SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-BIS[5-(3-METHYLISOXAZOLINO-2)]-1,1,3,3-TETRAPHENYLDISILOXANE

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Abstract. The addition of acetonitrile oxide to 1,3-divinyl-1,1,3,3-tetraphenyldisiloxane affords 1,3-bis[5-(3-methylisoxazolino-2)]-1,1,3,3-tetraphenyldisiloxane, the latter exists as a mixture of R,S- and R,R-diastereoisomers. The bond angle of Si-O-Si fragment in R,S-isomer equals 180(0)° and in R,R-isomer it is 172.8(2)°.

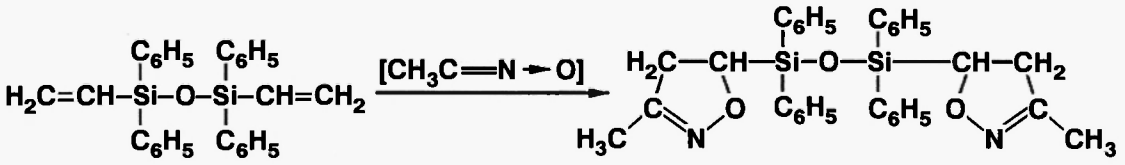
Introduction

X-ray diffraction studies of organosiloxanes have shown that their Si-O-Si fragment is extremely flexible [1-3]. According to Gibbs' quantum-chemical calculations [4] not much energy is needed to increase the bond angle of Si-O-Si from its optimal value, 140°, up to 180°. Recently it has been found that the bond angle in Si-O-Si fragment changes from 147° to 163° within the temperature range -100°C to 28°C [5]. On the other hand, the number of phenyl groups in disiloxane molecules influences the magnitude of the Si-O-Si angle [1,3]. The Si-O-Si fragment in hexaphenyldisiloxane is linear [2], the substitution of the phenyl group for hydrogen [3,6] or for methyl [7,8] leads to the disiloxane group bending. Both steric and electronic factors may be the reasons for this variation [9].

We have studied the interaction of 1,3-divinyl-1,1,3,3-tetraphenyldisiloxane with acetonitrile oxide in the [2+3] cycloaddition reaction. This reaction results in the introduction of the heterocyclic isoxazoline group in the 1,3-positions of disiloxane.

Results and Discussion

1,3-Divinyl-1,1,3,3-tetraphenyldisiloxane (1) reacts with acetonitrile oxide, generated by the dehydration of nitroethane with phenylisocyanate in the presence of the catalytic amount of triethylamine in benzene [10], affording 1,3-bis[5-(3-methylisoxazolino-2)]-1,1,3,3-tetraphenyldisiloxane (**2**):



1 **2 a,b**

The presence of two signals at -19.10 and -19.14 ppm in ^{29}Si NMR spectrum indicates that the product obtained exists as a mixture of two diastereoisomers.. It has been also confirmed by ^{1}H and ^{13}C NMR spectra. The low field signal in ^{1}H NMR spectrum, corresponding to the methine proton at C_5 of the isoxazoline ring, appears as two double doublets with approximately equal chemical shifts (4.31 and 4.37 ppm, respectively). The group of signals of the methylene protons at C_4 of the isoxazoline ring is in the high field (2.72, 2.78 ppm. and 2.83, 2.87 ppm). As seen from ^{13}C NMR spectrum the asymmetric centre at C_5 in the isoxazoline ring influences the signals of the phenyl group at the silicon atom.

We have separated the isomers by crystallization and determined their structures as the (R,S)- and (R,R)-diastereoisomers using an X-ray crystallographic method.

X-Ray analysis of the disiloxanes **2a** *and* **2b**

2a crystals were grown from acetonitrile and **2b** crystals - from ethyl acetate. Colourless crystals of these compounds were studied on the Syntex-P2, single - crystal diffractometer. The detailed crystal data and the measurement conditions are presented in Table 1.

Table 1. Crystal data and measurement conditions for compounds **2a** and **2b**.

