

Interactions in crystals LXXVIII [☆]. The structure of “naked” 9,10-bis(trimethylsilyl)anthracene radical anion

Hans Bock ^{a,*}, Manssur Ansari ^a, Norbert Nagel ^a, Rodney F.C. Claridge ^b

^a Chemistry Department, University of Frankfurt, Marie-Curie-Strasse 11, D-60439 Frankfurt, Germany

^b Chemistry Department, University of Canterbury, Christchurch, New Zealand

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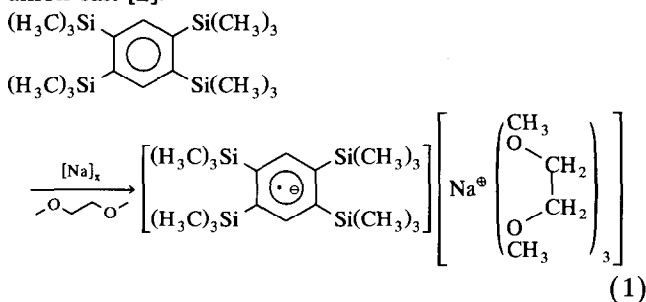
Abstract

Reduction of 9,10-bis(trimethylsilyl)anthracene at a sodium metal mirror under aprotic conditions and argon yields its radical anion, which is characterized by its ESR multiplet signal pattern. Crystallization from dimethoxyethane solution under aprotic conditions yields brown prisms of its solvent-separated radical anion salt. The structure, determined in a 130 K cold N₂ flow, is discussed in comparison with the analogously folded structure of the neutral molecule, literature examples and results of MNDO calculations.

Keywords: Silicon; ESR spectroscopy; 9,10-Bis(trimethylsilyl)anthracene; Solvent-separated radical anion salt

1. Starting point: the crystallization of solvent-separated ion pairs including those of organosilicon-substituted π compounds

Reduction of 1,2,4,5-tetrakis(trimethylsilyl)-benzene in dimethoxyethane solution at a sodium metal mirror yielded as planned [2–10] the solvent-separated radical anion salt [2]:



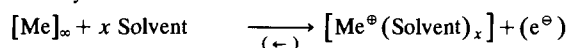
In general, conditions are now well established to crystallize from the usually dark-red ether solutions,

[☆] Part LXXVII see [1]. For a subsequent discussion of solvent-separated ion pairs see [2]. Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

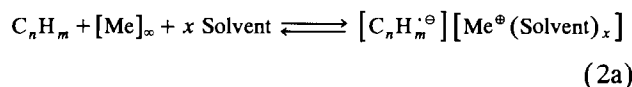
* Corresponding author.

which result from the rather unselective reduction using an alkaline metal mirror, and which contain a network of electron transfer, ion pair formation, solvation as well as aggregation equilibria [2–4], selectively the solvent-separated sodium radical anion salt [5–10]:

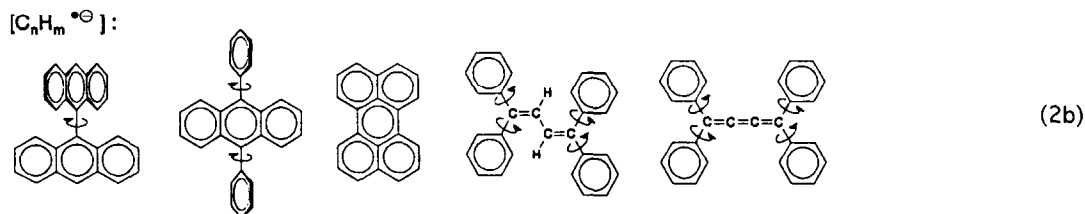
redox half-system I:



redox half-system II:



The seemingly surprising selectivity can be rationalized convincingly. Extended π systems (2b) such as provided by bianthryl [5,7], 9,10-diphenylanthracene [5,6], perylene [3,5,9], 1,1,4,4-tetraphenyl-1,3-butadiene [3,5,8] or 1,1,4,4-tetraphenylbutatriene [3,5] lack extensively charged individual centers for contact ion formation [3,10]. Sodium counter-cations Na⁺ are rather advantageous [3], because the first vertical ionization energy of Na, IE₁^v = 5.13 eV, and the hydration enthalpy of [Na⁺(H₂O)₁₇], $\Delta H_f = -390 \text{ kJ mol}^{-1}$ [11], both contribute to the low and therefore more gentle first reduction potential $E_{1/2}^{\text{Red}}(\text{Na}) = -2.71 \text{ V}$. In addition, its ionic radius $r = 97 \text{ pm}$, increasing to 113 pm for



