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Photoelectron spectra and molecular properties

CXXXVIII *. 1,4-Di[tris(trimethylsilyl)silyl]benzene: synthesis, structural analogy, photoelectron spectrum and ESR/ENDOR characterization of its radical anion **

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Abstract

1,4-Di[tris(trimethylsilyl)silyl]benzene $[(H_3C)_3Si]_3SiC_6H_4Si[Si(CH_3)_3]_3$, which contains eight silicon centers, has been synthesized and some of its molecular properties determined. For a single crystal structure determination, its isovalence-electronic and sterically more crowded carbon analogue, $[(H_3C)_3Si]_3CC_6H_4C[Si(CH_3)_3]_3$, was selected. It shows van der Waals interactions due to close lattice packing. Despite its shorter SiC bonds, however, no severe skeletal distortions due to overcrowding are observed; the contraction of the benzene *ipso* angles to 114° is due to the donor effect of the tris(trimethylsilyl)methyl substituents. The first vertical ionization energy of the title molecule, $IE_1^v = 7.37$ eV, is the lowest of all of these recorded up to now for 1,4-dialkyl or 1,4-disilyl substituted benzene derivatives; for the monosubstituted tris(trimethylsilyl)silyl derivative $[(H_3C)_3Si]_3SiC_6H_5$ the value is 8.04 eV. Cyclovoltammetric experiments in aprotic solution reveal a velocity-dependent irreversible oxidation above +1.28 eV and no electron insertion within the measurement range to -2.9 V. The reduction to the radical anion, however, can be achieved in THF solution containing [2.2.2]cryptand at a potassium metal mirror. According to the spin populations deduced from 1H and ^{29}Si ENDOR signal patterns, more than half of the spin is located in the two $[(H_3C)_3Si]_3Si$ groups. Results of molecular orbital (MO) calculations and comparison with equivalent molecular states of chemically related compounds allow rationalization of the effects of the $[(H_3C)_3Si]_3Si$ substituent, which acts as a strong electron donor in radical cations and as a strong electron acceptor in radical anions.

1. Introduction

Trimethylsilyl substituents in a β -position to a π -system or to a lone pair center are among the strongest electron donors known, especially for molecular cations [5–7]. This is shown, for instance, by the very large

lowering of their first vertical ionization energies ΔIE_1^v , relative to those of the parent compounds or even of their methyl derivatives [8,9]:

	$R-C\equiv C-R$	$\begin{array}{c} R \\ \diagup \\ C \\ \diagdown \\ R \end{array}$	$\begin{array}{c} R & & R \\ & \backslash & / \\ & C \\ & / & \backslash \\ R & & R \end{array}$	$\begin{array}{c} R & & R \\ & \backslash & / \\ & N \\ & / & \backslash \\ R & & R \end{array}$
				(1)
$R = H$	11.40	10.51	9.24	10.85
$-CH_3$	9.61	8.31	8.05	8.44
$-CH_2Si(CH_3)_3$	8.85	7.15	7.10	7.66
$\Delta IE_1^v(H/CH_2Si(CH_3)_3)$	2.55	3.36	2.14	3.91 eV

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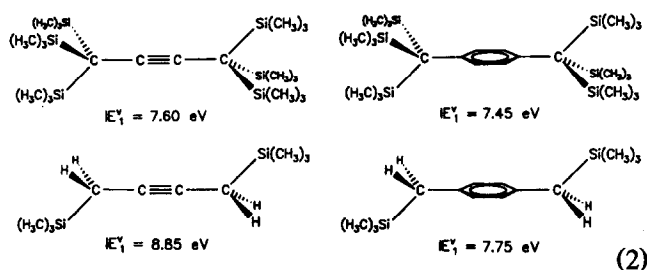
* Part CXXXVII see ref. 1, cf. also refs. 2–4.

** Dedicated to Professor M.G. Voronkov in recognition of his important contributions to organosilicon chemistry.

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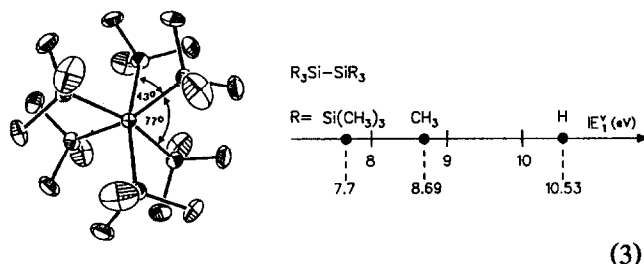
Obviously, there are individual differences depending on the molecular size, the substitution pattern and the effective nuclear charges at the substitution centers, and these can be rationalized in terms of first and

second order perturbation arguments [5,10]. On multiple substitution $[(H_3C)_3Si]_nH_{3-n}C$, the ionization energies fall further [8,9]:



These observations illustrate the extensive delocalization of the positive charge into the bulky ligands, which simultaneously shield the reactive radical cations generated and often allow their characterization by ESR/ENDOR spectroscopy in aprotic solutions [5,6,11,12].

Recently, we have determined the crystal structure of hexakis(trimethylsilyl)disilane [1], which like that of the sterically much more crowded tert-butyl derivative [13], shows cogwheel gearing of the two molecular halves, and thus within D_3 symmetry exhibits two different dihedral angles of 43 and 77°:

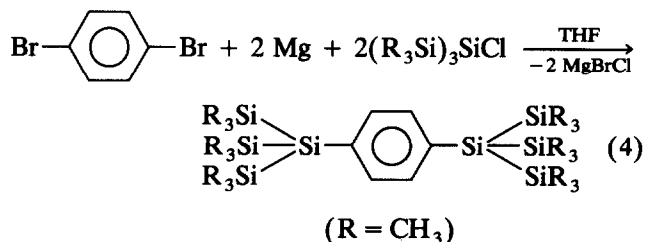


Furthermore, its first vertical ionization energy is the lowest so far observed for a disilane derivative [6]: PE spectroscopy gave a value of 7.70 eV, which is 3 eV (!) below that of the parent disilane and still 1.16 eV below that of the hexamethyl derivative [1]. Accordingly, the replacement of the central carbon in the $[(H_3C)_3Si]_3C$ -substituent by silicon enhances its donor effect. An additional comparison of the bulky $[(H_3C)_3Si]_3Si$ groups with simple $(H_3C)_3Si$ substituents, which already considerably stabilize π -radical anions [5,14], suggests that they also must be superior acceptors for negative charges.

