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Interactions in crystals. LXXIII [☆]. The structures of 1,2,4,5-tetrakis(trimethylsilyl)benzene and of its solvent-separated radical anion salt $[Na^{\oplus}(H_3COCH_2CH_2OCH_3)_3][((H_3C)_3Si)_4H_2C_6^{\cdot\ominus}]$

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Abstract

Reduction of 1,2,4,5-tetrakis(trimethylsilyl)benzene at a sodium-metal mirror under aprotic conditions and an argon atmosphere yields red needles of its solvent-separated radical anion salt. The structure, determined in a 150 K cold N_2 flow, is discussed in comparison with that of the neutral starting molecule, literature examples and results of MNDO calculations.

Keywords: Silicon; Interactions in crystals; Radical anion salt; MNDO calculations; 1,2,4,5-Tetrakis(trimethylsilyl)benzene; Single electron reduction

1. Starting point: the preparation of solvent-separated ion pairs and its application to organosilicon-substituted π-compounds

Conditions are now well-established for the selective crystallization of the solvent-separated sodium radical anion salt from the usually dark-red ether solutions, which result from the rather unselective reduction by a sodium metal mirror. These solutions contain a variety of species in equilibrium due to electron transfer, ion pair solvation and aggregation [2,3,4–9].

This surprising selectivity of crystallization can be easily understood by considering the following points. Extended π-radical anions, such as those provided by perylene [2,4,8], 9,10-diphenylanthracene [4,5], bianthryl [4,5], 1,1,4,4-tetraphenyl-1,3-butadiene [2,4,7] or 1,1,4,4-tetraphenylbutatriene [2,4] lack any extensively charged individual centers for contact ion formation [2,9]. Sodium countercations $Na^{\oplus}$ are favored [2] because the first vertical ionization energy of Na ($IE_1^v = 5.13$ eV) and the hydration enthalpy of $[Na^{\oplus}(H_2O)_{17}]$ ($\Delta H_f = -390$ kJ mol^{-1}) [10] both contribute to the low, and therefore more gentle, first reduction potential $E_{1/2}^{Red}$ (Na) $= -2.71$ V. Moreover, its ionic radius $r = 97$ pm, increasing to 113 pm for 30% covalent contribution [2,11], is of the right magnitude for the preferred six-fold, often octahedral coordination geometry. Last but not least, the choice of solvent is critical. For six-coordinate solvation of $Na^{\oplus}$ by an ether, the following increasing enthalpies (kJ mol^{-1}) have been calculated based on structural data: $[Na^{\oplus}(THF)_6]$ $-587 <$ $[Na^{\oplus}(DME)_3] - 671 < [Na^{\oplus}(diglyme)_2] - 677$ [4]. By considering all the above information we succeeded in growing even the black crystals of a solvent-separated naphthalene radical salt $[C_{10}H_8^{\cdot\ominus}][Na^{\oplus}(diglyme)_2]$ from diglyme solution after sodium-metal-mirror reduction according to Scheme 1 [1].

A search of the Cambridge Structural Database (December 1994) produced only two entries on structures of organosilicon-substituted benzene anion salts, both from the group in Sendai [12,13] (Schemes 2 and 3). The lithium-metal reduction of 1,2,4,5-tetrakis(trimethylsilyl)benzene in dimethoxy-ethane at room temperature yields brown needles of the corresponding bis(di-

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[☆] Part LXXII see Ref. [1] For a previous discussion of solvent-separated ion pairs see Ref. [2]. Part LXXIII dedicated to Professor H. Sakurai on the occasion of his 65th birthday.

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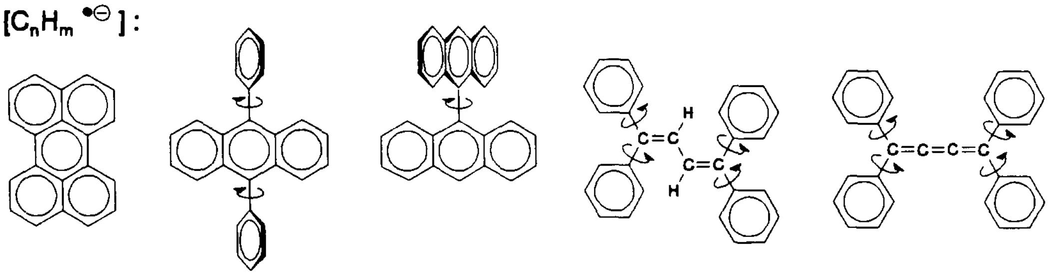
Redox-Halfsystem I: $[\mathrm{Me}]_\infty + x\ \mathrm{Solvent} \xrightarrow[(\leftarrow)]{} [\mathrm{Me}^{\oplus}\ (\mathrm{Solvent})_x] + (e^{\ominus})$

Redox-Halfsystem II: $C_nH_m + (e^{\ominus}) \rightleftarrows [C_nH_m{}^{\bullet\ominus}]$

