

Interactions in crystals

CX¹. The structure of 9,10-bis(diisopropylsilyl)anthracene and of its “naked” radical anion

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Abstract

To further explore anthracene derivatives with bulky 9,10-substituents and a bent molecular skeleton due to repulsive interactions with adjacent ring hydrogens, we have synthesized 9,10-bis(diisopropylsilyl)anthracene and determined its molecular structure. Reduction with lithium metal in THF solution under aprotic conditions and argon yields its radical anion, which has been characterized by its ESR and ENDOR signal patterns. Crystallization from the red THF solution following addition of an n-hexane layer yielded the radical anion as blue, air- and moisture-sensitive needles. Its structure, determined at 130 K in an N₂ flow, is discussed by comparison with that of the neutral molecule and those of 9,10-bis(trimethylsilyl)anthracene and its solvent-separated radical ion pair $[(\text{H}_3\text{C})_3\text{Si})_2\text{C}_{14}\text{H}_8^-]$ - $[\text{Na}^+(\text{DME})_3]$, and in the light of literature examples and the results of MNDO calculations.

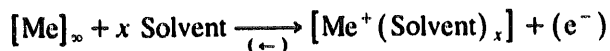
Keywords: Silicon; Anthracene derivatives; ESR spectra; ENDOR spectra; Radical anion; MNDO calculations; Crystal structure

1. Introduction: cation solvation vs. contact ion formation

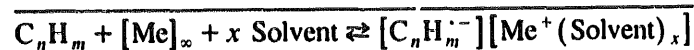
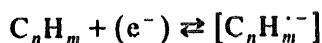
In our investigation of prototype interactions in molecular crystals such as hydrogen bridge-bonding, donor → acceptor aggregation or van der Waals forces [4], we have also studied extensively cation solvation [5] and the competing formation [6] of solvent-sharing contact ion multiples [6,7]. As an illustration of our approach, the recently reported crystallization and structural characterization of a “naked” naphthalene radical anion [8] and of the contact ion quintuple [rubrene⁴⁻(Na⁺THF₂)₄] containing the first isolated π-hydrocarbon tetraanion [9] are selected (Fig. 1).

Both surprising results (Fig. 1), the solvent-free naphthalene radical anion and the eight-fold THF-solvated tetrasodium salt of the rubrene tetraanion, are based on the same principle of optimum cation solvation [5] as an essential additional driving force for electron transfer from metal surfaces to molecules in solution:

Redox half-system I:



Redox half-system II:



(1)

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¹ For Part CXII, see Ref. [1]. For a preceding discussion of solvent-separated ion pairs of organosilicon substituted π-hydrocarbon radical anions, see Refs. [2,3]. Dedicated to Professor Robert Corriu.

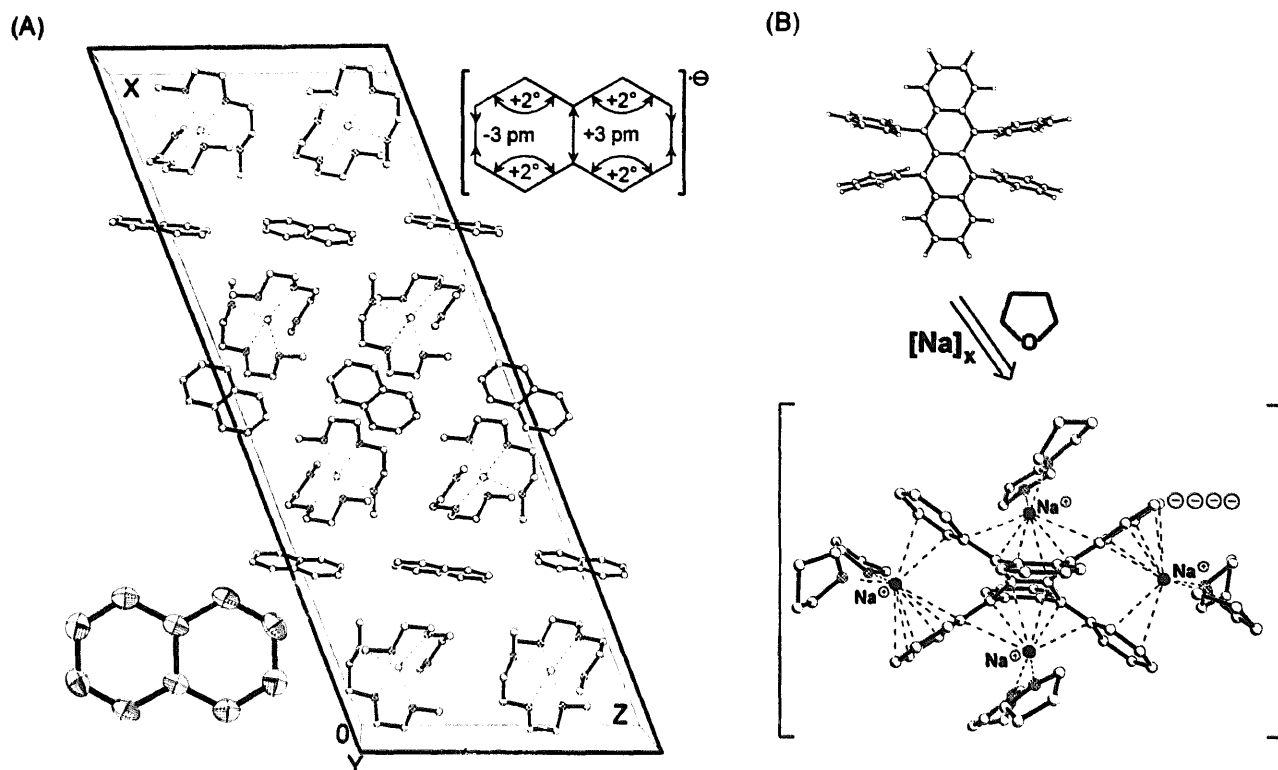
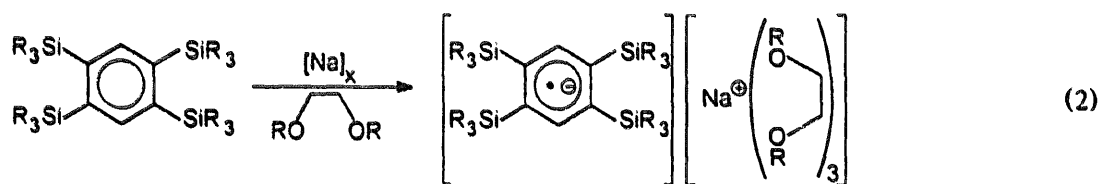


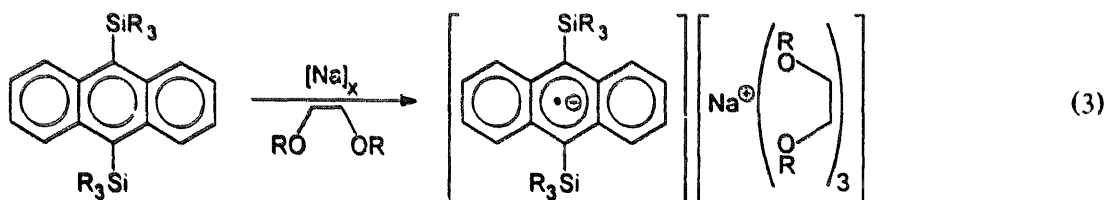
Fig. 1. Solvent-separated and solvent-shared contact ion multiples: (A) unit cell of naphthalene-bis(diglyme)sodium (monoclinic $C2/c$, $Z=8$) and radical anion structure (50% thermal ellipsoids, bond length and angle changes relative to naphthalene), (B) structure of $[\text{rubrene}]^{\bullet-}(\text{Na}^+(\text{THF})_4)_4$ generated by four-electron reduction of rubrene at a sodium metal mirror in THF solution.