The benzene π -system, which according to HMO theory has both degenerate highest occupied (e_{2g}) as well as lowest unoccupied (e_{2u}) levels [5,10], is well-suited for investigation of substituent perturbations by the bulky $[(H_3C)_3Si]_3Si$ groups. Depending on the positive or negative charge of the respective radical ion, either strong electron-donating [1,5] or electron-accepting [5,16] effects are expected. Experimental evidence

has already been provided for both effects; for instance, by photochemical reactions of tris(trimethylsilyl)benzene [15] such as the generation of trimethylsilylphenylsilylene by R_3SiSiR_3 elimination [16] or by the ESR spectroscopic characterization of its radical anion [17]. For further investigation, the 1,4-disubstituted-benzene derivative, $[(H_3C)_3Si]_3SiC_6H_4Si[Si(CH_3)_3]_3$, was selected, because its π -perturbation amounts to 2/3 of the maximum possible [5,10].

The monosubstituted derivative, tris(trimethylsilyl)silylbenzene, was first prepared 25 years ago from decaphenylcyclopentasilane by lithiation in the presence of R_3SiCl [15]. It can also be made by treatment of phenyltrichlorosilane with Li/R_3SiCl [18], or, with advantage, by the Grignard phenylation of tris(trimethylsilyl)chlorosilane in THF [2] (Experimental section). In contrast, a literature search [2] revealed no relevant entry for the title compound, but this was straightforwardly synthesized by the widely applicable 'one-pot *in situ*' Grignard procedure [19,20] (see Experimental section):



We also report below the crystal structure of the isovalence electronic, but sterically more congested carbon analogue [4,20], $[(H_3C)_3Si]_3CC_6H_4C[Si(CH_3)_3]_3$, the photoelectron spectra of the mono- and the 1,4-di(tris(trimethylsilyl)silyl)-substituted benzene derivatives [2], and the ESR/ENDOR-spectroscopic characterization of the disubstituted radical anion [3].

2. Experimental section

2.1. 1,4-Di(tris(trimethylsilyl)silyl)benzene

Magnesium chippings (0.25 g, 10.2 mmol) are dispersed in 3 ml dry THF under Ar and *ca.* 0.5 ml of a solution of 1.2 g (5.1 mmol) of *p*-dibromobenzene in 4 ml of dry THF were added, until an exothermic reaction began. On addition of 3.07 g (10.8 mmol) of tris(trimethylsilyl)chlorosilane in 3 ml of dry THF, the solution became opalescent. After addition of the rest of the *p*-dibromobenzene solution, the mixture was stirred 24 h at room temperature and then for 50 h, during which a white solid separated and the colour changed via green to red. Hydrolysis with 30 ml of H_2O at 300 K was followed by three extractions with 30 ml portions of diethyl ether. After drying over

Na_2SO_4 , the extract was evaporated. Addition of acetone to the oily residue gave a white solid, which was filtered off and purified by chromatography on silicagel (60 Å) with a 4:1 mixture of n-hexane and methyl acetate as eluent. Recrystallization from acetone gave 0.15 g (5%) of white crystals, m.p. 545 K. $^1\text{H-NMR}$ (CDCl_3 , TMS): δ 0.12 (s, 54H), 7.21 ppm (s, 4H). MS: $m/e = 571$ (M^+), 556 ($\text{M}^+ - \text{CH}_3$), 498 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$).

2.2. Tris(trimethylsilyl)silylbenzene [18]

Magnesium shavings in a baked-out three-necked flask (0.32 mg, 13.1 mmol) were dispersed in 5 ml of dry THF under Ar. To initiate formation of the Grignard reagent, 0.3 ml of a solution of 1.38 ml (2.06 g, 13.1 mmol) of bromobenzene in 3 ml of dry THF were added together with 1 drop of 1,2-dibromoethane. After addition of the remainder of the solution 30 min stirring and a further 20 min under reflux the cooled Grignard solution was added dropwise to a solution of 3.72 g (13.1 mmol) of tris(trimethylsilyl)chlorosilane in 10 ml of dry THF. The mixture was stirred for 2 d each at 295 K and a further 2d at 315 K and 20 ml of saturated aqueous NH_4Cl solution were then added slowly. After 3 extractions with 20 ml of diethyl ether, the combined extracts were dried, and the solvent evaporated to leave a colourless residue. Purification by vacuum sublimation at 10^{-2} mbar yields 2.77 g (65%) of a waxy solid with m.p. 356 K ([18]: 357–358 K). $^1\text{H-NMR}$ (CDCl_3 , TMS): δ 0.23 (s, 27H), 7.0–7.5 ppm (m, 5H). MS: $m/e = 325$ (M^+), 310 ($\text{M}^+ - \text{CH}_3$), 252 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$).

2.3. 1,4-Di(tris(trimethylsilyl)methyl)benzene [20]

Magnesium shavings (9.32 g, 384 mmol) were dispersed under Ar in 10 ml of dry THF and 48.6 ml (41.67 g, 384 mmol) of trimethylchlorosilane were added. After cooling to 273 K, a solution of 10 g (32 mmol) $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene in 50 ml of dry THF is added dropwise at such a rate as to avoid a too strongly exothermic reaction. The resulting solution was refluxed for 70 h, during which it turned to black-green and a white salt separated. After addition of 300 ml of 1 M HCl the aqueous layer was extracted three times with 70 ml of diethyl ether. The extract was dried over Na_2SO_4 and the solvent evaporated to leave a muddy residue, which after repeated recrystallization from acetone/n-hexane yielded 1.73 g (10%) large colourless octahedra with m.p. higher than 600 K. $^1\text{H-NMR}$ (CDCl_3 , TMS): 0.29 (s, 54H), 7.12 ppm (s, 4H). MS: $m/e = 539$ (M^+), 524 ($\text{M}^+ - \text{CH}_3$), 466 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$).

