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Multiplicity of Planar Hexasilylbenzene Dianions: Effects of Substituents and Countercations

Wataru Setaka, Keisuke Ebata,[†] Hideki Sakurai,*,[‡] and Mitsuo Kira*

Contribution from the Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

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Abstract: The electronic structure of various planar hexasilylbenzene dianions was investigated by ESR spectroscopy. Dilithium salts of a planar hexasilylbenzene (1,3,4,6,7,9-hexasila-1,1,3,3,4,4,6,6,7,7,9,9-dodecamethyltrindane) dianion (**1a**) show thermally accessible triplet ESR signals with the D value of 0.0963 cm^{-1}. The D value as well as the singlet−triplet energy difference (ΔE_{ST}) in **1a** is dependent on the countercations ($M^+ = Li^+$, K^+, and Rb^+), indicative of the significant ion-pair interaction. The related dilithium salts of hexasilylbenzene dianions **2a** and **3a**, where all CH_2 bridges in **1a** are replaced by O and NMe bridges, respectively, afford similar triplet ESR signals, but they are thermally less stable than **1a**, suggesting that the thermal distortion of the ring structure occurs more easily in **2a** and **3a** than in **1a**. The origin of the singlet ground state of **1a** ($M^+ = Li^+$) is ascribed to the ion-pair interaction with the countercations on the basis of qualitative MO consideration.

Introduction

Since neutral benzene with D_{6h} symmetry has two degenerate LUMOs, the dianion of benzene is expected to be triplet in the ground state, while the removal of the degeneracy by the Jahn−Teller effect may make the singlet state more stable, as shown in Figure 1 schematically.

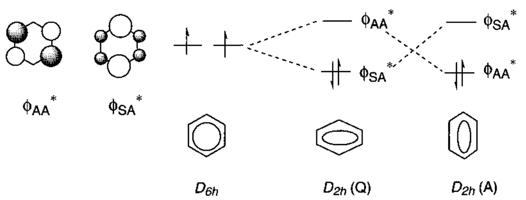
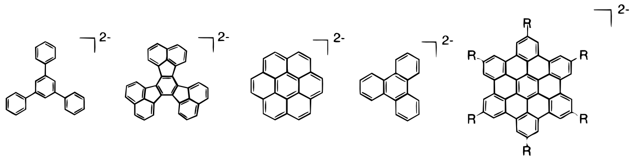


Figure 1. Schematic MO representation of D_{6h} benzene dianion and Jahn−Teller distorted D_{2h} quinoid (Q) and anti-quinoid (A) benzene dianions. ϕ_{SA} and ϕ_{AA} are symmetric and anti-symmetric with respect to the mirror plane bisecting the benzene ring plane, respectively. The second A in the suffix, which denotes the antisymmetric character of the orbitals under reflection to the ring plane, is not usually used but added to discuss the ion-pair interaction with two lithium ions.

Chart 1



Much attention has been focused for a long time on the electronic structure and the potential ferromagnetism of the dianions of benzene derivatives with higher symmetry than D_{3h}.[1] However, no experimental study of the parent benzene dianion has been reported so far, probably because of the high reduction potential of benzene and high reactivity of its dianion even if it is produced. Among benzene dianion derivatives studied so far, there are dianions of triphenyl benzene,[1a] decacyclene,[1a] coronene,[1b] triphenylene,[1c,d] and hexabenzocoronene[1e] (Chart 1). They are stabilized by significant delocalization of the anionic charges to the extended π-systems, where the electronic properties are substantially modified from parent benzene dianions; the 8π paramagnetic ring current as well as the exchange interaction expected in benzene dianion will be largely diminished by the delocalization. To elucidate the intrinsic electronic properties of benzene dianion, the electronic perturbation to the cyclic π system due to the effects of substituents should be minimized, even though they are required to stabilize the negatively charged molecules.

Since a carbanion is stabilized effectively by a trialkylsilyl group at the α-position due to the pπ^*−σ^*(Si−C) conjugation,[2]

[†] Present address: NTT Basic Research Laboratories, 3-1 Morinosato, Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan.

[‡] Present address; Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278-8501, Japan.

(1) For triplet benzene dianion derivatives, see; (a) Jesse, R. E.; Biloen, P.; Prins, R.; van Voorst, J. D. W.; Hoijtink, G. J. *Mol. Phys.* **1963**, *6*, 633. (b) Glasbeek, M.; van Voorst, J. D. W.; Hoijtink, G. J. *J. Chem. Phys.* **1966**, *45*, 1852. (c) van Willigen, H.; van Broekhoven, J. A. M.; de Boer, E. *Mol. Phys.* **1967**, *12*, 533. (d) van Broekhoven, J. A. M.; van Willigen, H.; de Boer, E. *Mol. Phys.* **1968**, *13*, 101. (e) Gherghel; L.; Brand, J. D.; Baumgarten, M.; Müllen, K. *J. Am. Chem. Soc.* **1999**, *121*, 8104. See also for triplet benzene dication derivatives: (f) Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* **1991**, *113*, 2322. (g) Thomaides, J.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970. (h) Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Vasquez, C.; Krusic, P. J.; Ward, M. D.; Wasserman, E.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 381. (i) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965. (j) Gabe, E. J.; Morton, J. R.; Preston, K. F.; Krusic, P. J.; Dixon, D. A.; Wasserman, E.; Miller, J. S. *J. Phys. Chem.* **1989**, *93*, 5337. (k) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749. (l) Breslow, R. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 199 and references therein. (m) Dixon, D. A.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 211 and references therein.