It is the thermodynamically favourable embedding of Na^+ counter cations via six-fold oxygen coordination by two diglyme ethers [5], that enforces the solvent-free crystallization of the naphthalene radical anions (Fig. 1(A)) or the energetically less advantageous O-coordination of two THF ethers [5], which vice versa promotes the competing π -hydrocarbon anion complexation of the four Na^+ counter cations (Fig. 1(B)). Concerning the solvation enthalpies for the six-fold ether-coordinated Na^+ complexes, the following increasing values of ΔH_f (kJ mol^{-1}) have been calculated based on structural data [5]: $[\text{Na}^+(\text{THF})_6] - 587 < [\text{Na}^+(\text{DME})_3] - 671 < [\text{Na}^+(\text{diglyme})_2] - 677$ [5].

The principle of solvent-free crystallization of radical anions, accompanied by the formation of strongly O-coordinated counter cations, can also be successfully applied to organosilicon compounds [2,3], such as the reduction of 1,2,4,5-tetrakis(trimethylsilyl)benzene in dimethoxyethane solution at a sodium metal mirror [3] ($\text{R} = \text{CH}_3$):



or of 9,10-bis(trimethylsilyl)anthracene [2] ($\text{R} = \text{CH}_3$):



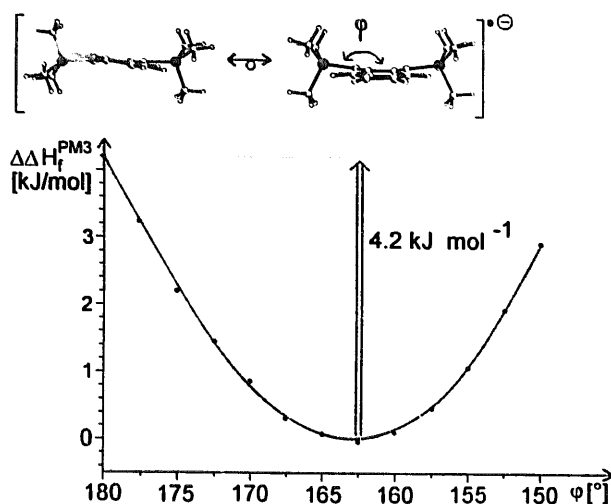
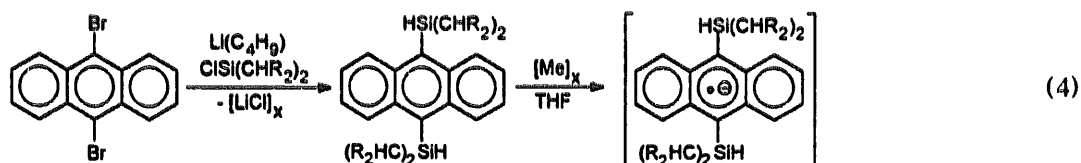


Fig. 2. PM3 open-shell enthalpy hypersurface for substituent out-of-plane bending in the radical anion of 9,10-bis(trimethylsilyl)anthracene [2].

The structure of the anthracenide radical anion has been determined [2] and a PM3 open-shell enthalpy hypersurface calculated for the substituent out-of-plane bending (Fig. 2). For a planarization of the skeleton [2], which is bent by 165° , a barrier of only 4 kJ mol^{-1} is predicted vs. 10 kJ mol^{-1} for the neutral molecule. These results suggest that for both the 9,10-bis(trimethylsilyl)anthracene and its radical anion considerably less strain is expected due to H/H repulsion between the methyl and the peri ring-hydrogens. Concomitantly, molecular dynamics should be fully activated at room temperature [2].

A search of the Cambridge Structural Database (February 1995) for anion salts of organosilicon-substituted cyclic carbon π systems has produced only two entries for the bis(dimethoxy)lithium contact ion triple of 1,2,4,5-tetrakis(trimethylsilyl)benzene dianion [10] with both Li^+ counter cations above and below the plane of the six-membered ring and for the bis(THF lithium) contact ion triple of hexakis(trimethylsilyl)benzene with both Li^+ on the same side [11]. Stimulated by the few crystallized organosilicon radical anion salts reported so far [2,3,10,11], as well as the partly drastic structural distortions caused by both sterical overcrowding (Fig. 2) and charge distribution (Fig. 1), we have synthesized 9,10-bis(diisopropylsilyl)anthracene via lithiation of 9,10-dibromo-anthracene and substitution with diisopropylchlorosilane (see Experimental section) ($\text{R} = \text{CH}_3$):



The radical anion generated by alkali metal reduction has been characterized in solution by ESR and ENDOR spectroscopy ($\text{Me} = \text{Na}, \text{K}$) and crystallized as an $[\text{Li}^+(\text{THF})_4]$ salt. The structures of both 9,10-bis(diisopropylsilyl)anthracene and its radical anion salt have been determined and, based on the structural data, their charge distribution calculated.

2. Experimental section

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

2.1. Preparation, crystallization and structure determination of 9,10-bis(diisopropylsilyl)anthracene

A slurry of 1 g of 9,10-dibromoanthracene (3 mmol) in 30 ml of tetrahydrofuran was cooled to -30°C and one equivalent of n-butyllithium (1.9 ml, 3 mmol) in hexane added within 5 min. The resulting deep red solution was

Table 1
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 9,10-bis(diisopropylsilyl)anthracene

Atom	x	y	z	U_{eq}
Si(1)	7450(1)	1977(1)	712(1)	53(1)
C(1)	6814(2)	-207(3)	-1255(2)	51(1)
C(2)	6727(2)	-1110(4)	-2140(2)	59(1)
C(3)	5724(2)	-1982(4)	-2446(2)	62(1)
C(4)	4844(2)	-1907(3)	-1862(2)	55(1)
C(5)	4880(2)	-961(3)	-925(2)	42(1)
C(6)	5918(2)	-77(3)	-601(2)	42(1)
C(9)	6048(2)	868(3)	327(2)	43(1)
C(10)	7581(4)	3754(5)	-190(5)	125(2)
C(11)	8536(6)	4340(10)	-400(8)	236(5)
C(12)	6544(4)	4858(5)	-194(4)	118(2)
C(13)	8730(2)	588(4)	860(3)	65(1)
C(14)	8437(3)	-1077(5)	1256(4)	105(2)
C(15)	9706(3)	1344(6)	1587(3)	98(1)

Equivalent isotropic U calculated as one third of the trace of the orthogonalized U_{ij} tensor.

stirred at room temperature for 10 min, diisopropylchlorosilane (453 mg, 3 mmol) added and the resulting pale yellow solution stirred for 15 min. After repeating the procedure with another equivalent of *n*-butyllithium, the mixture was hydrolyzed by adding 50 ml of H_2O . Three extracts with 30 ml each of diethyl ether were dried over Mg_2SO_4 and, after evaporation of all volatile components, a yellow residue remained. Crystallization from a 1:5 hexane/ethanol mixture yielded 775 mg (63.5%) 9,10-bis-(diisopropylsilyl)anthracene as pale yellow fluorescent crystals, m.p. 484 K. $^1\text{H-NMR}$ (CDCl_3 , TMS): 0.75 ppm (d, 12H), 1.2 ppm (d, 12H), 1.55 ppm (m, 4H), 4.77 ppm (t, 2H), 7.38 ppm (m, 4H), 8.45 ppm (m, 4H). Anal. Found: C, 76.08; H, 9.47. $\text{C}_{26}\text{H}_{38}\text{Si}_2$ Calc.: C, 76.80; H, 9.30.