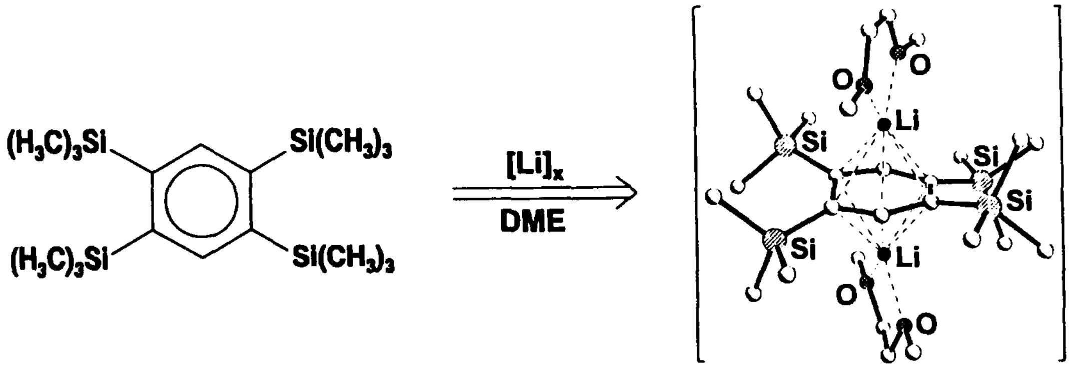
$$C_nH_m + [\mathrm{Me}]_\infty + x\ \mathrm{Solvent} \rightleftarrows [C_nH_m{}^{\bullet\ominus}]\,[\mathrm{Me}^{\oplus}\ (\mathrm{Solvent})_x]$$

$[C_nH_m{}^{\bullet\ominus}]$:

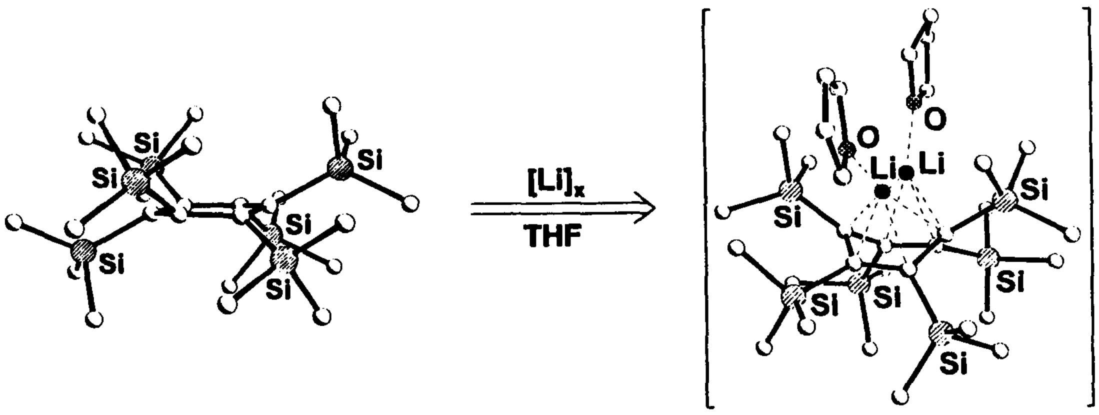


Scheme 1.

methoxylithium) contact ion triple with each countercation η^6-coordinated above and below the only slightly puckered six-membered carbon ring with contact distances $\mathrm{Li}^{\oplus} \cdots (\mathrm{C})_6^{2\ominus}$ of 187 pm [12]. Hexakis(trimethylsilyl)benzene (Scheme 3), which is highly overcrowded as demonstrated by torsion angles ω(SiC–CSi)



Scheme 2.



Scheme 3.

= 61° [13], is reduced by excess lithium metal in THF solution at room temperature to red crystals (Scheme 3) of a bis(THF lithium) contact ion triple with the two $Li^{\oplus}$ countercations on the same side of the dianion C_6 ring which is bent into a boat conformation [14,15]. The severe structural distortions, expected within a molecular state approach [16], can be reproduced by ab initio calculations on a 6-21G level [15].

1,2,4,5-Tetrakis(trimethylsilyl)benzene, easily accessible by in situ Grignard reaction from the corresponding tetrabromo derivative [17] (see Section 2), possesses a first vertical ionization energy of only 8.30 eV, i.e. lower by 0.95 eV than that of benzene [18]. On reduction by $[K]_\infty$ in DME solution with added di(cyclohexyl)-18-crown-6 [18], it yields a dark-red solution of its radical anion. Both the low first ionization energy and the fact that the radical anion exhibits relatively little benzene hydrogen coupling in its ESR spectrum [18] confirm a rather large first order perturbation on the antisymmetric levels of the formerly degenerate benzene E_{2g} and E_{2u} states. According to qualitative Hückel theory [19], the perturbation, $\delta\varepsilon_J^{(1)} = \Sigma b_J(c_{J\mu})^2$, should be unity, $\Sigma(c_{J\mu})^2) = 4 \times 0.25 = 1$, or the maximum possible for benzene acceptor substitution [16,18,19] (Scheme 4).

In order to determine the structures of both 1,2,4,5-tetrakis(trimethylsilyl)-benzene (with its steric overcrowding (Schemes 2 and 3)) and its radical anion (which exhibits distortions due to one-electron reduction) crystals suitable for X-ray structure analysis were grown.