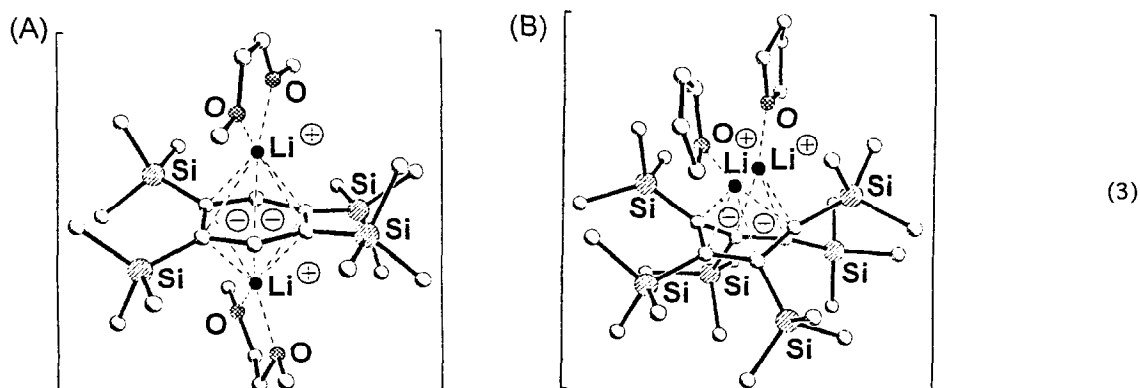
30% covalent contribution [3,12], is of the right size for the preferred sixfold and often octahedral coordination although the choice of the solvent is decisive. Based on structural data [5], for the sixfold-coordinate Na^{\oplus} solvation by different ethers, the following increasing enthalpies ΔH_f (kJ mol⁻¹) have been calculated: $[Na^{\oplus}(THF)_6] - 587 < [Na^{\oplus}(DME)_3] - 671 < [Na^{\oplus}(\text{diglyme})_2] - 677$ [5]. Using all the above information, for instance, we even succeeded in growing black crystals of a solvent-separated naphthalene radical anion salt, $[C_{10}H_8^{\bullet\ominus}][Na^{\oplus}(\text{diglyme})_2]$, from diglyme solution after sodium metal mirror reduction according to (2) [9] or even of the silyl-substituted benzene radical anion salt (1).

A search in the Cambridge Structural Database (February 1995) for anion salts of organosilicon-substituted cyclic carbon π systems has produced only two entries. Firstly the lithium metal reduction of 1,2,4,5-tetrakis(trimethylsilyl)benzene in dimethoxyethane at room temperature yields brown needles of the corresponding bis(dimethoxylithium) contact triple ion (3:A) with each one counter-cation η^6 -coordinated above and below the only slightly puckered six-membered carbon ring and contact distances $Li^{\oplus} \cdots (C)_6^{\ominus\ominus}$ of 187 pm [13]. The second example concerns hexakis(trimethylsilyl)benzene, which is heavily overcrowded as demonstrated by torsion angles $\omega(\text{SiC}-\text{CSi}) = 61^\circ$ [14] and can be reduced by excess lithium metal in tetrahydrofuran (THF) solution at room temperature to red crystals (3:B) of a bis(tetrahydrofurane lithium) contact triple ion with the two Li^{\oplus} counter-cations on the very same

side of the dianion C_6 ring bent into a boat conformation [15,16]. The severe structural distortion, expected within a molecular state approach [17], can already be reproduced by ab initio calculations on a 6–21 G level [16].

In order to gain further information on solvent-shared [3,4,8,9] and solvent-separated [2–4,7–10] contact ion multiples as well as in the potential formation of dianion salts [3,4,8] we have chosen 9,10-bis(trimethylsilyl)anthracene, for which a HMO π approach [18] predicts a low-lying non-degenerate unoccupied molecular orbital of b_{1u} irreducible symmetry representation and its largest possible substituent perturbation $\Sigma(c_{8,9/10})^2 = 2(0.44)^2 = 0.38$, in 9/10-positions. Unexpectedly, the neutral molecule is folded along its axis $C9 \cdots C10$ (Fig. 1) by an interplanar angle $\varphi = 161^\circ$ [19]. This experimental observation possibly can be traced to van der Waals interactions [20–24] between the bulky trimethylsilyl groups exhibiting a radius of 380 pm (!) [3] with the adjacent hydrogen atoms in 1,4,5- and 8-positions by overlap with their van der Waals radii of 120 pm [3]. A one-dimensional PM3 enthalpy hypersurface (Fig. 1) predicts for inversion only about 10 kJ mol⁻¹.

