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Diels–Alder reactions of C-phenylated siloles with 1,4-epoxy-1,4-dihydronaphthalene

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Abstract

Preparation of a novel type of cycloadducts composed of a 7-silanorbornene ring condensed to the 7-oxanorbornene moiety (**5**–**7**) is described and their spectroscopic features are discussed in detail. The X-ray data for **5** are also presented. Finally, formation of silanole **8** by nucleophilic cleavage of an *endocyclic* silicon–carbon bond in **7** is described. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 7-Silanorbornene; Diels–Alder reaction; High-pressure chemistry; Stereochemistry; X-ray

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1. Introduction

Recent research activity in the field of silole (1-silacyclopenta-2,4-diene) chemistry has considerably added to the understanding of their cycloaddition reactions and properties of the so formed cycloadducts [1]. In particular, a number of [4 + 2] cycloadditions of C-phenylated siloles and a variety of ethylenic [2–4] or acetylenic dienophiles [5,6], leading to diverse 7-sila[2.2.1]heptene and 7-sila[2.2.1]heptadiene derivatives, have been described. The latter compounds aroused considerable interest in the literature due to their intrinsic properties [1] and a great potential in synthetic chemistry [1,7]. Mechanisms and factors governing the ease of their thermolysis [5,6] and photolysis [8–10] have been extensively discussed. Less work has been reported on thermolysis and irradiation of 7-silanorbornene derivatives, presumably due to their less pronounced tendency to extrude silylene [11,12].

Herewith, we report on the synthesis and molecular geometry of a novel type of cycloadducts possessing 7-silanorbornene ring condensed with the 7-oxanorbornene moiety. To the best of our knowledge only the 7-germa analog of **5** has been reported in the literature so far [13] (see Scheme 1).

Our motivation for undertaking this study is prompted by our interest in the role of heteroatomic bridges in transmitting long-range π,π-interactions in geometrically fixed heteroatom analogous of fused norbornenes. As a part of this project, we recently reported on the electronic structure of 7-oxanorbornene adducts and their benzylated analogs [14,15]. Introduction of an $SiMe_2$ group at the bridgehead position of the bicyclic subunits in these compounds is of special interest in this regard due to low energy of the C–Si bond and its consequence on the conjugative interaction between σ-orbitals of the *endocyclic* C–Si bonds and the π-system [16]. Finally, the adducts **5**–**7** also offer an interesting set of model compounds for studying the influence of the phenyl groups on the stability towards nucleophiles, in addition to the thermal and photochemical processes. In this contribution we shall concentrate on their synthesis and structural characteristics.

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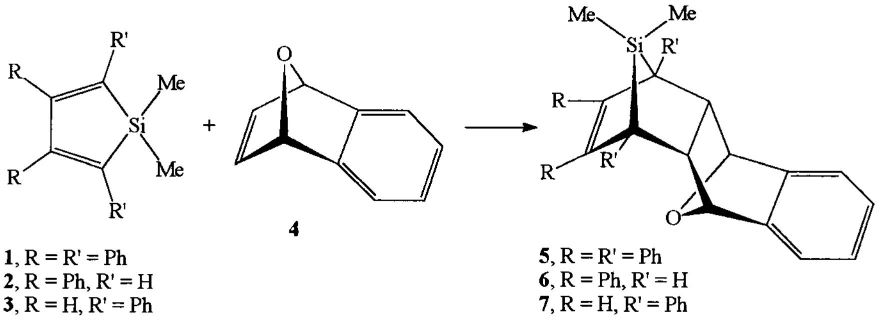

Scheme 1. Synthesis of **5**–**7**.

2. Results and discussion

2.1. Synthesis of adducts

Synthesis of compounds **5**–**7** was accomplished by allowing siloles **1**–**3** [17–19] to react with 1,4-epoxy-1,4-dihydronaphthalene (**4**) under conditions specified in Table 1. We shall commence discussion by considering results obtained for cycloaddition of **1** to **4**. In preliminary experiments cycloaddition of **1** to **4** has been attempted at the room temperature (r.t.) (Table 1, run 1). The reaction was found to be very sluggish, resulting after mixing for 2 weeks in roughly 17% conversion to **5**. By raising the temperature to 110°C the same product **5** was isolated in the 78% yield, while under high pressure (10 kbar) a conversion of 92% was achieved (Table 1, runs 2 and 3). Compound **5**, the only product in all three cases, was purified by column chromatography on silica gel and fully characterized by spectroscopic and elemental analysis in addition to X-ray crystallography.

