

The Crystal and Molecular Structure of (2-Morpholinoethyl)diphenylsilanol

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(2-Morpholinoethyl)diphenylsilanol, $C_{18}H_{23}NO_2Si$, $M_r=313.5$, monoclinic, $P2_1/c$, $a=17.063(4)$, $b=10.863(3)$, $c=9.094(3)$ Å, $\beta=90.61(2)^\circ$, $V=1685.5$ Å³, $Z=4$, $D_x=1.27$ Mg m⁻³, $\mu(MoK\alpha)=0.154$ mm⁻¹, $F(000)=672$. Out of 2494 independent reflexions measured on an automatic diffractometer 1219 had significant intensities. The structure was solved by direct methods and refined by fullmatrix least-squares calculations to a final R -value of 0.054. The molecules are bonded by O-H...N hydrogen bonds [2.776(8) Å] thereby forming infinite chains which build up the structure. The morpholine ring has a chair form conformation.

The present structure determination forms part of a research project on organosilicon compounds. The title compound is of interest because of its close relationship to the anticholinergics pridinol (1,1-diphenyl-3-piperidino-1-propanol) and sila-pridinol ((2-piperidinoethyl)diphenylsilanol).¹ The sila-pridinol and (2-morpholinoethyl)diphenylsilanol are almost identical. The only difference is that a CH₂ in the piperidine ring of the former is substituted with an oxygen to form the morpholine ring in the latter. Nevertheless they do not crystallize isomorphously and the hydrogen bonding system is different. (2-Morpholinoethyl)diphenylsilanol was kindly supplied by Dr. Reinhold Tacke, *der Technischen Universität, Braunschweig*.

EXPERIMENTAL

The material was recrystallized from a mixture of ethanol and diethyl ether. A preliminary investigation of the crystals was made by oscilla-

tion and Weissenberg techniques. The systematic absences were: $0k0$ when k is odd and $h0l$ when l is odd which uniquely indicate the centrosymmetric monoclinic space group $P2_1/c$. A crystal with the dimensions $0.3 \times 0.25 \times 0.05$ mm was used for the data collection. Unit cell parameters derived from diffractometer measurements: $a=17.063(4)$, $b=10.863(3)$, $c=9.094(3)$ Å and $\beta=90.61(2)^\circ$. The intensities were measured on a Philips PW-1100 diffractometer with the ω - 2θ scan technique. Graphite monochromatized MoK α radiation ($\lambda=0.7107$ Å) was used and 2494 non-zero reflexions within $\sin \theta/\lambda=0.59$ Å⁻¹ were collected at a scan speed of 0.05°/s and with a scan width of 1.2°. Reference reflexions recorded at regular intervals during the data collection showed no significant changes in intensity. The measured intensities were corrected for Lorentz and polarization factors but not for absorption owing to the low μ -value. Out of the reflexions recorded 1275 with $|F_o| < 5\sigma(F_o)$ were excluded from further calculations.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods and Fourier synthesis using the SHELX program system.² From the E -map the positions of seven atoms could be established. In a subsequent Fourier synthesis the silicon atom was located. An additional Fourier synthesis gave the positions of the remaining non-hydrogen atoms. The positional parameters of the non-hydrogen atoms refined with isotropic thermal parameters yielded an R -value of 0.14. After two cycles of anisotropic refinement the R -value decreased to 0.12. A difference synthesis gave the positions of all hydrogen atoms. Further anisotropic refinement