Suitable single crystal growths were obtained by dispersing 1 g of the solid in 5 ml of acetone and

TABLE 1. Atomic coordinates and equivalent isotropic displacement factors ^a

	x	y	z	U_{eq}
Si(6)	3739(1)	4400(1)	2720(1)	52(1)
C(8)	3855(3)	3855(3)	3855(3)	34(1)
C(5)	4445(3)	4445(3)	4445(3)	31(1)
C(61)	2795(5)	3925(6)	2050(5)	81(3)
C(62)	4759(6)	4278(7)	2024(4)	89(3)
C(63)	3494(9)	5634(5)	2770(8)	129(5)
C(6)	5327(10)	4566(11)	4270(11)	38(5)
C(4)	4151(10)	4849(13)	5238(11)	48(6)

^a The molecule is highly symmetric; for ease of understanding the molecule is numbered clockwise without labelling of symmetry-equivalent atoms. For example, Si(2) and Si(3) are actually related to Si(1) by successive rotations about the crystallographic three-fold axis and the two ends of the molecule are related by a crystallographic inversion centre. Thus the angle Si(1)–C(1)–Si(1') would conventionally be Si(1)–C(1)–Si(1'), and so on. The benzene ring shows a three-fold disorder, but only one position is shown in Fig. 1.

adding about 10 ml of n-hexane until a clear solution was formed. After slow cooling (1 K h^{-1}) in a cryostat to 278 K the solution was kept at this temperature and after 1 d well-suited octahedral single crystals had formed.

2.4. Crystal structure determination of 1,4-Di(tris(trimethylsilyl)methyl)benzene

$\text{C}_{26}\text{H}_{58}\text{Si}_6$ (MW 539.26), cubic space group $Pa\bar{3}$ (Nr. 205), $Z = 4$, $a = 1523.1(7) \text{ pm}$, $V = 3533.3 \cdot 10^6 \text{ pm}^3$ (208 K), $\rho = 1.014 \text{ g cm}^{-3}$, μ (Mo $K\alpha$) = 1.5 cm^{-1} , Siemens AED-2 diffractometer, $3^\circ < 2\theta < 54^\circ$ (ω -scan), 4356 measured reflections, of which are 794 independent with $I > 2\sigma(I)$. Structure solution by direct methods (SHELXTL-PLUS), C and Si positions anisotropically refined, no H positions detected, $N = 794$, $NP = 61$, $R = 0.083$, $R_w = 0.089$ ($w = 1/\sigma^2(F) + 0.005F^2$), $\text{GOF} = 1.405$, residual electron density $+0.57/-0.31 \text{ e \AA}^{-3}$. Threefold disordering of the benzene ring; the carbon centers 1 and 2 are located on a threefold axis and the trimethylsilyl substituents around it (Table 1). Deviations in structural parameters (Fig. 1): $+2 \text{ pm}$, $+1^\circ$; angle sum of the six-membered ring $720^\circ + 1^\circ$. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56604, the names of the authors, and the literature citation.

2.5. Instrumentation

Photoelectron spectra were recorded on a spectrometer Leybold Heraeus UPG 200 equipped with a heated inlet system and coupled on line via an Atari Mega-ST to the VAX 11/750 of our group. They were

calibrated by reference to both the $2P_{3/2}$ ionization of Xe at 12.13 eV and that of Ar at 15.76 eV.

Cyclovoltammograms were obtained with a E & G Princeton Applied Research combination M173 (potentiostat), M175 (function generator) and RE 0074 (plotter). The closed cell contained a glassy carbon working electrode (GCE), a Pt counter electrode, and either an Ag/AgCl (oxidation) or saturated calomel (reduction) reference electrode (SCE). The solvents H_2CCl_2 and DMF ($c_H < 1$ ppm) as well as the conducting salt $R_4N^+ClO_4^-$ were purified under Ar, and the measurement performed under Ar.

Radical anion generation was carried out in a three-compartment glass apparatus. On a high vacuum line, the potassium mirror, the compound plus the [2.2.2]cryptand, and the solvent were respectively introduced into the three compartments and the vessel sealed off. After cooling in a cryostat to the temperature specified, a radical anion solution was generated by rotating the vessel and transferred to a capillary fitted into the cavity.

ESR/ENDOR spectra were recorded with a digitalized high-performance spectrometer Bruker 220 D/ESP 300, equipped with a field/frequency lock

TABLE 2. Selected bond lengths (pm, ± 2) and angles ($^\circ$, ± 1) in 1,4-di[tris(trimethylsilylmethyl)]benzene (cf. Experimental section)

Selected bond lengths			
Si(1)–C(1)	192.6(3)	Si(1)–C(11)	190.5(8)
Si(1)–C(13)	189.1(9)	Si(1)–C(12)	191.9(9)
Selected bond angles			
C(13)–Si(1)–C(1)	112.7(3)	C(11)–Si(1)–C(1)	112.8(3)
Si(1)–C(1)–Si(3)	110.1(2)	Si(1)–C(1)–C(2)	108.8(2)
C(12)–Si(1)–C(1)	113.9(4)	Si(1)–C(1)–Si(2)	110.1(2)
C(11)–Si(1)–C(12)	104.3(5)	C(11)–Si(1)–C(13)	106.4(3)
C(12)–Si(1)–C(13)	106.1(5)		

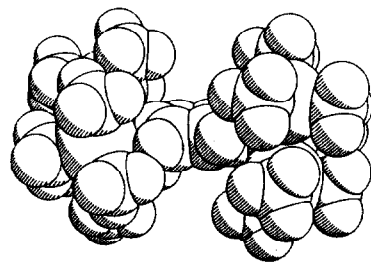
(standard: diphenylpicrylhydrazyl radical) and a constant temperature unit ER 4111 VT.

MO calculations have been carried out by use of standard MNDO [21] and HMO programs [10] on a VAX 11/750 computer.

3. Single crystal structure of 1,4-di[tris(trimethylsilyl)methyl]benzene

The molecular structure of hexakis(trimethylsilyl)disilane [1] reveals the presence of steric distortions by the bulky $(H_3C)_3Si$ substituents, although these are not as severe as those caused by tert-butyl groups [13], in which the SiSi bonds are replaced by considerably shorter SiC bonds. Thus the single crystal structure of the isosteric carbon analogue of the title compound, $[(H_3C)_3Si]_3CC_6H_4C[Si(CH_3)_3]_3$, was determined (Fig. 1 and Table 2) to provide information about whether the ortho ring hydrogens overlap sterically at all with some of the 18 peripheral methyl groups or whether the distances between them are shorter than the sum of their interference radii of 200 pm [22].