The ^{13}C-NMR spectrum of **5** exhibited 17 signals, whereas the ^{1}H-NMR spectrum featured only four sharp singlets in addition to the aromatic protons. Both spectra indicate a formation of [4 + 2] cycloadduct. This was further substantiated by COSY and HETCOR spectra. The absence of the three-bond coupling between $H_{4a(9a)}$ and $H_{9(10)}$ in the ^{1}H-NMR spectrum **5** supported either *endo,exo*- or *exo,exo*-stereochemistry of isolated product [20]. Finally, the NOE contacts between $H_{4a(9a)}$ and $H(Me_{11})$ (Fig. 1) revealed that the product had *endo,exo*-stereochemistry. This assignment was eventually confirmed by the X-ray crystal structure analysis, which will be discussed in the following section. The mass spectrum of **5** is also of some interest. It showed a low intensity peak for the molecular ion at *m*/*z* 558 (10). The base peak is found at *m*/*z* 176 (100) and was assigned to the 2,2-dimethyl-1,3-epoxy-2-silaindane ion, formation of which could be explained by the addition of dimethylsilylene to benzofuran. A similar process was proposed to explain the formation of the base peak in the MS spectrum of 7-germa analog of **5** [13]. In addition, a strong peak was observed at *m*/*z* 440 (90), which can be attributed to the 7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornadiene radical cation. Its formation could be rationalized in terms of retro Diels–Alder loss of benzofuran from **5**.

Table 1
Synthesis of compounds **5**–**7**

Run	Reactants	Conditions	Product	Yield[a]/%
1	**1**+**4**	CC$_4$, r.t., 2 weeks, 1 bar	**5**	15–17[b]
2	**1**+**4**	CC$_4$, 110°C, 40 h, 1 bar	**5**	78.3
3	**1**+**4**	CH$_2$Cl$_2$, r.t., 20 h, 10 kbar	**5**	92.4
4	**2**+**4**	CH$_2$Cl$_2$, r.t., 20 h, 10 kbar	**6**	99.6
5	**3**+**4**	CH$_2$Cl$_2$, r.t., 20 h, 10 kbar	**7**	95.1

[a] Isolated yield.

[b] Yield determined by ^{1}H-NMR.

Owing to their high performance in preparing **5**, high pressure conditions were also employed for the synthesis of adducts **6** and **7** (Table 1, runs 4 and 5). In both cases conditions identical to those used in preparation of **5** were applied, i.e. dienophile **4** was mixed with the silole (**2** or **3**) in CH$_2$Cl$_2$ at r.t. and a pressure of 10 kbar. The reaction was stopped after 20 h and the composition of the crude product analyzed by 1D and 2D ^{1}H- and ^{13}C-NMR spectroscopy, which indicated