Table 1. Final positional and thermal parameters for non-hydrogen atoms ($\times 10^4$). The e. s. d.'s are given in parentheses. The temperature factors are defined by: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23} \dots)]$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	2404(1)	4048(2)	619(2)	354(10)	316(10)	365(10)	34(10)	26(8)	37(10)
N	3810(3)	1108(4)	2140(5)	345(31)	317(31)	363(28)	-15(26)	6(23)	11(27)
O(1)	3020(2)	4775(4)	-419(4)	550(30)	422(28)	436(26)	-30(22)	154(22)	-50(24)
O(2)	4839(3)	-974(4)	1818(5)	560(35)	517(32)	750(34)	-23(29)	65(27)	231(29)
C(1)	2746(4)	2468(5)	1154(7)	344(39)	322(38)	538(42)	-21(32)	-41(33)	-2(31)
C(2)	3577(4)	2366(6)	1684(7)	453(45)	336(40)	465(43)	-3(32)	-36(34)	24(33)
C(3)	3752(4)	243(6)	904(6)	389(46)	458(45)	498(43)	-74(37)	-44(33)	46(36)
C(4)	4048(4)	-998(6)	1348(7)	646(54)	343(40)	686(47)	-55(41)	16(40)	122(44)
C(5)	4895(4)	-162(7)	3042(8)	516(53)	598(52)	656(49)	-25(44)	-55(40)	129(42)
C(6)	4630(3)	1108(6)	2643(7)	317(40)	466(48)	639(44)	-38(38)	-74(34)	-25(35)
C(7)	2279(4)	5059(5)	2273(6)	401(39)	282(38)	291(35)	38(30)	-8(30)	57(31)
C(8)	2656(4)	6169(6)	2467(7)	476(42)	440(45)	436(40)	22(37)	10(33)	-31(38)
C(9)	2485(4)	6928(6)	3655(8)	729(60)	401(45)	553(48)	-78(40)	-5(45)	-68(42)
C(10)	1956(4)	6571(7)	4675(7)	573(55)	674(56)	452(48)	-155(42)	-17(41)	63(47)
C(11)	1588(4)	5457(8)	4529(7)	415(48)	765(59)	415(44)	-5(42)	59(36)	11(43)
C(12)	1742(4)	4709(6)	3348(7)	425(44)	421(41)	467(42)	26(37)	-51(35)	9(37)
C(13)	1423(3)	3869(6)	-284(6)	329(38)	417(42)	337(35)	-79(34)	61(30)	-48(36)
C(14)	1152(4)	4670(6)	-1352(7)	509(52)	590(49)	415(41)	50(39)	6(37)	29(41)
C(15)	393(5)	4549(8)	-1940(7)	704(63)	854(67)	391(44)	79(43)	-8(44)	266(51)
C(16)	-86(4)	3641(9)	-1457(8)	426(51)	984(69)	535(51)	-139(47)	-71(41)	81(49)
C(17)	167(4)	2846(7)	-400(8)	509(55)	621(53)	699(57)	-35(45)	2(43)	-14(43)
C(18)	910(4)	2967(6)	174(7)	365(45)	536(47)	573(45)	4(38)	-99(37)	122(38)

Table 2. Final positional parameters for the hydrogen atoms ($\times 10^3$) which all were given $U=0.05 \text{ \AA}^2$. Standard deviations in parentheses.

	x/a	y/b	z/c
H(O1)	319(3)	447(5)	-119(5)
H(1)a	263(3)	198(4)	29(5)
H(1)b	243(3)	215(4)	192(5)
H(2)a	398(3)	266(5)	94(5)
H(2)b	366(3)	293(4)	262(5)
H(3)a	322(3)	19(4)	56(5)
H(3)b	400(3)	55(4)	18(5)
H(4)a	403(3)	-156(4)	41(5)
H(4)b	369(3)	-142(4)	211(5)
H(5)a	453(3)	-46(4)	389(5)
H(5)b	544(3)	-5(5)	328(5)
H(6)a	501(3)	150(5)	195(5)
H(6)b	468(3)	168(4)	342(5)
H(8)	304(3)	641(4)	174(5)
H(9)	277(3)	763(5)	374(5)
H(10)	180(3)	705(5)	542(5)
H(11)	122(3)	518(5)	516(5)
H(12)	150(3)	393(5)	326(5)
H(14)	147(3)	538(4)	-163(5)
H(15)	24(3)	516(5)	-267(5)
H(16)	-56(3)	358(4)	-192(5)
H(17)	-17(3)	224(4)	-10(5)
H(18)	108(3)	240(5)	91(5)

of the non-hydrogen atoms lowered the R -value to 0.060. Weights were then applied to F_o according to $w=1.65/(\sigma^2(F_o)+0.0005F_o^2)$ and the positional and thermal parameters of the non-hydrogen atoms were refined anisotropically. In the last refinement cycles the parameters of the hydrogen atoms were refined with fixed isotropic thermal parameters ($U=0.05 \text{ \AA}^2$). The final $R_w=\Sigma w^{1/2} |F_o|-|F_c| / \Sigma w^{1/2} |F_o|$ was 0.048 and the conventional R was 0.054. A difference map based on the final parameters of all atoms showed no peak higher than 0.3 e\AA^{-3} . Final positional and thermal parameters for the non-hydrogen atoms are given in Table 1 and the positional parameters of the hydrogen atoms are given in Table 2. Atomic scattering factors were those of International Tables for X-Ray Crystallography.³ Lists of the final structure factors are available from the author.