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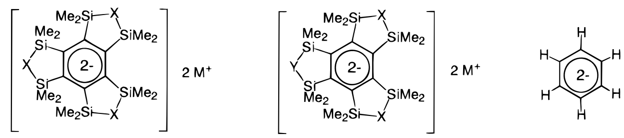
Chart 2



X = CH$_2$: **1a** (M = Li, K, Rb)
X = O : **2a** (M = Li).
X = NMe : **3a** (M = Li).

X = CH$_2$, Y = CH$_2$CH$_2$: **4a** (M = Li).
X = CH$_2$, Y = O : **5a** (M = Li).

hexasilylbenzene dianion is promising to be an experimental representative of benzene dianion. A dilithium complex of hexakis(trimethylsilyl)benzene dianion has been recently isolated and characterized as the first nonconjugated mononuclear benzene dianion, in addition to various other silylbenzene dianion dilithium complexes.[3] The structure of hexakis(trimethylsilyl)benzene dianion is highly distorted, however, into a boat form having a closed-shell electron system. The origin of this deformation is not attributable simply to the steric bulkiness of trimethylsilyl substituents but to the intrinsic property of benzene dilithium complex as shown by ab initio MO calculations.[4]

In a previous paper,[5] we have reported the synthesis, crystal structure, and ESR spectra of the dilithium complex of dianion **1a** (Chart 2), which is designed to have the constrained planar benzene ring structure by bridging the neighboring two silicon atoms of hexasilylbenzene by CH$_2$. In the molecular structure of a salt of **1a** [M$^+$ = Li$^+$ (quinuclidine)] determined by X-ray crystallography, the benzene ring is mostly planar, and two lithium ions are located above and below the ring on the C_3 axis. An ESR spectrum of a powder of **1a** (M$^+$ = Li$^+$) showed randomly oriented triplet signals with the zero-field splitting parameters D and E of 103.0 mT (0.0963 cm^{-1}) and 0 mT, respectively. The temperature dependence of the signal intensity ($\Delta m_s = 2$) revealed that the triplet state is not the ground state but the thermally accessible excited state with the singlet−triplet energy gap (ΔE_{ST}) of 1.0 kcal/mol.[6]

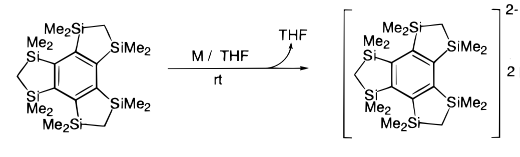
We wish herein at first to discuss the effects of countercations on the electronic structure of **1a**. The zero-field splitting parameters, ΔE_{ST} value, and the thermal stability of **1a** were found to be modified by the countercations (Na$^+$, K$^+$, Rb$^+$, and Cs$^+$), indicative of the significant ion-pair interaction in this system.

To investigate the effects of the bridging groups on the electronic properties of hexasilylbenzene dianions, dianions **2a** and **3a**, which are bridged by O and NMe, respectively, were prepared. Although **2a** and **3a** show similar triplet ESR signals to **1a**, the triplet states are thermally less stable than **1a**, because of the more flexible ring structure.

ESR studies of **4a** and **5a** have revealed how the removal of degeneracy is sensitive to the symmetry-lowering due to electronic and steric effects of substituents remote from the core degenerate π system.

Results and Discussion

Effects of Countercations. Whereas reduction of hexasilylbenzene **1** by lithium, potassium, and rubidium in THF gave readily the corresponding dianion salts **1a** (M$^+$ = Li$^+$, K$^+$, and Rb$^+$) (eq 1), preparation of the dianion salts having Na$^+$ and Cs$^+$ as counteranions was unsuccessful in similar reaction conditions. Reduction of hexasilylbenzene **1** with excess sodium metal in THF at room temperature gave immediately a black solution probably due to the formation of the corresponding dianion salts, but removal of solvent in vacuo after 10 min reaction reproduced neutral hexasilylbenzene **1** and Na metals probably due to the back-electron-transfer reaction. Reduction of **1** with cesium metal at room temperature gave an insoluble white powder, suggesting the facile decomposition of the generated dianion salt **1a** (M$^+$ = Cs$^+$) in this condition.



