

9,10-Disilylanthracene; synthesis, structure and fluorescence [☆]

Robert Schröck, Klaus Angermaier, Alexander Sladek, Hubert Schmidbaur ^{*}

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Received 26 May 1995

Abstract

For the preparation of the title compound, 9,10-dilithiumanthracene is treated with *p*-anisylchlorosilane to give 9,10-bis(*p*-anisylsilyl)anthracene (**1**) with high yields. The protodearylation of **1** with two equivalents of triflic acid affords 9,10-bis(trifluoromethanesulfonatosilyl)anthracene, which can be converted into 9,10-disilylanthracene (**2**) using LiAlH₄. The crystal structures of **1** and **2** have been determined by single-crystal X-ray diffraction. Solutions of **1** and **2** in common organic solvents show a violet fluorescence. The fluorescence spectra are compared with data on anthracene and 9,10-disubstituted derivatives.

Keywords: Silanes; Arylsilanes; Anthracenyl-silanes; Silyl-anthracenes; Silyl-arenes

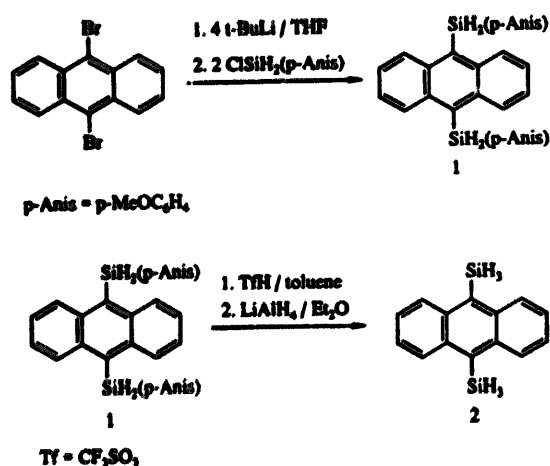
There is currently a rapidly growing interest in polysilylated hydrocarbons, which are precursors for polymeric organosilicon materials. Novel efficient coupling reactions for polysilylated arenes, e.g. dehydrogenative, oxidative and desilative coupling [1], give access to a wide structural variety of polymers. Polymers with tailored photophysical and photochemical properties are available from the coupling of individual monomers or mixtures of them [2]. In the present work we have therefore turned to simple silylated anthracenes, which have not been considered previously in this context. Owing to the special electronic structure of anthracene, and in particular of its 9,10-disubstituted derivatives, this family of compounds should offer new opportunities to modify the optical properties of homopolymers or heteropolymers [3]. In the past, 9,10-dihydro-disilylanthracenes were mainly used as key compounds for the generation of disilenes [4]. 9,10-Bis(trimethylsilyl)anthracene has first been reported in 1975 [5], and 9,10-bis(triethoxysilyl)anthracene has been prepared only recently [6]. There is virtually no information, however, about silyl anthracenes bearing solely hydrogen at the silicon atoms. We report the synthesis and properties of 9,10-bis(*p*-anisylsilyl)anthracene (**1**),

an arylated precursor, and of 9,10-disilylanthracene (**2**). Their crystal structures have been determined and their UV-visible absorption and fluorescence spectra recorded. Molecule **2** is of fundamental interest as the first substituent-free silyl anthracene.

The strategy for the preparation of the title compound was adopted from the synthesis of polysilylalkanes [7] and polysilylarenes [8], with 1,8-disilylnaphthalene [9] and 1,2-disilylbenzene [10] as prominent examples. In the three-step preparation of these compounds, the success of in-situ Grignard reactions is determining the overall yield. In the present case, no in-situ formation of a difunctional Grignard reagent is necessary, because 9,10-dilithiumanthracene and magnesiumanthracene are readily available [3,11]. Treatment of 9,10-dilithiumanthracene with *p*-anisylchlorosilane in tetrahydrofuran at low temperatures (–60°C) affords 9,10-bis(*p*-anisylsilyl)anthracene (**1**) as yellow crystals with high yields (75%) (melting point (m.p.), 218–219°C) [12] (Scheme 1). The *p*-anisyl protecting group was chosen because of its excellent leaving group properties, which were expected to be superior to those of the anthracenyl group. In the protodearylation at the silicon atoms with trifluoromethanesulfonic (triflic) acid, only a completely selective cleavage of the *p*-anisyl substituents with formation of the corresponding silyltriflate can lead to acceptable yields of the title compounds. Previous kinetic studies of protodearylation or protodesilylation reactions did not include anthracene compounds, and our experiments should thus allow us

[☆] Dedicated to Professor H.W. Roesky on the occasion of his 60th birthday.