The PM3 calculations in steps of $\Delta\varphi = 2.5^\circ$ (see Section 2) with each full geometry optimization yield a potential curve exhibiting an enthalpy-of-formation minimum at an angle $\varphi = 168^\circ$, i.e. close to the experimental value of $\varphi = 161^\circ$ [19]. With most of the points fitting a quadratic regression $\Delta\Delta H_f^{\text{PM3}} = 1.8492 - 22.0\varphi + 0.07\varphi^2$ ($R = 0.999$). On crossing the activation



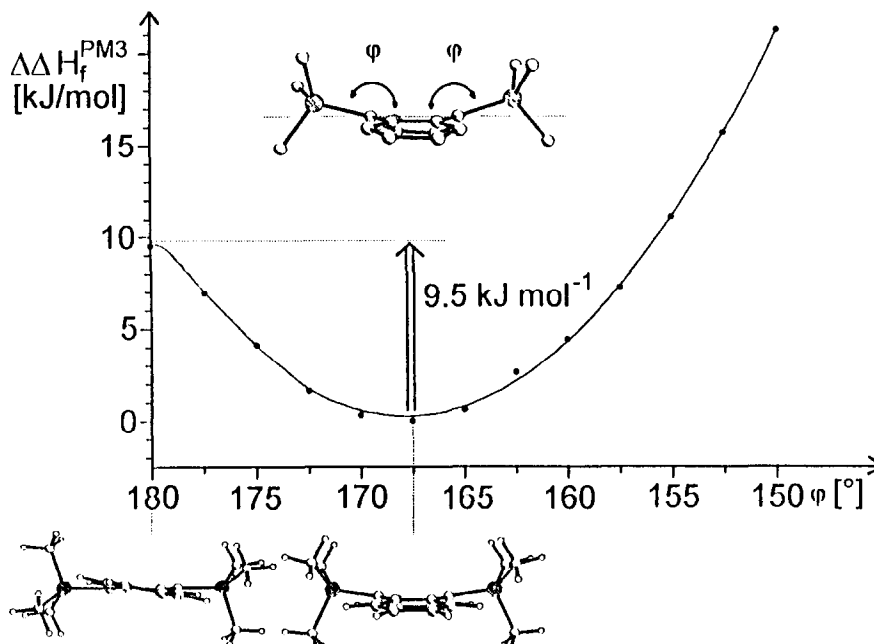


Fig. 1. Enthalpy hypersurface for substituent out-of-plane-bonding in 9,10-bis(trimethylsilyl)anthracene.

enthalpy barrier of 9.5 kJ mol^{-1} the cisoid arrangement of the two $(\text{H}_3\text{C})_3\text{Si}$ substituent changes into a transoid arrangement with a simultaneous inclination of the C(6) ring planes relative to the Si–C(9) \cdots C(10)–Si substituent axis.

Whatever the origin of the intricately small but significant deviation from the skeletal planarity of 9,10-bis(trimethylsilyl)anthracene (Fig. 1) might be, it is of interest whether on insertion of additional electrons its interplanar angle will increase, remain constant or decrease.

2. Experimental section

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

2.1. 9,10-Bis(trimethylsilyl)anthracene

The literature procedure [25] has been modified as follows: a slurry of 2 g (5.95 mmol) 9,10-dibromoanthracene in 30 ml of THF was cooled to -20°C and one equivalent of *n*-butyllithium (3.8 ml, 5.95 mmol) in *n*-hexane added within 5 min. The resulting deep-red solution was stirred at room temperature for 10 min, trimethylchlorosilane (646 mg, 5.95 mmol) added and the now pale-yellow solution stirred for 15 min. The above procedure has been repeated with an another equivalent of *n*-butyllithium. The mixture was hydrolyzed by adding 100 ml of H_2O and three times extracted with 30 ml of diethyl ether. All extracts were

dried over Mg_2SO_4 and all volatile components evaporated, yielding 1.75 g of a yellow oil. Crystallization from 20 ml ethanol yielded 14% of pale-yellow crystals of 9,10-bis(trimethylsilyl)anthracene with a melting point of 387 K (386–387 K [25]). $^1\text{H-NMR}$ (CDCl_3 , tetramethylsilane): 0.72 ppm (m, 18 H), 7.44 ppm (m, 4H), 8.42 (m, 4H) ppm. Anal. Found: C, 73.25; H, 8.21. $\text{C}_{20}\text{H}_{26}\text{Si}_2$ Calc.: C, 74.50; H, 8.07.

2.2. Tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide

A sodium mirror was generated by vacuum distillation of 50 mg (2.2 mmol) of sodium in a carefully dried Schlenk trap under argon and 10 ml of dry dimethoxyethane and 300 mg (0.93 mmol) of 9,10-bis(trimethylsilyl)anthracene were added. After 1 day, nearly all sodium had vanished, and 10 ml of *n*-hexane was added to the resulting dark-brown–red solution. After 2 days, brown prisms had grown, which despite of their extreme air and moisture sensitivity could be successfully subjected to X-ray crystallography.

