

Synthesis and Characterization of a [5.5]Paracyclophane-Containing Silicon by NMR Spectroscopy and X-ray Crystallography

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Received 17 November 1998; revised 5 February 1999

ABSTRACT: *The synthesis and characterization of 1,3,10,12-tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclophane obtained by reaction of 1,4-benzenedimethanol and dichlorodiphenylsilane is reported. The structure was established by mass spectrometry; ^1H , ^{13}C , and ^{29}Si NMR; and X-ray diffraction analysis. © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 351–354, 1999*

INTRODUCTION

In previous studies, we have reported that the reaction of 2,6-pyridinedimethanol with phenylboronic acid provides a tetrameric boronate ring system of 20 members [1], while the reaction of 2-salicylideneaminoethanol derivatives with the same acid yields monomeric or dimeric boronates depending on the number and position of the substituents in the ligand used [2,3]. This is in contrast to the behavior of transition metal ions and heavier elements of the main group that induce for both ligands the formation of monomeric [4,5] or trimeric complexes [6]. With respect to smaller main group elements, it has been reported that the reaction of 2,6-pyridinedimethanol or 1,3-benzenedimethanol with dichlorodimethylsilane or dichlorodiphenylsilane affords

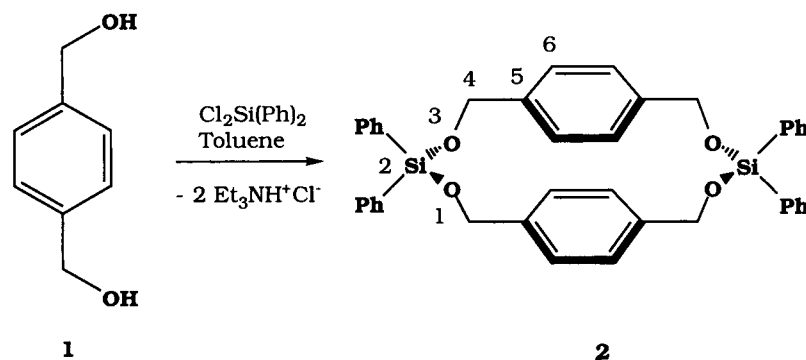
dimeric compounds of cyclophane-type structures [7,8]. Thereby, the formation of [2.2] and [2.2.2]cyclophanes with silicon–silicon bridging units has been reported [9], whereby the [2.2]cyclophane resulted in a bis(disilyl- η^6 -arene)metal complex with chromium [10]. The [2.3]-, [2.4]-, and [2.6]parasilacyclophanes were obtained from intramolecular $[2\pi + 2\pi]$ photocycloadditions [11]. Recently, [2.2]paracyclophanes with disilanylene bridges have been used as precursors in polymer syntheses [12].

RESULTS AND DISCUSSION

1,3,10,12-Tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclophane (**2**) was obtained by reaction of 1,4-benzenedimethanol with dichlorodiphenylsilane (Scheme 1) in toluene in the presence of triethylamine. The mass spectrum shows the molecular ion peak of $m/z = 636$ corresponding to the dimeric compound. An unequivocal ^1H and ^{13}C NMR spectral assignment was achieved by HETCOR and COLOC experiments. The ^1H and ^{13}C NMR spectra of **2** consist only of signals for a quarter of the molecule, so that the point group is D_{2h} . In the ^1H NMR spectrum, the singlet signal for the aromatic H-6 hydrogen atom is located at 6.95 ppm, 0.30 ppm upfield shifted in comparison to the corresponding hydrogen in 1,4-benzenedimethanol. The signal at -30.67 ppm in the ^{29}Si NMR spectrum is in agreement with the chemical shifts of other tetracoordinated silicon compounds [8,13]. The tetracoordination of the silicon atom is confirmed by the X-ray crystallographic

