hexakis(trimethylsilyl)benzenide[1]

Akira Sekiguchi, Keisuke Ebata, Chizuko Kabuto, and Hideki Sakurai*

Department of Chemistry and Organosilicon
Research Laboratory, Faculty of Science
Tohoku University, Aoba-ku, Sendai 980, Japan

Received October 22, 1990

The benzene dianion is theoretically of great interest,[2] although no experimental study has been reported so far.[3,4] We report herein the isolation, characterization, and unusual molecular structure of bis[(tetrahydrofuran)lithium(I)] hexakis(trimethylsilyl)benzenide, the first nonconjugated mononuclear benzene dianion.[5]

Reduction of hexakis(trimethylsilyl)benzene (**1**, 512 mg, 1.0 mmol)[6] with excess lithium metal (60 mg, 8.6 mmol) in dry oxygen-free THF (10 mL) at room temperature led to the formation of a dark red solution of the benzene dianion of **1** within 1 h. The solvent was removed in vacuo, and then dry degassed hexane was introduced by vacuum transfer. Crystallization from hexane afforded red crystals of bis[(tetrahydrofuran)lithium(I)] hexakis(trimethylsilyl)benzenide (**2**), $[Li(thf)]_2[(Me_3Si)_6C_6]$, containing two molecules of THF.[7] The dilithium benzene complex **2** is extremely air and moisture sensitive and readily reverted to the original benzene **1** on exposure to the air. The reactions with H_2O and D_2O produced 1,2,3,4,5,6-hexakis(trimethylsilyl)cyclohexa-1,4-dienes **3a**[8] and **3b**[9] respectively (scheme I).

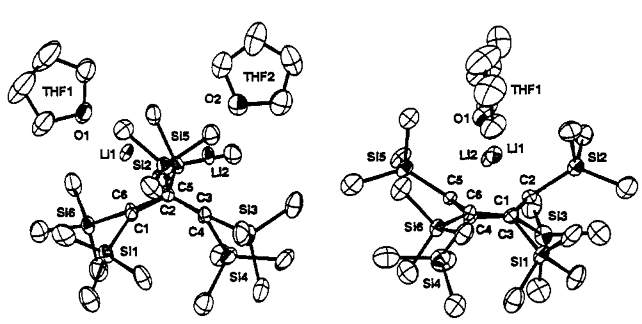
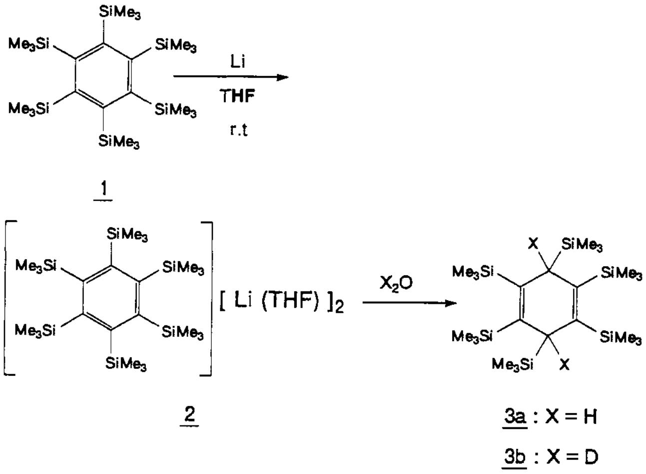


Figure 1. Molecular structure of $[Li(thf)]_2[(Me_3Si)_6C_6]$. Selected bond lengths (Å): C(1)–C(2), 1.527 (12); C(2)–C(3), 1.502 (12); C(3)–C(4), 1.400 (12); C(4)–C(5), 1.526 (12); C(5)–C(6), 1.493 (12); C(6)–C(1), 1.386 (12); C(1)–Si(1), 1.892 (9); C(2)–Si(2), 1.845 (9); C(3)–Si(3), 1.906 (9); C(4)–Si(4), 1.895 (9); C(5)–Si(5), 1.844 (9); C(6)–Si(6), 1.894 (9); Li(1)–C(1), 2.122 (18); Li(1)–C(2), 2.302 (18); Li(1)–C(5), 2.496 (20); Li(1)–C(6), 2.127 (18); Li(2)–C(2), 2.296 (18); Li(2)–C(3), 2.099 (20); Li(2)–C(4), 2.117 (20); Li(2)–C(5), 2.299 (18); Li(1)–O(1), 2.003 (18); Li(2)–O(2), 1.964 (18). Selected bond angles (°): C(6)–C(1)–C(2), 114.3 (7); C(1)–C(2)–C(3), 107.4 (7); C(2)–C(3)–C(4), 113.3 (7); C(3)–C(4)–C(5), 116.1 (7); C(4)–C(5)–C(6), 108.6 (7); C(5)–C(6)–C(1), 115.5 (7).