^{*} Corresponding author.



Scheme 1.

for the first time to place the anthracenyl unit in the published reactivity ranking [13].

Therefore the reaction mixture of the protodearylation, followed by a hydrogenation step, was carefully investigated in order to obtain information on the relative cleavage efficiency (*p*-anisyl vs. anthracenyl). Treatment of 9,10-bis(*p*-anisylsilyl)anthracene (1) with two equivalents of triflic acid at -60°C in toluene led to an air- and water-sensitive viscous oil with limited thermal stability. No attempts were made to isolate any of the components, and the reaction mixture was re-

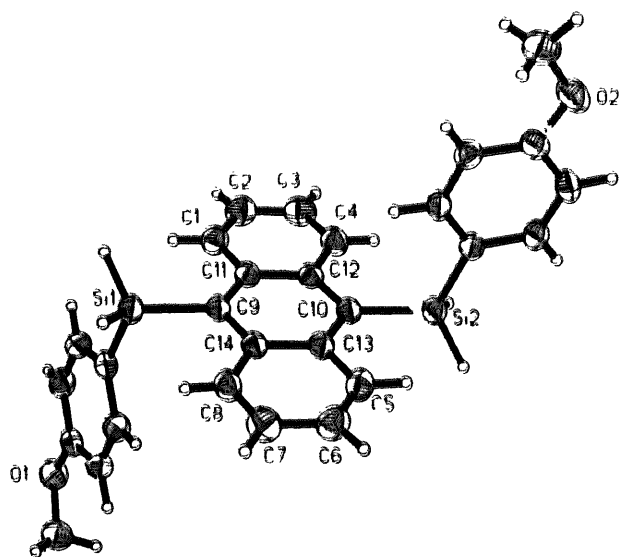


Fig. 1. Molecular structure of 9,10-bis(*p*-anisylsilyl)anthracene (1) with atomic numbering (ORTEP; 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond distances and angles are as follows: Si(1)–C(9), 1.892(2) Å; Si(2)–C(10), 1.884(2) Å; Si–H(average), 1.41 Å; C(9)–C(14), 1.412(3) Å, C(9)–C(11), 1.410(3) Å; C(11)–C(12), 1.439(3) Å; C(11)–C(1), 1.439(3) Å, C(1)–C(2), 1.349(3) Å; C(2)–C(3), 1.406(4) Å, C(3)–C(4), 1.350(3) Å; C(4)–C(12), 1.434(3) Å; C(11)–C(9)–Si(1), 119.6(2) $^{\circ}$; C(14)–C(9)–C(11), 118.7(2) $^{\circ}$; C(2)–C(1)–C(11), 122.2(2) $^{\circ}$; C(5)–C(6)–C(7), 120.7(2) $^{\circ}$; H(01)–Si(1)–H(02), 104.6(12) $^{\circ}$; C(9)–Si(1)–H(01), 113.6(8) $^{\circ}$.

