

An approach to stable organic molecules of the triplet state via organosilicon route

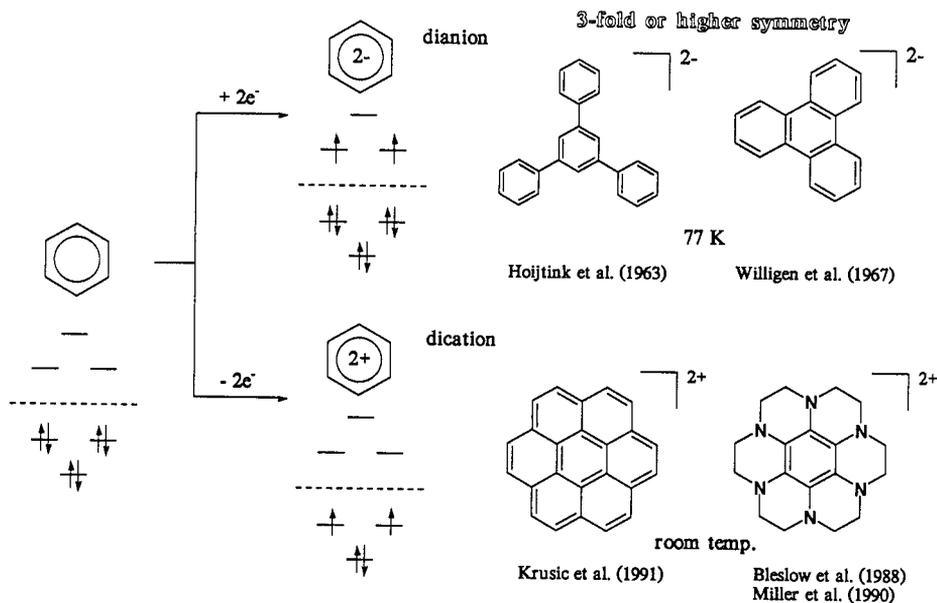
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ABSTRACT – Dianions of hexakis(trimethylsilyl)benzene and 1,2,4,5-tetrakis(trimethylsilyl)benzene are described. Although the former has a boat-deformed structure of non-aromaticity with two lithium atoms at the same side of the benzene ring, the latter has a planer structure of anti-aromaticity with two lithium atoms at the both side of the benzene ring. The dianion of specially designed hexasilylbenzene with three fused rings shows triplet ESR signals in the temperature range of 100–370 K.

INTRODUCTION

It is one of the most interesting and challenging subject to realize the stable triplet states for benzene dianions and dication. These are not only theoretically important but interesting as potential components of organic molecular ferromagnetic materials. The benzene ring accommodates normally 6π -electrons as an aromatic system. However, the benzene dianion and dication systems can be anti-aromatic, namely destabilized by conjugation as 8π - and 4π -electron systems. It is also an interesting possibility that these systems can have ground triplet states with two unpaired electrons, if they have appropriate symmetry.



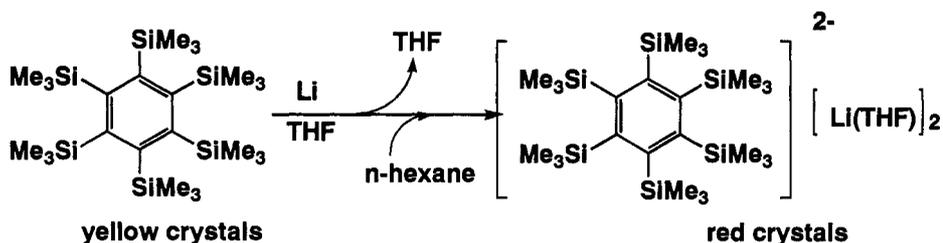
Recently, dications of coronene¹ and hexaazacorone² have been reported as the stable triplet at ambient temperature. The triplet ESR spectra were observed for 1,3,5-triphenylbenzene and

decacyclene dianions³ at 77 K and for the coronene dianion⁴ in the temperature range of -160 to + 60 °C.