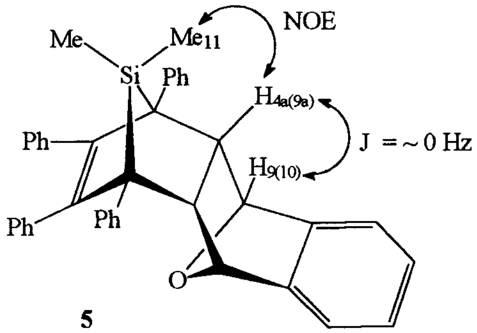

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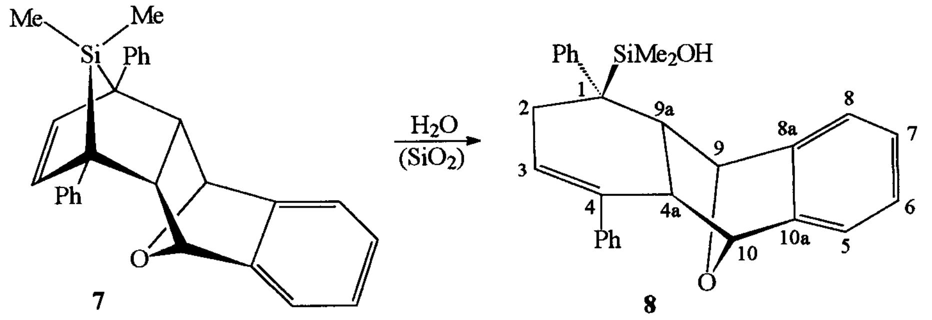
Fig. 1. NOE contacts in **5**.



Scheme 2. Formulation of **8** from **7**.

that in both cases only an *endo,exo*-adduct was formed in excellent yield. The most convincing evidence in favor of *endo,exo*-configuration came again from the NOE contacts between $H_{4a(9a)}$ and $H(Me_{11})$ encountered in the corresponding NOESY spectra.

It is interesting to mention that adducts **6** and **7** differ considerably in stability. This is best illustrated by their behavior during chromatographic purification. Though the adduct **6** (like **5**) could be purified by chromatography on silica gel with no sign of decomposition, chromatography of **7** led to exclusive formation of silanol **8** (Scheme 2).

The constitution of **8** was deduced on the basis of its IR and 1D/2D NMR spectra and by comparison with the NMR spectra of structurally related silanols. In particular, the appearance of the signals at 2.73, 2.99, and 6.48 ppm in the ^{1}H-NMR spectrum and their multiplicities allowed unequivocal conclusion on the presence of the $CH_2{-}CH{=}CPh$ fragment. This is further corroborated by the measured coupling constants between methylenic hydrogen atoms, $J(H_{2a}{-}H_{2b}) = 17$ Hz, and their coupling constants with the olefinic proton at C_3, $J(H_{2a}{-}H_3) = 2.0$ Hz and $J(H_{2b}{-}H_3) = 7.5$ Hz. ^{1}H-NMR and IR spectra also provided evidence of the presence of a hydroxyl group. Finally, the ^{13}C-NMR spectrum of **8** exhibited 22 signals ($C_5{-}C_8$ and $C_6{-}C_7$ could not be distinguished), suggesting that this molecule does not possess a plane of symmetry.

The formation of **8** can be explained by nucleophilic cleavage of one *endocyclic* silicon–carbon bond with water and finds precedent in previously described nucleophilic decomposition of various 7-silanorbornadiene derivatives [21,22]. Typical examples are provided by the conversion of 1,4,5,6,7-hexaphenyl-7-silanorbornadiene-2,3-dimethylcarboxylate to the corresponding naphtyldiphenylsilanol during chromatography on basic alumina [2] and by the reaction of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene with water [22]. Similar reaction has been also reported for 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorbornadiene [23].

Turning to the behavior of adducts **5**–**7** during chromatography, we may conclude that their sensitivity towards cleavage of an *endocyclic* Si–C bond depends strongly on the substitution pattern of the phenyl groups on the basic ring. It appears that substitution of the olefinic carbon atoms with the aromatic rings considerably stabilizes 7-silanorbornene skeleton. This in turn follows the trend observed in silylene formation from related phenyl substituted 7-silanorbornadienes [5,24].

2.2. X-ray data

The compound **5** crystallizes with two molecules of water in the triclinic $P\bar{1}$ space group, and the molecule possesses no symmetry plane. The molecular geometry and atom labeling scheme are shown in Fig. 2. Fig. 3 displays molecular unit cell packing. The related geometric properties are listed in Table 2 and Table 3, and atomic coordinates and equivalent isotopic thermal parameters are given in Table 4.

