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]

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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, β = 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

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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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Table I. Correlation Coefficients for Linear Relations between Measures of Electronegativity for 21 Main-Group Elements[a]

	ground state in atoms		valence state in molecules	
	μ	V_Q	V_x	X_M
ground state				
μ	1	0.985	0.964	0.951
V_Q		1	0.967	0.945
valence state				
V_x			1	0.989
X_M				1

[a] μ and V_Q are from ref 12; V_x is from ref 3; X_M is from ref 15.

Thirdly, the value of n_x/r_x is dependent on the valence state, charge, and ligand number of the central atom. This means it is general, as in Parr and Pearson's theory. Fourthly and most importantly, there are good linear correlations between V_x and the electronic chemical potential, μ, and the central electrostatic potential, V_Q, at r_μ, for the 21 main-group elements of ref 12. There μ was calculated as the Mulliken electronegativity of a ground-state atom,

$$\mu = (\mathrm{IP} + \mathrm{EA})/2 \qquad (2)$$

where IP and EA are the ionization potential and the electron affinity, respectively; r_μ is the radial distance at which the total electrostatic potential, $V(r_\mu)$, of a ground-state atom exactly equals its chemical potential, μ. V_Q is defined as Q/r_μ, where Q is the total electronic and nuclear charge inside a sphere of radius r_μ. The correlation coefficients have been determined, as shown in the second-last column of Table I.

A close linear relation between r_μ and the covalent radius has been noted previously.[12-14] Mulliken's scale of electronegativity, μ, for free atoms in the ground state was found to be strongly correlated with V_Q.[12]

Any atom in a molecule is in its energetically optimum valence state, not in the free ground state. The covalent radius is a particular measure of the size of an atom in a molecule[13] and is thus a valence-state property.

The parameters μ, $V(r_\mu)$, r_μ, and V_Q of atoms in valence states have been too difficult to calculate so far by absolute electronegativity theory. But valence-state ionization potentials, electron affinities, and Mulliken electronegativities have been calculated[15] by the semiempirical method of Hinze and Jaffe.[16] According to absolute electronegativity theory, the inherent Mulliken electronegativity scale, X_M, from the valence-state analogue of eq 2, the electronic chemical potential, μ, and Huheey's[17] parameter, *a*, are all approximately the same.

We have calculated the correlation coefficients for linear relations between four measures, μ, V_Q, V_x, and X_M, of electronegativity for the 21 main-group elements considered in ref 12. They are listed in Table I.

It is interesting to note in Table I that the two ground-state measures, μ and V_Q, correlate well with each other, but less well with the valence-state measures, V_x and X_M.

The simple V_x is strongly linked with X_M, as shown in Figure 1; the correlation coefficient is 0.989. This comparison means that the new scale, V_x, is theoretically reasonable and a good measure of the valence-state electronegativity. This explains the good correlations between V_x and bonding properties. V_x should be a basic parameter for diatomic and polyatomic properties.[5]

Parr and Pearson's absolute electronegativity theory is sophisticated, and Hinze and Jaffe's method is advanced. The new scale is not only theoretically reasonable and scientifically useful but also so simple that beginning chemistry students know the two parameters, n_x and r_x. On the basis of previous work[1-10] and this work, we predict that there is a good possibility (a) of using the new scale to simply correlate energies of polyatomic systems and (b) of introducing and teaching the new scale in introductory classes.

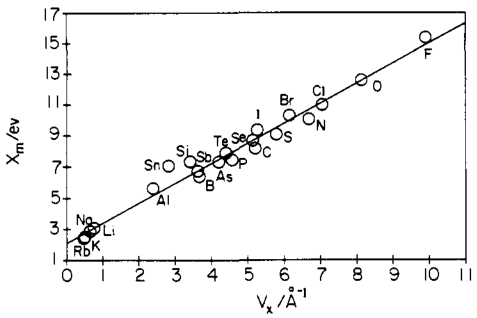

Figure 1. Relation between V_x and the chemical potentials of the valence states, X_M, for 21 main-group elements.

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Preparation and Photochemistry of Disilanyl Quinones: Formation of Novel Sila-*m*-quinomethane Intermediates[1]

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Recently, photochemical reactions of organosilicon compounds involving intermolecular charge transfer processes have received considerable attention from both synthetic and mechanistic viewpoints.[2] However, relatively few photoinduced intramolecular charge transfer reactions of organosilicon compounds have been reported.[3] We report herein the preparation and photoreactions of hitherto unknown disilanylbenzoquinones (**1**), an interesting class of organosilicon compounds containing both electron-withdrawing (benzoquinone) and electron-releasing (dislane) groups connected directly to each other.[4] Photochemical reactions of **1** resulted in the formation of novel sila-*m*-quinomethane intermediates.

2-(Pentamethyldisilanyl)-5-*tert*-butyl-1,4-benzoquinone (**1a**, R = *t*-Bu) was prepared by a series of reactions as indicated in Scheme I. 2-Bromo-5-*tert*-butyl-1,4-bis[(pentamethyldisilanyl)oxy]benzene (**2a**) was treated with 1.1 equiv of *t*-BuLi at −78 °C, and the resulting anion **3a** was warmed slowly to −20 °C. During the course of warming, spontaneous rearrangement occurred to give **4a**, which was oxidized with dichlorodicyanobenzoquinone (DDQ), without isolation, to **1a** in 43% overall

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