The Crystal and Molecular Structure of (3-Morpholinopropyl)diphenylsilanol

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(3-Morpholinopropyl)diphenylsilanol, $C_{19}H_{25}NO_2Si$, $M_r=327.5$, triclinic, space group $P\bar{1}$, $a=15.073(4)$ Å, $b=9.678(3)$ Å, $c=6.770(3)$ Å, $\alpha=99.04(2)°$, $\beta=95.84(2)°$, $\gamma=103.90(2)°$, $V=936.68$ Å^3, $Z=2$, $D_x=1.16$ Mg m^{-3}, $\mu(CuK\alpha)=1.146$ mm^{-1}, $F(000)=352$.

The intensities of 3308 unique reflexions were measured on an automatic diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares calculations using 3281 reflexions to a final R_w-value of 0.072. The molecules are held together by O−H···N hydrogen bonds [2.840(3) Å] thereby forming infinite chains which build up the structure. The morpholine ring has a chair form conformation.

The title compound is closely related to the anticholinergic drugs difenidol (1,1-diphenyl-4-piperidino-1-butanol) and sila-difenidol (3-piperidinopropyl)diphenylsilanol.[1] The present molecule and the sila-difenidol molecule differ only in that a CH_2 in the piperidine ring of the latter is substituted with an oxygen to form a morpholine ring. The structure of (3-morpholinopropyl)diphenylsilanol has been determined in order to compare it with the structure of sila-difenidol.[2] The material was kindly supplied by Dr. Reinhold Tacke, *der Technischen Universität, Braunschweig.*

EXPERIMENTAL

Large colourless crystals were obtained by recrystallization from a mixture of hexane and diethylether. A crystal with the dimensions $0.6\times0.7\times0.45$ mm was used for the data collection. Preliminary investigations using oscillation and Weissenberg techniques showed that the crystals were triclinic, space group $P1$ or $P\bar{1}$. Unit cell parameters derived from diffractometer measurements: $a=15.073(4)$ Å, $b=9.678(3)$ Å, $c=6.770(3)$ Å, $\alpha=99.04(2)°$, $\beta=95.84(2)°$ and $\gamma=103.90(2)°$. The intensities were measured on a Philips PW-1100 diffractometer with the $\omega-2\theta$ scan technique. Graphite monochromatized $CuK\alpha$ radiation ($\lambda=1.5418$ Å) was used. 3308 independent reflexions within sin $\theta/\lambda=0.61$ Å^{-1} were collected at a scan speed of $0.04°$ s^{-1} and with a scan width of $1.50°$. Seven reflexions were not measured because of too high intensities. Reference reflexions recorded at regular intervals during the data collection showed no significant changes in their intensities. After correction for Lorentz and polarization factors 27 reflexions with negative intensities were rejected. Because of the size of the crystal and the fact that $CuK\alpha$ radiation was used an absorption correction would have been desirable. Unfortunately the crystal was dismounted from the diffractometer before the necessary measurements for absorption correction were made.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods and Fourier synthesis using the program systems MULTAN 80[3] and SHELX,[4] respectively. The positions of all non-hydrogen atoms were easily established from the E-map. The intensity data showed that even the faintest reflexions had very low σF_o. To reduce the number of reflexions 1076 with $|F_o|<80\sigma(F_o)$ were excluded in the early stages of refinement. Two cycles of isotropic refinement followed by two cycles of anisotropic refinement of the non-hydrogen atoms gave