In addition to confirming the stereochemistry, the X-ray data show several interesting features of the molecular structure of **5**. The most striking among them is related to the pronounced deviation of the phenyl groups from the basic ring defined by the atoms C_2, C_3, C_{9a}, and C_{4a}. The deviation angles have values of 29.6, 137.5, 99.8, and 85.4° for the phenyl rings attached to the C1, C2, C3, and C4 positions, respectively. Particularly noticeable is the difference in orientation of the phenyl groups at the bridgehead positions. This is at variance with the situation encountered in previously published X-ray structures of various 7-silanorborn(adi)enes, where phenyl groups were found to assume perpendicular orientation to the basis ring. A typical example is provided by 9,9-dimethyl-1,2,3,4-tetraphenyl-1,4-silanaphthalene [8]. The interatomic distances within the 7-silanorbornene and 7-oxanorbornene subunits are in good accordance with the earlier X-ray data obtained for a number of their derivatives [10,25,26]. For instance, the *endocyclic* silicon–carbon bonds are slightly longer then the *exocyclic* $Si{-}C_{Me}$ bonds, the latter being of the same order of magnitude as in unstrained silanes [27]. A similar trend has been reported for a variety of 7-silanorbornadiene

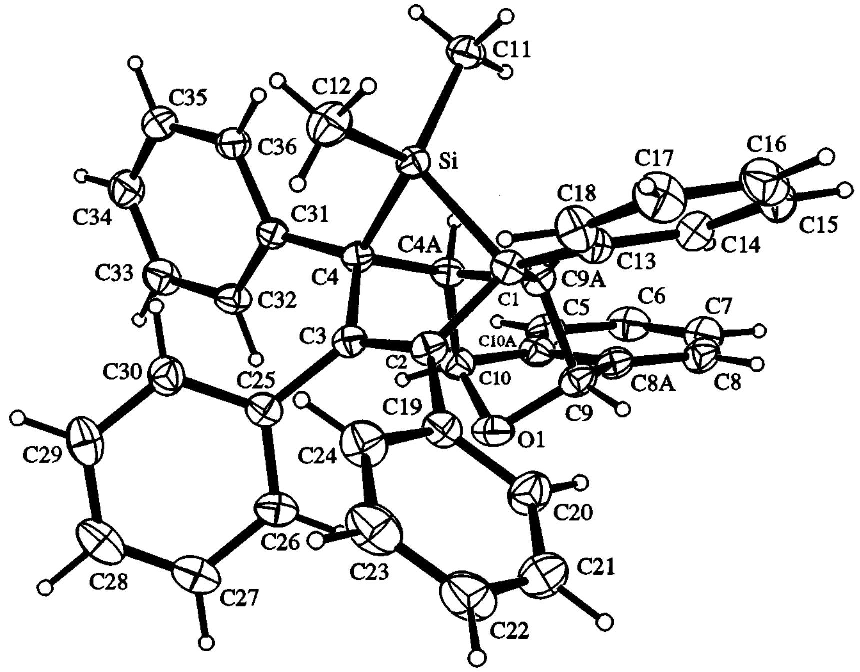


Fig. 2. Molecular structure of **5**.

derivatives and was explained in terms of delocalization of the electron density from the bridge Si–C bonds to the π-bonds [25]. We note in passing that π–σ^* type of orbital interaction between the π-system of the double bond and σ^* MOs of the bridging Si–C bonds would have the same effect. Similar trend, albeit less pronounced, is reflected in the C–O bond distances in the 7-oxanorbornene subsystem, which are slightly longer