Single crystals were grown by diffusion: addition of a 5 ml ethanol layer to a solution of 200 mg of 9,10-bis-(diisopropylsilyl)anthracene in 5 ml of carbon tetrachloride at 300 K yielded yellow prisms after two days.

2.1.1. Crystal structure determination

$\text{C}_{26}\text{H}_{38}\text{Si}_2$ (MW 702.10), monoclinic, $P2_1/c$ (No. 14), $Z = 2$, $a = 1181.2(1)$ pm, $b = 823.6(1)$ pm, $c = 1282.6(1)$ pm, $\beta = 96.81(1)^\circ$, $V = 1239.0(2) \times 10^6$ pm 3 (RT), $\rho = 1.090$ g cm $^{-3}$, $\mu(\text{Mo K}\alpha) = 0.15$ mm $^{-1}$, Siemens P4 diffractometer, $3^\circ < 2\theta < 51^\circ$ (ω -scan), 2566 measured reflections of which 2272 were independent, 131 parameters. Structure solution by direct methods (SHELXS-86), structure refinement using the program SHELXL-93, all non-hydrogen positions refined anisotropically. The hydrogens bound to silicon and to the anthracene skeleton were detected by difference Fourier synthesis; the hydrogens bound to carbon were placed in an idealized geometry and refined with fixed isotropic displacement parameters [$U(\text{H}_{\text{aromatic, methine}}) = 1.2U_{\text{eq}}(\text{C}_{\text{aromatic, methine}})$, $U(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model. The positions and isotropic displacement parameters of the hydrogens bound to silicon were refined, $R_1 = 0.0609$ (for 1882 reflections with $F_o > 4\sigma(F_o)$), $wR_2 = 0.1755$ (for all data), GOF 1.060, residual electron density 0.39/−0.38 e \AA^{-3} . The atom coordinates are listed in Table 1. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

2.2. Preparation, crystallization and structure determination of tetrakis(tetrahydrofuran)lithium-9,10-bis(diisopropylsilyl)anthracenide

In a carefully dried Schlenk trap and under argon, 20 mg of lithium metal (2.9 mmol) was submersed in 10 ml of dry tetrahydrofuran and 300 mg of 9,10-bis(diisopropylsilyl)anthracene (0.74 mmol) was added. The dark red solution resulting after two days was covered by a layer of 10 ml of hexane. Blue, extremely air- and moisture-sensitive crystals grew within three days.

2.2.1. Crystal structure determination

$\text{C}_{42}\text{H}_{70}\text{Li}_1\text{O}_4\text{Si}_2$ (MW 702.10), monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 1048.0(1)$ pm, $b = 1788.6(1)$ pm, $c = 2230.5(2)$ pm, $\beta = 94.37^\circ$, $V = 4168.8(6) \times 10^6$ pm 3 (130 K), $\rho = 1.119$ g cm $^{-3}$, $\mu(\text{Mo K}\alpha) = 0.12$ mm $^{-1}$, Siemens P4 diffractometer, $3^\circ < 2\theta < 48^\circ$ (ω -scan), 7128 measured reflections of which 6480 were independent, 447 parameters. Structure solution by direct methods (SHELXS-86), structure refinement using the program SHELXL-93, all C, Li, O and Si positions of the radical anion refined anisotropically, some carbon centres of THF molecules refined

on two positions with isotropic displacement parameters and fixed site occupation factors. The hydrogens bound to carbon were placed in an idealized geometry and refined with fixed isotropic displacement parameters [$U(\text{H}_{\text{aromatic,methine}}) = 1.2U_{\text{eq}}(\text{C}_{\text{aromatic,methine}})$, $U(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model, the positions and isotropic displacement parameters of the hydrogens bound to silicon were refined. $R_1 = 0.0553$ (for 4556 reflections with $F_0 > 4\sigma(F_0)$), $wR_2 = 0.1445$ (for all data), GOF 1.021, residual electron density $0.50 / -0.33 \text{ e } \text{\AA}^{-3}$. The atom coordinates are listed in Table 2. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

2.3. ESR / ENDOR spectroscopic investigation

The anion radical was generated in solution in a sealed glass apparatus by reaction of the parent compound in solvents with an alkali metal mirror distilled under high vacuum. ESR spectra were recorded on a Varian E9 spectrometer equipped with a dual cavity for g value determination (reference: perylene radical anion in THF, $g = 2.002656$) or on a digitalized high performance Bruker 220 D/ESP 300 spectrometer equipped with a field/frequency-lock (standard: diphenylpicryl hydrazyl radical). Both spectrometers are equipped with Bruker ER 4III VT variable temperature units.

ENDOR spectra were recorded on a Bruker spectrometer in ENDOR mode using Wavetek frequency synthesizers and an EIN A 300 power amplifier.

ESR spectra simulation was accomplished using the program EPRCALC on the Bruker ESP-1600/1620 Data System.

2.4. PM3 calculations

Starting from the crystal structure data and idealized CH bond lengths of 109 pm, the SCAMP IV/1 version of the MOPAC program (T. Clark, University of Erlangen) was used on our IBM work station RISC 6000/320 H.

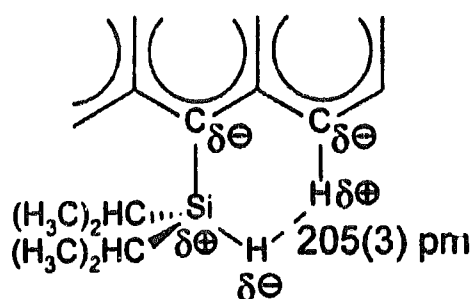
3. Results and discussion

3.1. Crystal structure of 9,10-bis(diisopropylsilyl)anthracene

The neutral compound crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$ molecules in the unit cell and the asymmetric unit contains half a molecule on a crystallographic centre of inversion. In the herringbone-like packing motif [12], the dihedral angle of the skeletal planes of adjacent molecules, related by the 2_1 screw axis, amounts to 76° and allows the hydrogens of the outer six-membered rings to point towards the π -system of neighbouring molecules (Fig. 3(A)).

The anthracene sub-unit of the molecule is planar within the accuracy of the structure determination (see Experimental section). All carbons of the six-membered rings deviated by less than 5 pm from the least-squares plane through these centres. Nevertheless, it may be possible that the molecule is slightly bent along the $\text{C9} \cdots \text{C9}(\#1)$ axis, as in 9,10-bis(trimethylsilyl)anthracene [13], and its radical anion [2] and that the crystallographic centre of inversion cover this geometric detail, inducing only weak disorder of the carbon centres of the anthracene skeleton, i.e. slightly enlarged anisotropic displacement parameters.