The X-ray diffraction study of 1,4-di[tris(trimethylsilyl)methyl]benzene revealed a cubic unit cell containing four molecules, the benzene rings of which are threefold disordered. The closest $C \cdots C$ distance between two molecules amounts to only 382 pm and thus is shorter than the sum of the interference radii of two methyl groups ([22]: 400 pm), and so there may be some Van der Waals bonding between their hydrocarbon shells, which are depicted in (5) with the hydrogen radii upscaled from 0.32 to 0.53:



(5)

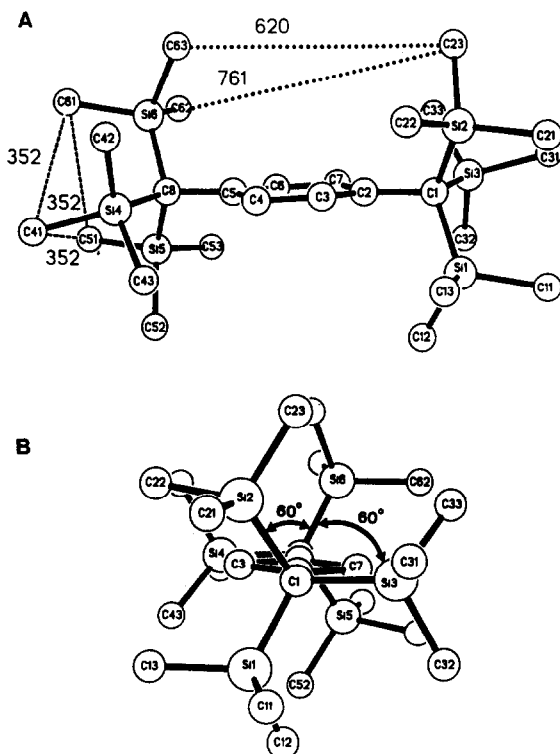


Fig. 1. Single crystal structure of 1,4-di[tris(trimethylsilyl)methyl]benzene not showing the threefold disordering of the benzene rings: (A) CC axial and (B) side view of a selected benzene ring position to reveal the staggered conformation of the six $(H_3C)_3Si$ groups (cf. Table 2).

dering or to the lattice packing, can be recognized, and so an inversion center is the only molecular symmetry element. The benzene ring seems to be planar (Σ)CCC = 720°), but (again with some reservation because of the threefold disordering) shows *ipso* angles of only 114° at the substituted centers, which is consistent with the expected considerable electron donor effect of the $[(H_3C)_3Si]_3C$ groups [22,23]. This stretching of the benzene ring along the substituent axis, correspondingly widens all other ring angles to about 123° , and thus, together with the elongation of the C1–C2 and C5–C8 bonds to about 156 pm (Table 2), helps to reduce the interference between the ring hydrogens and the closest substituent methyl groups. The bulky $[(H_3C)_3Si]_3C$ groups are arranged in a staggered conformation and the inner C1–Si1 bonds of 193 pm length are slightly longer than those in $Si(CH_3)_4$ ([24]: 189 pm). There are no contacts between the methyl hydrogens belonging to the different molecular half-shells: subtraction of two H_3C interference radii each of 200 pm from the shortest non-bonded C...C distance of 618 pm measured (Fig. 1B), still leaves some 200 pm space between them. In contrast, within one half-shell there are three C...C distances of 352 pm, indicating considerable interlocking of the three outside H_3C groups, as further substantiated by the less than tetrahedral values of the (HC)–Si–(CH) angles of 104° and 106° between them (Table 2).

Overall, the presence of the bulky $[(H_3C)_3Si]_3C$ -substituents in the 1,4-positions of the benzene ring in their staggered conformation does not result in any marked steric distortion, and so in the case of the title compound, in which six Si–C bonds are replaced by Si–Si bonds, which are *ca.* 45 pm longer, no steric interaction is expected. Nevertheless, if the $[(H_3C)_3Si]_3Si$ ligands are viewed as half-shells (*cf.* (5)), the benzene π system is only just visible in the gap between the two shielding CH moieties.

4. Photoelectron spectra

A heated inlet system had to be used for recording of the PE spectra of the mono- and 1,4-di-[tris(trimethylsilyl)silyl]-substituted benzene derivatives (Fig. 2), which are both solids with rather low vapour pressures at room temperature (*cf.* Experimental section).

The PE spectra (Fig. 2) of both of the rather large molecules $C_{15}H_{32}Si_4$ and $C_{24}H_{58}Si_8$ exhibit each four ionization regions of overlapping bands, as expected by the electron counting “rule of thumb” [6], $\Sigma(np_E + 1s_H)/2$ [11], which predicts at least 35 and 61 ionizations within the He(I) measurement region between 6 and 21 eV. By comparison with the ionization patterns of chemically related compounds [6], they can be

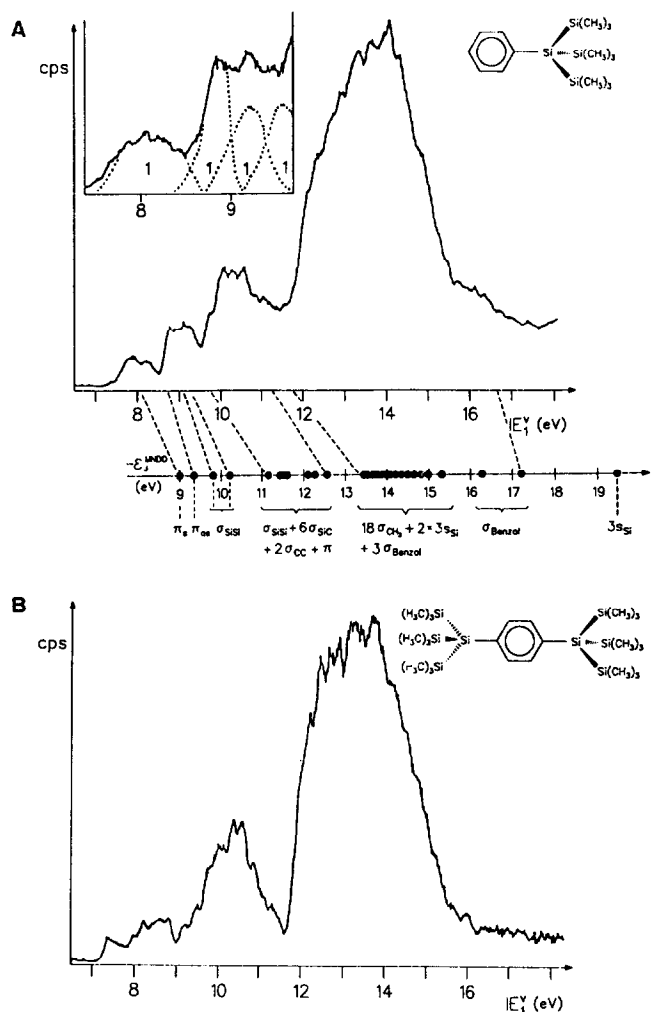
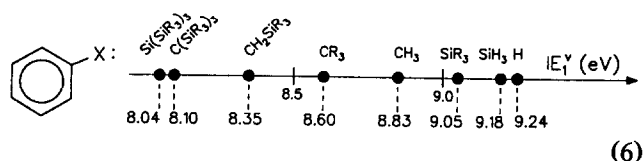