Compound	**2a**	**2b**
Formula	$C_{16}H_{16}NO_{1.5}Si$	$C_{32}H_{32}N_2O_3Si_2$
Molecular weight	274.39	548.78
Crystal system	monoclinic	triclinic
Space group	P $2_1/c$	P-1
Unit cell dimensions:	a = 8.547(2) Å $\alpha = 90^\circ$	a = 9.135(3) Å $\alpha = 73.56(2)^\circ$
	b = 10.466(3) Å $\beta = 116.87(2)^\circ$	b = 11.172(3) Å $\beta = 75.62(2)^\circ$
	c = 18.122(4) Å $\gamma = 90^\circ$	c = 15.309(3) Å $\gamma = 86.87(2)^\circ$
Cell volume	1446.0(6) $Å^3$	1451.3(7) $Å^3$
Z	4	2
Density (calculated)	1.260 g/cm^3	1.256 g/cm^3
F (000)	580	580
Crystal size	0.2x0.3x0.35 mm	0.15x0.3x0.35 mm
Radiation	Cu K_α graphite monochromated	
Wave length	1.54178 Å	
Absorption coefficient μ	1.396 mm^{-1}	1.391 mm^{-1}
2θ range for data collection	5.03 to 49.99°	3.10 to 49.97°
Scan mode	θ/θ	
Independent reflections collected	1349	2586
Data/restraints/parameters	1327/0/179	2557/0/353
Goodness-of-fit on F^2	0.989	1.03
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0646	R1 = 0.0642
R indices (all data)	R1 = 0.0725	R1 = 0.0718
Extinction coefficient	0.012(2)	0.0055(9)
Largest diff. peak and hole	0.233 and -0.370 $e/Å^3$	0.247 and -0.369 $e/Å^3$

Both structures were determined by direct methods (SHELXS-86 [11]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-93 [12]) employing unit weights. The nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms - isotropically. The fractional coordinates and the equivalent isotropic displacement parameters for the nonhydrogen atoms for compound **2a** are listed in Table 2 and for compound **2b** - in Table 3. Intramolecular distances and angles for both structures are reported in Table 4. Figures 1 and **2** show a perspective view of molecules **2a** and **2b**.

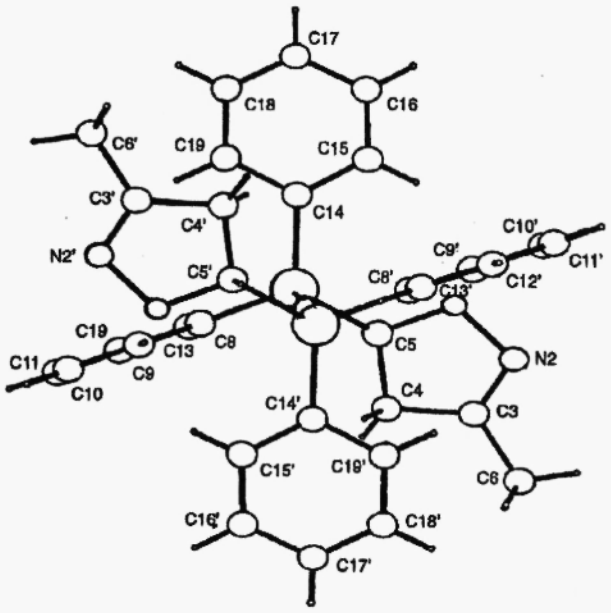


Fig. 1. X-Ray structure of (R,S)-1,3-bis[5-(3-methylisoxazolino-2)]-1,1,3,3-tetraphenyldisiloxane