(1)

1

1a (M$^+$ = Li$^+$, K$^+$, Rb$^+$)

The relative ease of the formation of dianion **1a** and its stability are explained in terms of the ionization potentials of alkali metals and the solvation energy of the metal cations.[7] Although lithium metal has relatively high ionization energy, lithium cation formed by the oxidation is small in size and effectively solvated. Therefore, **1** is reduced by lithium in THF to give stable dianion salt **1a** (M$^+$ = Li$^+$). Potassium and rubidium also reduce **1** easily to form **1a** (M$^+$ = K$^+$ and Rb$^+$) because of the low ionization energies of the metals. In the reaction of **1** with sodium metal, stable dianion may not be formed because of the endothermicity as the sum of the ionization energy of sodium metal and the solvation energy of sodium ion. Since cesium has the lowest ionization energy among investigated alkali metals, **1** will be reduced by cesium metal, but dianion salts **1a** (M$^+$ = Cs$^+$) may not be stabilized effectively by the electrostatic interaction in the ion pair due to the large ion radii of cesium ion.

The ESR spectra of powder of dianion salts **1a** (M$^+$ = K$^+$ and Rb$^+$) at room temperature are similar to that of **1a** (M$^+$ = Li$^+$) as shown in Figure 2; the spectral feature is characteristic of randomly oriented triplets having approximately 3-fold symmetry. The *g* values and zero-field splitting parameters of these dianion salts, *D* and *E*, determined by spectral simulation[8] are shown in Table 1. The *D* values of **1a** decrease with increasing size of the cations; 103.0, 89.0, and 86.5 mT for Li$^+$, K$^+$, and Rb$^+$, respectively. The averaged spin−spin distances between two electron spins are calculated using the point dipole approximation to be 2.08, 2.18 and 2.20 Å, for **1a** (M$^+$ = Li$^+$, K$^+$, and Rb$^+$, respectively).[9]

The dependence of the *D* values and hence the spin−spin distance of **1a** on the countercations will be the consequence of the contact ion-pair interaction in the dianion salts. The Coulomb energy between dianion **1a** and the cations, which is

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[3] (a) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464. (b) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081. (c) Sakurai, H. *Pure Appl. Chem.* **1994**, *66*, 1431.

[4] Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1991**, *113*, 7797.

[5] Ebata, K.; Setaka, W.; Inoue, T.; Kabuto, C.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 1335.

[6] It was once suggested incorrectly that **1a** (M$^+$ = Li$^+$) should have a ground-state triplet on the basis of the preliminary results of the temperature dependence of the ESR signal height ($\Delta m = 2$).[3c] However, the line-width of the $\Delta m = 2$ signal was found to be significantly temperature-dependent. To obtain more reliable data, we have determined the signal intensities for all hexasilylbenzene dianions investigated in this paper as the integrated area of the line.

[7] (a) Lambert, C.; Schleyer, P. v R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129. (b) Bock, H. et al. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550 and references therein.

[8] The ESR spectra were simulated using a program prepared by Professor Tero and Dr. Ikoma, Institute for Chemical Research Science, Tohoku University. We greatly appreciate their help.

[9] Intramolecular spin−spin distance is calculated according to the method reported by Breslow et al.: Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

Table 1. ESR Parameters of Hexasilylbenzene Dianion Salts

dianion	counter-cation	g	$\lvert D/\mathrm{cm}^{-1}\rvert$	$\lvert E/\mathrm{cm}^{-1}\rvert$	d/Å[a]	ΔE_{ST}/ (kcal mol^{-1})[b]	ΔH/ (kcal mol^{-1})[c]	ΔS/ (kcal mol^{-1} K^{-1})[c]
1a	Li^+	2.0035	0.0963	<0.001	2.08	1.0		
1a	K^+	2.0030	0.0832	<0.001	2.18	1.1		
1a	Rb^+	2.0030	0.0809	<0.001	2.20			
2a	Li^+	2.0025	0.0991	<0.001	2.06	1.1	1.0	7
3a	Li^+	2.0034	0.1001	<0.001	2.05	1.1	1.2	7
5a	Li^+	2.0030	0.0958	<0.0005	2.08	1.45		

[a] Average spin−spin distance calculated using the point-dipole approximation. [b] Singlet−triplet energy difference. Positive value means the singlet state is more stable than the triplet state. [c] Enthalpy (Δ*H*) and entropy (Δ*S*) for the distortion equilibrium in eq 4.

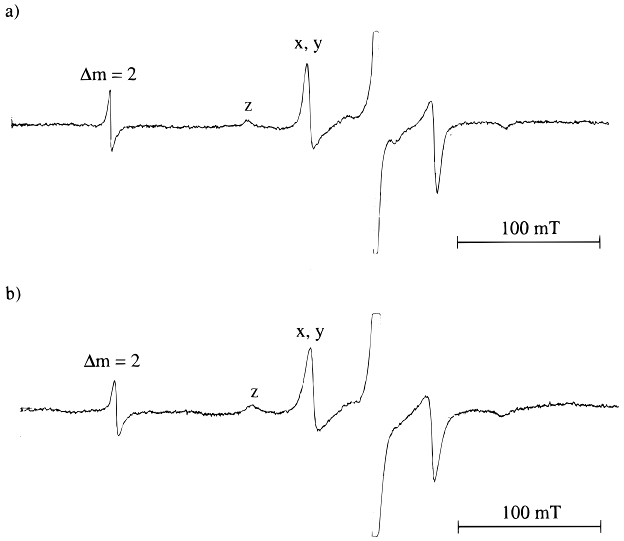

Figure 2. ESR spectra of powdered salts of hexasilylbenzene dianion **1a** at 20 °C: (a) $M^+ = K^+$; (b) $M^+ = Rb^+$. The central sharp lines are due to the corresponding anion radicals.