Fig. 2. He(I)PE spectra of (A) tris(trimethylsilyl)silyl-benzene at 330 K together with an expansion of the region between 7.3–9.8 eV, as well as Koopmans' assignment by MNDO eigenvalues and of (B) 1,4-di[tris(trimethylsilyl)silyl]benzene at 520 K.

roughly classified as follows: between 7 and 9 eV the low-energy benzene $\pi_{s,as}$ and σ_{SiSi} ionizations are expected, between 9 and 12 eV most of the σ_{SiC} and σ_{CC} ionizations, and between 12 and 16.5 eV numerous σ_{CH} ionizations as well as the remaining ones of σ_{SiC} and σ_{CC} type. In addition, at about 15 to 16 eV, bands are usually observed for radical cation states with dominant $3s_{Si}$ contribution [6,25]. Within this context, the PE spectroscopic investigations of the analogous toluene and *p*-xylene derivatives, $(R_3Si)_nH_{3-n}CC_6H_5$ and $(R_3Si)_nH_{3-n}CC_6H_4CH_3$ (SiR_3)_n, are relevant [6,8,10].

A more detailed discussion starts with advantage with the PE spectrum of the mono-substituted, smaller molecule tris(trimethylsilyl)silylbenzene (Fig. 2). Its first vertical ionization energy of only 8.04 eV, generating

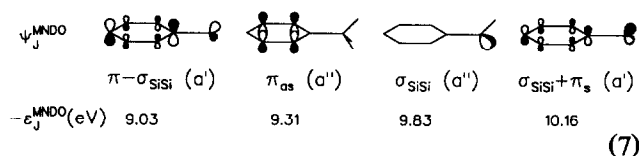
the radical cation ground state with predominant ($\pi_s - \sigma_{\text{SiSi}}$) contribution, is the lowest observed so far for silyl and alkyl benzene derivatives [6,9,26] ($\text{R} = \text{CH}_3$):



(6)

This sequence of substituents shifts has also been observed for the first vertical ionization energies of numerous other organosilicon compounds with π electron clouds, such as sulfides $\text{R}-\text{S}-\text{R}$ [13]. As pointed out in the Introduction, even the very large electron donating power of the substituent $\text{C}(\text{SiR}_3)_3$, containing three β trimethylsilyl groups [5,6,13], is exceeded by that of $\text{Si}(\text{SiR}_3)_3$, in which the central carbon has been replaced by an additional Si center of low effective nuclear charge.

The four lowest ionizations of $[(\text{H}_3\text{C})_3\text{Si}]_3\text{SiC}_6\text{H}_5$ (Fig. 2, insert) are straightforwardly assigned based both on comparison of equivalent M^{++} states of chemically related molecules [6,27] as well as a Koopmans' correlation, $\text{IE}_n^v = -\epsilon_j^{\text{MNDO}}$, with MNDO eigenvalues for the respective molecular orbitals Ψ_j^{MNDO} of C_s symmetry:



(7)

In the radical cation ground state at 8.04 eV there is considerable $\pi_s/\sigma_{\text{SiSi}}$ -mixing, as indicated by the rather broad ionization band (Fig. 2, insert) and also implied by the low first ionization energy of $\text{Si}(\text{SiR}_3)_4$ at 8.24 eV [28], and this allows the positive charge generated in the benzene π cloud to be extensively delocalized into the adjacent SiSi_3 skeleton. The second (π_{as}) M^{++} state, in which the nodal plane through the substituent bond (7) prevents any π interaction and the ionization energy of which, therefore, usually remains at the value for benzene around 9.24 eV, is shifted to 8.85 eV by the inductive effect of the $\text{Si}(\text{SiR}_3)_3$ substituent. The third PES band at about 9.2 eV (Fig. 2; insert: intensity ratio approximately 1:1:1) is assigned to a dominant σ_{SiSi} (a) radical cation state (7). The fourth ionization ($7: \sigma_{\text{SiSi}} + \pi_s$) is expected at about 9.7 eV underneath the second ionization region, which should also contain other M^{++} states with predominant σ_{SiSi} and σ_{SiC} contributions. Altogether, the MNDO calculation satisfactorily reproduces the observed PES band intensity pattern.

The extreme 1.2 eV lowering of the benzene π_s

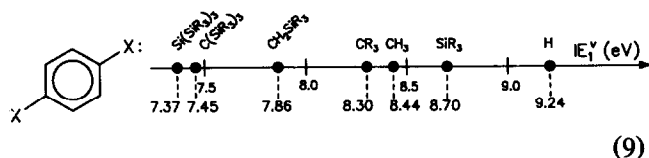
ionization (6) by the $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}$ substituent can be rationalized in terms of a combined first and second order perturbation approach [5,6,10]. Accordingly, the splitting of the degenerate benzene levels ($6: \text{H}$) is due to increasing second order π_s -interaction with the substituents and, to some smaller extent, to an accompanying first order inductive effect, which results from the difference in the effective nuclear charges $Z_{\text{eff}}(\text{Si}) < Z_{\text{eff}}(\text{C})$. For non-additive substituent perturbation as revealed by PE spectroscopy for organosilicon π systems with several β -trimethylsilyl groups [5,6,20], the dominant second order σ/π interaction can be transparently covered by an angle-dependent hyperconjugation model [20], e.g. for tris(trimethylsilyl)silyl benzene:

$$P_{\text{total}} = 9.24 - \text{IE}_1^v = \sum_{\sigma_{\text{SiSi}}} \langle \cos^2 \theta \rangle \quad (8)$$