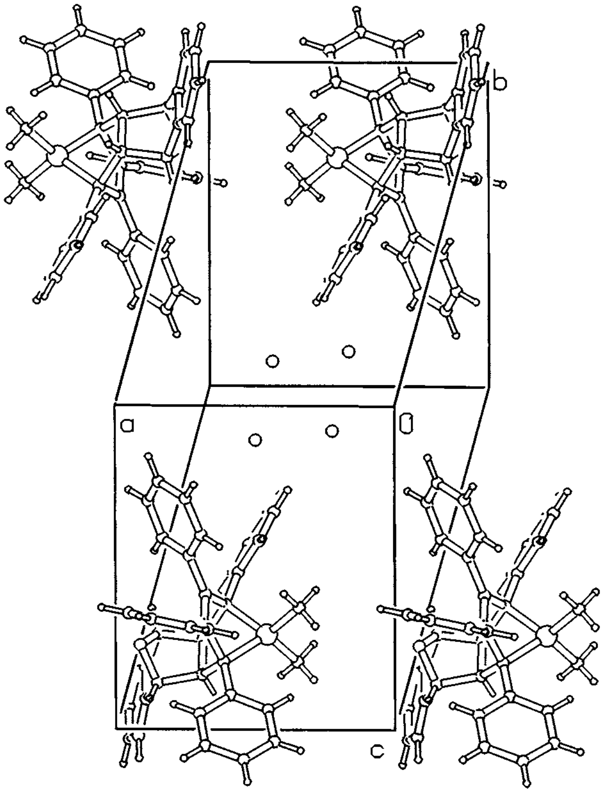


Fig. 3. Perspective view of part of the unit cell contents for $\mathbf{5} \cdot 2H_2O$.

Table 2
Interatomic bond distances for **5**[a]

Bond	Bond length/Å	Bond	Bond length/Å
Si–C1	1.927(3)	C10–C10A	1.515(5)
Si–C4	1.922(3)	C13–C14	1.389(5)
Si–C11	1.853(4)	C13–C18	1.396(5)
Si–C12	1.862(4)	C14–C15	1.384(6)
O1–C9	1.436(5)	C15–C16	1.359(7)
O1–C10	1.435(5)	C16–C17	1.382(7)
C1–C2	1.542(5)	C17–C18	1.374(6)
C1–C9A	1.564(4)	C19–C20	1.385(6)
C1–C13	1.496(5)	C19–C24	1.406(6)
C2–C3	1.345(5)	C20–C21	1.393(6)
C2–C19	1.485(5)	C21–C22	1.335(8)
C3–C4	1.537(4)	C22–C23	1.385(9)
C3–C25	1.480(5)	C23–C24	1.392(6)
C4–C4A	1.571(5)	C25–C26	1.386(5)
C4–C31	1.506(5)	C25–C30	1.400(5)
C4A–C9A	1.574(5)	C26–C27	1.389(6)
C4A–C10	1.549(5)	C27–C28	1.362(8)
C5–C6	1.389(7)	C28–C29	1.389(7)
C5–C10A	1.388(5)	C29–C30	1.387(6)
C6–C7	1.374(8)	C31–C32	1.401(5)
C7–C8	1.393(6)	C31–C36	1.395(5)
C8–C8A	1.385(6)	C32–C33	1.381(5)
C8A–C9	1.520(5)	C33–C34	1.402(6)
C8A–C10A	1.388(6)	C34–C35	1.368(6)
C9–C9A	1.570(5)	C35–C36	1.395(5)

[a] The numbering scheme is shown in Fig. 2.

Table 3
Selected valence angles (°) and torsion angles (°) for **5**[a]

C1–Si–C4	82.8(1)	C9–C9A–C4A	100.8(3)
C11–Si–C12	109.3(2)	C9A–C4A–C10	100.1(3)
C9–O1–C10	96.6(3)	C4A–C10–C10A	107.4(3)
C1–C2–C3	112.5(3)	C10–C10A–C8A	104.5(3)
C2–C3–C4	113.4(3)	C10A–C8A–C9	104.3(3)
C3–C4–C4A	109.1(3)	C8A–C9–C9A	105.9(3)
C4–C4A–C9A	107.9(3)	C2–C3–C4–C4A	60.5(2)
C4A–C9A–C1	108.2(3)	C3–C4–C4A–C9A	−56.2(2)
C9A–C1–C2	109.5(3)	C9A–C1–C2–C3	−58.9(2)
C9A–C1–C13	115.5(3)	C4A–C10–C10A–C8A	75.8(2)
C3–C2–C19	124.4(3)	C10A–C8A–C9–C9A	−72.4(2)
C2–C3–C25	123.8(3)	H9–C9–C9A–H9A	84.4(3)
C3–C4–C31	118.1(3)	H10–C10–C4A–H4A	−81.9(3)

[a] The numbering scheme is shown in Fig. 2.

than in 7-oxanorbornane moiety [26,28,29]. The measured bond angles are also within the range of the bond angles found in the structurally related compounds [25,26]. This holds in particular for the C_1–Si–$C_{(4)}$ and C_9–O–C_{10} bond angles, which are narrowed to 82.9(5) and 96.2(7)°, respectively.