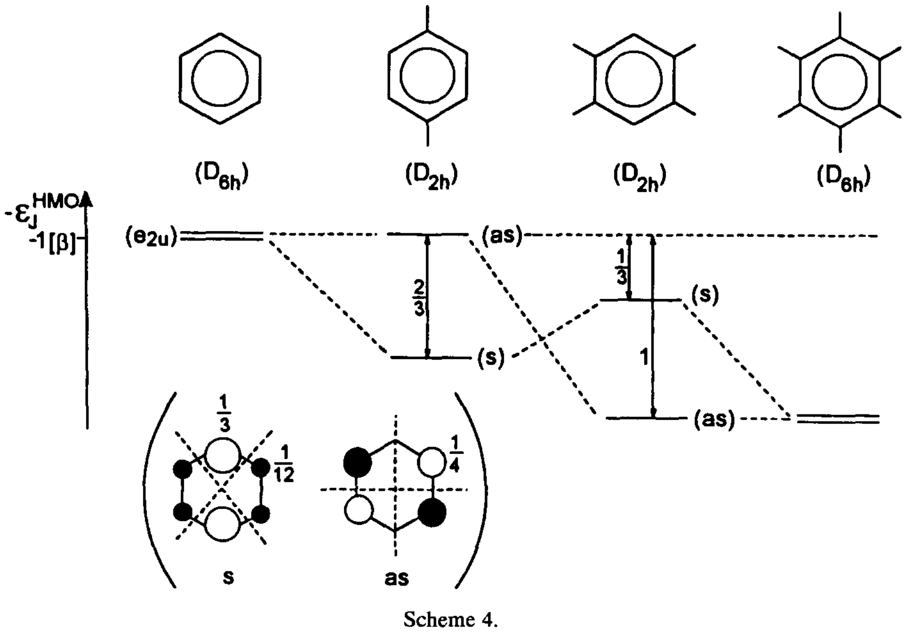
2. Experimental section

The solvents used, tetrahydrofurane, dimethoxyethane and hexane, were refluxed twice over Na/K alloy for 8 h and, after distillation, kept under dry argon.

2.1. 1,2,4,5-Tetrakis(trimethylsilyl)benzene [17,18]

Magnesium powder (4.5 g, 180 mmol) and trimethylchlorosilane (26 g, 220 mmol) were dispersed under argon in hexamethylphosphorictriamide (70 ml), and a solution of 1,2,4,5-tetrachlorobenzene (5.4 g, 25 mmol) in dry THF (50 ml) was added dropwise at a rate which avoided a strongly exothermic reaction. After heating the solution at 375 K for 2 d a white salt precipitated. The mixture was hydrolyzed by adding 100 ml of H_2O at 300 K and extracted with diethyl ether (3 × 75 ml). The extracts were dried over Mg_2SO_4 and all volatile components evaporated. Recrystallization of the white residue from ethanol (2 × 200 ml) yielded colorless crystals (4.5 g, 49%) with m.p. 445 K (444–446 K [1]). ^1H NMR ($CDCl_3$, TMS): 0.38 ppm (m, 36 H), 7.98 ppm (s, 2H). Anal. Calc. for $C_{18}H_{38}Si_4$: C 55.95; H 10.40%. Found: C 54.50; H 9.64%.

Single crystals with a suitable reflex profile for X-ray structure analysis were grown successfully by slow evaporation of a solution of 500 mg 1,2,4,5-tetrakis(trimethylsilyl)benzene in a mixture of 5 ml ethanol and 5 ml hexane at 300 K, which after 2 d yielded colorless prisms.



Scheme 4.

2.2. Crystal structure determination of 1,2,4,5-tetrakis-(trimethylsilyl)benzene

$C_{18}H_{38}Si_4$ (MW 366.84), orthorhombic, Pbca (No. 61), $Z = 4$, $a = 1076.7(1)$, $b = 1204.0(1)$, $c = 1876.4(1)$ pm, $V = 2432.5(2) \times 10^6$ pm^3 (200 K), $\rho = 1.002$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 0.24$ mm^{-1}, Siemens P4 diffractometer, $3° < 2\Theta < 53°$ (θ–2θ-scan), 3431 measured reflections, of which 2486 are independent, 113 parameters. Structure solution by direct methods (XS), structure refinement using the program SHELXL93; all C and Si positions anisotropically refined; all H atoms are positioned with idealized geometry and refined with individual isotropic displacement parameters using a