The total perturbation, $P_{\text{total}} = 9.24 - \text{IE}_1^v$, as experimentally determined by the shift of the π_s ionization IE_1^v relative to that of benzene at 9.24 eV (6), can be subdivided for a given conformation into bond specific ($8: \sigma_{\text{SiSi}}$) and angle-dependent ($8: \langle \cos^2 \theta \rangle$) π components of the adjacent bonds. Parametrization by insertion of $\text{IE}_1^v = 8.04$ eV for tris(trimethylsilyl)silylbenzene and assuming the conformation shown (8: $1 \cdot \cos^2 0^\circ + 2 \cdot \cos^2 60^\circ = 1.5$) yields $\sigma_{\text{SiSi}} = 0.8$ eV. Comparison with the values $\sigma_{\text{CSi}} = 0.68$ eV and $\sigma_{\text{CH}} = 0.27$ obtained analogously for $(\text{R}_3\text{Si})_n\text{H}_{3-n}\text{C}$ substituents [5,6,20] suggests that the σ/π interaction increases in the sequence $\sigma_{\text{CH}} < \sigma_{\text{CSi}} < \sigma_{\text{SiSi}}$ of decreasing effective nuclear charge at the bond centers. According to the MNDO assignment (7) of the lowest four $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}-\text{C}_6\text{H}_5$ radical cation states, its π_{as} ionization is also shifted by $9.24 - 8.85 = 0.4$ eV. This lowering, which cannot be rationalized in terms of π -conjugation, is reproduced by the π/σ_{SiSi} hyperconjugation approach for the given conformation with a nodal plane through the adjacent π center (8: $2 \cdot \cos^2 60^\circ = 0.5$) and the parametrization used ($P_{\text{total}} = 8.0$ eV $\cdot 0.5 = 0.4$ eV). Therefore, the alternative explanation of the $[(\text{H}_3\text{C})_3\text{E}]_3\text{E}$ ($\text{E} = \text{C}, \text{Si}$) substituent effects on the benzene π system by hyperconjugation (8) is preferable to the often used artificial subdivision into σ inductive and π conjugative components [5,6].

The PE spectrum of the disubstituted title compound (Fig. 2) proves that its first vertical ($\pi_s + \sigma_{\text{SiSi}}$) ionization is shifted even to as low as 7.37 eV, the

lowest value determined so far for 1,4-dialkyl- or 1,4-disilyl-benzene derivatives [6,29] ($R = \text{CH}_3$):



Comparison of the PE spectroscopically-determined benzene π_s ionization shift for two substituents (9: ΔIE_1^v ($2\text{H}/2 \text{ Si}(\text{SiR}_3)_3$) = 1.87 eV) with that observed for the monosubstituted derivative (6: ΔIE_1^v ($\text{H}/\text{Si}(\text{SiR}_3)_3$) = 1.20 eV) clearly demonstrates non-additivity. Again the hyperconjugation model (9) allows rationalization of the changes in the stabilization of the benzene $\pi_{s,as}$ radical cation states via delocalization of the positive charge into now six adjacent σ_{SiSi} bonds. For an analogous conformation (8: $2 \cdot \cos^2 0^\circ + 4 \cdot \cos^2 60^\circ = 3.0$), a slightly smaller parameter $\sigma_{\text{SiSi}} = 1.87 \text{ eV}/3.0 = 0.62 \text{ eV}$ results. For the π_{as} ionization of the assumed conformation accounting for the nodal plane through the adjacent π center (9: $4 \cdot \cos^2 60^\circ = 1.0$), the perturbation $P_{\text{total}} = 1 \cdot 0.62 \text{ V}$ predicts a shift to 8.6 eV. Therefore, the π_{as} ionization is expected within the second ionization region between 8 eV and 9 eV (Fig. 2), which according to the observed intensity ratio 1:5 for the first two PE bands should also contain four σ_{SiSi} ionizations.

In summary, the plausible rationalization of the benzene π radical cation perturbation by the strongly electron donating $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}$ substituents within a σ/π hyperconjugation model further supports the $\pi_s(-\sigma_{\text{SiSi}})$ assignment (9) for the record-low first vertical ionization of the title compound $[(\text{H}_3\text{C})_3\text{Si}]_3\text{SiC}_6\text{H}_4\text{Si}[\text{Si}(\text{CH}_3)_3]_3$.

5. Redox reactions in aprotic solution

A great variety of organosilicon compounds can be reduced in aprotic solution to their radical anions [5] and those with low first vertical ionization energies oxidized to their radical cations [5,6,11]. Most of these single electron transfer products are persistent, at least at low temperatures, and thus can be characterized by their ESR and ENDOR spectra, in part including ^{29}Si isotope coupling [12]. For the title compound, which both is an α -silyl substituted benzene and has a rather low first ionization energy IE_1^v of 7.37 eV, thermodynamically feasible redox reactions to both species $\text{M}^{\cdot-}$ and $\text{M}^{\cdot+}$ are expected. Cyclovoltammetric investigations in aprotic ($c_{\text{H}} < 1 \text{ ppm}$) H_2CCl_2 or $\text{DME}/0.1 \text{ M}$ $\text{R}_4\text{N}^+\text{ClO}_4^-$ solutions (cf. Experimental section), however, demonstrate that the oxidation peak poten-

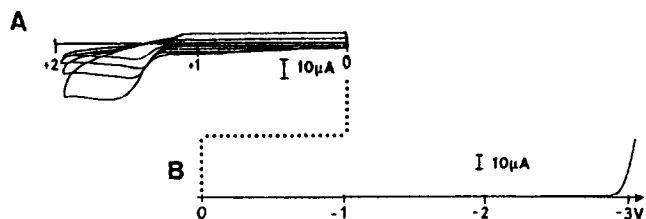


Fig. 3. Cyclovoltammograms of 1,4-di[tris(trimethylsilyl)silyl]benzene at 295 K: (A) oxidation between 0 and +2 V ($\text{H}_2\text{CCl}_2/0.1 \text{ M}$ $\text{R}_4\text{N}^+\text{ClO}_4^-$; GCE vs. Ag/AgCl ; $\bar{v} = 50$ to 500 mV s^{-1}); (B) reduction between 0 and -3 V ($\text{DMF}/0.1 \text{ M}$ $\text{R}_4\text{N}^+\text{ClO}_4^-$; GCE vs. SCE; $\bar{v} = 100 \text{ mV s}^{-1}$).

tial E° depends on the recording velocity (Fig. 3A: 1.28 V at 50 mV s^{-1} to 1.53 V at 500 mV s^{-1}), which indicates kinetic irreversibility, and that there is no reduction peak in the measurement range down to -2.9 V (Fig. 3B).