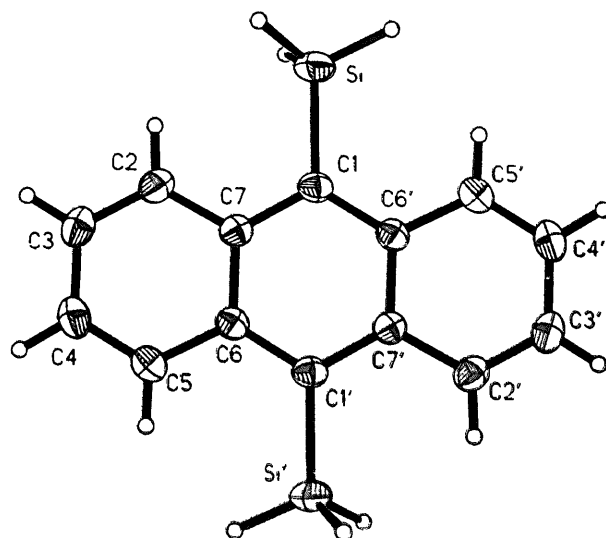


Fig. 2. Molecular structure of 9,10-disilylanthracene (2) with atomic numbering (ORTEP; 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond distances and angles are as follows: Si–C(1), 1.878(2) Å; Si–H(average), 1.35 Å; C(1)–C(7), 1.408(2) Å, C(1)–C(6'), 1.412(2) Å; C(7)–C(2), 1.431(2) Å; C(7)–C(6), 1.440(3) Å; C(2)–C(3), 1.352(3) Å; C(3)–C(4), 1.409(3) Å; C(4)–C(5), 1.353(3) Å; C(5)–C(6), 1.429(2) Å; C(7)–C(1)–Si, 118.2(1) $^{\circ}$; C(6')–C(1)–C(7), 119.3(2) $^{\circ}$; C(3)–C(2)–C(7), 122.4(2) $^{\circ}$; C(5)–C(4)–C(3), 120.2(2) $^{\circ}$; H(13)–Si–H(12), 109(2) $^{\circ}$, H(11)–Si–C(1), 111(1) $^{\circ}$.

duced at once with lithium aluminium hydride in diethyl ether (Scheme 1). The gas chromatography–mass spectroscopy (MS) analysis of the final products after an aqueous work-up showed about 40% of anthracene and 60% of 9,10-disilylanthracene (2). No significant amounts of 9-silylanthracene or 9-(*p*-anisylsilyl)anthracene were detected. The *p*-anisyl group has thus been shown to be superior as a leaving group over the anthracenyl group, but the differences are not great. 9,10-Disilylanthracene (2) can be isolated by extraction of the reaction mixture with hexane and sublimation at 40°C and 0.01 Torr (yield, 50%). Crystals suitable for X-ray crystallography were grown from hexane (yellow needles; m.p., $146\text{--}147^{\circ}\text{C}$). The analytical, MS and

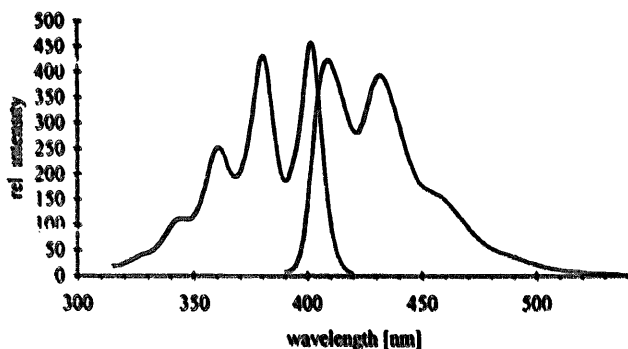


Fig. 3. Fluorescence and excitation spectrum of 9,10-bis(*p*-anisylsilyl)anthracene (1) (cyclohexane; excitation slit and emission slit, 5 nm; scan speed, 500 nm min⁻¹).

Table 1
Emission maxima of anthracene reference compounds

| Compound (solvent) | Fluorescence maxima (nm) |
|--|--------------------------|
| Anthracene (cyclohexane) [19] | 380, 400, 425, 450 |
| 9-Methylantracene (cyclohexane) [19] | 390, 415, 440, 470 |
| 9,10-Dichloroanthracene (cyclohexane) [19] | 405, 430, 460, 490 |
| 9,10-Diphenylantracene (cyclohexane) [19] | 410, 430, 460 |
| 9,10-(Si(OEt) ₃) ₂ anthracene (tetrahydrofuran) [6] | 420, 440, 460 |
| 9,10-Disilylanthracene (cyclohexane) | 405, 430, 455 |
| 9,10-(SiH ₂ - <i>p</i> -Anis) ₂ anthracene (cyclohexane) | 410, 430, 460 |

NMR spectroscopy data are in full agreement with the proposed formula [14].