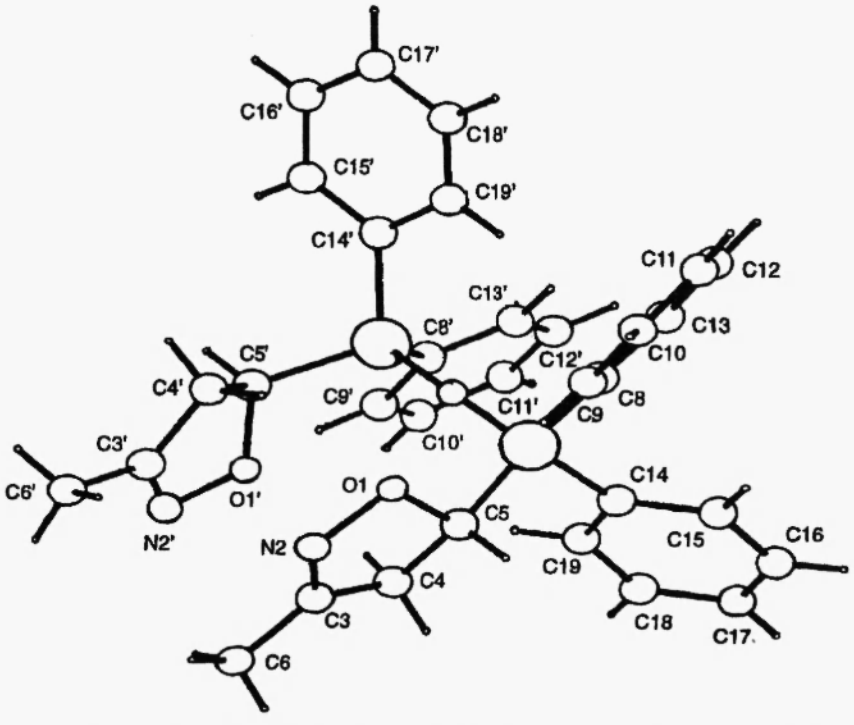


Fig. 2. X-Ray structure of (R,R)-1,3-bis[5-(3-methylisoxazolino-2)]-1,1,3,3-tetraphenyldisiloxane

Table 2. Atomic coordinates ($x 10^4$) and equivalent isotropic displacement parameters U(eq) ($Å^2 x 10^3$) for **2a**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Si(7)	6169(2)	789(1)	831(1)	58(1)
O(20)	5000	0	0	63(1)
O(1)	7989(4)	-1328(3)	1685(2)	73(1)
N(2)	9184(5)	-2221(4)	1630(2)	78(1)
C(3)	9843(6)	-1748(5)	1194(3)	74(1)
C(4)	9174(6)	-470(4)	866(3)	72(1)
C(5)	8276(6)	-109(4)	1390(3)	64(1)
C(6)	11102(7)	-2481(6)	1008(4)	117(2)
C(8)	6741(5)	2381(4)	591(3)	61(1)
C(9)	5886(6)	2942(5)	-180(3)	73(1)
C(10)	6349(8)	4145(5)	-317(3)	87(2)
C(11)	7640(8)	4799(5)	306(4)	92(2)
C(12)	8497(8)	4284(5)	1073(4)	91(2)
C(13)	8039(7)	3088(5)	1212(3)	82(2)
C(14)	4936(6)	938(4)	1449(3)	62(1)
C(15)	4881(7)	-9(5)	1961(3)	77(1)
O(16)	3927(8)	131(6)	2394(3)	94(2)
C(17)	3026(7)	1209(7)	2337(4)	93(2)
C(18)	3016(7)	2156(6)	1827(4)	97(2)
C(19)	3971(7)	2039(5)	1388(3)	84(2)

The isoxazoline rings in the centrosymmetric isomer **2a** (Fig.1) can be thought as to occupy *trans* positions to each other. The Si-O-Si angle is constrained to 180(0)° and Si-O is 1.608(1) Å. O1-C5-C4 plane in the isoxazoline ring deviates from the O1-N2-C3-C4 plane by 21.7°(3).

The isoxazoline rings in the isomer **2b** (Fig.2) are in *cis* positions to each other, the Si-O-Si bond angle equals 172.8(2)° and the Si-O distance is 1.611(3) Å. The isoxazoline rings have an envelope-like conformation. O1-C5-C4 plane deviates from O1-N2-C3-C4 plane by 27.4(3)°, and O1'-C5'-C4' plane from O1'-N2'-C3'-C4' plane - by 25.1(4)°.

Summing up the abovesaid it may be concluded that if the substitution of the phenyl group for the methyl group [8] or for hydrogen [6] leads to the disiloxane group bending then in the case of the isoxazoline group introduction depending on the spatial location of heterocycles to each other (*cis*- or *trans*-) the Si-O-Si fragment can be either bent or linear in the molecule **2**.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U(eq) ($Å^2 \times 10^3$) for **2b**.