2.3. ESR spectroscopic investigation

Radical anion generation was carried out in a three-compartment glass apparatus. In a high vacuum line, a sodium mirror has been generated by distillation at 10^{-6} mbar pressure and, after depositing both the compound and the solvent, the apparatus sealed off. After cooling in a cryostat to the temperature specified, a radical anion solution was generated by rotating the

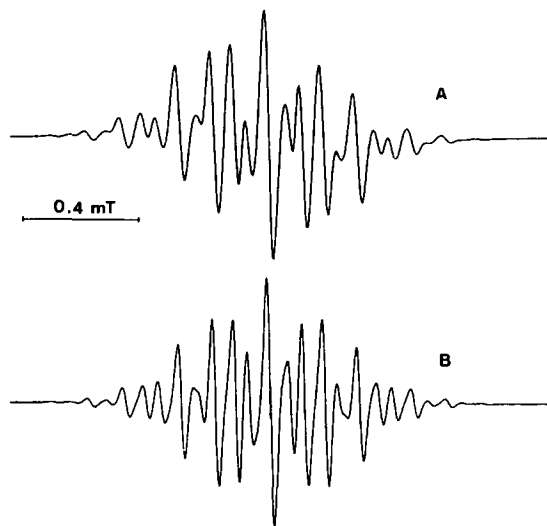


Fig. 2. Radical anion of 9,10-bis(trimethylsilyl)anthracene, generated in dimethoxyethane solution by a reduction at a sodium mirror: (A), ESR spectrum at 200 K; (B), spectrum simulated with coupling constants $a_{\text{H}} = 0.194$ and 0.121 mT as well as $a_{29\text{Si}} = 0.50$ mT.

apparatus vessel and transferred to a capillary fitting into the cavity of the ESR spectrometer.

ESR spectra were recorded with a digitalized high performance spectrometer Bruker 220 D/ESP 300, equipped with a field–frequency lock (standard, diphenylpicrylhydrazyl radical) and a constant temperature unit ER 4111 VT.

Simulation of the ESR spectrum (Fig. 3, spectrum B) has been accomplished by introducing the coupling constants read off predominantly from the satellites into the program ESR/SIMULATION II (author, Dr. B. Roth) and by improving the fit to the experimental spectrum by trial and error (Fig. 3, spectrum A).

2.4. Crystal structure determination of tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide

$\text{C}_{32}\text{H}_{56}\text{O}_6\text{Si}_2\text{Na}$ (molecular weight, 615.94); triclinic; $P\bar{1}$ (No. 2); $Z = 2$; $a = 1013.0(1)$ pm, $b = 1202.2(1)$ pm and $c = 1632.2(2)$ pm; $\alpha = 85.16(1)^\circ$, $\beta = 87.96(1)^\circ$ and $\gamma = 68.24(1)^\circ$, $V = 1839.4(5) \times 10^6$ pm³ (130 K); $\rho = 1.112$ g cm⁻³; $\mu(\text{Mo K}\alpha) = 0.15$ mm⁻¹; Siemens P4 diffractometer; $3^\circ < 2\theta < 48^\circ$ (ω scan), 6064 measured reflections of which 5699 are independent; 376 parameters. Structure solution by direct methods (XS); structure refinement using the program SHELXL93, all C, Na, O and Si positions refined anisotropically, all hydrogen atoms are positioned in idealized geometry and refined with fixed isotropic displacement parameters ($U(\text{H}_{\text{aromatic}}) = 1.2U_{\text{eq}}(\text{C}_{\text{aromatic}})$, $U(\text{H}_{\text{methylene}}) = 1.2U_{\text{eq}}(\text{C}_{\text{methylene}})$, $U(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$) using a riding model; R_1 (for 4656 $F_o > 4\sigma(F_o)$) = 0.0519; wR_2 (for all data) = 0.1417; goodness of fit, 1.065; residual electron density, 0.34, -0.33 electrons \AA^{-3} .

2.5. PM3 calculations

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

The enthalpy hypersurfaces for both 9,10-bis(trimethylsilyl)anthracene and its radical anion have been generated by varying the angles $\varphi(\text{Si}(1)\text{--C}(9)\cdots\text{C}(10))$ and $\varphi(\text{Si}_2\text{--C}(10)\cdots\text{C}(9))$ in steps of 2.5° and each optimizing the geometry by using the Fletcher–Powell subroutine.