The isopropyl groups and especially their centres C10 and C11 exhibit large anisotropic displacement parameters (Fig. 3(C)), caused by a disorder, which could not be resolved with a split model. Both isopropyl groups adopt a *gauche* conformation towards the plane of the ring system with dihedral angles $\omega_1(\text{C10-Si1-C9-C6}) = 72.3(3)^\circ$ and $\omega_2(\text{C13-Si1-C9-C6}) = -57.1(2)^\circ$, while the hydrogen H1, bound to Si1 according to the dihedral angle $\omega_3(\text{H1Si-Si1-C9-C6}) = -169(3)^\circ$, is largely coplanar to the anthracene sub-unit:



This location of H1Si therefore results in a short intramolecular contact of only 205(3) pm to the ring hydrogen H4(#1), significantly below two hydrogen van der Waals radii $2r_{\text{H}}^{\text{vdW}} = 240$ pm [14]. This small but significant overlap of van der Waals spheres would conventionally be considered repulsive [15]. However, this H...H interaction can be interpreted as energetically favourable: hydrogens bound to carbon centres of delocalized π -systems are weak acids, whereas hydrogens bound to silicon bear negative partial charges since silicon has a significantly

Table 2
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for tetrakis(tetrahydrofuran) lithium-9,10-bis(diisopropylsilyl)anthracenide

Atom	x	y	z	U_{eq}
Si(1)	3451(1)	6289(1)	1648(1)	25(1)
Si(2)	7970(1)	8529(1)	752(1)	31(1)
C(1)	5481(3)	5936(2)	710(1)	28(1)
C(2)	6422(3)	5638(2)	382(1)	33(1)
C(3)	7451(3)	6077(2)	257(1)	34(1)
C(4)	7500(3)	6813(2)	439(1)	30(1)
C(5)	5383(3)	9001(2)	1329(1)	31(1)
C(6)	4366(3)	9305(2)	1592(1)	33(1)
C(7)	3412(3)	8841(2)	1781(1)	32(1)
C(8)	3496(3)	8080(2)	1694(1)	29(1)
C(9)	4553(3)	6953(2)	1305(1)	22(1)
C(10)	6591(3)	7928(2)	938(1)	25(1)
C(11)	5514(3)	6680(2)	932(1)	23(1)
C(12)	6548(3)	7150(2)	772(1)	24(1)
C(13)	5515(3)	8227(2)	1227(1)	23(1)
C(14)	4522(3)	7742(2)	1418(1)	23(1)
C(15)	1845(3)	6129(2)	1217(1)	35(1)
C(16)	901(4)	6770(2)	1274(2)	60(1)
C(17)	1958(4)	5935(2)	557(2)	52(1)
C(18)	3139(3)	6462(2)	2463(1)	29(1)
C(19)	2418(4)	5802(2)	2702(2)	49(1)
C(20)	4376(3)	6586(2)	2852(2)	48(1)
C(21)	7703(4)	8982(2)	-12(2)	50(1)
C(22)	6564(5)	9498(3)	-64(2)	71(1)
C(23)	7585(5)	8391(3)	-508(2)	71(1)
C(24)	8569(3)	9261(2)	1318(2)	40(1)
C(25)	8726(4)	8951(2)	1955(2)	63(1)
C(26)	9864(4)	9573(2)	1136(2)	59(1)
Li(1)	8011(5)	7767(3)	3498(2)	36(1)
O(30)	7795(2)	6943(1)	2942(1)	37(1)
C(30)	8023(4)	6193(2)	3152(2)	52(1)
C(31)	8400(6)	5770(3)	2621(2)	43(2)
C(31')	7689(10)	5694(3)	2610(3)	46(2)
C(32)	7775(5)	6146(2)	2108(2)	74(2)
C(33)	7663(3)	6941(2)	2289(1)	36(1)
O(40)	6860(2)	8597(1)	3379(1)	41(1)
C(40)	6940(4)	9192(2)	3816(2)	51(1)
C(41)	5586(4)	9445(2)	3868(2)	56(1)
C(42)	4974(3)	9313(2)	3246(2)	48(1)
C(43)	5643(4)	8633(2)	3043(2)	52(1)
O(50)	7681(2)	7416(1)	4288(1)	43(1)
C(50)	8570(4)	7106(2)	4750(2)	55(1)
C(51)	7827(5)	6608(3)	5111(2)	98(2)
C(52)	6575(4)	6507(3)	4796(2)	71(1)
C(53)	6413(4)	7182(2)	4405(2)	53(1)
O(60)	9770(2)	8065(1)	3537(1)	50(1)
C(60)	10728(3)	7738(2)	3201(2)	47(1)
C(61)	11967(5)	8127(3)	3427(3)	46(2)
C(61')	11659(7)	8388(4)	3128(3)	50(2)
C(62)	11606(4)	8813(3)	3646(3)	91(2)
C(63)	10406(5)	8599(4)	3962(3)	40(2)
C(63')	10183(6)	8822(4)	3723(4)	42(2)

Equivalent isotropic U calculated as one third of the trace of the orthogonalized U_{ij} tensor.

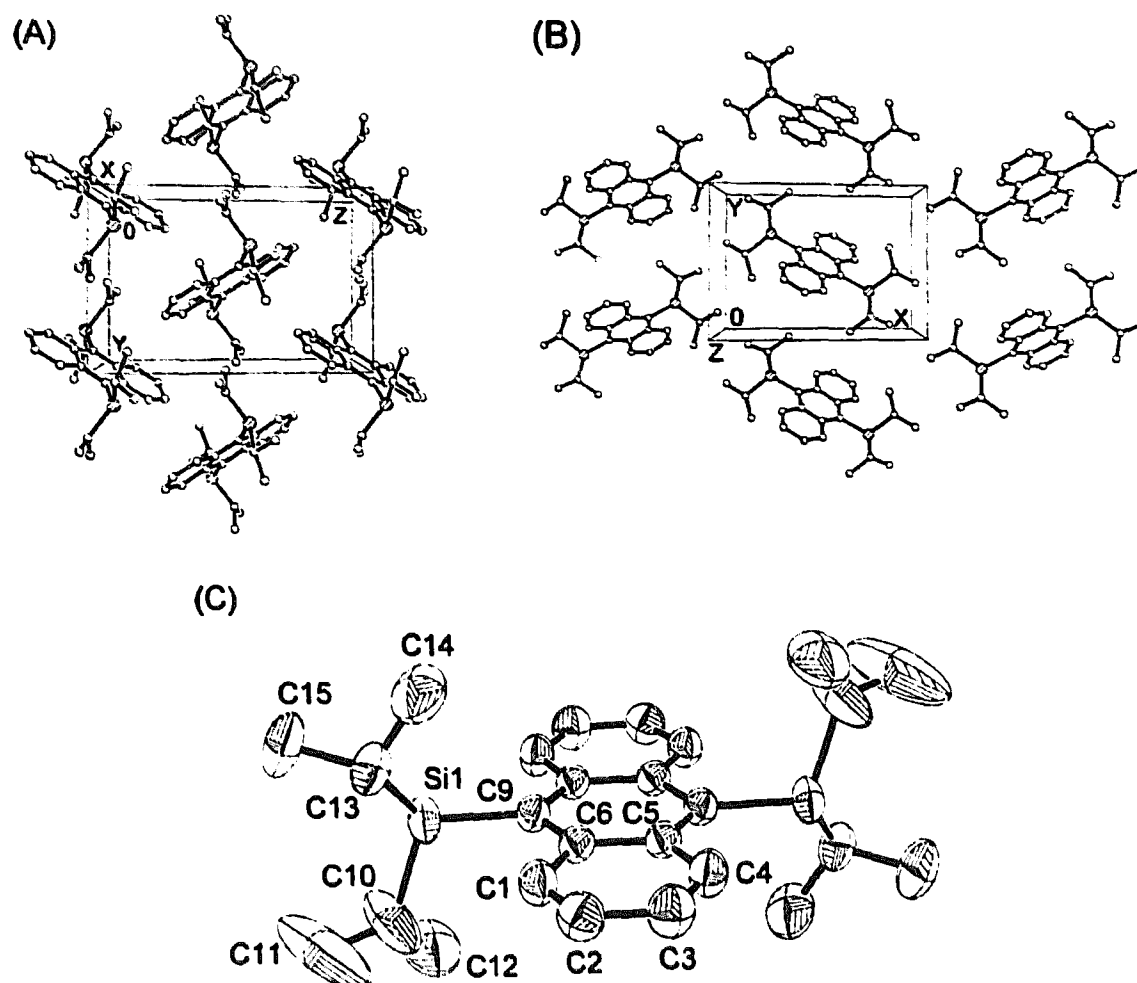


Fig. 3. Crystal structure of 9,10-bis(diisopropylsilyl)anthracene: unit cell (monoclinic $P2_1/c$, $Z = 2$) in the direction of (A) the a -axis, (B) the c -axis; (C) molecular structure (50% anisotropic displacement ellipsoids and numbering).