Despite the disappointing cyclovoltammetric results, radical cation generation from the title compound was attempted in aprotic H_2CCl_2 solution at 200 K using AlCl_3 , [30], SbF_5 , NO^+BF_4^- , Ag^+OCCF_3 and $(\text{BrH}_4\text{C}_6)_3\text{N}^+\text{SbCl}_6^-$ as oxidants. In none of the experiments, however, was a paramagnetic species detected by ESR spectra copy.

In contrast, the radical anion $[(\text{H}_3\text{C})_3\text{Si}]_3\text{C}_6\text{H}_4^{\cdot-}\text{Si}[\text{Si}(\text{CH}_3)_3]_3$ is readily formed on reduction in a THF solution containing [2.2.2]cryptand by a potassium metal mirror at 200 K and is stable up to 250 K. For the two sets of 4 and 54 hydrogens and the 2 and 6 equivalent ^{29}Si nuclei ($I = 1/2$, nat. abund. 4.67%) a total of $5 \times 55 \times 3 \times 7 = 5775$ ESR signals is expected. Of these only 11 are resolved in the ESR spectrum recorded (Fig. 4A): the ^1H ring quintet and a (satellite) triplet from the two ^{29}Si centers adjacent to the ring. The assignment is confirmed by simulation based on the ENDOR coupling constants (Figs. 4B and 4C; cf. subsequent discussion). Calibration with the perylene radical anion gave a value g of 2.00305.

The ENDOR experiments (Figs. 4B and 4C) resolved the rather small coupling of the 54 equivalent methyl hydrogens $a_{\text{H},2} = 0.007 \text{ mT}$ and also allow determination of the values of both $a_{\text{H},1}$, 0.166 mT for the benzene ring hydrogens and of $a_{29\text{Si}}$, 0.627 mT. The latter is due to the large ^{29}Si isotropic hyperfine coupling constant of -3381 MHz and split by each $\nu_{\text{Si}} = 2.965 \text{ MHz}$ around $a_{29\text{Si}}/2$ (Fig. 4C). The ^1H and ^{29}Si ENDOR coupling constants allow a satisfactory computer simulation of the ESR spectrum (Fig. 4A) except for the unresolved, and so not simulated, additional ^{29}Si septet in the outer satellite regions. Both couplings

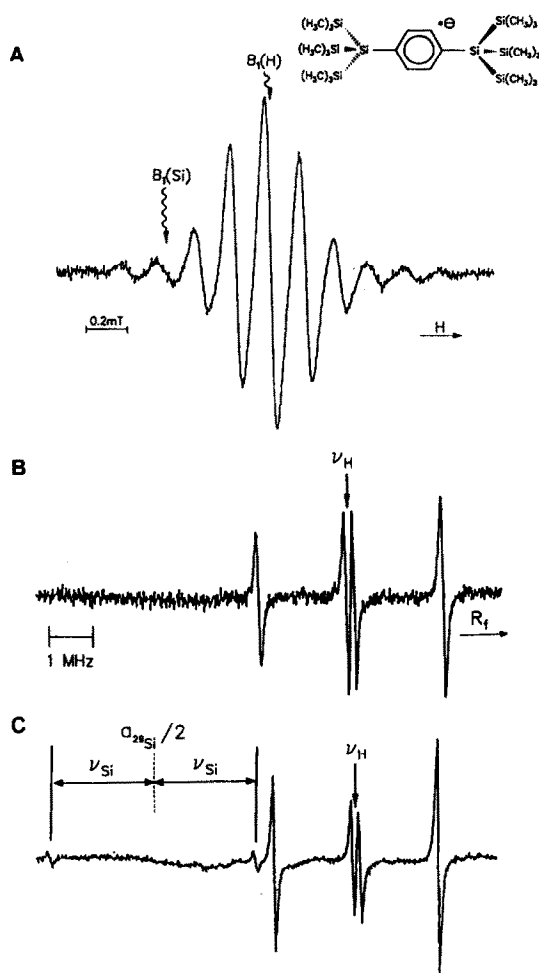
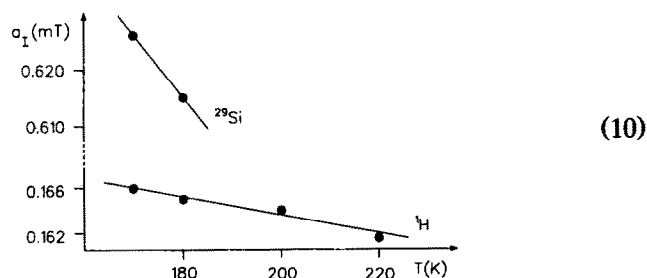


Fig. 4. Radical anion of 1,4-di[tris(trimethylsilyl)silyl]benzene, generated by reduction with potassium in THF/[2.2.2]cryptand solution at 200 K: (A) ESR spectrum; (B) as well as (C) ^1H and ^{29}Si ENDOR spectra recorded at 170 K on saturation of the ESR central ^1H quintet as well as the most intense ^{29}Si lines at frequencies $B_1(\text{H})$ and $B_1(\text{Si})$.