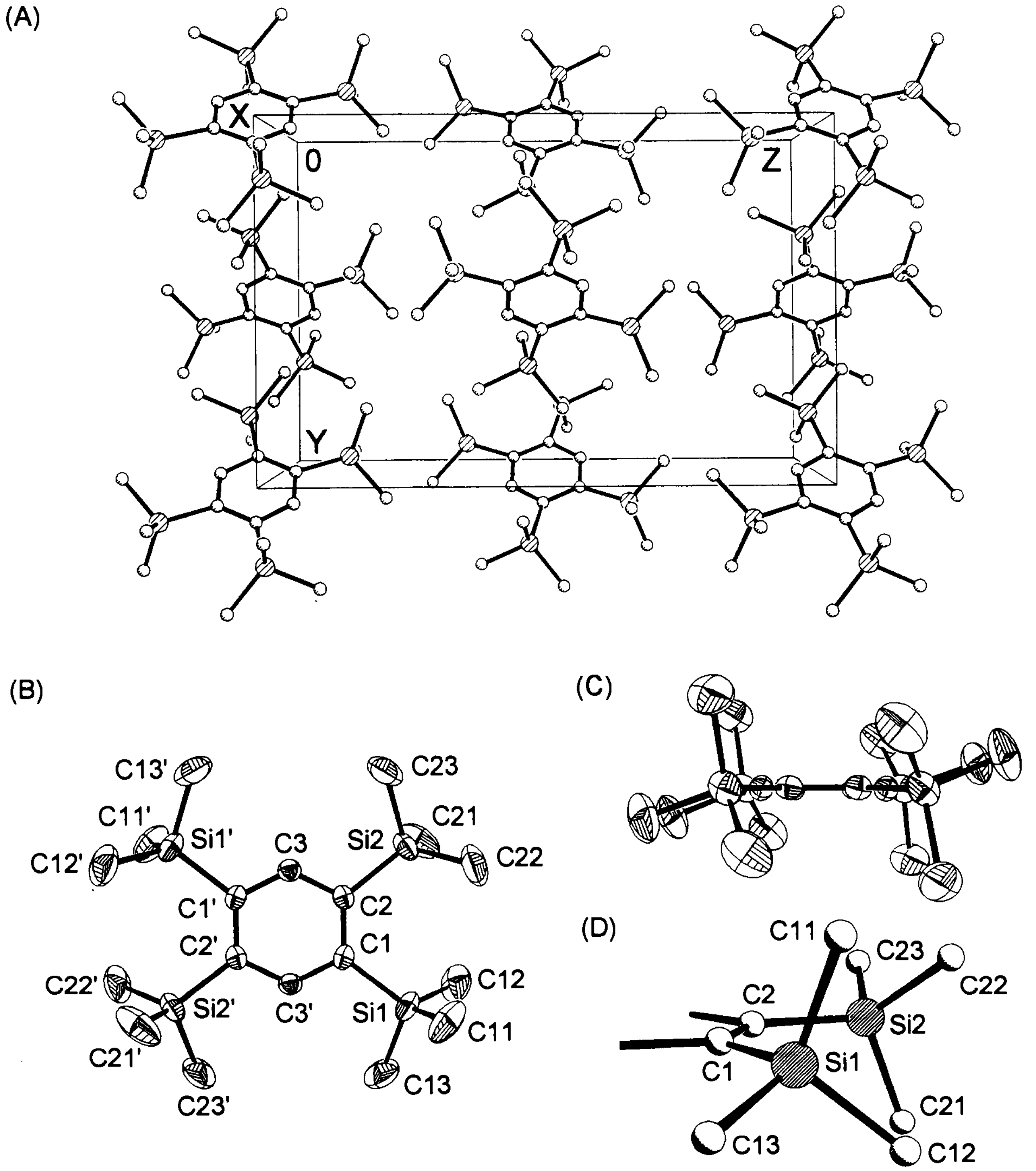


Fig. 1. Single crystal structure of 1,2,4,5-tetrakis(trimethylsilyl)benzene at 200 K: (A) unit cell (orthorhombic, *Pbca*, $Z = 4$) viewed in the X direction; and (B) molecular skeleton viewed perpendicular to the C6 plane including the numbering system of the individual centers (Table 1); (C) side view (50% thermal ellipsoids); and (D) section with two *ortho*-trimethylsilyl groups (◍: Si, O, C, without H, see text).

riding model. $R1$ (for 1867 $Fo > 4\sigma(Fo)$) = 0.0405, $wR2$ (for all data) = 0.1115, GOOF = 1.032 and residual electron density 0.30/ – 0.16 e $Å^{-3}$.

2.3. *Preparation and crystallization of tris(dimethoxyethane)sodium-1,2,4,5-tetrakis(trimethylsilyl)benzenide*

In a carefully dried Schlenk trap a sodium mirror was generated by vacuum distillation of 50 mg of sodium (2.2 mmol) and under argon. 10 ml Dry dimethoxyethane (10 ml) and 1,2,4,5-tetrakis(trimethylsilyl)benzene (300 mg, 0.82 mmol) were added. After 1 d nearly all the sodium metal had vanished and to the resulting dark red solution a layer of hexane (10 ml) was added. After 2 d red needles were obtained, which, despite of their extreme air- and moisture-sensitivity, could be successfully subjected to X-ray crystallography.

2.4. *Crystal structure determination of tris(dimethoxyethane)sodium-1,2,4,5-tetrakis(trimethylsilyl)benzenide*

$C_{30}H_{68}O_6Si_4Na$ (MW 660.19), orthorhombic, $Pca2_1$ (No. 29), $Z = 4$, $a = 1295.2(1)$, $b = 1526.8(1)$, $c = 2136.5(1)$ pm, $V = 4224.8(6) \times 10^6$ pm^3 (150 K), $\rho = 1.038$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 0.18$ mm^{-1}, Siemens P4 diffractometer, $3° < 2\Theta < 53°$ (ω-scan), 4767 measured reflections, of which 4378 are independent, 388 parameters. Structure solution by direct methods (XS), structure refinement with the program SHELXL93: all C, Na, O and Si positions refined anisotropically; all H atoms are positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U(H_{aromatic}) = 1.2$ $U_{eq}(C_{aromatic})$, $U(H_{methylene}) = 1.2$ $U_{eq}(C_{methylene})$, $U(H_{methyl}) = 1.5$ $U_{eq}(C_{methyl})$] using a riding model. $R1$ (for 3775 $Fo > 4\sigma(Fo)$) = 0.0395, $wR2$ (for all data) = 0.0928, GOOF = 1.050, residual electron density 0.34/ – 0.15 e $Å^{-3}$. The absolute structure was determined; the Flack enantiomorph polarity parameter [21] converged to $x = 0.0(1)$.