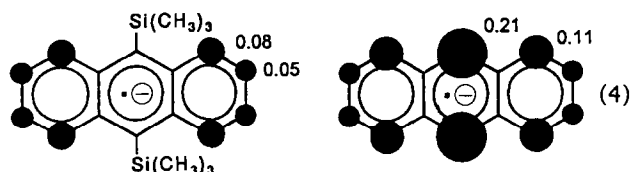
3. Results and discussion

3.1. ESR spectrum of 9,10-bis(trimethylsilyl)anthracenyl radical anion

The signal pattern recorded after generation at a sodium metal mirror of the blue diethyl ether or dimethoxy ethane solutions (cf. Section 2) at 200 K (Fig. 2, spectrum A), centered around $g = 2.0024$ as calibrated by perylene radical anion, is dominated by two set of hydrogen quintets with coupling constants $a_{\text{H}} = 0.194$ and 0.121 mT. No coupling from the 18 methyl hydrogen atoms was detected; the lines exhibited a widths of 0.03 mT and could not be resolved further. In addition, a ^{29}Si coupling ($I = 1/2$; natural abundance, 4.67%) of 0.50 mT was detected. This assignment of the ESR spectrum is supported by its satisfactory simulation (Fig. 2, spectrum B).

A McConnell approximation $a_{\text{H}} = |2.5 \text{ mT}| \rho_{\mu}^{\pi}$, would suggest the spin density distribution at the H-substituted centers as given in (4) compared with anthracene radical anion [26]. In agreement with the squared HMO coefficients [18] and with other 9,10-disubstituted anthracene radical anions [27] and organosilicon π radical anions [27], most of the spin density resides at the π centres 9 and 10 of the substituted anthracene. The assignments are supported by McLachlan-type calculations [28].

No temperature dependence of the ESR spectrum is observed; the blue radical anion solution in dimethoxyethane is stable for days. However, on further contact with the sodium mirror, the solution rapidly becomes red and the ESR signal vanishes owing to further reduc-



tion to the dianion. In diethyl ether solution, the 9,10-bis(trimethylsilyl)anthracene radical anion is unstable above 200 K, the colour changes to red, and the ESR signal fades rapidly.

3.2. Crystal structure of tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide

The compound crystallizes in the space group $P\bar{1}$ with one formula unit inside the unit cell. The radical

anions and the solvated sodium counter cations are stacked alternatively with the anthracene skeletal planes perpendicular to the stacking axis (Fig. 3(a)). Therefore the shortest intermolecular contacts are found between the centers of the anthracene ring and the dimethoxyethane molecules as well as between the dimethoxyethane molecules, where the shortest distances $C \cdots C$ are 344 pm. The negative charges—often disadvantageous to the close-packing principle—seem to prevent a π stacking

