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.

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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

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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).

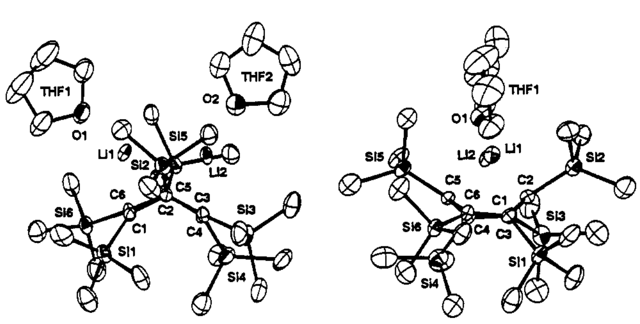
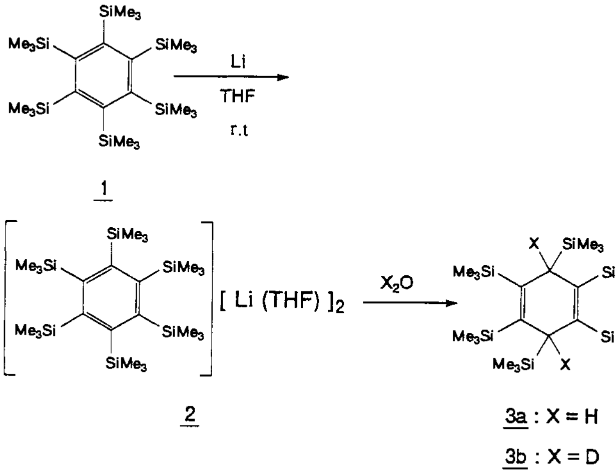


Figure 1. Molecular structure of $[Li(thf)]_2[(Me_3Si)_6C_6]$. Selected bond lengths (Å): C(1)–C(2), 1.527 (12); C(2)–C(3), 1.502 (12); C(3)–C(4), 1.400 (12); C(4)–C(5), 1.526 (12); C(5)–C(6), 1.493 (12); C(6)–C(1), 1.386 (12); C(1)–Si(1), 1.892 (9); C(2)–Si(2), 1.845 (9); C(3)–Si(3), 1.906 (9); C(4)–Si(4), 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



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(7) Compound **2**: highly hygroscopic and air-sensitive red crystals; ^{1}H 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); ^{7}Li 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; ^{1}H 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**: ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H, $SiMe_3$), 0.31 (s, 36 H, $SiMe_3$); ^{2}H 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.

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The structure of **2** has been unequivocally determined by X-ray crystallography as shown in Figure 1.[10] Several interesting features can be pointed out immediately. The most surprising one is the position of the lithium atoms. Both lithium atoms are located on the same side of the benzene ring. The Li-Li distance is only 2.722 Å despite the expected electrostatic repulsion. One THF molecule is coordinated to each lithium atom. So far reported, the cations in polynuclear aromatic dianions are located above and below the plane.[3]

Four aromatic carbons [C(1), C(3), C(4), C(6)] are nearly coplanar, while the C(2) and C(5) carbons are above the C(1)–C(3)–C(4)–C(6) plane by 0.656 and 0.578 Å, respectively. Consequently, the benzene ring is appreciably deformed into a boat form. The dihedral angles of C(1)–C(2)–C(3)/C(1)–C(3)–C(4)–C(6), C(4)–C(5)–C(6)/C(1)–C(3)–C(4)–C(6), and C(2)–C(1)–C(6)–C(5)/C(2)–C(3)–C(4)–C(5) are 47.0°, 41.0°, and 126°, respectively.

A theoretical consideration of the benzene dianion by ab initio calculation on the 6-21G level[2c] suggested that the antiaromatic benzene dianions could be stabilized to take a boat form with a folding angle of 167°. The degree of folding observed for **2** (folding angle: 126°) is much larger than that of the calculated degree of folding. The steric factors may play an important role to determine the structure of **2**.

The lengths of the C_{ar}–C_{ar} and C_{ar}–Si bonds in the benzene dianion **2** apparently differ from the values for **1** (average 1.413 Å and average 1.922 Å, respectively). In particular, the bond lengths of C(1)–C(6) (1.386 Å) and C(3)–C(4) (1.400 Å) are shortened, whereas the bond lengths of C(1)–C(2) (1.527 Å), C(2)–C(3) (1.502 Å), C(4)–C(5) (1.526 Å), and C(5)–C(6) (1.493 Å) are significantly stretched. The internal bond angles at C(1), C(3), C(4), and C(6) carbons range from 113.5° to 116.1° (cf. bond angles for C_{ar}–C_{ar}–C_{ar} of **1**: average 119.8°). However, the bond angles of both C(1)–C(2)–C(3) (107.3°) and C(4)–C(5)–C(6) (108.5°) largely changed owing to a large negative charge on C(2) and C(5). As a result, the bond lengths of C(2)–Si(2) (1.845 Å) and C(5)–Si(5) (1.844 Å) become short due to the increased C–Si bond order through p–σ^* interaction (cf. bond lengths for Si–C_{ar} of **1**: average 1.922 Å). Appreciable pyramidalization at C(1) and C(4) carbons can be noted.[11]

The molecular structure of **2** found in the crystals seems to be maintained in solution, on the basis of the NMR experiments. In the ^{1}H NMR spectrum taken in toluene-d_8 at 263 K, the signals of the trimethylsilyl groups appear at 0.46 (18 H) and 0.63 ppm (36 H). The signals of two equivalent THF molecules were also found. The carbons due to the trimethylsilyl groups can be observed at 7.55 and 8.39 ppm. The corresponding two sets of ^{29}Si signals can be seen at −25.5 and −14.3 ppm as well. The existence of two magnetically nonequivalent trimethylsilyl groups with an intensity ratio of 2:1 implies the structure of a boat form even in solution.