smaller effective nuclear charge than carbon and can be polarized more easily. A coulombic interaction between H1Si and H4(#1) might therefore foster this short contact (Eq. (5)).

3.2. ESR / ENDOR spectra of 9,10-bis(diisopropylsilyl)anthracene radical anion

Reduction of the neutral molecule with sodium or potassium in solvents such as THF or DME forms blue solutions of the radical anion. Reduction in the presence of added crown ether or 2.2.2-cryptand in DME to inhibit any possible ion pairing gives a green solution. In all solvents identical spectra are observed with little or no temperature

Table 3
Selected bond lengths and angles for 9,10-bis(diisopropylsilyl)anthracene

Bond lengths			
Si1–C10	188.3(4)	Si1–C13	188.8(3)
Si1–C9	190.4(2)	C1–C2	135.0(4)
C1–C6	143.0(3)	C2–C3	140.1(4)
C3–C4	135.4(4)	C4–C5	142.9(3)
C5–C9(#1)	141.3(3)	C5–C6	144.4(3)
C6–C9	141.5(3)	C9–C5(#1)	141.3(3)
Si1–H1Si	136(3)		
Bond angles			
C10–Si1–C13	114.2(2)	C10–Si1–C9	110.3(2)
C13–Si1–C9	113.4(1)	C2–C1–C6	123.2(2)
C1–C2–C3	119.7(2)	C4–C3–C2	120.1(2)
C3–C4–C5	122.8(2)	C9(#1)–C5–C4	122.5(2)
C9(#1)–C5–C6	120.3(2)	C4–C5–C6	117.2(2)
C9–C6–C1	121.4(2)	C9–C6–C5	121.6(2)
C1–C6–C5	117.1(2)	C5(#1)–C9–C6	118.2(2)
C5(#1)–C9–Si1	122.7(2)	C6–C9–Si1	119.1(2)

Symmetry code, #1: $-x + 1, -y, -z$.

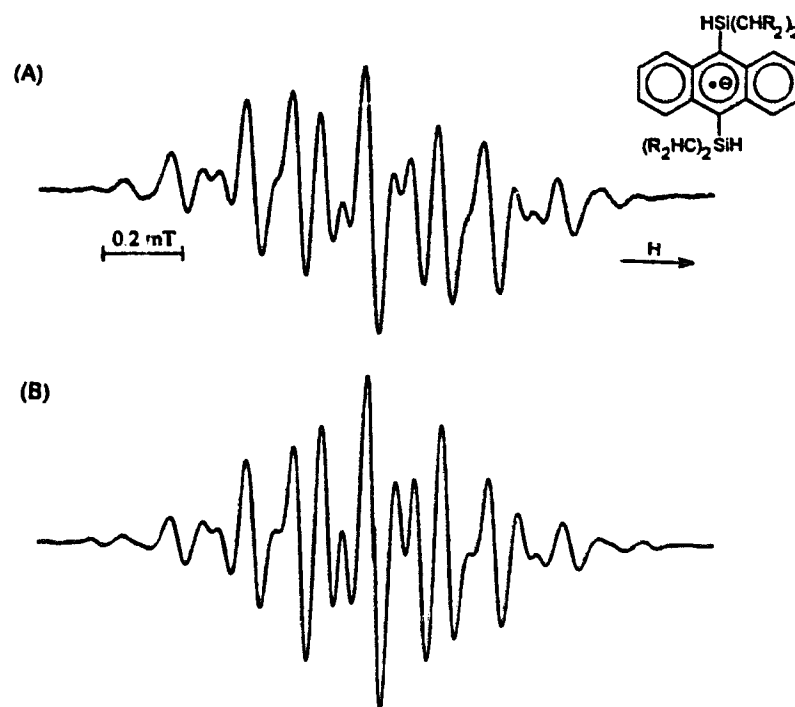
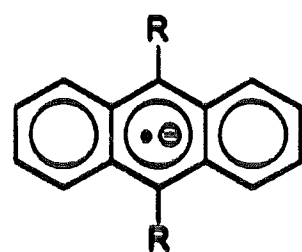


Fig. 4. Radical anion of 9,10-bis(diisopropylsilyl)anthracene generated by potassium mirror reduction: (A) ESR spectrum in tetrahydrofuran solution at 200 K, (B) simulated spectrum ($a_{\text{H}} = 0.207$ mT and 0.128 mT; $a_{29\text{-Si}}(4.67\%) = 0.47$ mT, line width 0.044 mT).

Table 4

ENDOR transition frequencies ν_{H} (MHz) and coupling constants a_{H} (mT) of the radical anions of 9,10-bis(diisopropylsilyl)anthracene (Fig. 5(A)) and 9,10-bis(trimethylsilyl)anthracene (Fig. 5(B))



R	Transition	ν_{H} (MHz)	a_{H} (mT)	$\overline{a_{\text{H}}}$ (mT)
SiH(CH(CH ₃) ₂) <i>I</i> _w 0.104 MHz 0.004 mT	1	5.747	0.205	0.20
	2	5.555	0.198	
	3	3.939	0.141	
	4	3.666	0.131	
	5	3.620	0.129	0.128
	6	3.394	0.121	
	7	0.529	0.019	0.019
	8	0.232	0.008	0.008
Si(CH ₃) ₃ <i>I</i> _w 0.096 MHz 0.003 mT	1	5.476	0.194	
	2	3.372	0.120	
	3	0.157	0.006	

dependence. At 200 K, the spectrum (Fig. 4(A), $g = 2.00251$, reference: perylene radical anion [16]) is characterized by two sets of hydrogen quintets with coupling constants $a_{\text{H}} = 0.207$ mT and 0.128 mT (Table 4).

For the radical anion of 9,10-bis(diisopropylsilyl)anthracene, no coupling from the hydrogens on the silicon centres or from those of the isopropyl groups can be detected. The lines exhibit a Gaussian line width of 0.044 mT and could not be resolved further by dilution. The ^{29}Si coupling ($I = 1/2$, nat. abundance 4.67%), however, is observed with a coupling constant $a_{29\text{-Si}} = 0.47$ mT. The assignment of the ESR signal pattern can be confirmed by simulation (Fig. 1(B)).

Further reduction of the radical anion solution with sodium or potassium metal mirrors leads to red solutions of the dianion and loss of the ESR signal. In an attempt to reduce 9,10-bis(diisopropylsilyl)anthracene with lithium metal in tetrahydrofuran solution, the red dianion formed immediately.