The molecular structures of **1** and **2** have been determined by single-crystal X-ray diffraction studies. 9,10-Bis(*p*-anisylsilyl)anthracene (**1**) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell [15]. The individual molecules have no crystallographically imposed symmetry. The crystal packing shows no anomalies regarding intermolecular contacts, and the bond angles and bond distances are within the normal range (Fig. 1). The atoms C(9) and C(10) as well as the silicon atoms lie in the plane of the anthracene frame unlike the situation for example in 9,10-bis(trimethylsilyl)anthracene [5].

9,10-Disilylanthracene (**2**) crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell [15]. By symmetry the compound has a center of inversion which is situated in the middle of the central ring of the anthracene. The anthracene framework is planar and the bond angles and bond distances are in the expected range (Fig. 2). 9,10-Dimethylantracene shows a similar structure in the solid state [18].

Compounds **1** and **2** show a violet fluorescence in most common organic solvents. A 10^{-6} M solution of 9,10-bis(*p*-anisylsilyl)anthracene (**1**) in cyclohexane has an absorption maximum in the excitation spectrum at 400 nm. The fluorescence spectrum has two emission maxima at 410 and 430 nm and a shoulder at 460 nm (Fig. 3). The absorption maximum in the excitation

spectrum of 9,10-disilylanthracene (**2**) appears at 395 nm, and the maxima in the fluorescence spectrum are blue shifted at 405 and 430 nm, with a shoulder at 455 nm, compared with **1** (Fig. 4). In Table 1 the emission maxima of anthracene reference compounds are listed for comparison [19]. Substitution with the *p*-anisylsilyl or silyl groups causes a red shift of the fluorescence wavelength compared with anthracene, which is larger than the shift induced by methyl substitution and approaches that of the phenyl substitution. π - σ interactions with Si-H bonds are the most likely origin of these phenomena.

To improve further the yield of the two-step preparation, more electron-rich substituents at silicon, such as veratrol, are being introduced in current studies. Dehydrogenative and desilanative coupling of 9,10-disilylanthracene with or without other silanes are also under investigation and will be the subject of future publications.

Acknowledgments

We thank J. Riede for establishing the X-ray data sets and M. Sandor for the measurement of the fluorescence spectra.

References and notes

- [1] H.-G. Woo, J.F. Walzer and T.D. Tilley, *Macromolecules*, **24** (1991) 6863; T. Sakakura, O. Kumberger, R.P. Tan, M.-P. Arthur and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, (1995) 193.
- [2] R.D. Miller and J. Michl, *Chem. Rev.*, **89** (1989) 1359; S. Bourg, R.J.P. Corriu, M. Enders and J.J.E. Moreau, *Organometallics*, **14** (1995) 564.
- [3] E.J. Corey and W.L. Mock, *J. Am. Chem. Soc.*, **84** (1962) 685; *US Pat. 3354190*, 4 January 1965, Esso Research and Engineering Co. (Inv. H.E. Ramsden); W. Carruthers and G.E. Hall, *J. Chem. Soc. B*, (1966) 861; R.J. Bose, J. Ross and M.S. Wrighton, *J. Am. Chem. Soc.*, **99** (1977) 6119; B. Bogdanović, S.-T. Liao, M. Schwickardi, P. Sikorsky and B. Spliethoff, *Angew. Chem.*, **92** (1980) 845; K. Müllen, T. Meul, P. Schade, H. Schmickler and E. Vogel, *J. Am. Chem. Soc.*, **109** (1987) 4992; D.A. Loy, H. Small and K.J. Shea, *Organometallics*, **12** (1993) 1484.
- [4] G.J.D. Peddle, D.N. Roark, A.M. Good and S.G. McGeachin, *J.*