RESULTS AND DISCUSSION

The atomic numbering is given in the schematic drawing of the molecule (Fig. 1). The bond

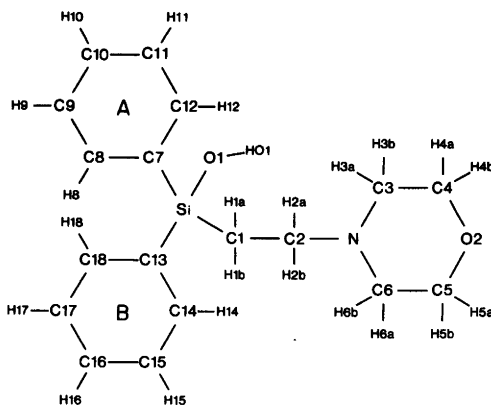


Fig. 1. The (2-morpholinoethyl)diphenylsilanol molecule, showing the numbering scheme of the atoms.

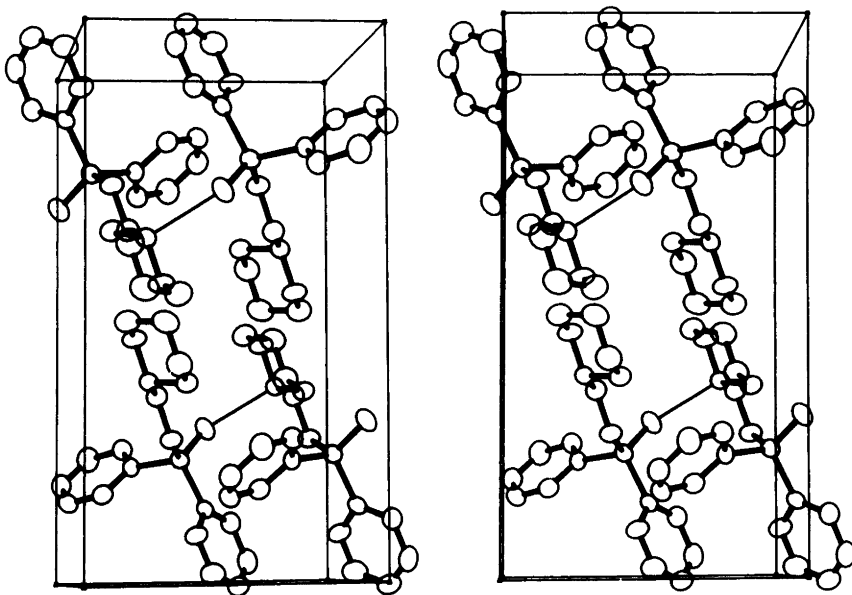
distances and angles uncorrected for the effects of thermal motion are given in Table 3. The C-H distances are in the range of 0.85–1.05 Å. The bond lengths and bond angles are normal and in good agreement with those given for sila-pridinol.¹ As seen in Table 3 the phenyl rings are slightly distorted. The substitution of a hydrogen atom with a silicon atom in a benzene ring causes the endocyclic angle of the carbon atom involved to close up.⁴ This is a common feature when a phenyl ring is attached to a silicon atom.^{1,5,6} In the present structure these endocyclic angles are 117.1(5) and 116.8(6)° for the phenyl rings A and B, respectively.

The planarity of the phenyl ring A is satisfactory, the largest deviations from the least-squares plane being $-0.010(8)$ and $+0.012(8)$ Å for the atoms C(7) and C(8), respectively. The phenyl ring B is also planar as no carbon atom deviates more than $0.004(8)$ Å from the least-squares plane. The morpholine ring has a chair form conformation. The atoms N and O(2) deviate $-0.675(7)$ and $+0.668(7)$ Å, respectively, from a least-squares plane through the carbon atoms C(3)–C(6). This conformation is the same as the piperidine ring exhibits in the sila-pridinol molecule.¹

The angle between the phenyl rings is 99.0° and the angles between the phenyl rings and the least-squares plane through the morpholine ring are 83.1 and 58.6° for phenyl ring A and B, respectively. Tacke *et al.*¹ have investigated the structure in solution of (2-morpholinoethyl)-

Table 3. Intramolecular bond distances (Å) and angles (°) with estimated standard deviations in parentheses.