related to the surface charge per unit area of metal cations, will decrease with increasing size of the alkali metal ions.[10] With decreasing the Coulomb energies, the anionic charges in **1a** will be delocalized more to silyl-substituents to stabilize the system. The average spin−spin distance in **1a** will thus increase with increasing size of the metal ions. Similar countercation dependence of the *D* values has been observed in triplet states of triphenylene dianions.[1d]

The temperature dependence of the ESR signal intensity of **1a** ($M^+ = K^+$; $\Delta m_s = 2$) is compared with that of **1a** ($M^+ = Li^+$) in Figure 3. By fitting the experimental points with the Bleany−Bowers equation (eq 2),[11] the singlet state was found

$$I = \frac{3e^{-\Delta E_{ST}/RT}}{1 + 3e^{-\Delta E_{ST}/RT}}\frac{C}{T} \tag{2}$$

to be the ground state for **1a** ($M^+ = K^+$) with the energy gap between the singlet and the triplet states (ΔE_{ST}) of 1.1 kcal/mol, which is slightly larger than that for **1a** ($M^+ = Li^+$; 1.0 kcal/mol), probably due to the larger distance between two unpaired electrons in the former. A similar change in ΔE_{ST} depending on spin−spin distances has been observed in cyclopentadienyl cation systems.[12] The ESR signal intensity of **1a** ($M^+ = Rb^+$) was not enough to examine the temperature dependence.

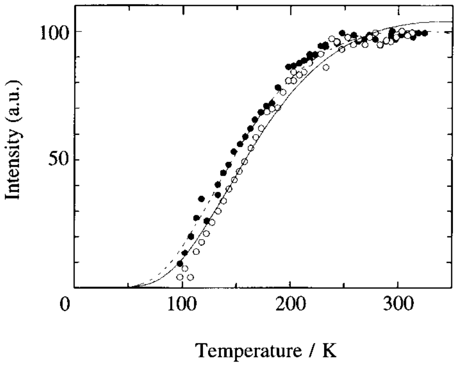

Figure 3. Temperature dependence of the ESR signal intensities ($\Delta m_s = 2$) of **1a** and curve-fitting with the Bleany−Bowers equation: (●) $M^+ = Li^+$ (ΔE_{ST} = 1.0 kcal/mol); (○) $M^+ = K^+$ (ΔE_{ST} = 1.1 kcal/mol).

Effects of Bridging Atoms. As shown in a previous paper, methylene bridging is important to prevent deformation from planar benzene ring geometry in **1a**.[5] To investigate the effects of the bridging groups on the geometry and electronic structure of hexasilylbenzene dianion, oxygen and nitrogen-bridged hexasilylbenzenes, **2** and **3**, were synthesized. ESR studies of the powder of the corresponding dianion salts **2a**, **3a**, and **4a** ($M^+ = Li^+$) have shown that the bridging groups play important roles not only to hold the benzene ring planar but to modify the electronic structure of hexasilylbenzene dianion.

Reduction of **2** and **3** by excess lithium metal in dry oxygen-free THF and then removal of solvent gave the black powder of **2a** ($M^+ = Li^+$) and **3a** ($M^+ = Li^+$). ESR spectra of the powder of **2a** and **3a** at room temperature (Figure 4) are characteristic of randomly oriented triplets having approximately 3-fold symmetry ($E = 0$) similarly to the spectra of **1a**. The *D* values of **2a** and **3a** are 106.0 mT (0.0991 cm^{-1}) and 107.0 mT (0.1001 cm^{-1}), respectively.[8] The *D* values of **2a** and **3a** are comparable to that of **1a** with the same countercations, indicating that the spin−spin distance is independent of bridging atoms.

Whereas dianions **2a** and **3a** ($M^+ = Li^+$) are thermally stable even at high temperatures (∼400 K) like **1a**, the temperature dependence of the ESR signal intensities ($\Delta m_s = 2$) of **2a** and **3a** is remarkably different from that of **1a** ($M^+ = Li^+$) as shown in Figure 5. The signal intensity of **1a** increases monotonically with increasing temperature but those of **2a** and **3a** decreased in the higher temperature region than 170 K. The simple Bleany−Bowers equation (eq 2)[11] is not applicable to the temperature dependence for **2a** and **3a**, while the dependence for **1a** is satisfactorily reproduced using the equation through the whole temperature region as shown in the previous section.

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(10) (a) Hart, A. J.; O'Brien, D. H.; Russell, C. R. *J. Organomet. Chem.* **1974**, *72*, C19. (b) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2981. (c) Takahashi, K.; Kondo, Y.; Asami, R. *Org. Magn. Reson.* **1974**, *6*, 580. (d) House, H. O.; Prabhu, A. V.; Philips, W. V. *J. Org. Chem.* **1976**, *41*, 1209. (e) O'Brien, D. H.; Hart, A. H.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (f) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427.

(11) Bleany, B.; Bowers, K. D. *Proc R. Soc.* (London) **1952**, *A214*, 451.