The ENDOR spectrum of 9,10-bis(diisopropyl)anthracene radical anion (Fig. 5(A)) was recorded at 200 K and demonstrates that the hydrogen ENDOR line pairs corresponding to the observed ESR multiplets are split, indicating a conformational equilibrium (Table 4).

The activation of a conformational equilibrium of the bis(diisopropylsilyl)anthracene radical anion in THF solution at 200 K is substantiated by comparison with the ENDOR spectrum of the 9,10-bis(trimethylsilyl)anthracene radical anion [2] (Fig. 5(B)), which exhibits no line splitting because the rotation of the trimethylsilyl groups leads to equivalent conformations.

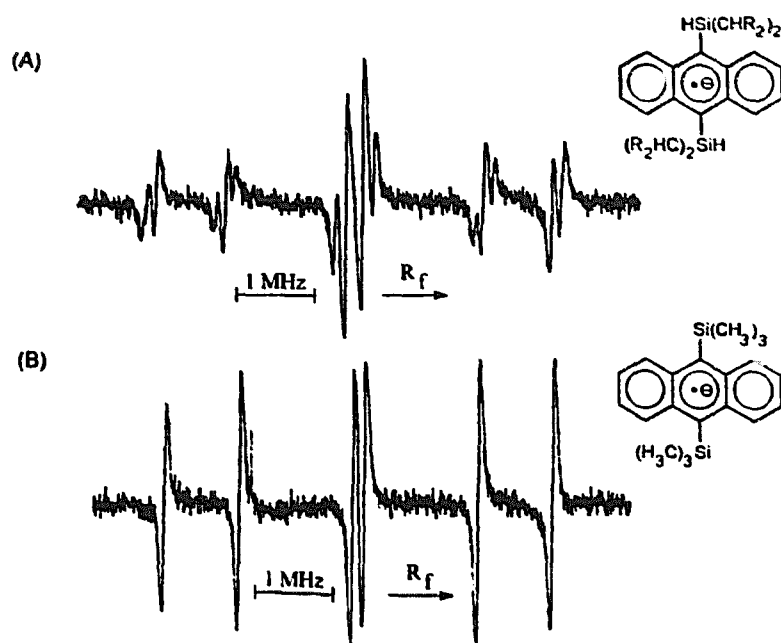
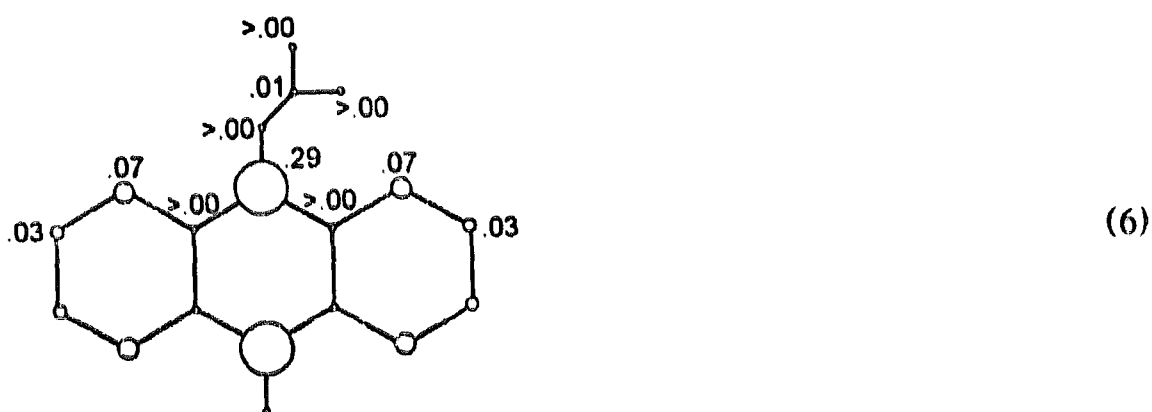


Fig. 5. ENDOR spectra of radical anions generated by potassium mirror reduction: (A) radical anion of 9,10-bis(diisopropylsilyl)anthracene in THF crown ether 18K6 solution at 200 K, (B) radical anion of 9,10-bis(trimethylsilyl)anthracene in DME solution at 210 K.

The following assignment of ENDOR transitions in the 9,10-bis(diisopropyl)anthracene radical anion is suggested. The average of transitions 3 to 6 corresponds to the smaller one (Table 4). Transitions 7 and 8 are readily assigned to the silicon hydrogen and the isopropyl hydrogen coupling by comparison with other 9,10-disubstituted anthracene radical anions such as the 9,10-bis(trimethylsilyl) derivative (Fig. 5(B)). Concerning the π spin populations at the individual centres, a PM3 open-shell calculation suggests that the larger hydrogen coupling should originate from the hydrogens in 1, 4, 5 and 8 positions:



As expected [17], the carbon π centres 9 and 10 with highest coefficients in the lowest unoccupied molecular orbital accumulate a substantial spin population. Surprisingly, no spin was found at the silicon centres [18–20].

3.3. Crystal structure of tetrakis(THF)lithium-9,10-bis(diisopropylsilyl)anthracenide

The lithium salt of 9,10-bis(diisopropylsilyl)anthracene crystallizes from a THF solution in the monoclinic space group $P2_1/n$ with one radical anion and one THF-solvated Li^+ cation inside the asymmetric unit (Fig. 6(A)). The crystal structure consists of stacks of radical anions alternating with THF-solvated lithium cations (Fig. 6(B)). The anions are stacked with the anthracene plane perpendicular to the stacking direction. This packing motif corresponds to that in the previously reported tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide [3]. In contrast, however, the succeeding radical anions are twisted against each other by about 90° along the stacking direction.

The tetra(THF)-solvated Li^+ counter cation is coordinated by four THF oxygens forming an almost ideal tetrahedron with contact distances $\text{Li} \cdots \text{O}$ between 191.5(6) and 192.8(6) pm and angles $\text{O} \cdots \text{Li} \cdots \text{O}$ between $102.9(3)$ and $117.4(3)^\circ$ (Fig. 6(C) and Table 5).

The 9,10-bis(diisopropylsilyl)anthracene radical anion, the bond lengths and angles of which are largely comparable with those of the neutral molecule (Tables 2 and 5), is folded along its $\text{C9} \cdots \text{C10}$ axis by an angle of 169° between the two anthracene halves and the silicon centres Si1 and Si2 are slightly bent by an average angle of 7° out