Table 1
Selected bond lengths (pm) and angles (°) of 1,2,4,5-tetrakis(trimethylsilyl)benzene

Selected bond lengths			
C1–C2	141.4(2)	C2–Si2	189.3(2)
C2–C3	140.4(2)	Si1–C11	187.1(3)
C2–C3′	140.3(2)	Si1–C12	187.4(3)
C1–Si1	189.7(2)	Si1–C13	187.0(3)
Selected bond angles			
C2–C1–C3′	116.9(2)	C2–C1–Si1	128.7(1)
C1–C2–C3	117.1(2)	C1–C2–Si2	129.1(1)
C2–C3–C1′	125.9(2)	C3′–C1–Si1	114.4(1)
		C3–C2–Si2	113.8(1)

2.5. *PM3 calculations*

Using the crystal structure data, PM3 calculations were performed with idealized CH bond lengths of 109 pm using the SCAMP IV/1 version of the MOPAC program (T. Clark, University Erlangen) on our IBM workstation RISC 6000/8320 H.

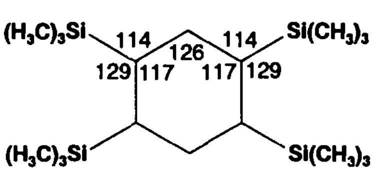
3. Results and discussion

3.1. *Crystal structure of 1,2,4,5-tetrakis(trimethylsilyl)-benzene*

The neutral compound crystallizes in the orthorhombic space group $Pbca$ with $Z = 4$ molecules inside the unit cell (Fig. 1(A)) and the asymmetric unit contains half a molecule located around a center of inversion.

The crystal packing of the individual molecules (Fig. 1(A)) is largely determined by the bulky substituents, which obviously prevent any π-stacking of the benzene rings. The shortest intermolecular distance (C ··· C 359 pm) is found between the (C22) methyl group and the (C1) ring center of an adjacent molecule. All intermolecular distances (C ··· C) between the various methyl groups are > 390 pm and most of them outside the $C(H_3) \cdots (H_3)C$ van der Waals sum limit of about 400 pm [2,23–26].

The molecular skeleton $C_6H_2Si_4$ (Fig. 1(B,C), Table 1) is close to planar — in contrast to the highly distorted chair conformation of the hexakis(trimethylsilyl)substituted derivative (Scheme 3) [13] — and all C–C and Si–C bond lengths (Table 1) correspond to standard values. The steric repulsion between the bulky trimethylsilyl groups, however, is demonstrated by the severe distortions of the angles inside and outside the six-membered ring (Scheme 5).



Scheme 5.

The bond angles at the unsubstituted ring carbons are opened to 126°, whereas those at the substituted ring centers are closed to 117°. The outside angles CCSi to the (trimethyl)silicon centers differ by 129–114 = 15°. The spatial overcrowding of the $(H_3C)_3Si$ substituents, which exhibit van der Waals radii of 380 pm [2], is also reflected in their conformational arrangement: both tetrakis(trimethylsilyl)benzene (solid lines, Scheme 6) and tetra(butyl)benzene [27] (dashed lines, Scheme 6) exhibit in their (quite similar) molecular structures a steri-