Silyl groups can stabilize either cationic or anionic centers by either $\alpha(\text{Si-C})-\pi$ or $\sigma-\pi^*$ conjugation. Therefore, silyl-substituted benzene systems are of considerable interest to construct the corresponding dianion or dications. In this paper, we describe recent results of investigations on such systems.

BIS[(TETRAHYDROFURAN)LITHIUM(I)] HEXAKIS(TRIMETHYLSILYL)BENZENIDE

As a part of studies on persilylated π -electron systems, particularly on persilylated benzenes,⁵ we are interested in the formation of dianions of hexakis(trimethylsilyl)benzene (1).^{5c} Reduction of hexakis(trimethylsilyl)benzene (1) with excess lithium metal in dry oxygen-free THF at room temperature led to the formation of a dark red solution of the benzene dianion of 1 within one hour. 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), containing two molecules of THF. 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 structure of 2 has been unequivocally determined by X-ray crystallography as shown in Fig. 1. 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. To each lithium atom, one THF molecule is coordinated. So far reported, the cations in polynuclear aromatic dianions are located above and below the plane.⁶

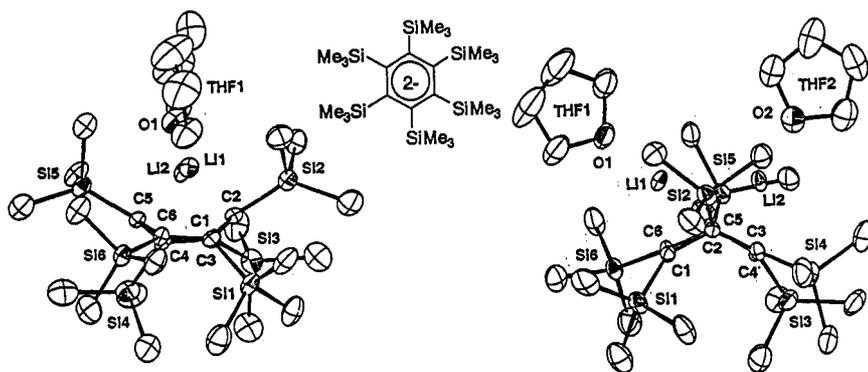


Fig. 1. Molecular Structure of $[\text{Li}(\text{thf})_2][(\text{Me}_3\text{Si})_6\text{C}_6]^{2-}$

Four aromatic carbons [C(1), C(3), C(4), C(6)] are nearly coplanar, while C(2) and C(5) carbons are above the C(1)–C(3)–C(4)–C(6) plane by 0.656 Å and 0.578 Å, respectively. Consequently, the benzene ring is appreciably deformed into a boat form. A theoretical consideration of the benzene dianion by *ab initio* calculation on the 6–21G level⁷ suggested that the anti-aromatic 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. The structure of the ligand benzene reflects the properties of the Ψ_s orbital of **1** as shown in Fig. 2.