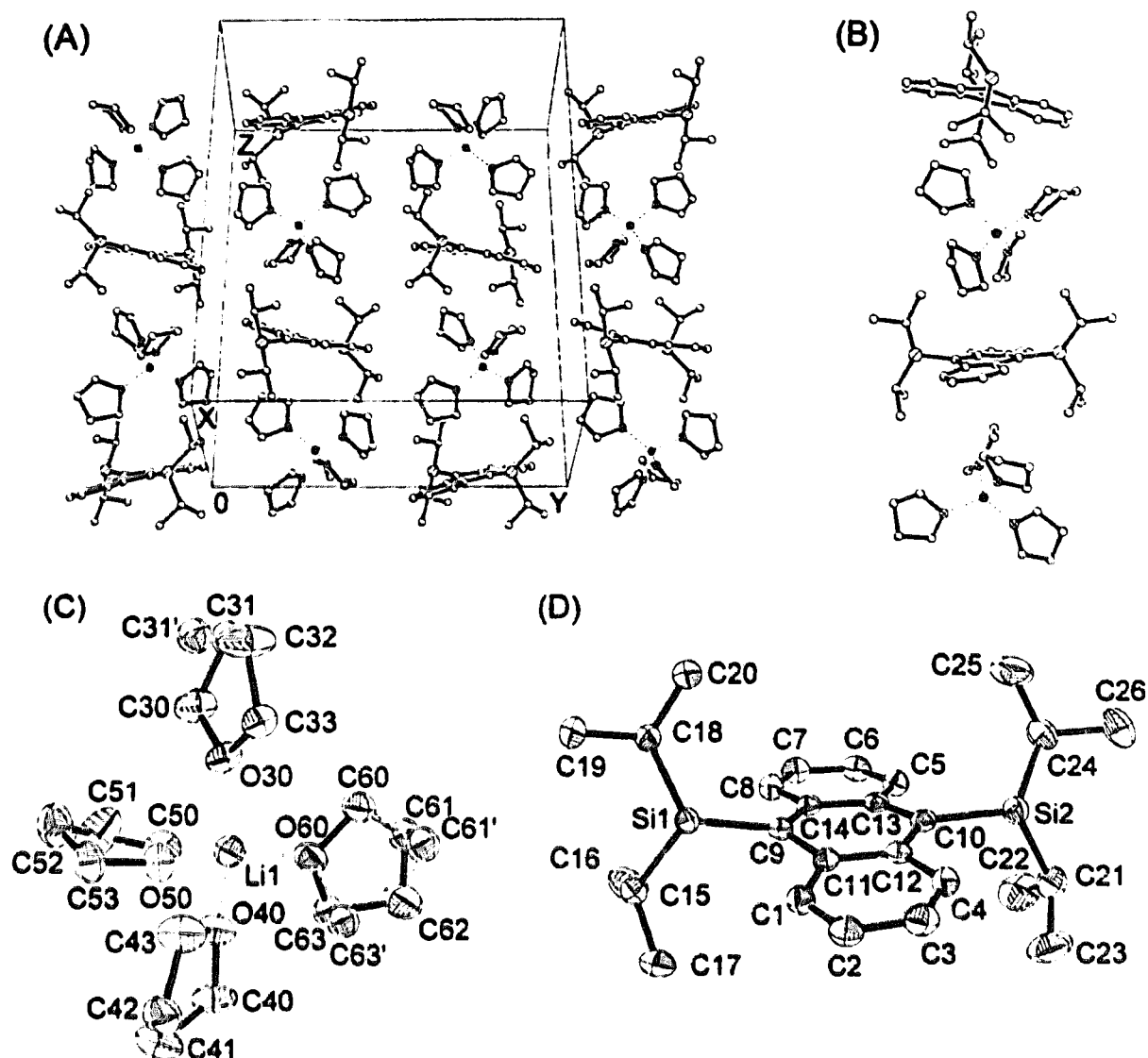
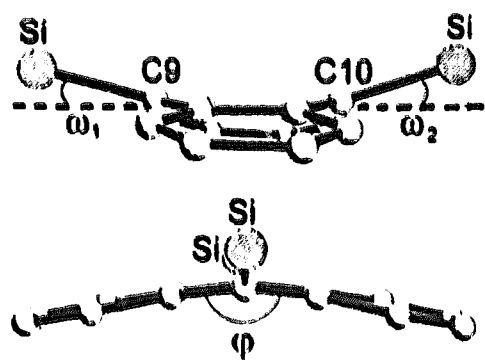


Fig. 6. Crystal structure of tetrakis(THF)lithium-9,10-bis(diisopropylsilyl)anthracene: (A) crystal packing, (B) stacking of alternating cations and anions, (C) molecular structure of the THF-solvated cation, and (D) the radical anion (50% anisotropic displacement ellipsoids and labelling scheme).

of the $C9 \cdots C10$ axis (Fig. 6(D) and Table 5). Relative to the chemically closely related 9,10-bis(trimethylsilyl)anthracene radical anion [2], only small changes are observed:



SiR_3	$\omega_1 + \omega_2$ [°]	φ [°]
$SiH(CH_2CH_3)_2$	4 + 10	169
$Si(CH_3)_3$	18 + 18	165

(7)

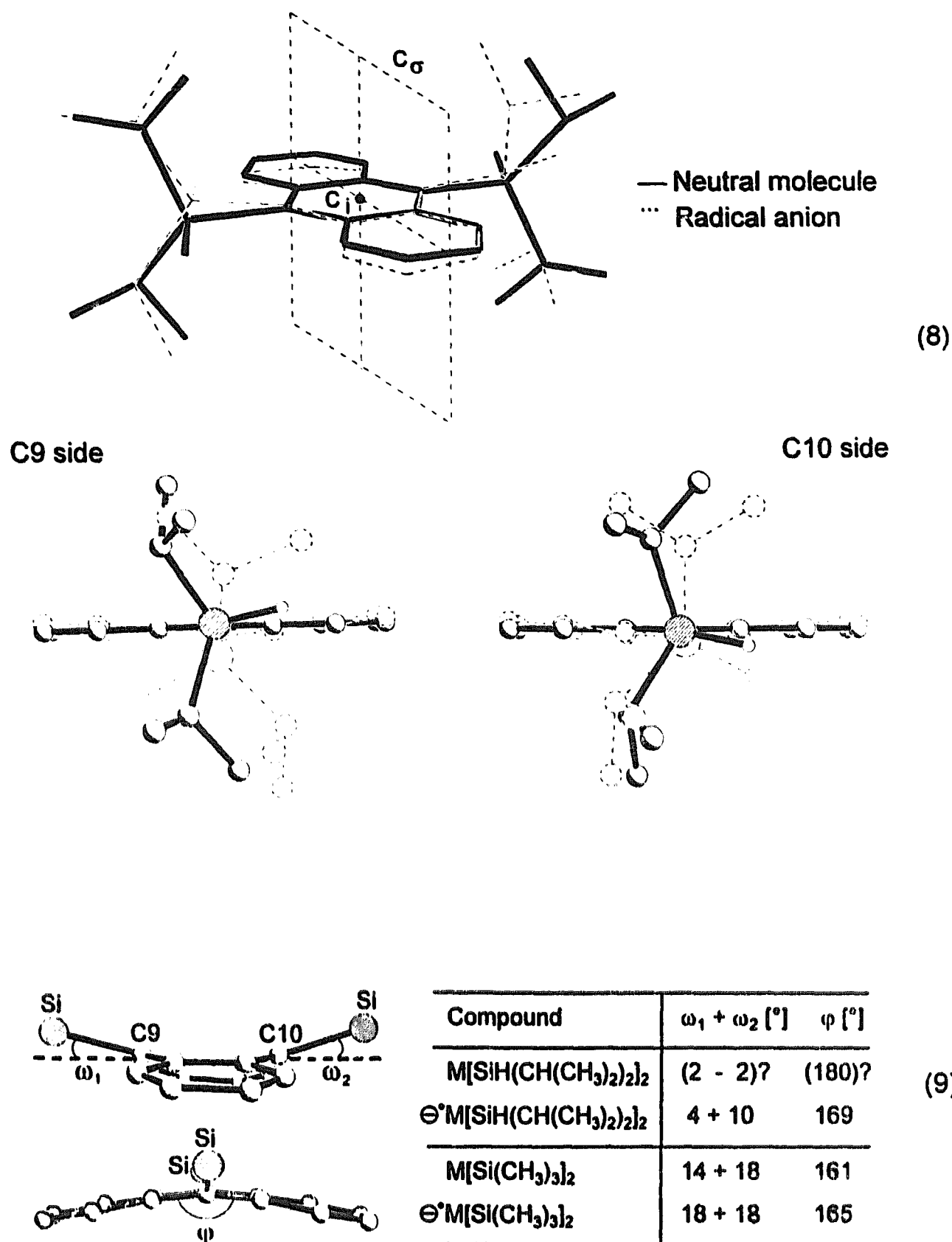
Both 9,10-bis(trialkylsilyl)-substituted anthracene radical anions differ only slightly, but significantly, in their structures. In the trimethylsilyl derivative, with presumably a sterically somewhat more demanding bulky substituent, the interplanar angle φ is smaller by 4° but the Si centre bending out of the $SiC \cdots CSi$ axis is larger by about 10°.