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: $exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2klb^*c^*U_{23}\ldots)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	2394(1)	3824(1)	6481(1)	444(4)	436(4)	478(4)	62(3)	116(3)	153(3)
O1	3399(2)	4240(2)	7903(3)	510(9)	544(9)	630(10)	99(8)	47(8)	161(7)
O2	5298(2)	1423(3)	-2185(4)	521(10)	810(13)	869(14)	-138(11)	230(9)	178(9)
N	3806(2)	2008(2)	-176(3)	459(10)	482(10)	497(10)	30(8)	102(8)	191(8)
C1	2364(2)	2455(3)	4154(4)	560(13)	512(12)	502(12)	44(10)	123(10)	204(10)
C2	3120(2)	2914(3)	2857(4)	572(13)	495(12)	503(12)	60(10)	144(10)	190(10)
C3	3149(2)	1655(3)	1245(4)	559(13)	512(12)	524(13)	72(10)	136(10)	190(10)
C4	4769(2)	2462(3)	836(4)	511(13)	590(14)	636(15)	-42(11)	52(11)	175(11)
C5	5424(2)	2692(4)	-681(5)	522(14)	716(17)	866(20)	-113(15)	180(13)	103(12)
C6	4373(2)	1007(4)	-3203(5)	616(15)	810(18)	685(17)	-112(14)	213(13)	200(13)
C7	3703(2)	717(3)	-1740(4)	544(13)	605(14)	570(14)	-77(11)	105(11)	177(11)
C8	2227(2)	5524(3)	5694(4)	464(11)	430(11)	548(12)	53(9)	98(9)	128(9)
C9	1379(2)	5885(3)	5685(5)	510(13)	584(14)	782(17)	243(12)	190(12)	183(11)
C10	1224(2)	7058(3)	4897(6)	618(16)	676(17)	1041(23)	275(16)	165(15)	292(13)
C11	1909(2)	7896(3)	4085(5)	756(17)	464(13)	913(20)	222(13)	125(15)	177(12)
C12	2751(2)	7580(3)	4070(5)	728(17)	461(12)	738(17)	127(12)	196(13)	23(11)
C13	2911(2)	6424(3)	4885(5)	503(13)	523(13)	709(15)	78(11)	180(11)	124(10)
C14	1428(2)	3092(3)	7871(4)	505(12)	537(12)	489(12)	144(10)	102(9)	190(10)
C15	845(2)	1697(3)	7266(4)	620(14)	539(13)	620(14)	130(11)	133(11)	163(11)
C16	114(2)	1201(4)	8294(5)	666(17)	748(18)	808(19)	339(15)	124(14)	42(14)
C17	-54(2)	2086(4)	9922(5)	630(16)	1058(24)	761(19)	442(18)	278(14)	234(16)
C18	508(3)	3450(4)	10568(5)	813(19)	964(22)	577(15)	172(14)	270(14)	398(17)
C19	1239(2)	3941(3)	9554(4)	686(15)	627(14)	544(14)	89(11)	182(11)	224(12)

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

	x	y	z
H1A	247(2)	148(3)	458(4)
H1B	184(2)	228(3)	342(4)
H2A	300(2)	366(3)	208(4)
H2B	370(2)	330(3)	366(4)
H3A	331(2)	90(3)	198(4)
H3B	245(2)	131(3)	56(4)
H4A	483(2)	171(3)	154(4)
H4B	488(2)	335(3)	170(4)
H5A	538(2)	343(3)	−126(4)
H5B	606(2)	293(3)	−12(4)
H6A	429(2)	16(3)	−419(4)
H6B	430(2)	180(3)	−387(4)
H7A	379(2)	−9(3)	−109(4)
H7B	307(2)	47(3)	−249(4)
H9	97(2)	532(3)	618(4)
H10	54(2)	724(3)	483(4)
H11	180(2)	868(3)	366(4)
H12	323(2)	816(3)	351(4)
H13	347(2)	613(3)	483(4)
H15	92(2)	111(3)	627(4)
H16	−36(2)	22(3)	783(4)
H17	−65(2)	175(3)	1043(4)
H18	48(2)	408(3)	1167(4)
H19	161(2)	486(3)	1004(4)
HO1	350(2)	368(3)	828(4)

an R-value of 0.086. A subsequent difference synthesis revealed the positions of all hydrogen atoms. Two further cycles of anisotropic refinement of the non-hydrogen atoms lowered the R-value to 0.067. The hydrogen atoms were then refined isotropically in two cycles which resulted in an R-value of 0.064. Weights were then applied to F_o according to $w=1.00/\sigma^2(F_o)$ $+0.0003F_o^2$. In the last refinement based on all data (3281 reflexions) the non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were refined with fixed isotropic thermal parameters ($U=0.05$ Å^2) until the shifts were all below the e.s.d.'s. The final $R_w=\Sigma w^{1/2}||F_o|-|F_c||/\Sigma w^{1/2}|F_o|$ was 0.072 with a conventional $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ of 0.067. A difference Fourier synthesis based on the final parameters of all atoms showed no peak higher than 0.26 e Å^{-3}. The final positional and thermal parameters of the non-hydrogen atoms are given

in Table 1 and the positional parameters of the hydrogen atoms are given in Table 2. The atomic scattering factors used were those of International Tables for X-Ray Crystallography.[5] Lists of the final structure factors are available on request from the author.