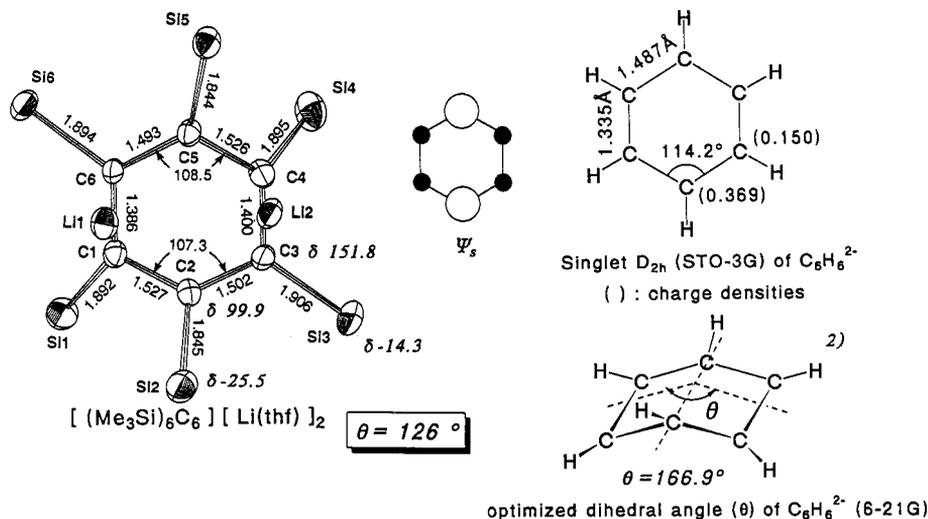
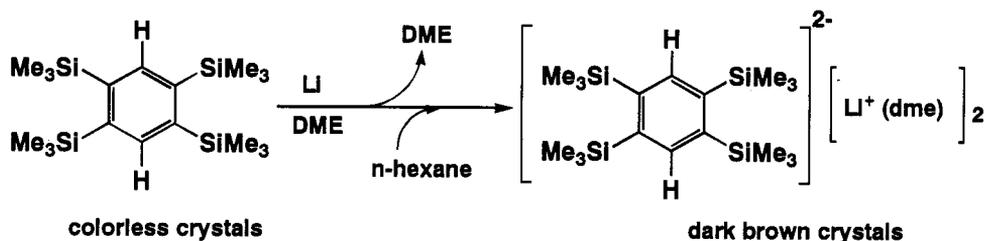


Fig. 2. Structure of the hexakis(trimethylsilyl)benzene dianion

The geometry (planar or nonplanar) and electronic state (singlet or triplet) of the benzene dianion is theoretically of great interest.^{7,8} Large stabilization of the 8π system by folding has been indicated. Indeed, as stated above, the hexakis(trimethylsilyl)benzene dianion–dilithium complex (**2**), as the first nonconjugated mononuclear benzene dianion, was highly distorted into a boat form having a closed shell electron system. The fact that the deformation is not attributable to the steric hindrance of bulky trimethylsilyl substituents is indicated experimentally^{5c} and theoretically.⁹ In any event, **2** was neither a triplet-state molecule nor an anti-aromatic molecule.

BIS[(DIMETHOXYETHANE)LITHIUM(I)]-1,2,4,5-TETRAKIS(TRI-METHYLSILYL)BENZENIDE. A NOVEL ANTI-AROMATIC BENZENE DIANION OF THE FIRST $6C-8\pi$ SYSTEM

Next, we have examined generation of dianions from 1,2,4,5-tetrakis(trimethylsilyl)benzene (**3**).



Reduction of **3** with lithium metal in dry-oxygen free dimethoxyethane (DME) at room temperature immediately led to a dark brown solution of the benzene dianion of **3**. The solvent was removed

in vacuo and then dry degassed hexane was introduced by vacuum transfer. Crystallization from hexane afforded dark brown crystals of bis[[dimethoxyethane]lithium(I)]-1,2,4,5-tetrakis(trimethylsilyl)benzenide **4**, $[\text{Li}(\text{dme})]_2[1,2,4,5-(\text{Me}_3\text{Si})_4\text{C}_6\text{H}_2]$.

The structure of **4** was also determined by X-ray crystallography. The ORTEP drawing of the molecular geometry of **4** is shown in Fig. 3. In this case, the two lithium atoms are perfectly located above and below the center of the benzene ring, and each lithium atom is coordinated by one DME as a bidentate ligand.