3.4. Changes due to single-electron reduction of 9,10-bis(diisopropylsilyl)anthracene

The structure determinations for both the neutral molecule (Fig. 3 and Table 2) and the radical anion (Fig. 6 and Table 5) enable us to note the following rather small changes [3]. The bond lengths and angles of 9,10-bis(diisopropylsilyl)anthracene on insertion of a single electron remain almost constant. A significant change, however, is observed both in the overall molecular symmetry, which shifts from inversion to mirror symmetry, and in the conformation of the diisopropylsilyl substituents (Eq. (7)). One consequence is that the silicon hydrogen bonds

Si1–H1Si and Si2–H2Si are now both twisted out of the least-squares plane of the anthracene carbons by 26° and, therefore, no longer form contacts (Eq. (5)) of 205 pm distance to the peri ring-hydrogens.

For the chemically closely related anthracene derivatives with $\text{SiH}(\text{CH}(\text{CH}_3)_2)$ or $\text{Si}(\text{CH}_3)_3$ substituents, the following angle changes (see Eq. (6)) relative to the neutral molecules are summarized:

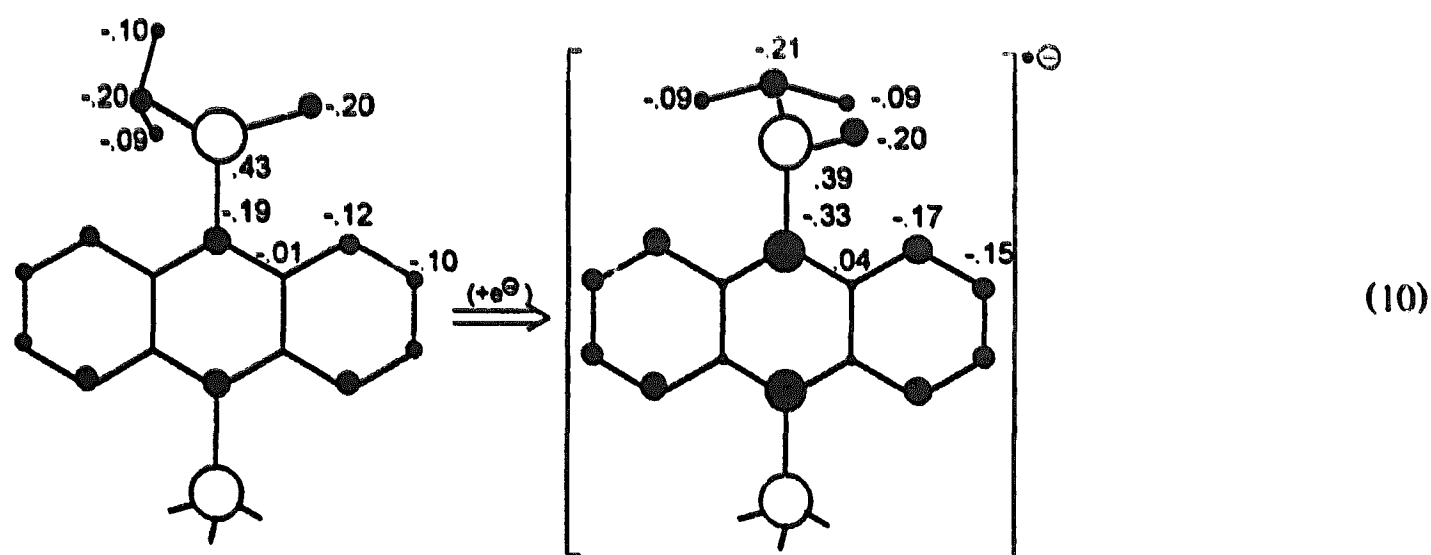


Comparison with the previously investigated [2] trimethyl silyl compounds is extremely helpful, because as pointed out already the structure determination with the molecule on a crystallographic centre of inversion does not yield unambiguous information on the bending angles (Eq. (9), in brackets). Most likely, both are bent, and consequently the angle changes on one-electron reduction also remain small (as confirmed by many literature examples [3] in which severe molecular distortions are only observed after the insertion of a second electron to generate the respective dianion).

Table 5
Selected bond lengths, contact distances (pm) and angles (deg) for tetrakis (THF)lithium-9,10-bis(diisopropylsilyl) anthracenide

<i>Bond lengths</i>			
Si1–C9	186.1(3)	Si1–C15	189.5(3)
Si1–C18	189.7(3)	Si2–C10	187.3(3)
Si2–C21	188.8(4)	Si2–C24	189.3(3)
C1–C2	137.9(4)	C1–C11	141.9(4)
C2–C3	137.9(5)	C3–C4	137.7(4)
C4–C12	142.3(4)	C5–C6	136.9(4)
C5–C13	141.2(4)	C6–C7	139.0(5)
C7–C8	137.8(4)	C8–C14	141.5(4)
C9–C14	143.4(4)	C9–C11	144.0(4)
C10–C12	143.8(4)	C10–C13	144.3(4)
C11–C12	143.9(4)	C13–C14	144.4(4)
Si1–H1Si	141(3)	Si2–H2Si	143(3)
<i>Contact distances</i>			
Li1–O30	192.8(6)	Li1–O40	191.9(6)
Li1–O50	192.5(6)	Li1–O60	191.5(6)
<i>Bond angles</i>			
C9–Si1–C15	116.3(1)	C9–Si1–C18	116.5(1)
C15–Si1–C18	107.5(1)	C10–Si2–C21	112.5(2)
C10–Si2–C24	118.2(1)	C21–Si2–C24	108.9(2)
C2–C1–C11	123.3(3)	C3–C2–C1	119.3(3)
C4–C3–C2	119.8(3)	C3–C4–C12	123.2(3)
C11–C9–Si1	120.3(2)	C12–C10–C13	117.6(3)
C12–C10–Si2	120.5(2)	C13–C10–Si2	121.9(2)
C1–C11–C12	117.4(3)	C1–C11–C9	121.4(3)
C12–C11–C9	121.2(3)	C4–C12–C10	122.3(3)
C4–C12–C11	116.9(3)	C10–C12–C11	120.7(3)

Based on the structural coordinates determined, PM3 closed- and open-shell calculations have been performed to approximate the difference in charge distribution:



Again surprisingly [18–20] most of the additional charge accumulates in the anthracene π system, increasing its total charge by about -0.70 , i.e. $2/3$ of the additional one electron. Contrary to the many literature examples, the two silicon centres localize only a minimal fraction of about $(+4.3) - (+0.39) \sim 0.05$, despite the known large π spin population of unsubstituted anthracene radical anions in which almost half of the spin is ESR-detected at the ring-bridging centres 9 and 10 [2].

Altogether, crystallization and structure determination of organosilicon π systems and their radical anions provide essential information on single electron reductions. The extra electron is largely distributed within the large, 14 carbon centre π system and, therefore, at best small and predominantly conformational changes are observed.

Acknowledgements

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