It is also interesting to note that the double bond in the 7-silanorbornene part of the molecule is practically planar, in contrast to the situation encountered in related hydrocarbons and 7-oxanorbornene derivatives [28,29]. A plausible explanation of this feature rests on lowering of the π-electron density of the double bond due to its transfer to the low lying vacant MOs [30] of the silicon bridge. An alternative explanation based on the propensity of the double bond to conjugation with the neighboring phenyl groups is excluded due to a pronounced distortion of the phenyl groups from the plane of the double bond.

3. Conclusions

Cycloadducts **5**–**7** prepared within this study present the first examples of 7-silanorbornenes linked to the 7-oxanorbornene ring via a common C–C bond. Diels–Alder reaction used for their preparation is highly stereospecific, as evidenced by exclusive formation of *endo*,*exo*-adducts. This finding is at variance with the earlier proposal for stereochemistry of the 1,4-dimethylgermano-9,10-epoxy-1,2,3,4-tetraphenyl-1,4,4a,9,9a,10-hexahydroanthracene analog, which was supposed exclusively on the basis of ^{1}H-NMR spectral data [13], indicating that additional investigations of the structure of this compound might be desirable.

4. Experimental

Melting points were measured on a Kofler apparatus and are uncorrected. The ^{1}H- and ^{13}C- 1D/2D NMR spectra were recorded on a Varian Gemini 300 spectrometer and were referred to TMS. IR spectra were measured on an IR Perkin–Elmer 297 instrument. MS spectra were recorded on an EXTREL FTMS 2001 DD spectrometer. High pressure experiments were carried out in an 14 kbar apparatus supplied by A. Hofer, Mülheim/Ruhr, Germany.

Siloles **1** and **3** were prepared by known methods [17,18]. Silole **2** was obtained in 48.2% yield according to the procedure described by Tamao et al. [19]. Con-

Table 4
Final fractional atomic coordinates ($\times 10^4$) and equivalent isotopic thermal parameters ($\times 10^2$ Å^2) for Compounds **5**·2H$_2$O

	x	*y*	*z*	U_{eq} [a]
Si	4991(1)	878(1)	1645(1)	38.6(4)
O1	252(3)	8171(3)	665(2)	56(1)
OW1	6268(5)	5598(3)	4565(3)	100(2)
OW2	3660(5)	6001(3)	4692(4)	107(3)
C1	3111(4)	7599(3)	1310(3)	39(2)
C2	2598(4)	8206(3)	2267(3)	41(1)
C3	2908(3)	9267(3)	2453(2)	39(1)
C4	3726(3)	9614(3)	1686(3)	38(1)
C4A	2713(4)	8914(3)	545(3)	38(1)
C5	307(4)	8577(4)	−1724(3)	55(2)
C6	−295(5)	7734(5)	−2717(3)	64(2)
C7	−682(5)	6654(4)	−2870(3)	64(2)
C8	−485(4)	6360(4)	−2034(3)	55(2)
C8A	11(4)	7205(3)	−1046(3)	47(2)
C9	570(4)	7240(3)	35(3)	48(2)
C9A	2325(4)	7668(3)	319(3)	38(2)
C10	1118(4)	8925(3)	290(3)	48(2)
C10A	493(4)	8298(3)	−880(3)	48(2)
C11	6023(4)	8583(3)	602(3)	53(2)
C12	6291(5)	9197(4)	2920(3)	63(2)
C13	3197(4)	6506(3)	1151(3)	44(1)
C14	2715(4)	5620(3)	184(3)	52(2)
C15	2946(5)	4658(3)	55(4)	62(2)
C16	3631(6)	4531(4)	872(4)	68(3)
C17	4109(6)	5394(4)	1846(4)	69(3)
C18	3897(5)	6356(3)	1977(3)	56(2)
C19	1832(4)	7664(3)	2898(3)	45(1)
C20	559(5)	6723(4)	2445(4)	62(2)
C21	−126(6)	6236(4)	3062(5)	78(3)
C22	402(7)	6653(5)	4096(4)	80(3)
C23	1672(7)	7595(5)	4577(4)	78(3)
C24	2405(5)	8094(4)	3985(3)	61(2)
C25	2503(4)	10033(3)	3306(3)	42(1)
C26	1023(4)	9850(3)	3348(3)	52(2)
C27	648(5)	10551(4)	4167(4)	64(3)
C28	1740(6)	11443(4)	4942(4)	69(3)
C29	3234(6)	11654(4)	4921(3)	64(2)
C30	3613(5)	10955(3)	4106(3)	52(2)
C31	4379(4)	10818(3)	1931(2)	39(1)
C32	3485(4)	11454(3)	2020(3)	47(2)
C33	4056(5)	12549(3)	2202(3)	57(2)
C34	5590(5)	13048(3)	2301(4)	61(2)
C35	6499(4)	12454(3)	2234(3)	56(2)
C36	5900(4)	11348(3)	2044(3)	46(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tenzor.

