The Stereochemistry of Chloro-bis(N-morpholino)phenylsilane

Gerald Huber, Annette Schier, Hubert Schmidbaur*

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

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Silylamines, Aminosilanes, Symmetry, NMR Data, Crystal Structure

Treatment of phenyltrichlorosilane with an excess of morpholine and N-lithium-morpholide in pentane/toluene affords only the disubstitution product Cl(Ph)Si(Mor)₂ with Mor = O(CH₂CH₂)₂N-. The third halogen atom is not replaced owing to sterical hindrance. The title compound crystallizes with two independent molecules in the unit cell. These two molecules can be classified as enantiomers, because a disrotatory twist of the two morpholino ligands away from the potential mirror plane induces a chiral conformation. In benzene solution there is racemization owing to completely free rotation, chair/boat interconversion, and nitrogen inversion of the morpholino groups on the NMR time scale, but all CH₂ protons remain anisochronous (diastereotopic).

Introduction

Aminosilanes (silylamines, silazanes) are useful synthons for the construction of silicon-nitrogen frameworks [1 - 3]. For a close approach to silicon nitride structures, complete substitution of all halogen atoms in a halosilane precursor is necessary. However, as the number of amino functions present at a given silicon atom is increased, steric congestion is soon encountered which prevents extensive or complete substitution [4]. Needless to say, already a set of diethylamino groups -N̸É₂ groups is much more difficult to accommodate as compared to dimethylamino groups -N̸É₂. These difficulties can be avoided if the two ethyl groups are tied together as in pyrrolidine, piperidine, or morpholine. In the latter an oxygen atom forms the bridge between the β carbon atoms and narrows the cone angle of the amine.

In the course of pertinent studies of morpholinosilanes [5, 6] the title compound was prepared and its stereochemistry investigated. Although the structure is generally straightforward, some details merit special comments as shown in this short report.

Preparative, Spectroscopic, and Structural Results

The title compound is readily available by treatment of phenyltrichlorosilane with an excess of

* Reprint requests to Prof. Dr. H. Schmidbaur.

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Fig. 1. Structures of the two independent molecules a and b in the unit cell of Cl(Ph)Si(Mor)₂. The molecules are mirror images and represent the two enantiomers. (ORTEP, 50% probability; H-atoms omitted for clarity):

a) Selected bond lengths [Å] and angels [°]: Si1-N11 1.680(2), Si1-N12 1.695(2), Si1-C10 1.851(3), S1-N11-C11 2.0823(10), N11-Si1-N12 111.25(11), N11-Si1-C10 112.36(11), N12-Si1-C10 113.69(12), N11-Si1-C11 107.90(9), N12-Si1-C11 105.47(9), C10-Si1-C11 112.36(11), C14-N11-Si1 127.3(2), C14-N11-Si1 120.9(2), C15-N12-C18 111.6(2), C15-N12-Si1 123.6(2), C18-N12-Si1 124.2(2);

b) Selected bond lengths [Å] and angels [°]: Si2-N21 1.686(2), Si2-N22 1.690(2), Si2-C70 1.846(3), Si2-C12 2.090(10), N21-Si2-N22 112.01(12), N21-Si2-C70 111.4(2), N22-Si2-C70 112.59(12), N21-Si2-C12 108.17(9), N22-Si2-C12 106.42(9), C70-Si2-C12 111.4(2), C24-N21-C21 111.4(2), C24-N21-Si2 122.0(2), C21-N21-Si2 126.5(2), C25-N22-C28 111.1(2), C25-N22-Si2 122.1(2), C28-N22-Si2 126.6(2).

suggests that there is unrestricted rotation of all substituents, as well as rapid ring inversion of the chair conformation and inversion at the nitrogen atoms of the morpholino rings. This leads to virtual mirror symmetry for the molecule as a whole, and local mirror symmetry for each individual substituent. However, the methylene hydrogen atoms of the morpholino rings are diastereotopic (anisochronous) and show separate triplet signals. This splitting is well resolved for the NCH₂ groups, but leads only to a broadening for the CH₂O groups, which are further away from the center of prochirality. The assignments are supported by data for related N-morpholino compounds [5, 6].

