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STRUCTURE OF BIS(*o*-PHENYLENEDIOXY)DIMETHYLSILANE *

J.A. HAWARI, E.J. GABE, F.L. LEE, M. LESAGE and D. GRILLER*
Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A OR6 (Canada)

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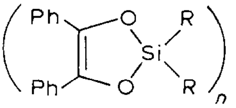
Summary

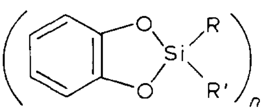
The reaction of dichlorodimethylsilane with 1,2-dihydroxybenzene yielded bis(*o*-phenylenedioxy)dimethylsilane as a crystalline product. An X-ray diffraction study of this material showed that it adopts a dimeric structure. The configuration at the silicon atoms was approximately tetrahedral and the Si–O bond lengths were 1.63 and 1.65 Å. The phenyl rings were in parallel planes separated by a distance of 0.83 Å.

Introduction

In recent studies of organosilicon compounds, we have investigated the chemistry of cyclic silicon enolates, **1** [1]. The structures of these materials, and the extent to which they are mono- or oligomeric, are difficult to determine using conventional techniques since they are readily hydrolysed and thermolyzed. However, some structural insights can be gleaned from studies of the related 1,2-dihydroxybenzo derivatives, **2**, which are far more resistant to hydrolysis and thermolysis than their silicon enolate relatives [2].



(1, R = Me or Ph)



(2a, R = R' = Me;
2b, R = Me; R' = Ph;
2c, R = R' = Ph)

Compounds **2a–2c** have been investigated using NMR spectroscopy [2] which supports the existence of a monomer–dimer equilibrium in chloroform solvent at 59°C. However, ebullioscopic molecular weight measurements [2] in benzene at

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80°C revealed that, at this higher temperature, **2b** and **2c** were largely dissociated into monomers.

In view of the overall complexity of this problem, we have determined the crystal structure of **2a** so as to confirm that it is indeed dimeric in the crystal, and to establish the conformational properties, and the nature of the silicon–oxygen bonding which appears to be so easily disrupted when the crystals are dissolved.

Experimental

Materials. Compound **2a** was prepared by the literature method [2]. The crude product was washed repeatedly with cold pentane, and was then recrystallized several times from pentane until the crystals had a constant melting point (88–90°C). The final yield was 67%.

Spectroscopy. NMR spectra were recorded on a Bruker B-VT 1000 spectrometer using $CDCl_3$ as solvent.

X-ray crystallography. A crystal of approximately 0.5 × 0.5 × 0.5 mm was selected for analysis after attempts to cut others had failed. Crystallographic details for the compound $C_{16}H_{20}Si_2O_4$, were: monoclinic, space group $P2_1/c$, a 6.2368(6), b 12.877(1), c 10.877(1) Å, β 103.91(1) Å, $Z = 4$, D_{cal} 1.30 Mg m^{-3}.

Diffraction intensities were collected with graphite monochromatized Mo-K_α radiation, using the $\theta/2\theta$ scan technique, and profile analysis [3]. Data were collected to $2\theta_{max}$ 60°, and gave a total of 2758 measurements of which 2491 were unique and 1598 were considered to be significant, with $I_{net} > 2.5\sigma(I_{net})$. The usual Lorentz and polarization factors were applied, but absorption corrections were not considered to be necessary as μ 0.22 mm^{-1}. The cell dimensions were obtained by least squares refinement of the setting angles of 60 reflections with $2\theta > 40°$ (λ(Mo-$K_{\alpha1}$) 0.70932 Å).

The structure was solved by a literature method [4] and H atoms were located from difference maps. The structure was refined with full matrix least squares, and the final agreement factors were R_f 0.046 and R_w 0.031 for the reflections considered to be significant and R_f 0.082 and R_w 0.031 when all of the data were included, using weights based on counting statistics.

All calculations were performed with the National Research Council PDP-8e system of programs [5], which had been adapted to run on a VAX computer. Scattering factors were taken from the International Tables for X-ray crystallography [6].

Results and discussion

X-ray crystallography. The X-ray diffraction study of **2a** showed that it existed as a dimer in the crystal, consisting of two equivalent $C_8H_{10}SiO_2$ units arranged around a crystallographic center of symmetry. The distances, angles, and the atomic labelling are shown in Fig. 1, while Fig. 2 gives a stereoview of the molecule.

The phenyl rings lie in parallel planes which are separated by 0.83 Å (Fig. 2). The silicon atoms are situated at a distance of 0.33 Å from these planes, while the oxygen atoms lie close to the planes of their neighbouring phenyl rings.

In **2a** the Si–O bond lengths (1.63 and 1.65 Å) are similar to those previously reported for tetrahedral silicon (1.61–1.67 Å) [7,8]. Moreover, the Si–C bond lengths

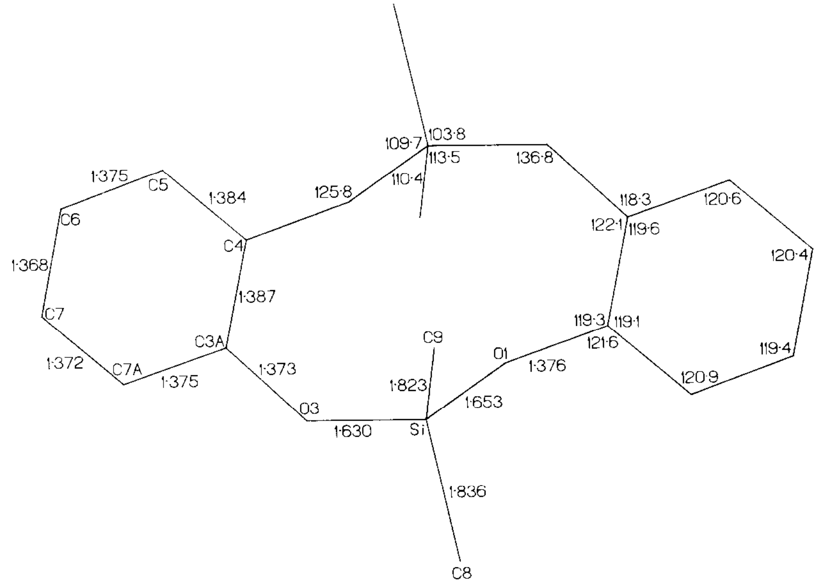

Fig. 1. Bond lengths and angles for **2a**. Estimated standard deviation of bond lengths are 0.015 Å for Si–O, 0.03 for Si–C and 0.03–0.04 Å for other bonds; those for bond angles range from 0.1–0.2°.

