Planar Hexasilylbenzene Dianion with Thermally Accessible Triplet State

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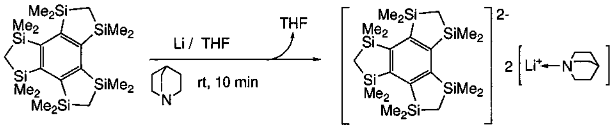
Received November 19, 1997

It is well recognized that, since benzene derivatives with D_{3h} or higher symmetry have 2-fold degenerate highest bonding and lowest antibonding π-orbital levels, the corresponding dianions and dications are potentially triplet states. Although a number of dianions and dications of benzene derivatives with ground or thermally accessible triplet states have been known so far,[1] most of them have more extended π systems such as coronene, triphenylene, and 1,3,5-triphenylbenzene. A recent experimental study of hexakis(trimethylsilyl)benzene dilithium[2] as well as a theoretical study of benzene dilithium[3] has revealed that they are singlet states with a nonplanar ring system, i.e., a boat form with doubly bridged lithium cations. As an approach to a triplet benzene dianion without stabilization by any extra π systems, we have investigated lithium metal reduction of a hexasilylbenzene, 1,3,4,6,7,9-hexasila-1,1,3,3,4,4,6,6,7,7,9,9-dodecamethyltrindane (**1**),[4] which is designed as a persilylbenzene that resists deformation from planar ring geometry. Actually, the corresponding benzene dilithium complex is almost planar in the solid state and shows thermally accessible triplet ESR signals.

When **1** was mixed with excess lithium metal in dry oxygen-free tetrahydrofuran at room temperature, a dark-brown solution of 1^{2-} was obtained within a few minutes (eq 1). After the solvent was removed in vacuo, $1^{2-}[Li^+(thf)_n]_2$ (**2a**) was isolated as amorphous black solid. Benzene dianion salt **2a** was extremely air- and moisture-sensitive. A similar reduction in the presence of quinuclidine ($C_7H_{13}N$, 2 mol) as a ligand for lithium cation followed by recrystallization from toluene gave single crystals of 1^{2-} $[Li^+(C_7H_{13}N)]_2$ (**2b**).



(1)

1 **2b**

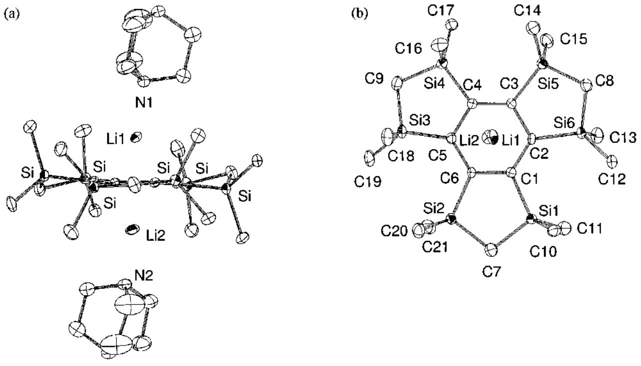


Figure 1. Molecular structure of **2b**: (a) side view; (b) top view (quinuclidine is omitted for clarity). Selected bond lengths (Å): C1−C2, 1.470(9); C2−C3, 1.511(9); C3−C4, 1.443(9); C4−C5, 1.494(9); C5−C6, 1.486(9); C6−C1, 1.448(9); C1−Si1, 1.883(7); C2−Si2, 1.853(7); C3−Si3, 1.861(7); C4−Si4, 1.871(7); C5−Si5, 1.864(7); C6−Si6, 1.864(7); Si1−C7, 1.878(9); Si6−C7, 1.861(9); Si2−C8, 1.872(9); Si3−C8, 1.865(9); Si4−C9, 1.864(9); Si5−C9, 1.872(9); Li1−N1, 2.040(16); Li2−N2, 2.014(16). Selected bond angles (deg): C6−C1−C2, 121.6(6); C1−C2−C3, 118.7(6); C2−C3−C4, 119.9(6); C3−C4−C5, 120.8(6); C4−C5−C6, 119.1(6); C5−C6−C1, 119.9(6); Si6−C6−C1, 114.1(5); Si1−C1−C6, 113.5(5); Si2−C2−C3′ 113.2(5); Si3−C3−C2, 112.3(5); Si4−C4−C5, 112.7(5); Si5−C5−C4, 112.8(5); Si1−C7−Si6, l05.0(5); Si2−C8−Si3, l04.3(4); Si4−C9−Si5, l03.6(4).