Crystals of Cl(Ph)(OC₄H₄N₂)₂Si (from toluene) are monoclinic, space group P2₁/c with Z = 8 formula units in the unit cell. The lattice contains two independent molecules with no sub-van-der-Waals contacts. There are no solvent molecules included. The morpholino groups have standard chair conformations but feature a planar configuration at the nitrogen atoms.

None of the two molecules has any crystallographically imposed symmetry. Inspection of the structures shows that the deviation from the potential mirror symmetry is indeed very significant. The phenyl rings are neither coplanar with, nor perpendicular to the planes defined by the individual atom triples Cl-Si-C (Figures 1a,b). The pairs of morpholino groups are not mirror images with respect to these planes because of a rotation about the Si-N bonds in opposite directions. Each of the two molecules is thus chiral.

Although not required by crystal symmetry, the two independent molecules are mirror images and closely represent two enantiomers.

Discussion

The title compound is thus a molecule with the potential for internal mirror symmetry (point group C₃). When locked in the crystal lattice, there are two chiral conformers which are approximately mirror images. The low-symmetry conformation is probably required by the congestion of the four substituents at the silicon atoms. In solution there is virtually free rotation of all substituents (phenyl and morpholino) about their C/N-Si bonds, and equally unhindered inversion at the nitrogen atoms and interconversion of the ring conformers of the morpholino groups.
Experimental Part

General: Standard equipment for handling of sensitive compounds has been employed throughout. - NMR: Jeol GX 400, solution in CDCl3 at 23 °C. - MS: GC/MS with mass-selective detector HP 5971 A (El 70eV).

Chloro-bis(N-morpholino)phenylsilane
To a solution of morpholine (5.23 ml, 60 mmol) in a solvent mixture (v:v = 1:1) of pentane and toluene (200 ml), phenyltrichlorosilane (1.60 ml, 10 mmol) was slowly added at r. t. After stirring for 10 h a suspension of N-lithium morpholide [10 mmol, from 2.61 ml (30 mmol) of morpholine and equivalent quantities of n-butyllithium in hexane] in toluene (40 ml) was added and the mixture again stirred for 24 h at r.t. After filtration the solvent was removed from the filtrate in a vacuum and the residue taken up with pentane. Cooling of this solution to -30 °C caused precipitation of the product as colourless crystals. Yield 1.80 g (58%); m.p. 70 °C. - 'H NMR: δ = 2.72 and 2.73 (t each, 7H, NCH2), 3.32 (br. t, 7H, OCH2), 7.13 (m, 3H, Hm.p), 7.60 (m, 2H, Ho). - 13C{'H } NMR: δ = 45.5 (NCH2), 68.0 (OCH2), 128.5 (Cp), 131.0 (Cm), 133.2 (C0), 135.2 (C,). - 29Si{'H } NMR: δ = -21.1. - MS (El, 70 eV) m/z: 312 [M+], 226 [M+ -NC4H8O], 142 [2F(C2H5)].

Elemental analysis: C14H21ClN2O2Si (312.87)
Calcd C 53.8 H 6.8 N 8.9 %.
Found C 53.7 H 6.8 N 8.9 %.

Crystal structure determination
A suitable single crystal (from toluene) was sealed in a glass capillary and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp but not for absorption effects [μ(Mo Kα) = 3.2 cm⁻¹]. The structure was solved by direct methods and refined by full matrix least-squares calculations against F². The thermal motion of all non hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions (Uiso(H) = 0.08 Å²).

Crystal data for C14H21ClN2O2Si
Mr = 312.87, colorless crystals, monoclinic, a = 11.575(1), b = 29.856(2), c = 9.322(1) Å, β = 99.44(1)°, space group P 21/c, Z = 8, V = 3177.9(5) Å³, ρcalc = 1.308 g cm⁻³, F(000) = 1328; T = -74 °C. 5032 measured and 4795 unique reflections [(sin θ/λ)max = 0.60 Å⁻¹; Rint = 0.0272]; 361 refined parameters, wR2 = 0.0912, R = 0.0387 for 4785 reflections used for refinement. Residual electron densities: +0.28/-0.22. The function minimized was: wR2 = [(Σw(Fo - Fe)²)/Σw(Fo)²]¹/²; w = 1/[(σ²(Fo)² + (ap)² + bp)²].

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