	x	y	z	U(eq)		x	y	z	U(eq)
Si(7)	-1124(1)	1470(1)	2750(1)	62(1)	Si(7')	2345(1)	2319(1)	1738(1)	64(1)
O(2)	577(3)	1982(3)	2247(2)	68(1)					
C(1)	-2317(4)	2933(3)	1343(2)	75(1)	O(1')	2429(4)	1772(3)	135(2)	80(1)
N(2)	-2486(5)	2946(4)	430(3)	78(1)	N(2')	1931(5)	2288(5)	-714(3)	82(1)
C(3)	-2086(6)	1908(5)	298(4)	71(1)	C(3')	1524(6)	3396(5)	-719(4)	72(1)
C(4)	-1544(6)	1032(5)	1067(3)	69(1)	C(4')	1653(6)	3801(5)	70(3)	73(2)
C(5)	-2187(5)	1636(4)	1841(3)	62(1)	C(5')	2066(6)	2809(5)	480(4)	72(1)
C(6)	-2075(8)	1658(6)	-615(4)	105(2)	C(6')	917(7)	4160(6)	-1538(4)	102(2)
C(8)	-2049(6)	2346(5)	3598(3)	67(1)	C(8')	3476(5)	950(5)	2178(4)	68(1)
C(9)	-3235(7)	3135(5)	3458(4)	85(2)	C(9')	4267(6)	253(5)	1593(4)	78(2)
C(10)	-3882(8)	3805(6)	4059(5)	106(2)	C(10')	5076(6)	-795(6)	1926(6)	93(2)
C(11)	-3336(8)	3747(6)	4827(5)	103(2)	C(11')	5115(7)	-1127(6)	2843(6)	99(2)
C(12)	-2174(7)	2982(6)	5004(4)	91(2)	C(12')	4367(8)	-475(7)	3430(5)	99(2)
C(13)	-1546(6)	2293(5)	4394(4)	79(2)	C(13')	3558(6)	548(6)	3114(4)	86(2)
C(14)	-1125(6)	-210(5)	3359(4)	68(1)	C(14')	2812(5)	3669(4)	2139(3)	63(1)
C(15)	-2152(7)	-759(6)	4209(4)	89(2)	C(15')	4117(6)	4383(6)	1699(4)	85(2)
C(16)	-2208(9)	-2047(7)	4571(5)	110(2)	C(16')	4122(7)	5400(6)	1966(5)	94(2)
C(17)	-1339(11)	-2786(7)	4120(7)	119(3)	C(17')	3481(8)	5717(5)	2689(5)	87(2)
C(18)	-311(10)	-2273(7)	3289(6)	114(2)	C(18')	2205(7)	5022(6)	3149(4)	83(2)
C(19)	-216(7)	-1013(5)	2935(4)	88(2)	C(19')	1879(6)	4017(5)	2887(4)	77(2)