The molecular structure of **2b** determined by X-ray crystallography[5] is shown in Figure 1. One lithium atom is located above the benzene ring and the other below; each lithium atom is coordinated by one quinuclidine. The distances between a lithium atom and the benzene ring plane are 1.667 (Li1) and 1.717 Å (Li2), and all distances between benzene carbons and lithium atoms are approximately equal (2.196−2.322 Å, av 2.245 Å). As expected, the benzene ring of **2b** is mostly planar in contrast to that of hexakis(trimethylsilyl)benzene dilithium;[2] the torsion angles of all sets of four connected aromatic carbons of **2b** are only 0.96−3.78° (the average value, 2.22°). All interior angles of the benzene ring are almost 120° (118.7−121.6°, total 720.0°). However, the benzene ring of **2b** is significantly distorted from D_{6h} symmetry to quinoid D_{2h} structure; the bond lengths of C1−C2 (1.470 Å), C2−C3 (1.511 Å), C4−C5 (1.494 Å), and C5−C6 (1.486 Å) are longer than those of C1−C6 (1.448 Å) and C3−C4 (1.443 Å). Positions of the Si atoms slightly deviate up and down alternately from the benzene ring plane; torsion angles of $Si-C_{ar}-C_{ar}-Si$ are 2.0−12.9° (av 6.5°). A five-membered ring of C1−C6−Si2−C7−Si1 is approximately flat, while the others are puckered. The benzene planes of **2b** are regularly stacking along the axis in the crystal. The shortest distance between centers of the two benzene rings in the crystal is 10.7 Å, being indicative of no significant intermolecular spin−spin interaction in the solid state.

An ESR spectrum of a powder of **2b** (Figure 2)[6] at room temperature is characteristic of randomly oriented triplets having approximately 3-fold symmetry with the simultaneous appearance of a signal due to $\Delta m_s = 2$; the zero-field splitting parameters D

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(4) Hexasilylbenzene **1** was prepared by the intramolecular trimerization of 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-1,4,6,9,11,14-hexasilacyclopentadeca-2,7,12-triyne with octacarbonyldicobalt in 46% yield: Ebata, K.; Matsuo, T.; Inoue, T.; Otsuka, Y.; Kabuto, C.; Sekiguchi, A.; Sakurai, H. *Chem. Lett.* **1996**, 1053.

(5) A single crystal of **2b** with dimensions of 0.25 × 0.l0 × 0.25 mm was sealed in a capillary glass tube. Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at −120 °C. A total of 9710 reflections with $3° < 2\theta < 55°$ were collected. Crystal data: $Si_6N_2C_{35}Li_2H_{68}$; MW = 699.33; monoclinic; $a = 12.779(4)$ Å, $b = 17.301(3)$ Å, $c = 19.199(4)$ Å, $\beta = 94.90(2)°$; $V = 4229.0(19)$ Å^3; space group $P2_1/n$; $Z = 4$; $D_{calcd} = 1.098$ g/cm^3. The structure was finally refined anisotropically for Si, N, C, and Li (observed) and isotropically for H (calculated) to give an R factor of 0.0816 ($R_w = 0.0898$) for 4063 reflections with $F_o > 4\sigma(F_o)$.

(6) The ESR spectra were recorded on an X-band ESR spectrometer (Varian E-12) in the range of 110−400 K.

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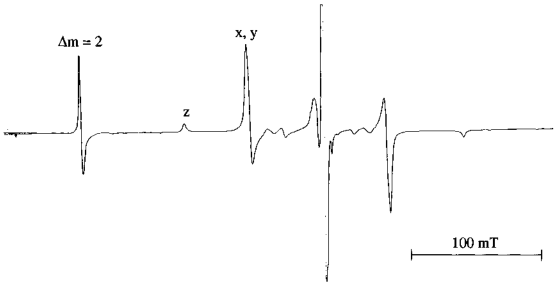

Figure 2. ESR spectrum of powder of **2b** at 20 °C. The central sharp line is due to the corresponding anion radical.