(12) (a) Breslow, R.; Jaun, B.; Kluttz, R. Q.; Xia, C. *Tetrahedron* **1982**, *38*, 863. (b) McGlynn, S. P.; Azumi, T.; Kinoshita, M. In *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1979; p 98.

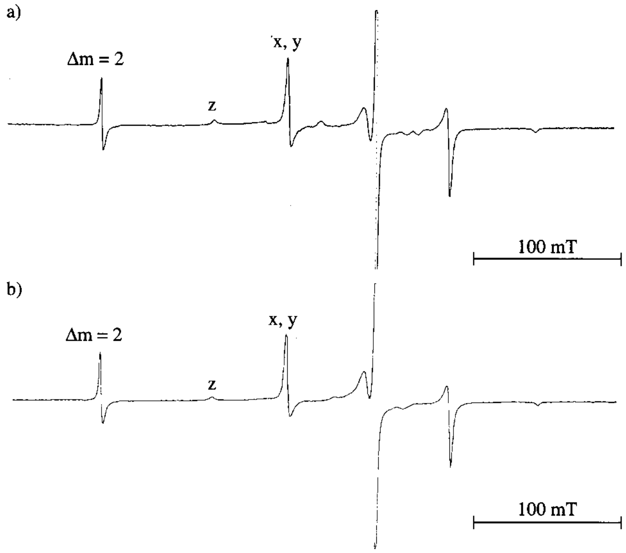

Figure 4. ESR spectra of powdered dilithium salts of hexasilylbenzene dianions **2a** and **3a** at 20 °C: (a) **2a**, (b) **3a**. The central sharp lines are due to the corresponding anion radicals.

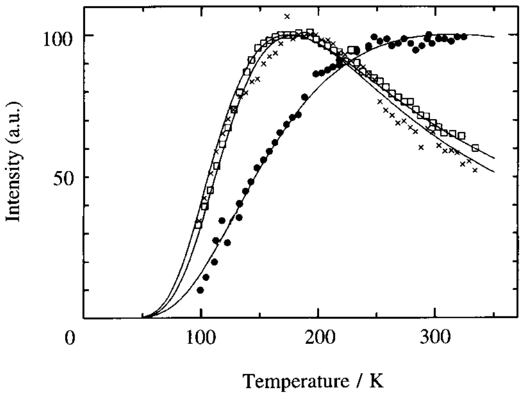

Figure 5. Comparison of the temperature dependence of the ESR signal intensities ($\Delta m_s = 2$) among **1a**−**3a** ($M^+ = Li^+$): (●) **1a**; (□) **2a**; (×) **3a**. Solid lines are obtained by curve-fitting with the Bleany−Bowers equation for **1a** and with the modified Bleany−Bowers equation for **2a** and **3a.**

The temperature dependence of the signal intensities for **2a** and **3a** is explained by taking the distortion of the geometry of the benzene ring from the planar D_{3h} structure at higher temperatures into account. In this situation, the population of the triplet state is determined not only by the thermal equilibrium between the singlet and triplet states at the D_{3h} structure but also by the population (eq 3)

$$\frac{|D_{3h}|}{|D_{3h}| + |\mathrm{DS}|} = \frac{1}{1 + K} = \frac{1}{1 + \mathrm{e}^{-\Delta G/RT}} \tag{3}$$

of the D_{3h} structure in the equilibrium between the D_{3h} and the distorted singlet structures (DS) (eq 4)

$$\underset{\text{(thermally accessible triplet)}}{\textit{\textbf{D}}_{\textbf{3h}}\ \textit{\textbf{benzene dianion}}} \overset{K}{\rightleftharpoons} \underset{\text{(singlet ground state)}}{\textit{\textbf{Distorted benzene dianion (DS)}}} \tag{4}$$

the triplet signal intensity (I) is described by the following modified Bleany−Bowers equation (eq 5)

$$I = \frac{1}{1 + \mathrm{e}^{-\Delta G/RT}} \frac{3\mathrm{e}^{-\Delta E_{\mathrm{ST}}/RT}}{1 + 3\mathrm{e}^{-\Delta E_{\mathrm{ST}}/RT}} \frac{C}{T} \tag{5}$$

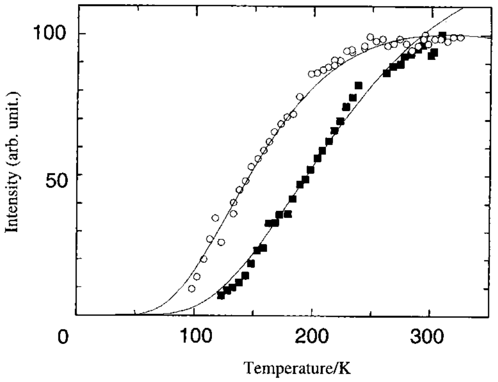

Figure 6. Comparison of the temperature dependence of the ESR signal intensities of **5a** ($M^+ = Li^+$, solid square) with those of **1a** ($M^+ = Li^+$, open circle). Solid lines are the curve-fitting with the Bleany−Bowers equation ($\Delta E_{\mathrm{ST}} = 1.45$ and 1.0 kcal/mol for **5a** and **1a**, respectively).