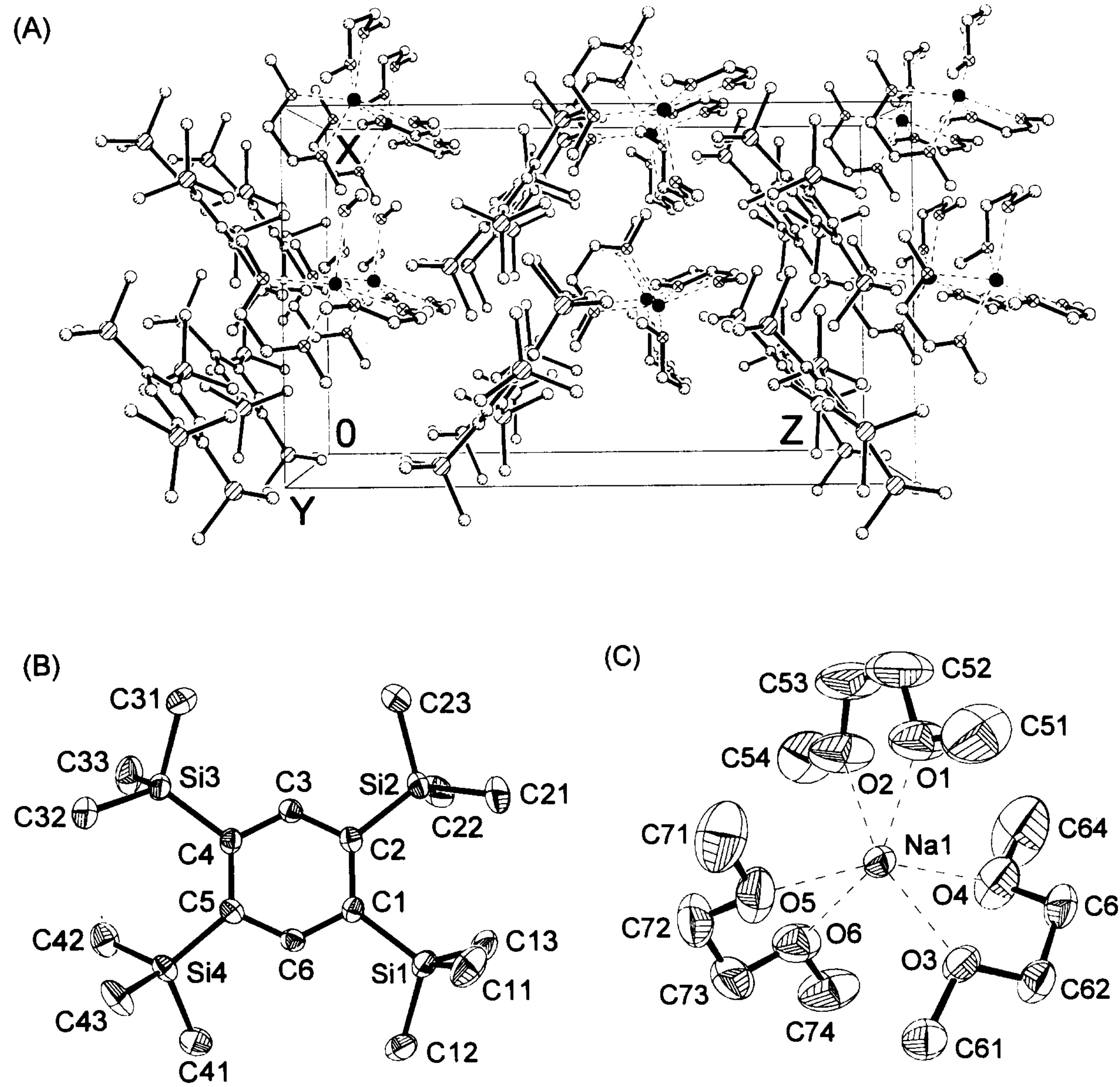
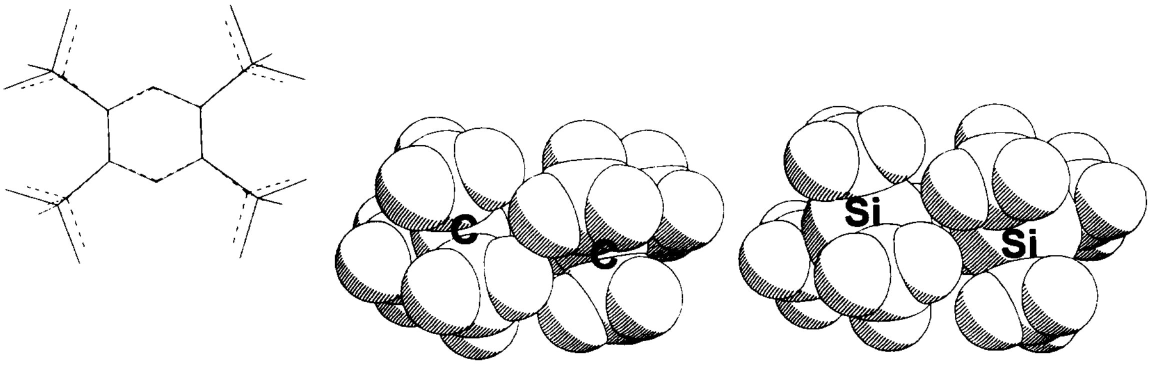


Fig. 2. Single crystal structure of tris(dimethoxyethane)sodium-1,2,4,5-tetrakis(trimethylsilyl)benzenide at 150 K: (A) unit cell (orthorhombic, *Pca*21, $Z = 4$) in Y direction, molecular skeleton including numbering of the centers of (B) the radical viewed perpendicular to the C_6 plane with 50% thermal ellipsoids and (C) the threefold dimethoxyethane-solvated sodium cation with 50% thermal ellipsoids.



Scheme 6.

cally favorable cog-like gearing of the methyl groups, best illustrated by space filling representations of the $(H_3C)_3Si–C–C–Si(CH_3)_3$ and $(H_3C)_3C–C–C–C(CH_3)_3$ fragments (Scheme 6).

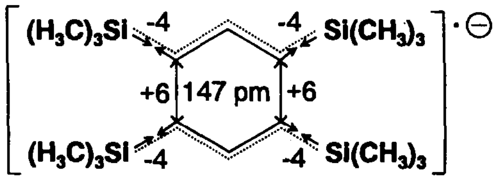
According to both the principle of structure correlation and empirical force field calculations [28], this conformational arrangement (Scheme 6) represents the global energy minimum for adjacent t-butyl groups and, obviously, can be extended to trimethyl silyl groups in close proximity.

3.2. Crystal structure of tris(dimethoxyethane)sodium-1,2,4,5-tetrakis(trimethylsilyl)benzenide

The radical anion crystallizes as a solvent-separated ion pair $[M^{\cdot\ominus}]\,[Na^{\oplus}(DME)_3]$ in the noncentrosymmetric, orthorhombic space group $Pca2_1$ with four formula units in the unit cell and, accordingly, one ion pair inside the asymmetric unit.

In the crystal structure of the tris(dimethoxyethane)-sodium-1,2,4,5-tetrakis(trimethylsilyl)benzenide, the radical anions as well as the solvated $Na^{\oplus}$ cations are arranged in stacks along the *Y* axis (Fig. 2(A)). The shortest intermolecular C–C distances (356 pm) are found between ring and methyl carbon centers of the radical anions and the solvent.