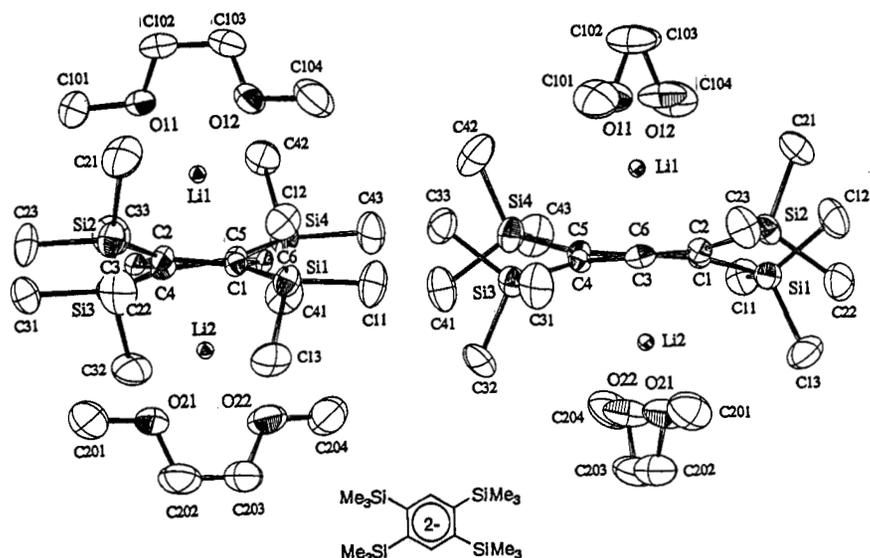


Fig. 3. Molecular structure of 1,2,4,5-tetrakis(trimethylsilyl)benzene dianion

The distances between lithium atoms and the mean plane of the benzene ring are 1.870 Å (Li1) and 1.868 Å (Li2), and the distances between benzene carbons and lithium atoms are approximately equal (av. 2.366 Å). The benzene ring is *nearly planar*, contrary to the case of **2**. The bond lengths of $\text{C}_{\text{ar}}-\text{Si}$ (av. 1.824 Å) are shortened due to the increased bond order (cf. $\text{C}_{\text{ar}}-\text{Si}$ in Ph_4Si : 1.872 Å).

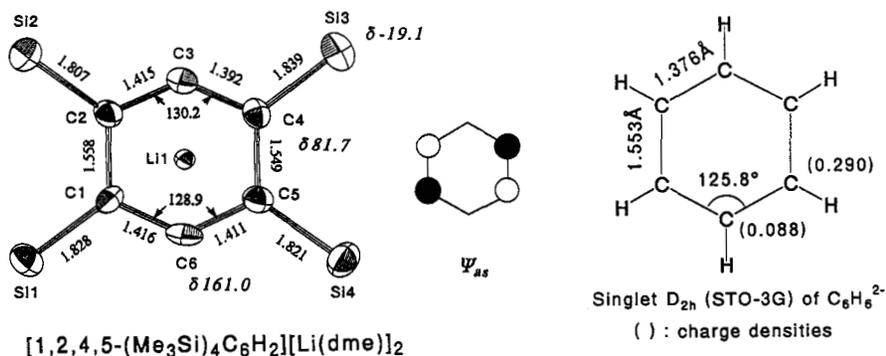


Fig. 4. Structural features of tetrakis(trimethylsilyl)benzene dianion

The bond lengths of C(2)–C(3) (1.415 Å), C(3)–C(4) (1.392 Å), C(5)–C(6) (1.411 Å), 3 and C(6)–C(1) (1.416 Å) are almost as the same as aromatic C–C bond distances (1.40 Å), whereas the bond lengths of C(1)–C(2) (1.558 Å) and C(4)–C(5) (1.549 Å) are appreciably elongated. The internal bond angles at C(1), C(2), C(4), and C(5) carbons range from 113.5° to 115.3°. However, the bond angles of both C(2)–C(3)–C(4) (130.2°) and C(5)–C(6)–C(1) (128°) are widened considerably. The molecular structure is in good accordance with that of the calculated form (D_{2h}) of $C_6H_6^{2-}$. The geometry of **2** seems to be reflected by Ψ_{as} LUMO of **3** (Fig. 4).

Of particular interest in NMR spectra of **4** is 7Li resonance at 10.7 ppm, being observed at the lowest magnetic field among the organolithium compounds reported so far. For comparison, 7Li signal of $[Li(thf)]_2[(Me_3Si)_6C_6]$ (**2**) was observed at -1.48 ppm owing to the nonaromaticity. In contrast to **4**, 7Li of lithium cyclopentadienide (LiCp) was reported to be -8.60 ppm in Et_2O due to the strong shielding.