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Contract Grant Sponsor: CONACYT
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SCHEME 1

study (Tables 1 and 2). The bond angles at the silicon atom vary from $104.5(1)$ to $113.2(1)^\circ$, the C(8)–Si(1)–C(14) bond angle being the largest and O(2)–Si(1)–C(14) being the smallest one. In the solid state, the symmetry (Ci) of the molecule is lower than in solution; the aromatic rings of the 1,4-benzenedimethoxy group are not perfectly eclipsed (Figure 1) but have a glide of 1.385 \AA . The distance between them is 3.909 \AA , being 0.45 \AA larger than the distance in other cyclophane-type structures with two disilanylene bridges [9]. The silicon–silicon distance is 8.748 \AA . The distortion of the tetrahedral geometry at the silicon atom can also be seen from the difference between the C(8)–Si(1)–O(1)–C(20) and C(14)–Si(1)–O(2)–C(1) torsion angles with values of -179.8 and -166.4° , respectively. Figure 2 depicts the molecular packing in the unit cell, dashed lines showing distances of 6.946 \AA between aromatic rings.

CONCLUSIONS

The paracyclophane **2** is air stable, soluble, and does not decompose in solution for several weeks; it therefore presents better perspectives as an ion cage than the macrocyclic boronates that we have reported so far. Thus, this compound could be used in rotaxane chemistry [14] and, due to the cavity size, also for the complexation of transition metals.

Experimental

^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Jeol GSX270 equipment, whereby Hetcor and Coloc experiments were performed to assign the spectra adequately. The ^{29}Si NMR spectrum was recorded with the Inept pulse sequence [15]. Chemical shifts (ppm) are relative to $(\text{CH}_3)_4\text{Si}$. The mass spectrum was obtained on an HP 5989A spectrometer. The melting point was obtained on a Gallenkamp MFB-595 apparatus and is uncorrected. The elemental mi-

TABLE 1 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{40}\text{H}_{36}\text{O}_4\text{Si}_2$ (**2**). $U(\text{eq})$ is Defined as One-third of the Trace of the Orthogonalized U_j tensor.

	x	y	z	$U(\text{eq})$
Si (1)	2133.4 (6)	2255.1 (8)	4601.3 (7)	44.9 (3)
O (1)	3010.7 (14)	1730 (2)	3961 (2)	50.2 (5)
O (2)	2164.9 (15)	1476 (2)	5721.4 (15)	49.5 (5)
C (1)	2973 (2)	1590 (3)	6706 (2)	56.6 (8)
C (2)	4021 (2)	1042 (3)	6609 (2)	45.5 (7)
C (3)	4152 (2)	-217 (3)	6536 (3)	54.2 (8)
C (4)	5114 (2)	-725 (3)	6445 (2)	51.1 (8)
C (5)	5970 (2)	30 (3)	6441 (2)	45.1 (7)
C (6)	5837 (2)	1288 (3)	6512 (3)	56.1 (8)
C (7)	4882 (2)	1788 (3)	6591 (2)	55.0 (8)
C (8)	2453 (2)	3905 (3)	4900 (2)	52.5 (8)
C (9)	1772 (3)	4609 (3)	5365 (3)	71.7 (10)
C (10)	1988 (4)	5826 (4)	5646 (3)	93.2 (13)
C (11)	2878 (4)	6358 (4)	5465 (4)	100 (2)
C (12)	3576 (4)	5700 (4)	5002 (4)	97.7 (15)
C (13)	3359 (3)	4477 (3)	4716 (3)	69.3 (10)
C (14)	776 (2)	2010 (3)	3770 (2)	50.1 (7)
C (15)	458 (3)	2482 (5)	2738 (3)	101 (2)
C (16)	-537 (3)	2244 (5)	2087 (3)	115 (2)
C (17)	-1230 (3)	1545 (4)	2457 (3)	82.3 (11)
C (18)	-969 (3)	1104 (4)	3494 (4)	91.6 (13)
C (19)	28 (3)	1336 (3)	4139 (3)	73.3 (10)
C (20)	2966 (2)	466 (3)	3615 (3)	57.2 (8)

TABLE 2 Selected Bond Lengths (\AA) and Angles (deg) for $\text{C}_{40}\text{H}_{36}\text{O}_4\text{Si}_2$ (**2**)