where K and ΔG are the equilibrium constant and the free energy difference in the equilibrium in eq 3, respectively:

The experimental temperature dependence of the ESR signal intensities of **2a** and **3a** was well fitted by eq 5. The reason for the drastic decrease of the intensities for **2a** and **3a** from 150 to 330 K is thus attributed to the significant contribution of the distorted structures (DS) in the temperature region, owing to more flexible Si−O−Si and Si−N−Si linkages compared with Si−C−Si linkage.[13] The ΔH values for the distortion equilibrium in eq 4 are small for **2a** and **3a** (1.0 and 1.2 kcal/mol, respectively), while the ΔE_{ST} values of **1a**, **2a**, and **3a** are independent of the bridging atoms (1.1 kcal/mol).

Dilithium complex of hexasilylbenzene dianion **4a** having a more flexible ethylene bridge showed no triplet ESR signals, being good in accord with the boat form like hexakis(trimethylsilyl)benzene dianion[3a] as determined by NMR spectroscopy (see Experimental Section).

Effects of Symmetry-Lowering by Introducing Two Different Bridging Groups. Whereas the orbital degeneracy in D_{3h} benzene is expected to be removed by very small electronic perturbation of a substituent, there has been no experimental study on how the degeneracy is sensitive to the symmetry-lowering by a substituent remote from the core degenerate π system. In this context, we have investigated ESR spectra of the dilithium salt of 1,3,4,6,7,9-hexasila-2-oxa-trindane dianion (**5**), where one bridging methylene in **1** is replaced by oxygen; **5** no longer has 3-fold symmetry, but C_{2v} symmetry in a rigorous sense. An ESR study of dianion **5a** has revealed that the ΔE_{ST} value is significantly larger than those for **1a**−**3a** with D_{3h} local symmetry.

The dilithium complex of hexasilylbenzene dianion **5a** ($M^+ = Li^+$) shows randomly oriented triplet signals in the ESR spectrum, similarly to that of **1a**; the D and E values and g factor of **5a** are 102.5 mT (0.0958 cm^{-1}), < 0.5 mT (0.0005 cm^{-1}), and 2.0030, respectively, which are very close to those for **1a** (Table 1).

In Figure 6, the temperature dependence of the ESR signal intensity of **5a** is compared with that for **1a**. Interestingly, the ΔE_{ST} value for **5a** (1.45 kcal/mol) determined using the Bleany−Bowers equation is larger by 0.45 kcal/mol than that of **1a**. The increase of the ΔE_{ST} value of **5a** compared with **1a** is ascribed to the difference in the electronic effects between oxygen and

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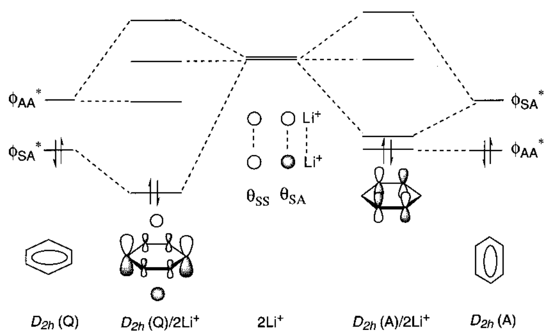

Figure 7. Qualitative MO interaction diagram between D_{2h}(Q) and D_{2h}(A) benzene dianions with two lithium ions in the ion-pair complexes. To represent the relative energy levels between hexasilylbenzene dianion and lithium in the ion-pair, ϕ_{SA} and ϕ_{AA} energy levels are located at lower levels than those of the 2s orbitals (LUMO) of lithium ions, while the relationship should not be realized in the parent benzene dianion–dilithium complex.

methylene remote from the core benzene. The result constitutes the first estimation of the destabilization energy of a benzene dianion triplet due to lowering symmetry by remote substituents.

Ion-Pair Interaction as a Possible Explanation for Singlet Ground States of Planar Benzene Dilithiums. The simple Hückel theory for planar benzene dianion **6a** predicts that the Jahn–Teller distortion to quinoid (D_{2h}(Q)) and anti-quinoid (D_{2h}(A)) structures may make the singlet state more stable than the triplet state with D_{6h} symmetry, if the exchange energy is smaller than the stabilization by the distortion (Figure 1). However, ab initio MO calculations have shown that the triplet state of the D_{6h} benzene dianion is 8.3 kcal/mol[14a] and 5.5 kcal/mol[14b] more stable than the D_{2h}(Q) singlet state at the R(O)-HF/4-31G level and the CCSD(T)/6-31G*//RHF/6-31G* level, respectively.[15] Although we need to consider the conical intersection associated with the Jahn–Teller interaction[16] to describe fully the singlet surface of the planar benzene dianion, the available theoretical results are not compatible with our experimental results for planar hexasilylbenzene dianion **1a** ($M^+ = Li^+$), which is singlet with the D_{2h}(Q) structure.