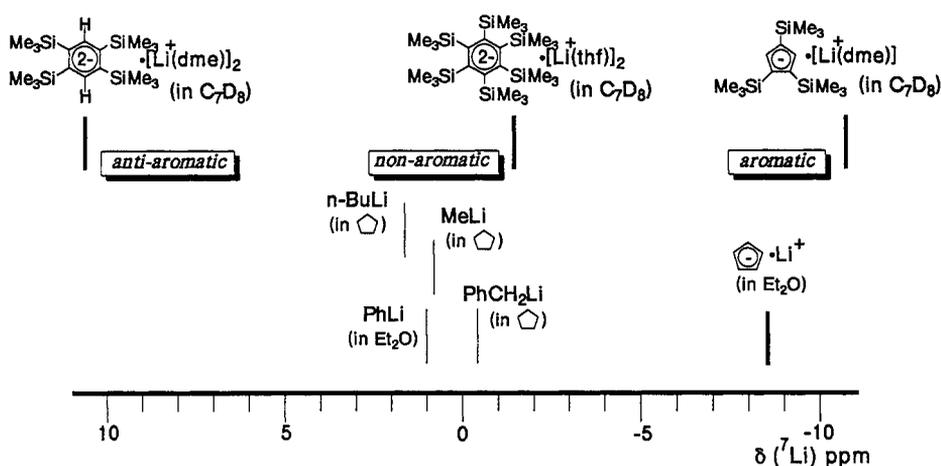
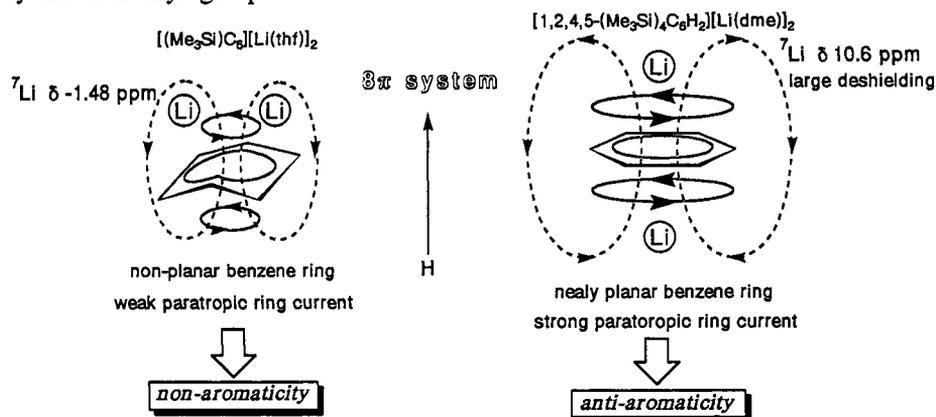


Fig. 5. 7Li NMR chemical shifts of organolithium compounds

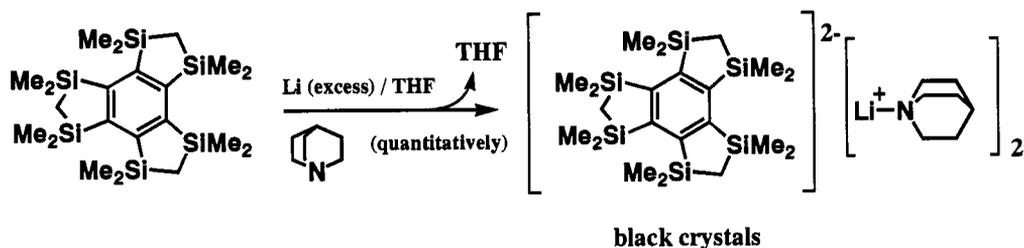
The appreciable down-field shift is caused by the high deshielding effect on the lithium atoms by the paratropic ring current resulting from 8π antiaromatic system. Based on these spectroscopic properties, the molecular structure of **4** found in the crystals is persisted in solution. Thus, the benzene dianion **4** has the nearly planar anti-aromatic character so as to stabilize the anionic charge by the four silyl groups.