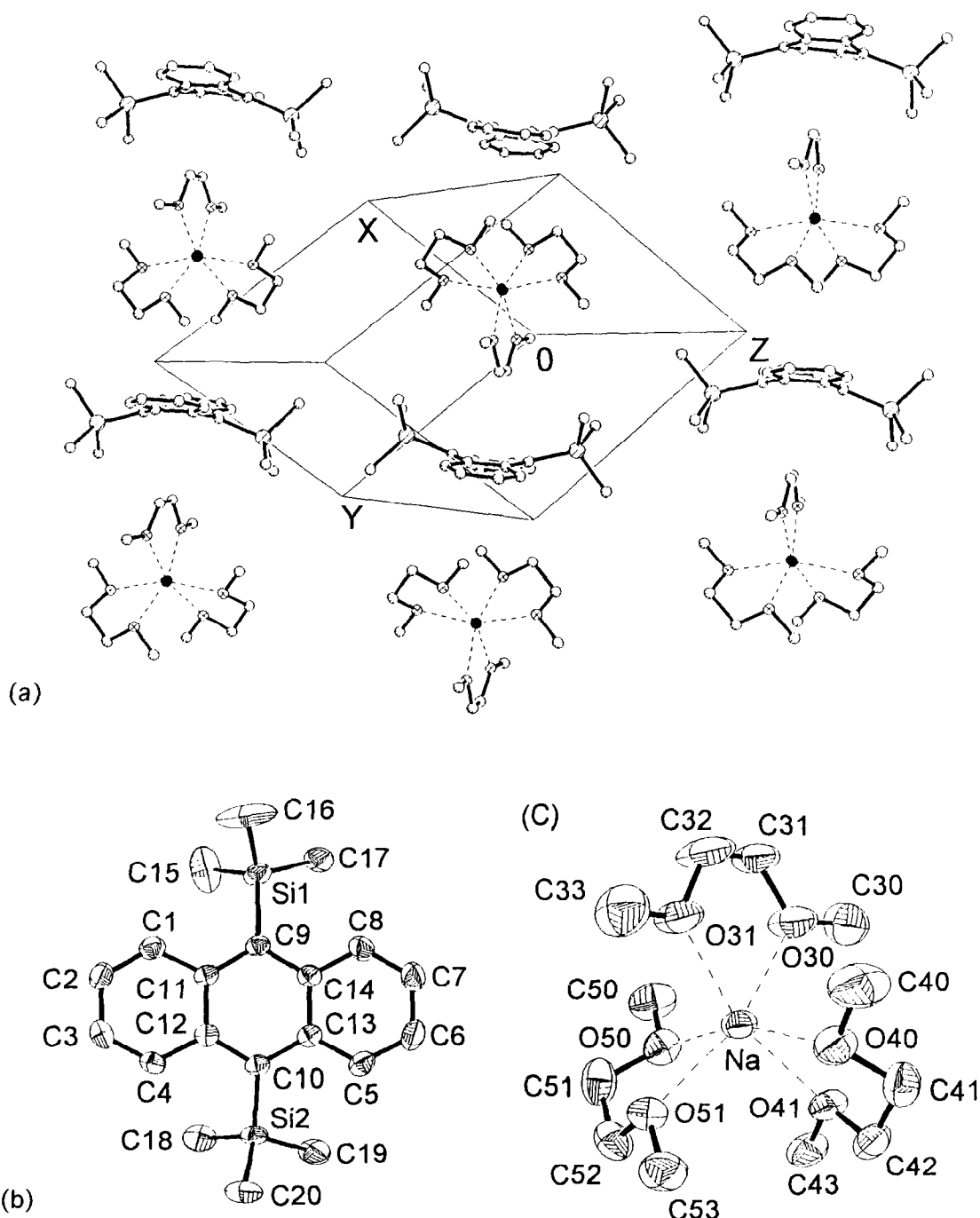


Fig. 3. Crystal structure of tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide at 130 K: (a) unit cell (triclinic; $P\bar{1}$; $Z = 2$) with mixed stacks of the anions and cations; (b) the radical anion viewed perpendicularly to the anthracene plane and (c) the threefold dimethoxyethane-solvated sodium cation (50% thermal ellipsoids).