Table 4. Bond lengths (Å) and angles (°) for **2a** and **2b**

Compound **2a**		Compound **2b**		
Si(7)-O(2)	1.608(1)	1.611(3)	1.612(3)	Si(7')-O(2)
Si(7)-C(8)	1.843(4)	1.844(5)	1.838(5)	Si(7')-C(8')
Si(7)-C(14)	1.859(5)	1.841(5)	1.841(5)	Si(7')-C(14')
Si(7)-C(5)	1.871(5)	1.864(5)	1.870(5)	Si(7')-C(5')
O(2)-Si(7) #1	1.608(1)			
O(1)-N(2)	1.420(5)	1.440(5)	1.438(5)	O(1')-N(2')
O(1)-C(5)	1.446(5)	1.447(5)	1.449(6)	O(1')-C(5')
N(2)-C(3)	1.261(6)	1.253(6)	1.263(6)	N(2')C(3')
C(3)-C(4)	1.471(6)	1.474(7)	1.479(7)	C(3')-C(4')
C(3)-C(6)	1.479(7)	1.498(7)	1.481(7)	C(3')-C(6')
C(4)-C(5)	1.515(6)	1.506(6)	1.504(7)	C(4')-C(5')
C(8)-C(9)	1.382(6)	1.379(7)	1.393(7)	C(8')-C(9')
C(8)-C(13)	1.385(6)	1.391(7)	1.395(7)	C(8')-C(13')
C(9)-C(10)	1.375(6)	1.362(8)	1.389(8)	C(9')-C(10')
C(10)-C(11)	1.354(7)	1.357(9)	1.356(9)	C(10')-C(11')
C(11)-C(12)	1.356(7)	1.357(8)	1.347(9)	C(11')-C(12')
C(12)-C(13)	1.368(7)	1.373(7)	1.364(8)	C(12')-C(13')
C(14)-C(15)	1.374(6)	1.399(7)	1.383(7)	C(14')-C(15')
C(14)-C(19)	1.392(7)	1.376(7)	1.385(7)	C(14')-C(19')
C(15)-C(16)	1.370(7)	1.386(9)	1.375(8)	C(15')-C(16')
C(16)-C(17)	1.343(8)	1.331(10)	1.344(8)	C(16')-C(17')
C(17)-C(18)	1.352(8)	1.372(10)	1.355(8)	C(17')-C(18')
C(18)-C(19)	1.379(8)	1.357(9)	1.364(7)	C(18')-C(19')
O(2)-Si(7)-C(8)	111.21(14)	110.8(2)	109.5(2)	O(2)-Si(7')-C(8')
O(2)-Si(7)-C(14)	109.03(14)	110.5(2)	108.0(2)	O(2)-Si(7')-C(14')
C(8)-Si(7)-C(14)	110.4(2)	110.6(2)	112.1(2)	C(8')-Si(7')-C(14')
O(2)-Si(7)-C(5)	106.8(2)	108.1(2)	108.7(2)	O(2)-Si(7')-C(5')
C(8)-Si(7)-C(5)	106.8(2)	110.4(2)	111.0(2)	C(8')-Si(7')-C(5')
C(14)-Si(7)-C(5)	112.6(2)	106.3(2)	107.5(2)	C(14')-Si(7')-C(5')
Si(7)#1-O(2)-Si(7)	180.0	172.8(2)		Si(7)-O(2)-Si(7')
N(2)-O(1)-C(5)	107.9(3)	106.4(3)	107.0(4)	N(2')-O(1')-C(5')
C(3)-N(2)-O(1)	108.9(4)	108.0(4)	108.4(4)	C(3')-N(2')-O(1')
N(2)-C(3)-C(4)	114.1(4)	115.0(5)	114.1(5)	N(2')-C(3')-C(4')
N(2)-C(3)-C(6)	121.1(5)	120.4(5)	120.7(5)	N(2')-C(3')-C(6')
C(4)-C(3)-C(6)	124.7(5)	124.4(5)	125.2(5)	C(4')-C(3')-C(6')
C(3)-C(4)-C(5)	100.8(4)	99.4(4)	100.5(4)	C(3')-C(4')-C(5')
O(1)-C(5)-C(4)	103.3(3)	103.5(4)	103.5(4)	O(1')-C(5')-C(4')
O(1)-C(5)-Si(7)	111.1(3)	111.5(3)	111.2(3)	O(1')-C(5')-Si(7')
C(4)-C(5)-Si(7)	114.9(3)	117.6(3)	116.9(3)	C(4')-C(5')-Si(7')
C(9)-C(8)-C(13)	117.2(4)	115.6(5)	116.3(5)	C(9')-C(8')-C(13')
C(9)-C(8)-Si(7)	123.2(3)	122.5(4)	124.0(4)	C(9')-C(8')-Si(7')
C(13)-C(8)-Si(7)	119.5(3)	121.8(4)	119.7(4)	C(13')-C(8')-Si(7')
C(10)-C(9)-C(8)	120.5(4)	122.0(5)	122.0(6)	C(10')-C(9')-C(8')
C(11)-C(10)-C(9)	120.3(5)	120.5(6)	118.6(6)	C(11')-C(10')-C(9')

Table 4. Bond lengths (Å) and angles (°) for **2a** and **2b**

Compound **2a**		Compound **2b**		
C(10)-C(11)-C(12)	120.9(5)	120.2(5)	121.2(6)	C(10')-C(11')-C(12')
C(11)-C(12)-C(13)	119.0(5)	118.9(6)	120.7(6)	C(11')-C(12')-C(13')
C(12)-C(13)-C(8)	122.0(4)	122.8(5)	121.2(5)	C(12')-C(13')-C(8')
C(15)-C(14)-C(19)	116.8(4)	116.3(5)	115.5(5)	C(15')-C(14')-C(19')

Table 4. Bond lengths (Å) and angles (°) for **2a** and **2b** (continued)

Compound **2a**		Compound **2b**		
C(15)-C(14)-Si(7)	123.2(4)	122.3(4)	123.0(4)	C(15')-C(14')-Si(7')
C(19)-C(14)-Si(7)	119.9(4)	121.0(4)	121.5(4)	C(19')-C(14')-Si(7')
C(16)-C(15)-C(14)	121.4(5)	119.5(6)	121.7(5)	C(16')-C(15')-C(14')
C(17)-C(16)-C(15)	121.0(5)	122.0(7)	121.0(5)	C(17')-C(16')-C(15')
C(16)-C(17)-C(18)	119.6(5)	119.7(7)	118.8(5)	C(16')-C(17')-C(18')
C(17)-C(18)-C(19)	120.5(5)	119.1(6)	120.9(5)	C(17')-C(18')-C(19')
C(18)-C(19)-C(14)	120.8(5)	123.3(6)	122.1(5)	C(18')-C(19')-C(14')

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z

Experimental

^{1}H, ^{13}C, ^{29}Si NMR spectra were measured on a WH-360/DS (Bruker) instrument at 360.1 MHz, 90.56 MHz and 71.50 MHz, respectively.