$a_{\text{H},1}$ and $a_{29\text{Si}}$ exhibit each negative temperature gradients:



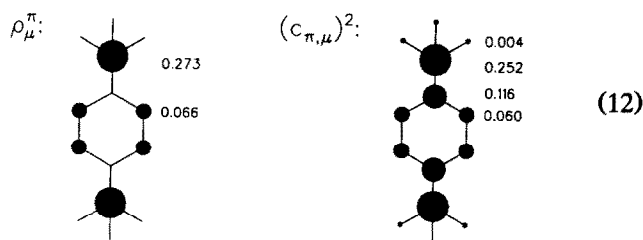
These are probably due to intensified deformation vibrations of the trimethylsilyl groups [12], which enhance the σ/π interactions and thus reduce the in-plane couplings. For an effective rotation volume V_{eff}

$\approx 1300 \text{ \AA}^3$, estimated from standard bond lengths, and for an optimum temperature of 180 K, an optimal rotation correlation time $\tau_{\text{R}}^{\text{opt}} = V_{\text{eff}} \cdot \eta / kT = 1.3 \text{ ns}$ results. On its insertion together with the usual [12] parameter $B \approx 1 \times 10^{-6}$ into the equation for the ENDOR effect, $\tau_{\text{R}}^{\text{opt}} = 200 (B/TrA^2)^{0.5}$, a TrA^2 value below 1 MHz^2 is obtained. This rather low anisotropy of the coupling is one of the conditions for a successful ^{29}Si ENDOR experiment [12].

The π spin distribution ρ_{μ}^{π} in $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}-\text{C}_6\text{H}_4\text{Si}^-\text{Si}[(\text{CH}_3)_3]_3$ can be estimated both from the measured coupling constants $a_{\text{H}}/a_{\text{Si}}$ and from HMO coefficients $(c_{\text{J}\mu}^{\text{HMO}})^2$ calculated with literature parameters [17] ($h_{\text{C}} = 0.0$, $h_{\text{Si}} = -0.95$, $h_{\text{Si}(\text{R}3)} = -2.0$, $k_{\text{CC}} = 1.00$, $k_{\text{CSi}} = 0.70$, $k_{\text{SiSi}} = 0.20$), which are both correlated by the McConnell equation:

$$a_{\text{H}/\text{Si}} = |Q_{\text{H}/\text{Si}}| \rho_{\mu}^{\pi} \approx |Q_{\text{H}/\text{Si}}| (c_{\text{J}\mu}^{\text{HMO}})^2 \quad (11)$$

By use of the known proportionality factors for radical anions of benzene derivatives, $|Q_{\text{H}}| = 2.5 \text{ mT}$ [31] and $|Q_{\text{Si}}| = 2.3 \text{ mT}$ [32], the “experimental” spin populations ρ^{π} are obtained:



The calculated spin populations $\rho_{\mu}^{\pi} \approx (c_{\text{J}\mu}^{\text{HMO}})^2$ agree satisfactorily and, in addition, provide some clues about those at the ‘dark centers’ that are not accessible by ESR/ENDOR experiments. Accordingly, more than half of the total spin is delocalized into the bulky $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}$ substituents, which thus act in π radical anions as strong electron acceptors. The analogous π -spin delocalization into α -trimethylsilyl substituents is, as expected less, extensive for instance, in the radical anion of 1,2-bis(trimethylsilyl)ethylene, $\text{R}_3\text{Si}-\text{HC}=\text{CHSiR}_3^-$, ESR spectroscopy shows that 2/3 of the total spin populates the central $\text{C}=\text{C}$ bond, and only 1/6 is delocalized into each of the $(\text{H}_3\text{C})_3\text{Si}$ substituents [14].

The rather strong acceptor effect of $[(\text{H}_3\text{C})_3\text{Si}]_3\text{Si}$ substituents was further confirmed by re-examining the ESR spectrum of the radical anion of tris(trimethylsilyl)silylbenzene [17] (see Fig. 5), which had been prepared for PE spectroscopic M^{+} state comparison (cf. Experimental section and preceding chapter).

The satisfactorily resolved [7] ESR spectrum shows the doublet of the para hydrogens and each triplets for

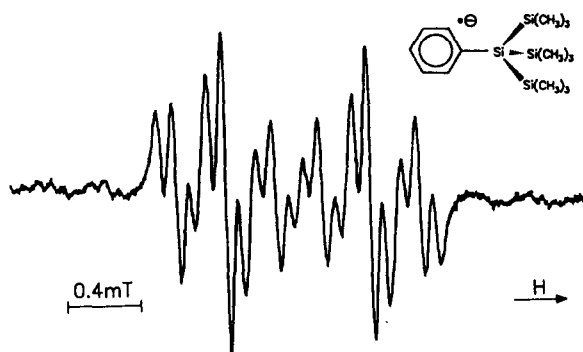
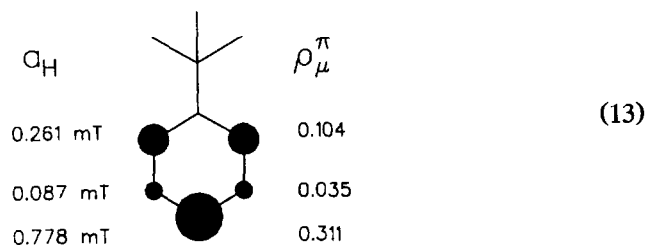


Fig. 5. ESR spectrum of tris(trimethylsilyl)silylbenzene radical anion, generated by K/[2.2.2]cryptand reduction in THF at 170 K (calibration with perylene radical with perylene radical anion confirms $g = 2.0030$ [17]).

the ortho and meta ones; ^{29}Si satellites cannot be assigned with certainty. By use of the McConnell relation (11), spin populations can again be estimated:



Comparison with those for the disubstituted benzene radical anion (12) provides additional insight. At the unsubstituted para ring center there is a rather high spin population. This has to be viewed, however, in the light of the lop-sided substitution: thus the average value for both the *ortho* and *meta* centers $(0.104 + 0.035)/2 = 0.0695$, resembles that derived for the symmetrically 1,4-disubstituted benzene radical anion (12). Summations of the ESR spectroscopically derived spin densities, $\sum_{\mu} \rho_{\mu}^{\pi} = 0.589$, and addition of the value $\rho_{1,4} = 0.11$ for the ESR-spectroscopically "dark" 1,4-centers in the disubstituted radical anion (12) yields a difference of $1 - 0.7 = 0.3$. This reasonable approximation demonstrates beyond doubt that also in the mono-substituted radical anion a considerable amount of spin and, assuming parallelity, of the negative charge is delocalized into the powerful electron acceptor group $\text{Si}[\text{Si}(\text{CH}_3)_3]_3$.

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