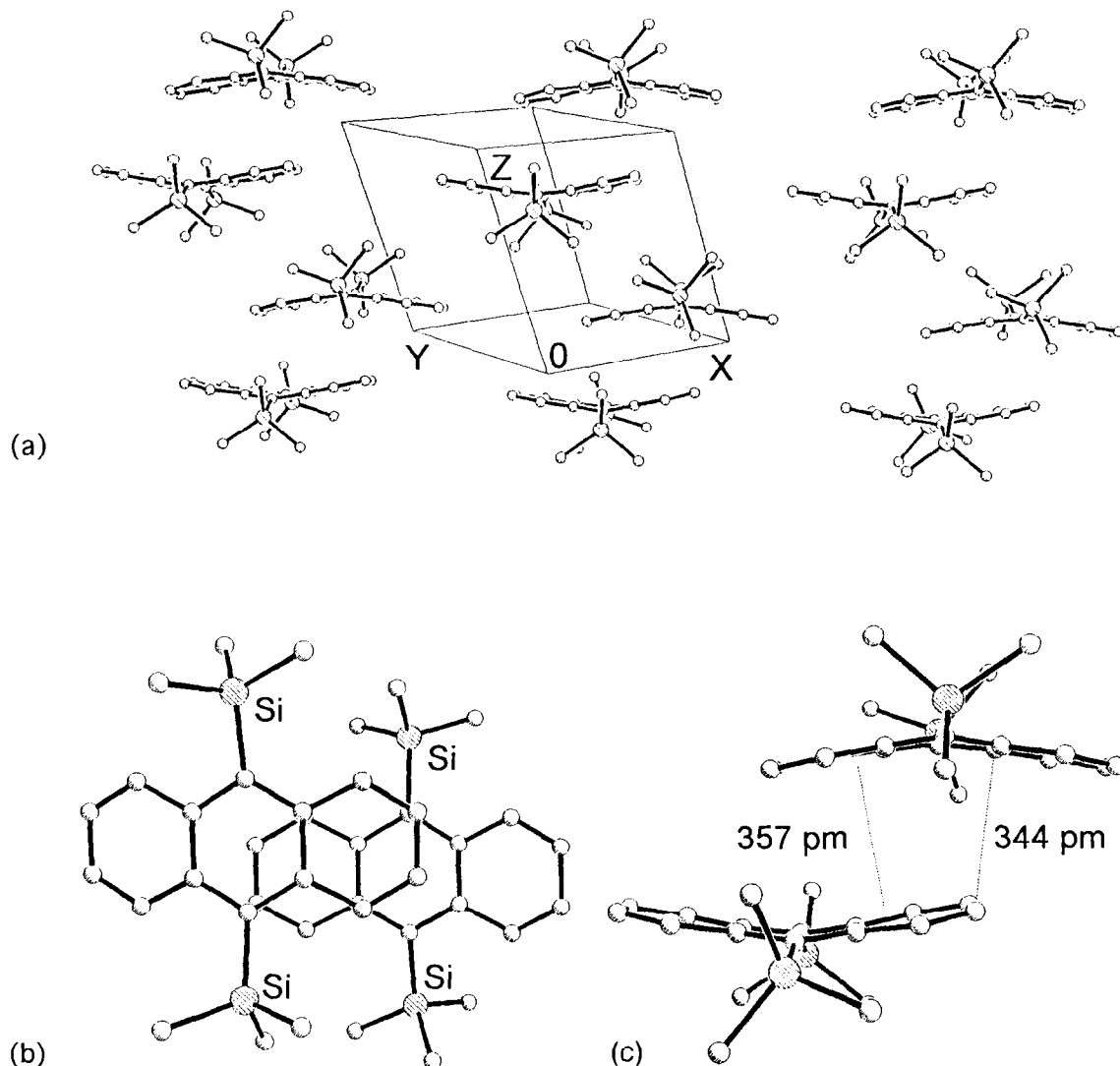


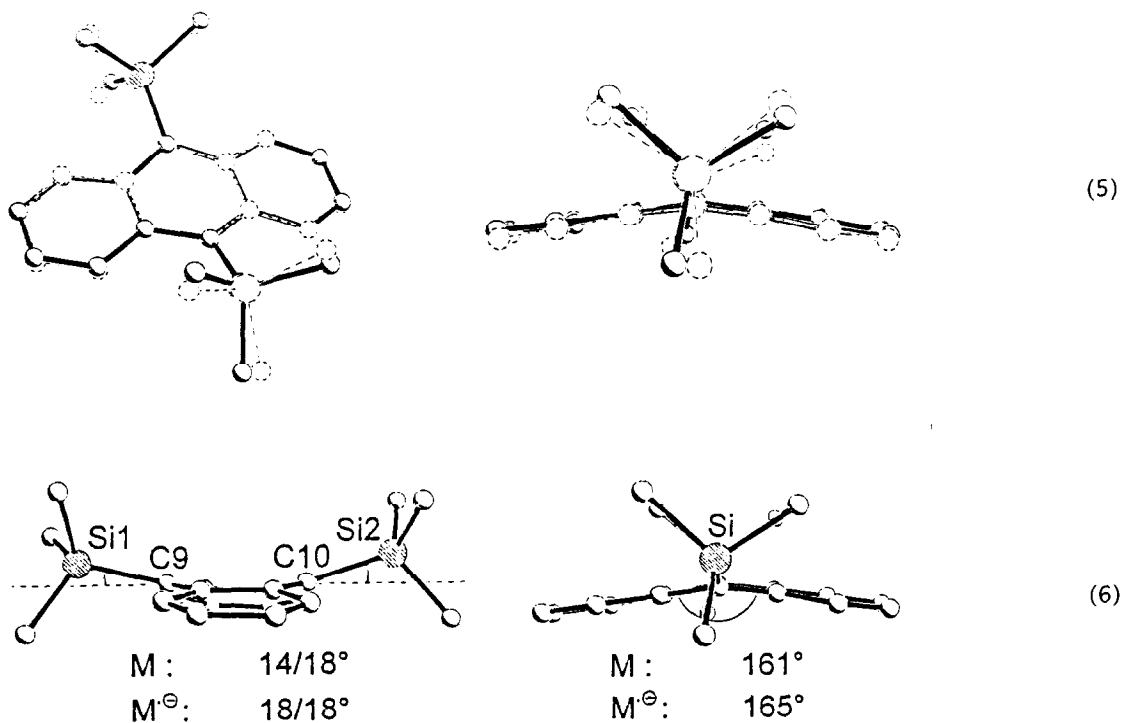
Fig. 4. Crystal structure of 9,10-bis(trimethylsilyl)anthracene at 293 K [19]: (a) unit cell (triclinic; $P\bar{1}$; $Z=2$) with molecular stacks; (b) arrangement of adjacent molecules perpendicular to their skeletal planes and (c) viewed along the anthracene planes.

of the anthracene fragments in contrast to with the crystal structure of the neutral compound (Fig. 4(a)). [19], in which the molecules despite their bulky trimethylsilyl substituents form weak van der Waals contacts between their π systems. Each one anthracene half-fragment of two molecules is oriented coplanar to the other one with an interplanar distance of about 357 pm and a shortest intermolecular distance C...C (between C(7) and C(11)) of 344 pm (Figs. 4(b) and 4(c)).