trary to the original procedure, excess of naphthalene was removed by sublimation prior to isolation of crude **2**. The crude product was purified by column chromatography, SiO_2, using hexane as eluent.

*4.1. General procedure for the preparation of adducts **5**–**7** at high pressure*

In the autoclave filled with a highly viscous mineral oil, which is used as pressure-transducing medium, the sealed polytetrafluoroethylene (PTFE) tube containing a solution of silole (2 mmol) and epoxynaphthalene **4** (288.3 mg, 2 mmol) in CH_2Cl_2 (4 ml) was pressurized to 10 kbar at r.t. for 20 h. After the pressure was released, the solvent was evaporated and the crude product purified as described hereafter.

*4.2. 11,11-Dimethyl-9,10-epoxy-1,4-silano-1,2,3,4-tetraphenyl-1,4,4a,9,9a,10-hexahydroanthracene (**5**)*

Purified by column chromatography (SiO_2) using light petroleum–ethyl acetate 9.5 : 0.5 as eluent. White crystals, yield 92.4%, m.p. 214–216°C; IR (KBr, cm^{-1}): 1600, 1500, 1460, 1440, 1250, 1075, 910, 850, 750, 700; ^{1}H-NMR ($CDCl_3$) δ 0.09 (s, 3H), 0.62 (s, 3H), 3.29 (s, 2H), 5.73 (s, 2H), 6.79–7.35 (m, 24H); ^{13}C-NMR ($CDCl_3$) δ -6.65, -3.35, 51.69, 52.84, 82.10, 118.66, 124.74, 125.27, 126.45, 126.89, 127.80, 128.78, 130.07, 138.75, 139.38, 141.29, 147.55; MS (-10 eV) m/z 558 (M^+, 15), 540 (20), 484 (15), 440 (90), 382 (10), 330 (12), 304 (37), 176 (100). Anal. Calc. for $C_{40}H_{34}OSi$: C, 85.98; H, 6.13. Found: C, 85.97; H, 6.39.

Adduct **5** was also prepared by mixing **1** and **4** in CCl_4 at r.t. for 15 days or in the sealed tube at 110°C for 40 h. After evaporation of solvent the crude product was purified as indicated above.

*4.3. 3,4-Diphenyl-11,11-dimethyl-9,10-epoxy-1,4-silano-1,4,4a,9,9a,10-hexahydroanthracene (**6**)*

Purified by column chromatography (SiO_2) using light petroleum–ethyl acetate 9.5 : 0.5 as eluent. White crystals, yield 95.1%, m.p. 160–160°C; IR (KBr, cm^{-1}) 1595, 1490, 1440, 1240, 1200, 1120, 1115, 910, 840, 750, 700; ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.25 (s, 3H), 2.52 (t, 2H, $J = 1$ Hz), 2.72 (t, 2H, $J = 1$ Hz), 5.19 (s, 2H), 7.07–7.24 (m, 14H); ^{13}C-NMR ($CDCl_3$) δ -7.95, -1.56, 40.90, 47.99, 83.75, 118.56, 125.73, 126.08, 127.95, 128.24, 136.85, 141.40, 147.92; MS (-70 eV) m/z 406 (M^+, 100).