Thermally Stable Triplet Hexasilylbenzene Dianion

As demonstrated by the above two examples, to achieve the mononuclear benzene dianions of the stable triplet state, it is necessary to design a system with a planar rigid structure and at least three-fold symmetry (*i. e.* D_{3h}). In this section, synthesis, crystal structures, and ESR spectra of the dianion dilithium complex of the hexasilylbenzene (**5**), which is designed to keep planarity of the benzene ring in the anti-aromatic 8π dianion state and to hold a rigid structure by fixing with three $-\text{Me}_2\text{Si}-\text{CH}_2-\text{SiMe}_2-$ chains.

Hexasilylbenzene (**5**) was prepared by the intramolecular trimerization reaction of 1,1,4,4,6,6,9,9,11,11,14,14-dodecamethyl-1,4,6,9,11,14-hexasila-cyclopentadeca-2,7,12-triyne with octacarbonyl-dicobalt. Reduction of **5** with excess lithium metal in dry oxygen-free tetrahydrofuran at room temperature gave a dark-brown solution of 5^{2-} within one hour. After removal of the solvent *in vacuo*, amorphous black solids of $1^{2-}[\text{Li}^+(\text{thf})_n]_2$ were remained. The dianion 1^{2-} was extremely air- and moisture-sensitive. Reduction of **5** with Li in the presence of quinuclidine ($\text{C}_7\text{H}_{13}\text{N}$) as ligand for the lithium cation gave the crystalline solids of $1^{2-}\cdot[\text{Li}^+(\text{C}_7\text{H}_{13}\text{N})]_2$ (**6**). Suitable single crystals for X-ray crystallography were obtained from a toluene solution.



The structure of **6** was determined by X-ray crystallography. The ORTEP drawing of the molecular geometry of **6** is shown in Fig. 6. The two lithium atoms are perfectly located above and below the center of the benzene ring, and each lithium atom is coordinated by one quinuclidine as a ligand. The benzene ring is slightly distorted from the regular hexagonal D_{6h} symmetry to the quinoid D_{2h} structure. Positions of the Si atoms slightly deviate up and down alternately from the benzene ring plane. The torsion angles of $\text{Si}-\text{C}_{\text{ar}}-\text{C}_{\text{ar}}-\text{Si}$ are 2.0 – 12.9° (average: 6.5°). The five membered ring of $\text{C}1-\text{C}6-\text{Si}6-\text{C}7-\text{Si}1$ is approximately flat, while others are puckered slightly. Therefore, the molecule does not have a precise 3-fold symmetry but the degree of the distortion is rather small.

The ESR spectrum displayed by powder of **6** (Fig. 7) at room temperature is characteristic of randomly oriented triplets having approximately 3-fold symmetry (very small E value: 0.0012 cm^{-1}). This species is surprisingly stable at higher temperature (100°C), decomposing above 120°C . The zero-field splitting parameter D is 1030 G (0.0963 cm^{-1}), and the g factors are $g_{xy} = 2.0297$ and $g_{zz} = 2.0056$. This D value is obviously larger than those of coronene dianion (575 G), coronene dication (632 G), and hexaazacoronene dication (597 G) whose π -systems are extended beyond the central benzene ring. The average distance between the two interacting electrons can be estimated from D to 3.0 \AA , which is in excellent agreement with the diagonal distances (average: 2.95 \AA) of the benzene ring of **6** determined by X-ray analysis. Accordingly, the spins are localized only in the benzene π -system.

The intensity of the $\Delta m = 2$ line of the triplet spectrum of **6** showed reversible thermal dependency as shown in Fig. 8. The question of whether the observed triplet state of **6** is the ground state is not easy to answer at this moment. However, this is the first example of organic triplet

molecule whose ESR spectrum is observed in a wide temperature range. Apparently, the spectrum obeys the Curie law $I = C/T$ as expected for a ground state triplet above 200 K. Further works are in progress.