Large localization of the negative charge on the two carbon atoms in the benzene ring [C(2) and C(5)] is shown by ^{13}C as well as ^{29}Si NMR spectra. Thus, in ^{13}C NMR, the two carbons appear at 99.9 ppm and the other four carbons appear at 151.8 ppm. The former appreciably shifted to upfield due to the location of the negative charge. As well, ^{29}Si resonances of the trimethylsilyl groups attached to these carbons can been seen at higher field (−25.5 ppm) than the others (−14.3 ppm). These spectroscopic data are in good accordance with the structure found in the crystals. Details of NMR studies including a dynamic process will be reported elsewhere.[12]

Acknowledgment. We are grateful for the financial support of the Ministry of Education, Science, and Culture of Japan (Specially Promoted Research No. 02102004).

Supplementary Material Available: ORTEP drawing of **2** with numbering and tables of details of X-ray experiment, atomic parameters, anisotropic temperature factors, and bond distances and angles (9 pages); listing of observed and calculated structure factors for **2** (24 pages). Ordering information is given on any current masthead page.

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(10) A single crystal of **2** was sealed in a capillary glass tube for data collection. Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (50 kV, 200 mA) with graphite-monochromatized Mo Kα radiation (λ = 0.709 26 Å). The data collection was carried out at 13 °C by using a crystal of dimensions 0.3 × 0.3 × 0.7 mm. A total of 9550 reflections with $2\theta = 50°$ were collected. Crystal data: $Si_6O_2C_{32}Li_2H_{70}$; MW = 669.1; monoclinic; $a = 43.784$ (20), Å, $b = 11.469$ (0) Å, $c = 20.230$ (1) Å, $\beta = 115.81$ (2)°; $V = 9148.4$ (60) Å^3; space group $C2/c$; $Z = 8$; $D_{calcd} = 0.97$ g/cm^3. The structure was finally refined anisotropically for Si, O, C, and Li and isotropically for H to give an R factor of 0.109 for 4787 reflections with $F_o > 3\sigma(F_o)$. The unsatisfactorily high R value is due to the high anisotropic factor of the THF.

(11) The C(1) and C(4) carbons lie above the Si(1)–C(2)–C(6) plane by 0.188 Å and the Si(4)–C(3)–C(5) plane by 0.214 Å, respectively.

(12) In preliminary studies, dilithium complexes of both hexakis(dimethylsilyl)benzene and hexakis(methylsilyl)benzene, which are presumably planar in structure, show similar NMR results to **2**, and it is concluded that preference of the boat structure for hexasilylbenzenes is not due to the steric factor of the bulky trimethylsilyl group.

Theoretical Support for a New Electronegativity Scale

Yu-Ran Luo and Philip D. Pacey*

Department of Chemistry, Dalhousie University
Halifax, Nova Scotia, Canada B3H 4J3

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Recently, a new scale of electronegativity has been introduced to correlate heats of formation of alkyl derivatives.[1,2] The new scale is the simplest of all available electronegativities and is defined as

$$V_x = n_x/r_x \qquad (1)$$

Here n_x is the number of valence electrons in the bonding atom in the group X, and r_x is the covalent radius of the atom. Values for all main-group atoms were listed in ref 3. V_x will be called the covalent potential.

Contrary to expectations, this simplest scale gave the least scatter and the highest correlation coefficient for heats of formation of alkyl derivatives,[3] ionization potentials,[4] and Lewis acid strengths.[5] The new scale has also been used very satisfactorily for estimating group parameters,[6] heats of formation of silicon-containing compounds,[7] and homopolar bond dissociation energies.[8] In unpublished work,[9] it has been extended to the propagator of the σ inductive effect, to heteropolar bond dissociation energies, to bond energies of silicon compounds, and to a theoretical model of bond cleavage. When it was used to correlate with homolysis and heterolysis bond energies, the agreement of most estimated values with experiment was within experimental accuracy (±1 kcal/mol).[8,9] The covalent potential was also used by Walsh[10] to correlate the divalent state stabilization energies of SiX_2. Surprisingly, the simplest scale always gave the best results. We will examine possible reasons for these advantages in this communication.

We have found that powerful theoretical support for the new scale of electronegativity comes from the absolute electronegativity theory of Parr and Pearson.[11] Firstly, the dimension of V_x is energy divided by charge, like electronegativity in Parr and Pearson's theory. Secondly, the value of n_x/r_x is a "global" atomic property, which is consistent with Parr and Pearson's theory.

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