The six contact distances between the dimethoxyethane oxygen atoms and the sodium counter-cation range from 233 to 244 pm and correspond to standard values [5]. The relatively large radical anion (2) can effectively delocalize its negative charge and, therefore, only small structural changes with respect to the neutral molecule are observed (Table 1); differences in bond lengths do not exceed 4 pm and those of angles within

Table 1
Selected bond lengths (pm), angles ($^\circ$) and contact distances (pm) in tris(dimethoxyethane)sodium-9,10-bis(trimethylsilyl)anthracenide

Selected bond lengths			
Si1–C9	186.7(2)	C9–C11	143.3(3)
Si2–C10	186.6(2)	C11–C1	141.5(3)
Si2–C18	187.7(3)	C1–C2	137.5(4)
Si2–C19	187.7(3)	C2–C3	138.7(4)
Si2–C20	197.9(3)	C11–C12	144.4(3)
Selected bond angles			
Si1–C9–C11	120.5(2)	C1–C11–C12	117.3(2)
C9–Si1–C15	111.0(2)	C9–C11–C12	120.0(2)
C11–C9–C14	117.4(2)	C1–C2–C3	119.3(2)
C1–C11–C9	122.8(2)	C2–C1–C11	123.2(2)
Selected contact distances			
Na1–O30	233.8(2)	Na1–O41	233.5(2)
Na1–O31	234.4(2)	Na1–O50	244.1(2)
Na1–O40	241.4(2)	Na1–O51	232.9(2)



the anthracene skeleton 2°. A one-on-top-of-the-other projection (5) illustrates that even the torsional angles of the trimethylsilyl groups deviate only by a little.

Most surprising is the almost constant folding of the two anthracene planes on one-electron reduction (6) in contrast with the rather larger changes on oxidation of

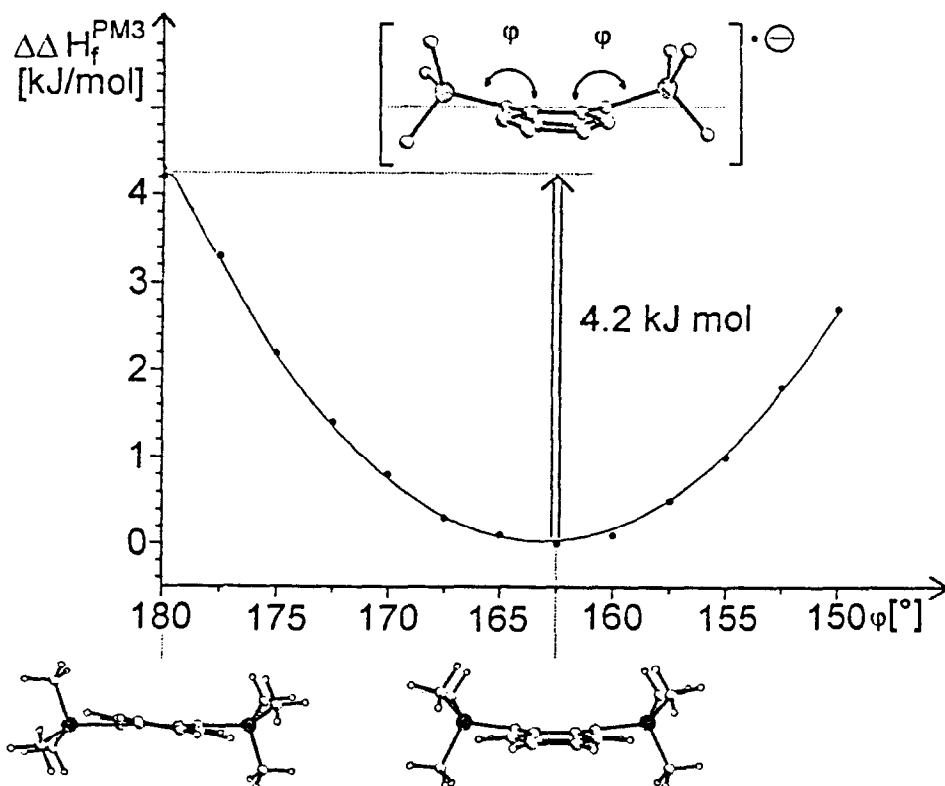


Fig. 5. Enthalpy hypersurface for substituent out-of-plane-bending in the radical anion of 9,10-bis(trimethylsilyl)anthracene (cf. Fig. 1).

thianthrene and its derivatives to iso(valence)electronic radical cations [29,30].

In conclusion, therefore, another enthalpy hypersurface (compare Fig. 1) for the 9,10-bis(trimethylsilyl)-anthracene radical anion has been approximated by PM3 open-shell calculations (Fig. 5). With respect to the potential for the neutral molecule Fig. 1 the potential minimum is shifted by about 5° to $\varphi = 163^\circ$ and the barrier of inversion reduced by about 5 kJ mol^{-1} to only about 4 kJ mol^{-1} .

Acknowledgments

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