*4.4. 1,4-Diphenyl-11,11-dimethyl-9,10-epoxy-1,4-silano-1,4,4a,9,9a,10-hexahydroanthracene (**7**)*

Slightly-yellow powder; yield 99.6%, m.p. 66–68°C; IR (KBr, cm^{-1}) 1600, 1490, 1260, 1245, 910, 750, 700; ^{1}H-NMR ($CDCl_3$) δ 0.06 (s, 3H), 0.15 (s, 3H), 3.37 (s, 2H), 5.32 (s, 2H), 6.47 (s, 2H), 7.19–7.45 (m, 14H); ^{13}C-NMR ($CDCl_3$) δ -9.35, -3.73, 50.00, 52.00, 82.00, 118.39, 124.71, 125.78, 126.41, 128.77, 133.82, 142.90, 147.88; MS (-10 eV) m/z 407 (MH^+, 10), 230 (100).

*4.5. 1,4-Diphenyl-1-hydroxydimethylsila-9,10-epoxy-1,2,4a,9,9a,10-hexahydroanthracene (**8**)*

Compound **8** was obtained by column chromatography (SiO_2) of the crude product **7** using dichloromethane as eluent. White crystals; yield 64%, m.p. 132–133°C; IR (KBr, cm^{-1}) 3450, 1600, 1495, 1460, 1445, 1250, 1030, 855, 820, 775, 745, 695; ^{1}H-NMR ($CDCl_3$) δ -0.13 (s, 3H), -0.03 (s, 3H), 1.65 (br s, 1H), 2.73 (br d, 1H, $J = 17.0$ Hz), 2.99 (dd, 1H, $J = 7.5$, 17.0 Hz), 3.04 (d, 1H, $J = 6.0$ Hz), 3.20 (d, 1H, $J = 6.0$ Hz), 5.04 (s, 1H), 5.08 (s, 1H), 6.48 (dd, 1H, $J = 2.0$, 7.5 Hz), 7.14–7.54 (14H, m); ^{13}C-NMR ($CDCl_3$) δ -2.42, -1.75, 28.75, 37.17, 42.52, 45.80, 81.99, 85.69, 117.70, 119.71, 125.20, 125.84, 126.38, 126.44, 126.94, 127.45, 128.78, 140.68, 140.82, 144.89, 145.65, 147.88.

*4.6. Determination of crystal structure of **5***

A colorless prism was used for unit cell determination and orientation matrix in the data collection procedure. Data were measured at r.t. on a Philips PW1100 (STOE upgraded) automatic difractometer. Three standard reflections measured every 1.2 h showed no evidence of crystal decay. The structure was solved in a straightforward manner by routine application of the direct methods program SOLVER (in NRCVAX). Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were included in the structure factor calculation as fixed contributors at geometrically expected positions. The waters of crystallization OW1 and OW2 show positional disorder to some extent, although separated at the distance characteristic for normal O–H···O hydrogen bond (O···O 2.753 Å). From this reason, the water molecule hydrogen atoms could not be located from the difference Fourier map. All calculations were performed on a personal computer using NRCVAX for structure solution, ORTEPII for asymmetric unit diagram and PLUTON for unit cell packing diagram [31,32].

Crystal data for $C_{40}H_{34}OSi \cdot 2H_2O$: Triclinic, space group: $P\bar{1}$, $a = 9.6586(5)$, $b = 14.0204(9)$, $c = 14.1051(8)$ Å, $\alpha = 110.845(5)$, $\beta = 96.284(5)$, $\gamma = 107.425(5)°$, $V = 1652.4(2)$ Å^3, $M_r = 594.79$, $Z = 2$, Mo–$K_\alpha = 0.71073$ Å, $D_{calc} = 1.187$ g cm^{-3}, $\mu = 0.09$ mm^{-1}, no. of reflections measured 7514, no. of unique reflections 7217, no. of reflections with $I_{net} > 2\sigma(I_{net})$ 4689, $R = 0.080$, $R_w = 0.138$, $S = 1.03$.

5. Supporting information

Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters and an atom-numbering scheme are available on request from the Cambridge Crystallographic Data Centre.

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