(1.84 Å) are close to that measured for tetrahedral phenylsilane (1.84 Å) [9], and for the tetrahedral ladder chain hydrogen-bonded dimers of di-t-butylsilanediol [8]. The six angles around Si (103.8–113.5°) including O(1)–Si–O(3) (106.5°) and C(8)–Si–C(9) (112.7°) are in the range expected for a configuration which is approximately tetrahedral. Remarkably, the Si–O–C angle (136.8°) is relatively large which indicates the presence of π-interaction between the lone pair of oxygen and the *d*-orbitals of silicon. Similar interactions have been suggested for methylsilyl ethers [10] and siloxanes [11]. The C–C bond lengths in the phenylene rings (1.387 Å) did not show a substantial deviation from the normal value of 1.399 Å measured for the C–C bonds in benzene [12].

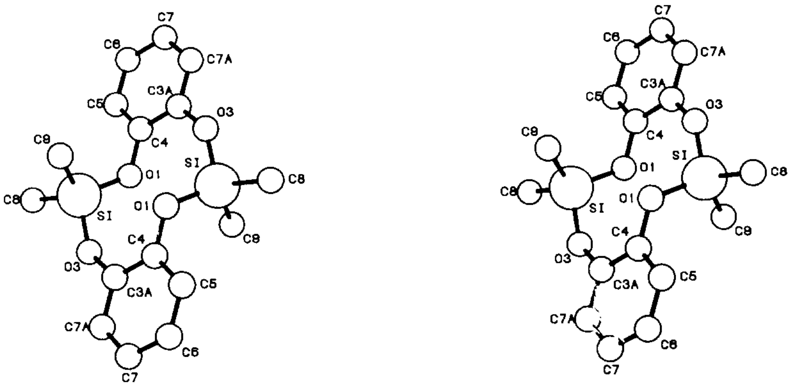

Fig. 2. A stereoview of **2a**.

The above observations show that **2a** is a dimer in the crystal in which the atoms are all connected by normal bond lengths and angles. There is no suggestion that the dimer is a loose association of two monomers. Why then does the dimer readily fragment to monomers in solution?

The answer to this question must be that the conformation adopted in the crystal minimizes steric interactions within this molecule. Indeed, models show that the conformation adopted in the crystal is essentially the only one available that relieves steric interaction between the methyl groups attached to silicon, and other parts of the molecule. In fact, small-ring motions, which must obviously occur in solution, immediately bring about strong interactions between these methyl groups and the nearest hydrogens of the aryl rings as well as transannular interactions. It must be these restrictive steric forces which make conversion to the monomer favourable.

NMR spectroscopy. The NMR spectrum of **2a** has been investigated by two groups [2,13]. However, their results and conclusions need to be reevaluated in the light of our own X-ray and NMR data.

We have measured the ^{13}C NMR spectrum of **2a** in $CDCl_3$ at room temperature, where it exists predominantly as the dimer. Remarkably, only four absorptions were observed with the following chemical shifts, $\delta(CDCl_3)$ 144.96, 122.74, 121.57 and -2.04 ppm which were in good agreement with the data reported by Cragg and Lane [2].

Two of the assignments are straightforward. That at -2.04 ppm is associated with the $SiMe_2$ groups while the peak at 144.96 ppm is almost certainly due to aryl carbon atoms bonded to oxygen. The two remaining peaks (δ 122.74 and 121.57 ppm) were originally thought to indicate that the four residual carbon atoms in each phenyl ring had identical chemical shifts and that the rings themselves were not in magnetically equivalent environments.

It is of course possible that, in solution, the dimer of **2a** will adopt conformations in which the aryl groups are not equivalent, and so we must admit the possibility of the above assignment. However, our X-ray results show that, in the crystal, the aryl rings are related by symmetry. The carbon atoms in a given aryl group are equivalent in pairs and each of these pairs has a magnetically equivalent partner pair in the opposite ring. Hence we would expect to find only three resonances for the aryl carbon atoms and do not require any adventitious equivalence of the chemical shifts.

Finally, the spectrum described herein is at variance with that described by Meyer, Klein and Weiss [13] who reported peaks at 120.99 and 113.33 ppm. While the peaks were detected as minor resonances by Cragg and Lane [2], they were absent in our spectra suggesting that Meyer et al. [13] were dealing with a compound which was not **2a**.

Supplementary Material

Tables of atomic parameters, $U_{i,j}$ values, torsion angles and structure factors are available on request, from the authors.

Conclusions

X-ray analysis of bis(*o*-phenylenedioxy)dimethylsilane (**2a**) has shown that it crystallizes as a fully bonded dimer and does not exist, in the solid, as two loosly associated monomer units. The proximity of the methyl groups to other parts of the molecule suggest that steric compression supplies the driving force which converts the dimer to monomer in solution at elevated temperatures. An analysis of the structure implies that the ^{13}C NMR spectrum of this material was incorrectly assigned in earlier work.

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