The melting points were determined on a "Digital melting point analyzer" (Fisher), the results are given without correction.

1,3-Divinyl-1,1,3,3-tetraphenyldisiloxane was bought from Gelest.

Synthesis of 1,3-bis[5-(3-methylisoxazolino-2)]-1,1,3,3-tetraphenyldisiloxane

Nitroethane (0.01 mol) and triethylamine (2 drops) in dry benzene (20 ml) are added dropwise for 4 h to the reaction mixture of 1,1-divinyl-1,1,3,3-tetraphenyldisiloxane (0.01 mol), phenylisocyanate (0.02 mol) and triethylamine (1 ml) in dry benzene at room temperature. After some minutes CO_2 begins to evolve and diphenylurea precipitates. The mixture is heated for 4 h at 70-80°C. After cooling to room temperature diphenylurea is filtered off and the solvent removed using a rotary evaporator. The solid residue is dissolved in hot ethyl acetate and put into a refrigerator for 24 h. The substance precipitated (**2b**) is filtered off, the residue evaporated and recrystallized from acetonitrile (**2a**). The total yield is 30%.

2a m.p. = 176°C (recrystallized from acetonitrile)

^{1}H NMR (360.1 MHz, $CDCl_3$/TMS) δ (ppm): 1.88 (s, 6H, CH_3), 2.83 (dd, 2H, J = 11.8 Hz, J = 16.3 Hz, CH), 2.87 (ddq, 2H, J = 1.2 Hz, J = 14.4 Hz, J = 16.3 Hz, CH), 4.31 (dd, 2H, J = 11.8 Hz, J = 14.4 Hz, SiCH), 7.3 (m, 12H, $H_{arom.}$), 7.6 (m, 8H, $H_{arom.}$).

^{13}C NMR (90.56 MHz, $CDCl_3$/TMS) δ (ppm): 12.77 (CH_3), 41.89 (C-5), 71.74 (C-4), 127.91($C^{m}_{arom.}$), 127.95 (C^{m}_{arom}), 130.39 ($C^{p}_{arom.}$), 132.74 (C^{i}_{arom}), 133.52 (C^{i}_{arom}), 134.67 ($C^{o}_{arom.}$), 134.95($C^{o}_{arom.}$), 155.36 (C-3).

^{29}Si NMR (71.50 MHz, $CDCl_3$) δ (ppm) - 19.10

2b m.p. = 146°C (recrystallized from ethyl acetate)

^{1}H NMR (360.1 MHz, $CDCl_3$/TMS) δ (ppm): 1.82 (s, 6H, CH_3), 2.72 (ddq, 2H, J = 1.2 Hz, J = 14.7 Hz, J = 16.3 Hz, CH), 2.78 (dd, 2H, J = 11.2 Hz, J = 16.3 Hz, CH), 4.37 (dd, 2H, J = 11.2 Hz, J = 14.7 Hz,

SiCH), 7.4 (m, 12H, $H_{arom.}$), 7.7 (m, 8H, $H_{arom.}$)

^{13}C NMR (90.56 MHz, $CDCl_3$/TMS) δ (ppm): 12.71 (CH_3), 41.85(C-5), 71.61 (C-4), 127.91($C^m_{arom.}$), 127.96 ($C^m_{arom.}$), 130.35 ($C^p_{arom.}$), 132.89 ($C^i_{arom.}$), 133.65 ($C^i_{arom.}$), 134.64 ($C^o_{arom.}$), 134.96 ($C^o_{arom.}$), 155.26 (C-3)

^{29}Si NMR (71.50 MHz, $CDCl_3$) δ (ppm): -19.14

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Received: November 22, 1995 - Accepted: December 14, 1995 - Accepted in revised camera-ready format: January 16, 1996