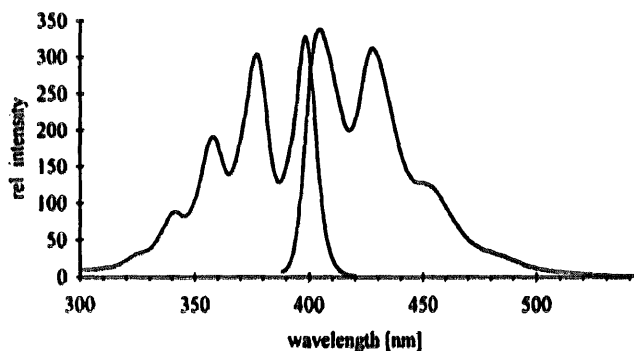


Fig. 4. Fluorescence and emission spectrum of 9,10-disilylanthracene (**2**) (cyclohexane; excitation slit and emission slit, 5 nm; scan speed, 500 nm min⁻¹).

- Am. Chem. Soc.*, 91 (1969) 2807; H. Sakurai, K. Oharu and Y. Nakadaira, *Chem. Lett.*, (1986) 1797.
- [5] H. Cho and R.G. Harvey, *J. Org. Chem.*, 40 (1975) 3097; H. Lehmkuhl, A. Shakoob, K. Mehler, C. Krüger, K. Angermund and Y.-H. Tsay, *Chem. Ber.*, 118 (1985) 4239.
- [6] K.J. Shea, D.A. Loy and O. Webster, *J. Am. Chem. Soc.*, 114 (1992) 6700.
- [7] R. Hager, O. Steigelmann, G. Müller, H. Schmidbauer, H.E. Robertson and D.W.H. Rankin, *Angew. Chem.*, 102 (1990) 204; H. Schmidbauer, J. Zech, D.W.H. Rankin and H.E. Robertson, *Chem. Ber.*, 124 (1991) 1952; J. Zech and H. Schmidbauer, *Eur. J. Solid State Inorg. Chem.*, 29 (1992) 5; S. Bommers and H. Schmidbauer, *Chem. Ber.*, 127 (1994) 1359.
- [8] C. Rüdinger, H. Beruda and H. Schmidbauer, *Chem. Ber.*, 125 (1992) 1401; R. Schröck, K. Angermaier and H. Schmidbauer, *Z. Naturforsch.*, 50b (1995) 613.
- [9] R. Schröck, K. Angermaier, A. Sladek and H. Schmidbauer, *Organometallics*, 13 (1994) 3399.
- [10] R. Schröck, A. Sladek and H. Schmidbauer, *Z. Naturforsch.*, 49b (1994) 1036.
- [11] W. Neugebauer, T. Clark and P. von Ragué Schleyer, *Chem. Ber.*, 116 (1983) 3283; B.F. Duerr, Y.-S. Chung and A.W. Czarnik, *J. Org. Chem.*, 53 (1988) 2120.
- [12] Anal. Found: C, 73.9; H, 5.9; Si, 12.3. $C_{28}H_{26}Si_2O_2$ calc.: C, 74.6; H, 5.8; O, 7.1; Si, 12.5%. 1H NMR ($CDCl_3$, 400 MHz): δ 3.75 (s, 6H, OMe), 5.68 (s, $^1J(SiH) = 201$ Hz, 4H, SiH_2), 6.85 and 7.51 (d each, $J = 8$ Hz, 8H, H *p*-Anis), 7.49 (dd, $J = 7, 3$ Hz, 4H, H Ant), 8.60 (dd, $J = 7, 3$ Hz, 4H, H Ant) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.0 (OMe), 114.1, 132.0, 136.9, 161.1 (C *p*-Anis), 121.6 (m, C 9/10), 125.5 (dd, C 2/3/6/7), 129.5 (dm, C 1/4/5/8), 137.0 (m, C 11/12/13/14) ppm. ^{29}Si NMR ($CDCl_3$, 79 MHz): δ -48.3 (m, $^1J(SiH) = 201$ Hz, $^3J(SiH) = 6$ Hz, SiH_2) ppm. MS (electron impact (EI), 70 eV): 450 [M^+], 419 [$M^+ - OMe$], 313 [$M^+ - SiH_2(p-Anis)$], 205 [$M^+ - SiH_2(p-Anis) - p-Anis$], 178 [$M^+ - 2 SiH_2(p-Anis)$].
- [13] E. Hengge and E. Eberhardt, *Monatsh. Chem.*, 110 (1979) 39; A.R. Bassindale and T. Stout, *J. Organomet. Chem.*, 271 (1984) C1.