Si—O(1)	1.625(4)	C(7)—C(8)	1.377(8)
Si—C(1)	1.875(6)	C(8)—C(9)	1.392(8)
Si—C(7)	1.876(6)	C(9)—C(10)	1.357(9)
Si—C(13)	1.866(6)	C(10)—C(11)	1.369(9)
C(1)—C(2)	1.496(7)	C(11)—C(12)	1.375(8)
C(2)—N	1.481(7)	C(12)—C(7)	1.400(8)
N—C(3)	1.468(7)	C(13)—C(14)	1.380(8)
C(3)—C(4)	1.493(8)	C(14)—C(15)	1.403(9)
C(4)—O(2)	1.412(8)	C(15)—C(16)	1.357(10)
O(2)—C(5)	1.423(8)	C(16)—C(17)	1.360(9)
C(5)—C(6)	1.495(9)	C(17)—C(18)	1.373(9)
C(6)—N	1.468(7)	C(18)—C(13)	1.381(8)
O(1)—Si—C(1)	113.2(3)	Si—C(7)—C(8)	124.0(5)
O(1)—Si—C(7)	105.1(3)	C(7)—C(8)—C(9)	121.1(6)
O(1)—Si—C(13)	112.2(3)	C(8)—C(9)—C(10)	120.5(6)
C(1)—Si—C(7)	111.4(3)	C(9)—C(10)—C(11)	119.6(6)
C(1)—Si—C(13)	107.1(3)	C(10)—C(11)—C(12)	120.4(6)
C(7)—Si—C(13)	107.8(3)	C(11)—C(12)—C(7)	121.1(6)
Si—C(1)—C(2)	116.3(4)	C(12)—C(7)—C(8)	117.1(5)
C(1)—C(2)—N	114.2(5)	C(12)—C(7)—Si	118.8(5)
C(2)—N—C(3)	111.1(5)	Si—C(13)—C(14)	122.4(5)
N—C(3)—C(4)	110.5(5)	C(13)—C(14)—C(15)	120.7(7)
C(3)—C(4)—O(2)	112.7(6)	C(14)—C(15)—C(16)	120.1(7)
C(4)—O(2)—C(5)	107.7(5)	C(15)—C(16)—C(17)	120.2(7)
O(2)—C(5)—C(6)	111.4(5)	C(16)—C(17)—C(18)	119.5(7)
C(5)—C(6)—N	111.1(5)	C(17)—C(18)—C(13)	122.7(6)
C(6)—N—C(3)	107.2(5)	C(18)—C(13)—C(14)	116.8(6)
C(6)—N—C(2)	109.8(5)	C(18)—C(13)—Si	120.6(5)

**Fig. 2.** Stereoview (ORTEP⁷) of the crystal structure. The drawing is essentially seen along *b*. Hydrogen atoms are omitted for clarity. Thin lines represent hydrogen bonds.

diphenylsilanol with IR and ^1H NMR spectroscopy. These studies indicate that the present molecule, in non-polar solvents, exists as a monomer and that the molecule forms strong intramolecular O-H \cdots N hydrogen bonds which force the Si-CH₂-CH₂-N group into a *gauche* conformation. In the crystal structure however, the torsion angle Si-CH₂-CH₂-N is 178.1° which shows that the silyl moiety and the morpholine ring are in *trans* conformation to each other. This is the same conformation as has been established for the sila-pridinol molecule in the solid state.¹ The packing of the molecule is shown in Fig. 2 which is a view down the *b* axis. The (2-morpholinoethyl)diphenylsilanol molecules are linked by intermolecular hydrogen bonds forming infinite chains running in the *c* axis direction. Each molecule is linked to another by the hydrogen bond O(1)-HO(1) \cdots N where the symmetry code for the N atom is *x*, 1/2-*y*, -1/2+*z*. The geometry of this bond is characterized by an O \cdots N distance of 2.776(8) Å and an O-H \cdots N angle of 168(3)°.

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REFERENCES

1. Tacke, R., Strecker, M., Sheldrick, W. S., Ernst, L., Heeg, E., Berndt, B., Knapstein, C.-M. and Niedner, R. *Chem. Ber.* 113 (1980) 1962.
2. Sheldrick, G. M. *SHELX. Program for Crystal Structure Determination*, Univ. of Cambridge, England 1975.
3. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
4. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr. B* 31 (1975) 221.
5. Glidewell, C. and Sheldrick, G. M. *J. Chem. Soc. A* (1975) 3127.
6. Párkányi, L. and Bocelli, G. *Cryst. Struct. Comm.* 7 (1978) 335.
7. Johnson, C. K. *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1970.

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