As shown in a previous section, the D value as well as ΔE_{ST} in **1a** is dependent on the countercations. The X-ray crystallography also suggests that there exists the significant ion-pair interaction in **1a** ($M^+ = Li^+$ quinuclidine); the benzene ring is distorted to a quinoid structure and the two lithium ions are located above and below the benzene ring with the distance of 1.69 Å between a lithium ion and the ring plane.[5] The singlet ground state of **1a** ($M^+ = Li^+$) may originate from the ion-pair interaction with the countercations. As shown in Figure 7, in planar benzene dilithium, an antisymmetric combination of the two s orbitals (θ_{SA}) can interact only with ϕ_{SA}*, while a symmetric combination of two vacant s orbitals on lithium cations (θ_{SS}) can interact with neither ϕ_{SA}* nor ϕ_{AA}* orbital of benzene. Thus, the HOMO of D_{2h}(Q) complex is stabilized, while the HOMO of D_{2h}(A) complex remains unperturbed. By this type of MO interaction, the D_{2h}(Q) singlet may become the most stable state in a planar benzene dilithium like **1a** ($M^+ = Li^+$), whereas the detailed assessment of electronic and steric effects of the outer rings is required for supporting this explanation.

Experimental Section

General Methods. ESR spectra were recorded on a Varian E-12 and a Bruker ESP-300E spectrometers. ^{1}H NMR (300 MHz) spectra were obtained on a Bruker AC-300 FT spectrometer. ^{13}C and ^{29}Si NMR spectra were collected at 75.5 and 59.6 MHz, respectively. Chemical shifts are based on the resonances of the deuterated solvents. Mass spectra and high-resolution mass spectra were obtained on a Shimadzu QP-1000 and a JEOL JMS D-300 mass spectrometers. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. All solvents were dried and degassed over a potassium mirror in vacuo prior to use.

Materials. Preparation of methylene-bridged hexasilylbenzene **1** was described previously.[5,17]

***O*-Bridged Hexasilylbenzene (2). Method A.** Hexakis(bromodimethylsilyl)benzene[18] (2.0 g, 2.3 mmol) was dissolved in diethyl ether (40 mL). To this solution was added water (5 mL) and then stirred for 10 min. Evaporation of the solvent afforded 1,3,4,6,7,9-hexasila-1,1,3,3,4,4,6,6,7,7,9,9-dodecamethyl-2,5,8-trioxatrindane (**2**, 1.0 g, 2.2 mmol, 95%) as a colorless solid, which was recrystallized from ethanol.

Method B. 2 was prepared in 46% yield using the intramolecular trimerization reaction of 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-5,10,15-trioxa-1,4,6,9,11,14-hexasila-cyclopentadeca-2,7,12-triyne with octacarbonyldicobalt in octane.[19]

2: colorless crystals; mp 266 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.43 (s, 36 H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 2.6, 152.3; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ 14.9; UV (hexane) λ_{max}/nm (ϵ) 256 (sh, 6000), 242 (sh, 11500), 218 (68000).

***N-Me*-Bridged Hexasilylbenzene 3.**To a three-necked flask (100 mL), dry methylamine (~10 mL), diethyl ether (30 mL), and hexakis(bromodimethylsilyl)benzene[16] (2.04 g, 2.27 mmol) were placed at −20 °C. After stirring for 10 min under argon, the mixture was slowly warmed to room temperature to give a white precipitate. After stirring further for 3 h, triethylamine (3 mL) and THF (5 mL) were added to the reaction mixture, which was stirred for an additional 8 h at room temperature. The resulting triethylammonium bromide, was filtered off under argon. Evaporation of the solvent afforded 2,5,8-triaza-1,3,4,6,7,9-hexasila-1,1,2,3,3,4,4,5,6,6,7,7,8,9,9-pentadecamethyltrindane (**3**, 1.03 g, 89%) as colorless crystals, which were recrystallized from ethanol: mp 214 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.31 (s, 36 H), 2.58 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 1.1 (SiCH$_3$), 26.4 (NCH$_3$), 151.3; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ 4.44; MS *m/z* (%) 507 (M$^+$,7), 492 (l00); UV (hexane) λ_{max}/nm (ϵ) 255 (sh, 8200), 240 (sh, 15800), 218 (67400); Anal. Calcd for $C_{21}H_{45}Si_6N_3$: C, 49.60; H, 8.93, N, 8.27. Found. C, 49.74; H, 8.63, N, 8.25.

Hexasilylbenzene Having an Ethylene and Two Methylene Bridges 4. Compound **4** was prepared in 44% yield by using the reaction of 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-1,4,6,9,11,14-hexasila-cyclohexadeca-2,7,12-triyne (**6**) with octacarbonyldicobalt in octane. Triyne **6** was synthesized with a similar method described in ref 17.

4: colorless crystals; ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.16 (s, 4 H), 0.31 (s, 12 H), 0.39 (s, 12 H), 0.41 (s, 12 H), 0.89 (s, 4 H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 1.1, 2.1, 3.9, 151.9, 154.9, 156.3; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ −7.9, 4.8, 6.3; MS *m/z* (%) 476 (M$^+$,100), 461 (32), 73 (50). HRMS Calcd for $C_{22}H_{44}Si_6$: 476.2059. Found: 476.2038.