and E are 103.0 mT (0.0963 cm^{-1}) and 0 mT and $g_{xy} = g_{zz} = 2.0035$.[7] The D value is remarkably larger than those of coronene dianion (57.5 mT),[1e] coronene dication (63.2 mT),[1a] and hexaazacoronene dication (59.7 mT)[1b] with extended π systems. Using a cyclic π electron triplet model,[8] the averaged distance between the two electron spins is calculated to be 2.4 Å, indicating that the electron spins in **2b** are almost confined within the benzene ring; the spin−spin distance is shorter than the diagonal distances of the benzene ring of **2b** (av 2.95 Å) determined by X-ray analysis. Benzene dilithium **2a** without quinuclidine ligand displays the same triplet ESR spectrum at room temperature. No decomposition of **2a** or **2b** is observed at <120 °C.

The temperature dependence of the signal intensity ($\Delta m_s = 2$) of **2b** is shown in Figure 3. The signal intensity increases with increasing temperature between 100 and 300 K, as expected for a thermally excited triplet. The energy gap between the triplet state and the singlet ground state (ΔE_{ST}) is estimated to be only 1.0 kcal/mol, as determined by curve-fitting with the Bleany−Bowers equation (eq 2).[9]

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

It is interesting to note that **2b**, the closest system of planar benzene dianion ($C_6H_6^{2-}$) among the known derivatives for the moment, is a singlet ground state (ESR) with a quinoid ring structure (X-ray). In contrast, ab initio MO calculations of $C_6H_6^{2-}$ constrained to the planar ring geometry have shown that the triplet state (D_{6h}) is lower in energy than the singlet states with Jahn−Teller-distorted quinoid and antiquinoid benzene structures (D_{2h}).[10] The discrepancy between theory and experiment is ascribed to silyl-substituent effects, insufficient levels of ab initio MO calculations, or significant ion-pair interaction between lithium cations and benzene dianion.[12]

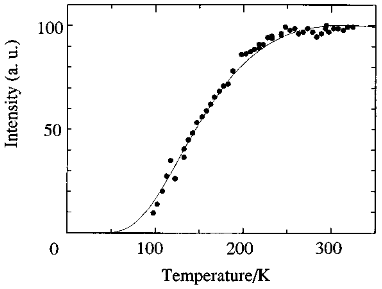

Figure 3. Temperature dependence of the ESR signal intensity of **2b** ($\Delta m_s = 2$) and the curve-fitting with the Bleany−Bowers equation (ΔE_{ST} = 1.0 kcal/mol).

Acknowledgment. We are grateful to Dr. E. Wasserman (Du Pont) for his helpful discussion and to the Ministry of Education, Science, and Culture of Japan for the financial support (Specially Promoted Research No. 02102004).

Supporting Information Available: X-ray experimental details and tables of positional parameters, thermal parameters, bond lengths, and angles (17 pages). See any current masthead page for ordering information and Web access instructions.

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(7) The ESR parameters were determined using the simulation program prepared by Professor Tero and Dr. Ikoma, Institute for Chemical Research Science, Tohoku University. A very small splitting of H_x and H_y peaks is observed at 120 K, indicating that the trigonal symmetry is lost in the rigorous sense.

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(10) The triplet $C_6H_6^{2-}$ (D_{6h}) has been reported to be more stable than the singlet quinoid (S_Q) and antiquinoid (S_A) structures with ΔE_{ST} values of −9.19 and −8.29 kcal/mol, respectively, at the R(O)HF/4-31G level.[11a] Theoretical calculations by ourselves at the QCISD(T)/6-31G*//R(O)HF/6-31G* level gave similar results, where the ΔE_{ST} values are −5.36 and −3.02 kcal/mol for S_Q and S_A, respectively.

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(12) During a theoretical study of planar benzene dilithium complexes, a singlet with a similar quinoid structure to **2b** was found as an energy minimum at the RHF/6-31G* level, where the lengths of long and short C−C bonds are 1.497 and 1.348 Å, and the two lithium atoms are located at the opposite side of the benzene ring plane with each other with the distance between lithium and benzene plane of 1.66 Å. No minimum was found for the D_{6h} triplet or antiquinoid structure of a singlet benzene dilithium. Details will be reported in a forthcoming paper.