Scheme I



---

(1) Chemistry of Organosilicon Compounds. 274.

(2) (a) Jesse, R. E.; Hoytink, G. J. *Chem. Phys. Lett.* **1967**, *1*, 109. (b) Nakayama, M.; Ishikawa, H.; Nakano, T.; Kikuchi, O. *J. Mol. Struct.* (THEOCHEM), **1989**, *184*, 369. (c) Podlogar, B. L.; Glauser, W. A.; Rodriguez, W. R.; Raber, D. J. *J. Org. Chem.* **1988**, *53*, 2127. For theoretical studies on the interaction between lithium and benzene, see: (d) Jebli, R.; Volpilhac, G. F.; Hoarau, J.; Achard, F. *J. Chem. Phys.* **1984**, *81*, 13. (e) Morton-Blake, D. A.; Corish, J.; Beniere, F. *Theor. Chim. Acta* **1985**, *68*, 389.

(3) The crystal structures of lithium complexes of naphthalene, anthracene, and fluorene have been reported. (a) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339. (b) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7346. (c) Rhine, W. E.; Davis, J.; Stucky, G. *J. Am. Chem. Soc.* **1975**, *97*, 2079. (d) Bladauski, D.; Broser, W.; Hecht, H. J.; Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979**, *112*, 1380. However, nonconjugated mononuclear benzene dianion is hitherto unknown. See the following reviews. (e) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982. (f) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (g) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169.

(4) It is documented that cocondensation of lithium with benzene diluted in argon produces lithium benzene complexes such as LiC_6H_6, $Li(C_6H_6)_2$, and $Li_2C_6H_6$. (a) Manceron, L.; Andrews, L. *J. Am. Chem. Soc.* **1988**, *110*, 3840. See also the following papers. (b) McCullough, J. D.; Duley, W. W. *Chem. Phys. Lett.* **1972**, *15*, 240. (c) Moore, J. C.; Thornton, C.; Collier, W. B.; Delvin, J. P. *J. Phys. Chem.* **1981**, *85*, 350.

(5) In the course of our investigation of dianion chemistry, we have recently reported ethylene dianions. Sekiguchi, A.; Nakanishi, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 3748.

(6) Sakurai, H.; Ebata, K.; Kabuto, C.; Sekiguchi, A. *J. Am. Chem. Soc.* **1990**, *112*, 1799.

(7) Compound **2**: highly hygroscopic and air-sensitive red crystals; ^1H NMR (300 MHz, toluene-d_8, 263 K) δ 0.46 (s, 18 H, $SiMe_3$), 0.63 (s, 36 H, $SiMe_3$), 1.35 (m, 8 H, THF), 3.47 (m, 8 H, THF); ^{13}C NMR (75.5 MHz, toluene-d_8, 263 K) δ 7.55 ($SiMe_3 \times 4$), 8.39 ($SiMe_3 \times 2$), 25.5 (THF), 68.7 (THF), 99.9 (C_{ar}), 151.8 (C_{ar}); ^{29}Si NMR (59.6 MHz, toluene-d_8, 263 K) δ −25.5 (Si × 2), −14.3 (Si × 4); ^7Li NMR (116.6 MHz, toluene-d_8, 263 K) δ −1.48 ppm (from LiCl in MeOH); UV (hexane) λ_{max}/nm (ϵ) 389 (10 200), 328 (11 400), 207 (40 000).

(8) Compound **3a**: mp 271–272 °C; ^1H NMR (C_6D_6) δ 0.25 (s, 18 H, $SiMe_3$), 0.31 (s, 36 H, $SiMe_3$), 3.85 (s, 2 H, C=CCH); ^{13}C NMR (C_6D_6) δ 3.68 ($SiMe_3$), 46.3 (C=CCH), 147.4 (C=C); ^{29}Si NMR (C_6D_6) δ −6.62 (Si × 4), 0.68 (Si × 2); UV (hexane) λ_{max}/nm (ϵ) 253 (7500), 214 (25 000); high-resolution MS calcd for $C_{24}H_{56}Si_6$ 512.2998, found 512.2996.

(9) Compound **3b**: ^1H NMR (C_6D_6) δ 0.25 (s, 18 H, $SiMe_3$), 0.31 (s, 36 H, $SiMe_3$); ^2H NMR (46.1 MHz, C_6H_6) δ 3.8 ppm; high-resolution MS calcd for $C_{24}H_{54}D_2Si_6$ 514.3123, found 514.3131.

0002-7863/91/1513-1464$02.50/0