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6: colorless crystals; ^{1}H NMR (300 MHz, CDCl$_3$) δ -0.08 (s, 4 H), 0.12 (s, 12 H), 0.22 (s, 24 H), 0.61 (s, 4 H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ -2.5, 1.2, 1.3, 3.1, 8.6, 113.7, 114.9, 115.1; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ -20.0, -19.9, -14.8; MS *m*/*z* (%) 476 (M$^+$,500), 461 (45), 403 (100), 73 (50). HRMS Calcd for $C_{22}H_{44}Si_6$: 476.2059. Found: 476.2040.

Hexasilylbenzene Having an Oxygen and Two Methylene Bridges 5. Compound **5** was prepared in 20% yield by using the reaction of 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-5-oxa-1,4,6,9,11,14-hexasilacyclopentadeca-2,7,12-triyne (**7**) with octacarbonyldicobalt in octane. Triyne **7** was synthesized with a similar method described in ref 19.

5: colorless crystals; mp 243 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ -0.92 (s, 4 H), 0.35 (s, 12 H), 0.42 (s, 12 H), 0.44 (s, 12 H); ^{13}C NMR (75.5 MHz, CDCl$_3$) 0.3, 2.9, 3.4, 153.2, 154.6, 155.8; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ 6.7, 7.2, 14.9; MS *m*/*z* (%) 464 (M$^+$,36), 449 (100), 217 (32), 73 (98). HRMS Calcd for $C_{20}H_{40}OSi_6$: 464.1695. Found: 464.1694.

7: colorless crystals; mp 126 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ -0.12 (s, 4 H), 0.23 (s, 24 H), 0.24 (s, 12 H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 1.5, 2.3, 3.1, 113.6, 113.8, 115.3; ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ -20.2, -19.5, -18.7; MS *m*/*z* (%) 464 (M$^+$,10), 449 (100), 73 (57). HRMS Calcd for $C_{20}H_{40}OSi_6$: 464.1695. Found: 464.1700.

Preparation of Dialkali−Metal Complexes of Hexasilylbenzene Dianions. Preparation of dilithium complexes of methylene-bridged hexasilylbenzene **1a** ($M^+ = Li^+$) was described in a previous contribution.[5]

1a ($M^+ = K^+$ or Rb^+). Methylene-bridged hexasilylbenzene **1** (30 mg, 0.06 mmol) and potassium or rubidium metal (1 mmol) were placed in a Schlenk tube with a magnetic stirrer. After degassing, dry oxygen-free THF (0.5 mL) was introduced by vacuum transfer, and the mixture was stirred at room temperature for 2 days. After the solvent was removed in vacuo, **1a** ($M^+ = K^+$ or Rb^+) was obtained as a black solid.

2a and 3a ($M^+ = Li^+$). To a mixture of lithium metal (70 mg, 10 mmol), quinuclidine (50 mg, 0.45 mmol), and **2** or **3** (0.06 mmol) in a Schlenk flask was introduced dry oxygen-free THF (0.5 mL) by vacuum transfer. The mixture was stirred for 10 min at room temperature to give a dark-red solution of the corresponding dianion. Evaporation of the solvent afforded **2a** or **3a** ($M^+ = Li^+$) as a black solid.

4a ($M^+ = Li^+$). A mixture of **4** (30 mg, 0.06 mmol), lithium metal (70 mg, 10 mmol), and THF (0.5 mL) was stirred for 0.5 h to give a dark-red solution of the dianion. Evaporation of the solvent afforded **4a** as diamagnetic red crystals.

4a: red crystals; ^{1}H NMR (300 MHz, toluene-d_8, 298 K) δ 0.12 (s, 3 H), 0.15 (s, 3 H), 0.39 (s, 3 H), 0.42 (s, 3 H), 0.47 (s, 3 H), 0.52 (s, 3 H), 0.69 (s, 3 H), 1.31 (m, 8 H), 3.47 (m, 8 H); ^{13}C NMR (75.5 MHz, toluene-d_8, 298 K) δ 2.29, 3.68, 3.93, 3.95, 4.02, 4.25, 4.36, 4.45, 4.92, 5.38, 5.41, 6.13, 6.80, 8.76, 11.04, 13.67, 25.59, 69.69, 81.17 (m), 99.73 (m), 139.52, 157.11, 158.60, 160.74; ^{29}Si NMR (59.6 MHz, toluene-d_8, 298 K) δ -17.6, -15.1, -6.6, -4.9, -4.1, -3.6; ^{7}Li NMR (116.6 MHz, toluene-d_8, 298 K) δ 0.03, 0.18.

5a ($M^+ = Li^+$). To a mixture of lithium metal (70 mg, 10 mmol), quinuclidine (50 mg, 0.45 mmol), and **5** (0.06 mmol) in a Schlenk flask was introduced dry oxygen-free THF (0.5 mL) by vacuum transfer. The mixture was stirred for 10 min at room temperature to give a dark-red solution of the corresponding dianion. Evaporation of the solvent afforded **5a** ($M^+ = Li^+$) as a black solid.

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Supporting Information Available: An ESR spectrum of **5a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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