Si(1)–O(2)	1.634 (2)	O(2)–Si(1)–O(1)	111.1 (1)
Si(1)–O(1)	1.634 (2)	O(2)–Si(1)–C(8)	111.2 (1)
Si(1)–C(8)	1.850 (3)	O(1)–Si(1)–C(8)	106.6 (1)
Si(1)–C(14)	1.851 (3)	O(2)–Si(1)–C(14)	104.5 (1)
O(1)–C(20)	1.431 (4)	C(8)–Si(1)–C(14)	113.2 (1)
O(2)–C(1)	1.436 (3)	C(20)–O(1)–Si(1)	119.7 (2)
C(1)–C(2)	1.510 (4)	C(1)–O(2)–Si(1)	124.8 (2)
C(2)–C(3)	1.377 (4)	O(2)–C(1)–C(2)	113.0 (2)
C(2)–C(7)	1.380 (4)	O(1)–C(20)–C(5a)	112.5 (2)

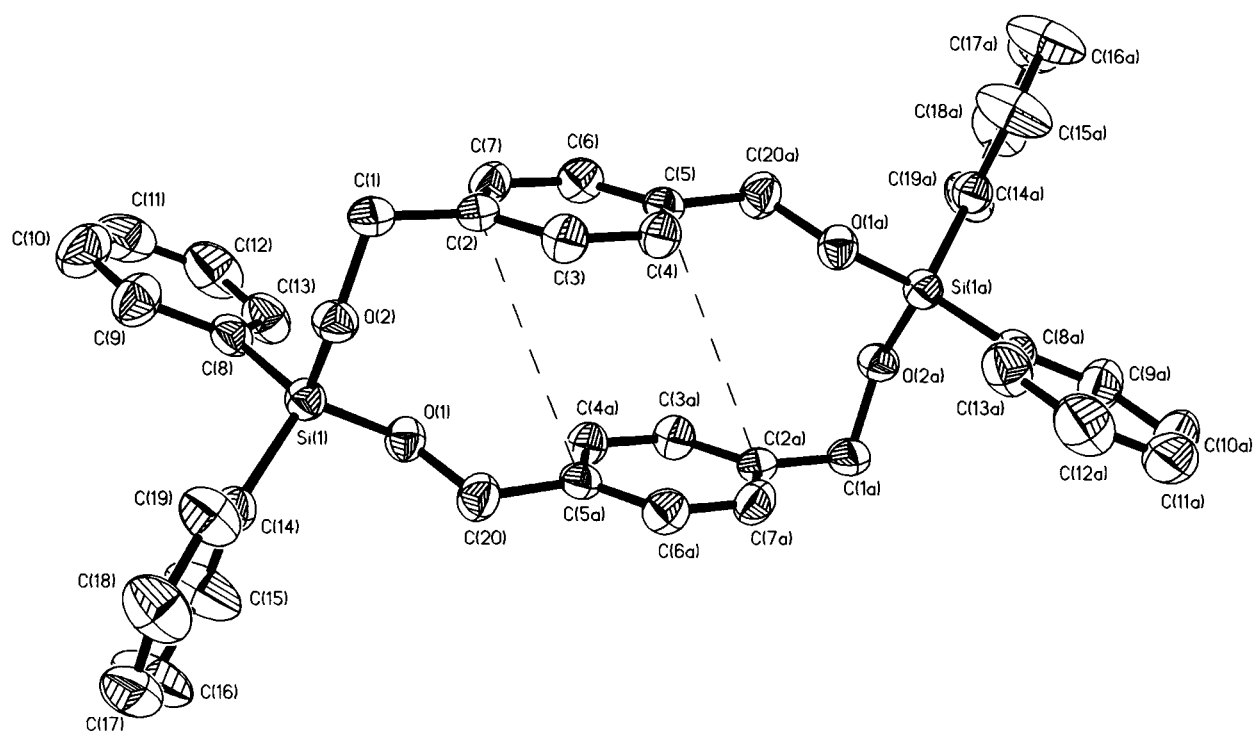


FIGURE 1. Molecular structure of 1,3,10,12-tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclophane (**2**).

croanalysis was performed by Oneida Research Services (Whitesboro, NY). The X-ray crystallographic study was done on an Enraf Nonius CAD4 diffractometer, $\lambda_{(\text{MoK}\alpha)} = 0.71069 \text{ \AA}$, graphite monochromator, $T = 293 \text{ K}$, $\omega/2\theta$ scan, range $2 < \theta < 25^\circ$.