- [14] Anal. Found: C, 71.4; H, 6.0; Si, 23.2. $C_{14}H_{14}Si_2$ Calc.: C, 70.6; H, 5.9; Si, 23.5%. 1H NMR ($CDCl_3$, 400 MHz): δ 4.80 (s, $^1J(SiH) = 204$ Hz, 6H, SiH_2), 7.56 (dd, $J = 7, 3$ Hz, 4H, H Ant), 8.47 (dd, $J = 7, 3$ Hz, 4H, H Ant) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 124.5 (m, C 9/10), 125.6 (dd, C 2/3/6/7), 129.2 (dm, C 1/4/5/8), 136.9 (m, C 11/12/13/14) ppm. ^{29}Si NMR ($CDCl_3$, 79 MHz): δ -74.5 (qm, $^1J(SiH) = 204$ Hz, SiH_2) ppm. MS (EI, 70 eV): 238 [M^+], 207 [$M^+ - SiH_3$], 178 [$M^+ - 2 SiH_3$].
- [15] Crystal data for 1: $C_{28}H_{26}O_2Si_2$; $M_r = 450.67$; triclinic; space group, $P\bar{1}$; $a = 5.914(1)$ Å, $b = 11.850(1)$ Å and $c = 17.085(1)$ Å; $\alpha = 80.86(1)^\circ$, $\beta = 88.86(1)^\circ$ and $\gamma = 81.27(1)^\circ$; $V = 1168.4$ Å³; $Z = 2$; $D_c = 1.281$ g cm⁻³; $F(000) = 476$; $\mu(Mo K\alpha) = 1.75$ cm⁻¹; 5057 reflections measured; 5052 unique; 5052 observed. Structure solution by direct methods, with all missing atoms located by successive difference Fourier syntheses, refinement of 393 parameters converged at $wR2 = 0.1224$, and at $R = 0.0396$ for 3485 observed reflections with $F_0 > 4\sigma(F_0)$ respectively; maximum and minimum residual electron densities in the difference Fourier map were 0.33 and -0.22 electrons Å⁻³ respectively; the program used was SHELXL-93 [16]; $T = -68^\circ C$; Enraf-Nonius CAD4 diffractometer; $\gamma(Mo K\alpha) = 0.71069$ Å.
- Crystal data for 2: $C_{14}H_{14}Si_2$; $M_r = 238.43$; monoclinic; space group, $P2_1/n$; $a = 8.002(1)$ Å, $b = 5.225(1)$ Å and $c = 15.345(2)$ Å; $\beta = 103.76(1)^\circ$; $V = 623.2$ Å³; $Z = 2$, $D_c = 1.271$ g cm⁻³; $F(000) = 252$; $\mu(Mo K\alpha) = 2.5$ cm⁻¹; 1520 reflections measured; 1243 unique; 1104 observed ($F_0 > 4\sigma(F_0)$). Structure solution by direct methods, with all missing atoms located by successive difference Fourier syntheses; refinement of 136 parameters converged at $R = 0.0369$ and $R_w = 0.0400$, $w = [\sigma^2(F_0) + 0.000279 F_0^2]^{-1}$; maximum and minimum residual electron densities in the difference Fourier map were 0.39 and -0.37 electrons Å⁻³ respectively; the program used was SHELXL-PC [17]; $T = -68^\circ C$; Enraf-Nonius CAD4 diffractometer; $\lambda(Mo K\alpha) = 0.71069$ Å. Further details of the X-ray structure determinations have been deposited at Fachinformationzentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the CSD number 59033.
- [16] G.M. Sheldrick, *SHELXL-93, Program for the Refinement of Structures*, University of Göttingen, Göttingen, 1993.
- [17] *SHELXL-PC*, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
- [18] J. Iball and J.N. Low, *Acta Crystallogr., Sect. B*, 30 (1974) 2203.
- [19] I.B. Berlmann, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1971.