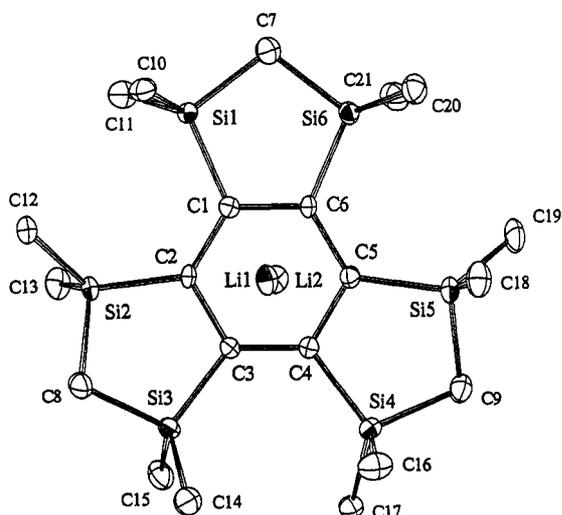


Fig. 6. Molecular structure of the dianion 6.

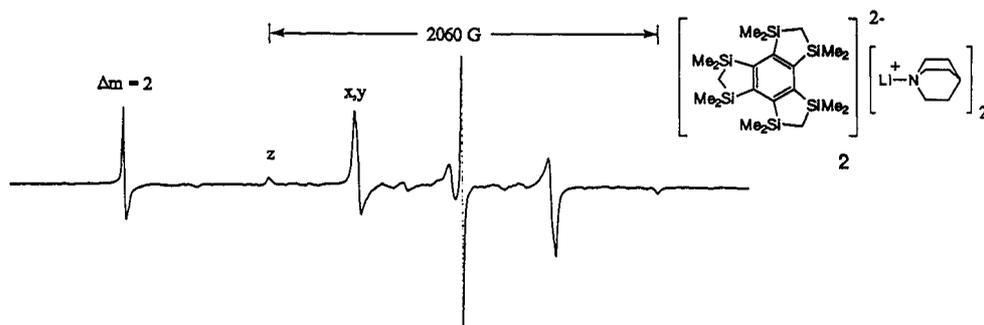


Fig. 7. Triplet ESR spectrum of 6.

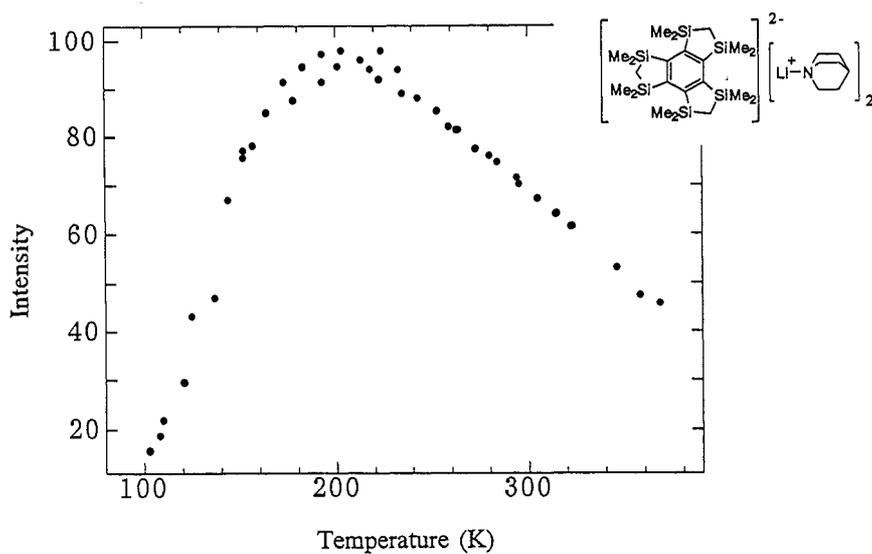


Fig. 7. Temperature dependence of the ESR signal of the $\Delta m = 2$ line of 6

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