Each sodium cation is solvated by three dimethoxyethane molecules and therefore does not come into contact with the radical anions. The contact distances $Na^{\oplus} \cdots O$ between the centres of the cation $Na^{\oplus}$ and the dimethoxyethane oxygen range from 231 to 242 pm, corresponding to standard values. The six $Na^{\oplus} \cdots O$ links form an irregular polyhedron around the sodium countercation (Fig. 2(C)).

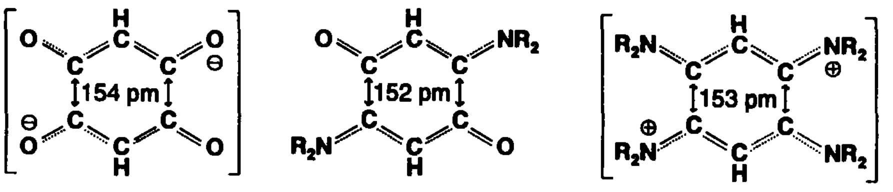


Scheme 7.

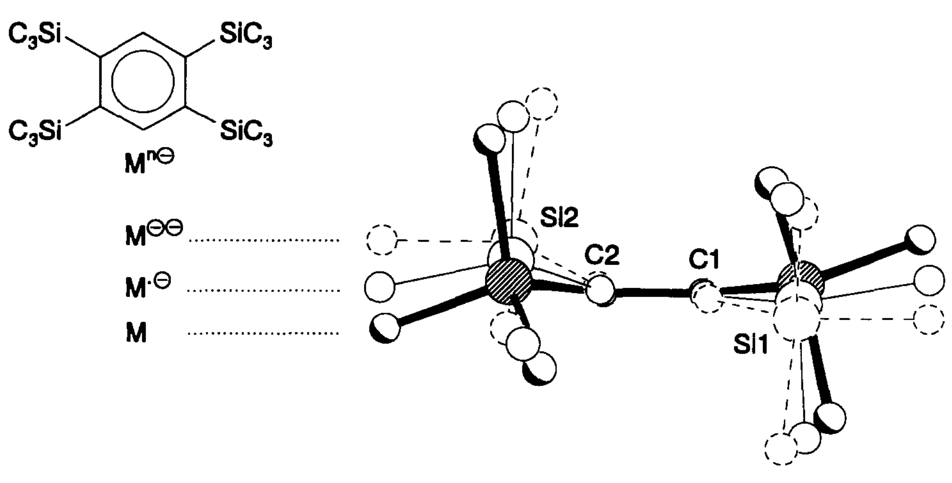
The one-electron reduction of 1,2,4,5-tetrakis(trimethylsilyl)benzene (Scheme 2) using a metal mirror causes significant structural changes (Scheme 7, Δd in pm).

The largest differences are observed for the two C–C bonds between the substituted ring centers, which stretch by 6 pm from 141 pm in the neutral molecule to 147 pm in the radical anion and for the four bonds C_{ring}–Si, which are each shortened by 4 pm. All of these changes add up to a cyanine distortion [2], as with 2,5-dihydroxyhydroquinone dianion, neutral 2,5-bis(dialkylamino)quinones or 1,2,4,5-tetrakis(dimethylamino)-benzene dication, in all of which an even number of π-electrons are delocalized over an odd number of centers forming two strongly delocalized chains connected by weakened bonds (Scheme 8).

The six-membered ring of the radical anion (Scheme



Scheme 8.



Scheme 9.

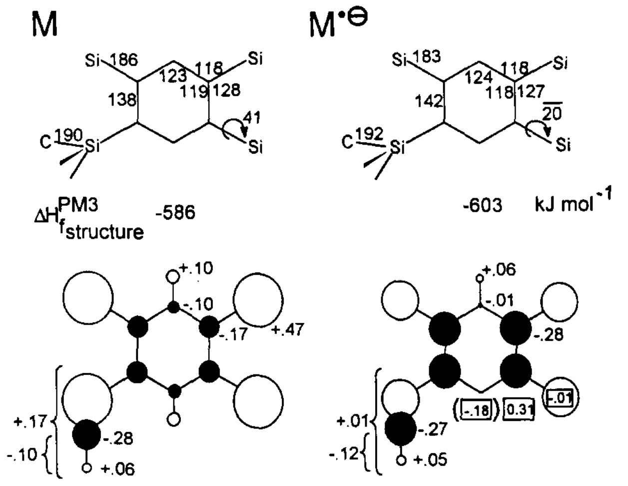
7) is no longer fully planar, as in the neutral molecule, but slightly distorted by ring torsions $|\omega_{\mathrm{ring}}| \leq 8°$. The ring angles CCC of 128° for the HC ring centers and 116° for the trimethylsilyl-substituted ones are comparable to those of the neutral molecule (Fig. 1 and Table 1). The same is observed for the wide outside angles of the ring ($\sphericalangle$CCSi = 129°; Scheme 5) between the sterically overcrowded trimethylsilyl substituents. The maximum deviation of the silicon centers from an idealized least-squares plane through the ring carbons is 28 pm – which differs from the neutral molecule with its C_6Si_4 skeletal plane.

1,2,4,5-Tetrakis(trimethylsilyl)benzene is one of the few compounds [2] for which the structures of the neutral molecule M (Fig. 1), its radical anion $M^{\cdot\ominus}$ (Fig. 2) and its dianion $M^{2\ominus}$ [12] have been determined. Structure superposition of half-molecule fragments, aligned horizontally with respect to the ring planes, shows significant, although moderate differences (Scheme 9).