Crystal Data for 2. Colorless cubic crystals of $\text{C}_{40}\text{H}_{36}\text{O}_4\text{Si}_2$ ($M = 636.87 \text{ g mol}^{-1}$) with crystal dimensions of $0.46 \times 0.36 \times 0.33 \text{ mm}^3$ crystallized in the monoclinic space group $\text{P}2_1/c$, $a = 12.945(3)$, $b = 10.811(2)$, $c = 12.573(3) \text{ \AA}$, $\beta = 102.95(3)^\circ$, $V = 1714.8(7) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.233 \text{ g cm}^{-3}$. A total of 6347 reflections were measured, of which 3005 were independent. Corrections were made for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86). Using SHELXS-93 [16], all nonhydrogen atoms were refined anisotropically by full-matrix least squares, and hydrogen atoms were fixed and refined with an overall isotropic thermal parameter. Refinements were based on F^2 with values $R = 0.0462$, $R_w = 0.1160$ from 1669 reflections with $F > 4\sigma(F)$ for 209 parameters, $s = 1.012$. Largest residual electron density peak/hole in the final difference map: $\rho_{\text{max}} = 0.275$, $\rho_{\text{min}} = -0.190 \text{ e/\AA}^3$.

Preparation of 1,3,10,12-tetraoxo-2,11-(diphenylsilylene)[5.5]paracyclophane (2). A solution of 0.10 g of 1,4-benzenedimethanol (0.72 mmol) and Et_3N

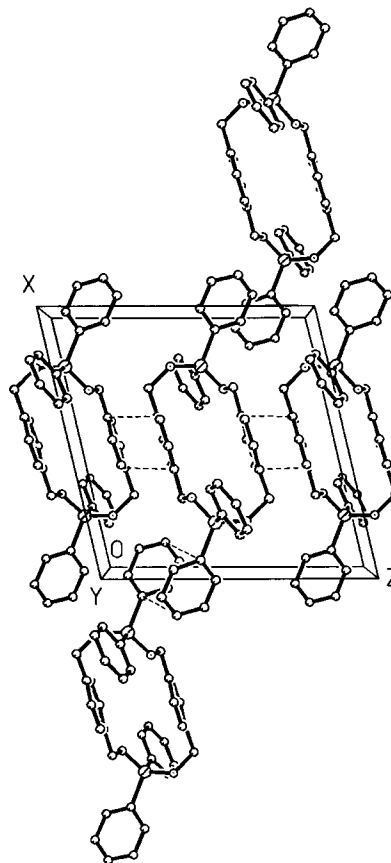


FIGURE 2. Molecular packing in the unit cell for compound **2**.

0.15 g (1.44 mmol) in 30 mL of toluene was cooled to 0°C, and 0.18 g (0.72 mmol) of dichlorodiphenylsilane was added dropwise. The mixture was allowed to warm to room temperature and brought to reflux for 24 hours. The precipitate containing Et₃NHCl was separated by filtration, and the solvent was removed under vacuum to afford a yellow oil. Et₂O was added, and 0.060 g (27.6%) of a white solid was obtained, mp 204–206°C. Suitable crystals for X-ray diffraction were obtained from chloroform. ¹H NMR (270.16 MHz, CDCl₃) δ: 4.68 (2H, s, CH₂), 6.95 (2H, s, H-6), 7.44–7.47 (3H, m, H-*m*, H-*p*), 7.78–7.781 (2H, dd, *J* = 2.2, 7.6 Hz, H-*o*) ppm; ¹³C NMR (67.94 MHz, CDCl₃) δ: 65.14 (C-4), 125.96 (C-6), 128.10 (C-*m*), 130.54 (C-*p*), 132.68 (C-*i*), 135.09 (C-*o*), 138.70 (C-5) ppm; ²⁹Si NMR (53.67 MHz, CDCl₃) δ: –30.67 ppm; MS *m/z* (%): 636 (M⁺, 37%), 558 (5), 361 (6), 319 (14), 211 (12), 199 (100), 104 (89), 78 (19). Anal. calcd for C₄₀H₃₆O₄Si₂: C, 75.43; H, 5.70. Found: C, 74.91; H, 5.87.

Full crystallographic data for **2** are deposited at the Cambridge Crystallographic Data Centre [17].

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