In the dianion [12], the bond lengths between the substituted ring carbons increase from 141 pm (M) via 147 pm ($M^{\cdot\ominus}$) eventually to 155 pm ($M^{\ominus\ominus}$), which corresponds to the value for a slightly elongated C–C single bond [29]. The angle $\sphericalangle$CCC does not vary significantly between radical anion and dianion, although this represents a contact ion triple (Scheme 3), and finally reaches 130° at the C(H) and 115° at the $C(SiR_3)$ centers. The C_6 ring distortion increases by 6° to a maximum ring torsion of $|\omega_{\mathrm{ring}}| < 14°$ and the deviation of the four silicon centers from the idealized least squares plane through the six ring carbon centers to a maximum of 54 pm [12]. Despite the striking structural displacement of the Si atoms on addition of negative charges (Scheme 9), in all of the tetrakis(trimethylsilyl)benzene structures determined the optimum conformational arrangement of the vicinal trimethylsilyl groups is retained. This spatial interlocking, characterized as cog-like with approximately C_2 symmetry within the individual $(H_3C)_3Si–C–C–Si(CH_3)_3$ fragments (Scheme 6), can be seen to differ with increasing charge $M \rightarrow M^{\cdot\ominus} \rightarrow M^{\ominus\ominus}$ in (Scheme 9).

Table 2
Selected bond length and contact distances (pm) and angles (°) in tris(dimethoxyethane)sodium-1,2,4,5-tetrakis(trimethylsilyl)benzene

Selected bond lengths			
C1–C2	146.6(4)	C2–Si2	185.8(3)
C2–C3	140.3(4)	Si1–C11	188.5(4)
C3–C4	140.1(4)	Si1–C12	186.5(4)
C1–Si1	185.0(3)	Si1–C13	188.5(4)
Contact distances			
Na1–O1	232.6(3)	Na1–O4	236.7(3)
Na1–O2	231.1(3)	Na1–O5	241.6(3)
Na1–O3	233.8(3)	Na1–O6	234.1(3)
Selected bond angles			
C2–C1–C6	115.5(3)	C2–C1–Si1	128.8(2)
C1–C2–C3	116.8(3)	C1–C2–Si2	127.7(2)
C2–C3–C4	127.2(3)	C6–C1–Si1	115.6(2)
		C3–C2–Si2	115.3(2)



Scheme 10.

3.3. Semiempirical calculation

Extensive PM3 calculations [30] have been carried out using the structure coordinates determined experimentally (Tables 1 and 2). The essential reoptimized structure parameters and the respective charge distributions are presented in Scheme 10. The calculated data are informative and, insofar as they can be checked against experimental values, reproduce these satisfactorily. Even if the structures (Figs. 1 and 2) are reoptimized using the respective subroutine in the PM3 program package (see Section 2), deviations are few and small. The most obvious of these is the incorporation of the steric overcrowding between adjacent bulky trimethylsilyl substituents: the calculated ring C–C bond length in between is too short by 3 pm for the neutral molecule M and by 5 pm for the radical anion M (Scheme 10). Furthermore, due to the parametrization, the SiC_{ring} bonds are 3 pm too short and the angle $\sphericalangle$CC(H)C is 3° too small for M and for $M^{\cdot}\ominus$. However, the twist angles ω(CC–SiC) of the silyl groups are nicely reproduced both in M and in $M^{\cdot}\ominus$.

The "gas phase" electron affinity, $M + e^{\ominus} \rightarrow M^{\cdot\ominus}$, estimated from the difference in the enthalpies of formation obtained for the structural data, $\Delta\Delta H_f^{\mathrm{PM3}} = -603 - (-586) = -17$ kJ mol^{-1} ≈ -0.18 eV seems to be very reasonable for an optimally four-fold acceptor-substituted molecule (Scheme 4). The accompanying changes in the charge distribution can be explained thus: in the neutral molecule M the large difference in effective nuclear charges $Z_{\mathrm{eff}}(C) \gg Z_{\mathrm{eff}}(Si)$ [16], causes quite some polarization $Si^{\delta\oplus}–C^{\delta\ominus}$, which can be summarized to -0.66 for the C_6H_2 ring and $4 \times +0.17 = +0.68$ for the four $(H_3C)_3Si$ groups. The additional electron transferred on metal reduction should predominantly increase the charges at the substituted ring centers by -0.44 and reduce the positive charges at the $(H_3C)_3Si$ groups by $4 \times (-0.16) = -0.64$ with the obvious difference being due to the uncounted HC ring centers. The calculated results further support the ESR/ENDOR- proven spin delocalization into trimethylsilyl substituents [16], which, in the special case of 1,4-di(tris(trimethylsilyl)silyl)benzene radical anion, $[((H_3C)_3Si)_3Si\text{-}C_6H_4\text{-}Si(Si(CH_3)_3)_3]^{\cdot\ominus}$, exceeds the experimentally determined spin population remaining in the C_6 ring π-system [22,23,25].

In conclusion, the nodal plane is emphasized, as established by the PM3 results with respect both to the overall charge distribution in the radical anion (Scheme 10: $M^{\cdot\ominus}$) and to the spin population (Scheme 10: □) calculated using the open-shell PM3 version [30]. All results support the perturbation argument (Scheme 4) based on the acceptor properties of α-trimethylsilyl substituents [16].

Acknowledgment

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References and notes

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