RESULTS AND DISCUSSION

The atomic numbering is shown in the schematic drawing of the molecule (Fig. 1). The bond distances and angles uncorrected for the effects of thermal motion are given in Table 3. The C−H distances are in the range of 0.85−1.08 Å. Although no absorption correction was made all bond lengths and bond angles are normal and in good agreement with those given for sila-difenidol,[2] sila-pridinol[6] and (2-morpholino-ethyl)diphenylsilanol.[7] The phenyl rings are slightly distorted. The deviation from a regular hexagonal geometry of the benzene ring upon substitution of a hydrogen atom with a silicon atom affects the bond lengths and bond angles.[8] In the present molecule this distortion is most pronounced in the angles C9−C8−C13 and C15−C14−C19 both of which are 116.3(2)°. Deformation of this magnitude are common in organosilicon compounds where benzene rings are attached to silicon atoms.[2,6,7,9,10] Both phenyl rings are planar. The maximum deviation from the least-squares plane is 0.010(4) Å for the atom C13 in ring A and −0.007(4) Å for the atom C17 in ring B. The morpholine ring has as expected a chair form conformation. The atoms N and O2 deviate −0.666(3) and 0.655(3) Å, respectively, from a least-squares plane through the carbon atoms C4−C7. The angle between the phenyl rings is 66.4(3)° which is less than the corresponding angle in pridinol,[6] sila-pridinol,[6] sila-difenidol[2] and in (2-morpholinoethyl)diphenylsilanol.[7] In these structures the angle is larger than 90°. The angles between the phenyl rings and the least-squares plane through the morpholine ring are 86.0(3)° (ring A) and 29.6(3)° (ring B).

The morpholinopropyl chain has an extended conformation. The torsion angles of the Si−C1−C2−C3 and C1−C2−C3−N fragments are 169.8(2) and 175.7(2)°, respectively. The distance between the phenyl centre and the nitrogen atom is for ring A 6.4 Å and for ring B 8.2 Å.

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

Si—O1	1.635(2)	C8—C9	1.404(3)
Si—C1	1.881(2)	C9—C10	1.385(4)
Si—C8	1.872(2)	C10—C11	1.371(4)
Si—C14	1.871(2)	C11—C12	1.376(4)
C1—C2	1.533(3)	C12—C13	1.382(4)
C2—C3	1.514(3)	C13—C8	1.398(3)
C3—N	1.468(3)	C14—C15	1.395(3)
N—C4	1.472(3)	C15—C16	1.391(4)
C4—C5	1.500(4)	C16—C17	1.370(5)
C5—O2	1.427(3)	C17—C18	1.363(5)
O2—C6	1.425(3)	C18—C19	1.385(4)
C6—C7	1.494(4)	C19—C14	1.392(3)
C7—N	1.471(3)		
O1—Si—C1	110.7(1)	Si—C8—C9	121.9(2)
O1—Si—C8	107.4(1)	Si—C8—C13	121.5(2)
O1—Si—C14	111.9(1)	C9—C8—C13	116.3(2)
C1—Si—C8	108.8(1)	C8—C9—C10	121.9(2)
C1—Si—C14	109.2(1)	C9—C10—C11	119.9(2)
C8—Si—C14	108.7(1)	C10—C11—C12	120.0(2)
Si—C1—C2	115.0(2)	C11—C12—C13	120.2(2)
C1—C2—C3	111.1(2)	C8—C13—C12	121.8(2)
C2—C3—N	115.3(2)	Si—C14—C15	122.6(2)
C3—N—C4	111.9(2)	Si—C14—C19	121.1(2)
C3—N—C7	109.2(2)	C15—C14—C19	116.3(2)
C4—N—C7	108.1(2)	C14—C15—C16	121.2(2)
N—C4—C5	110.5(2)	C15—C16—C17	120.4(3)
C4—C5—O2	112.2(2)	C16—C17—C18	120.0(3)
C5—O2—C6	109.4(2)	C17—C18—C19	119.7(3)
O2—C6—C7	110.6(2)	C14—C19—C18	122.5(2)
C6—C7—N	111.4(2)		
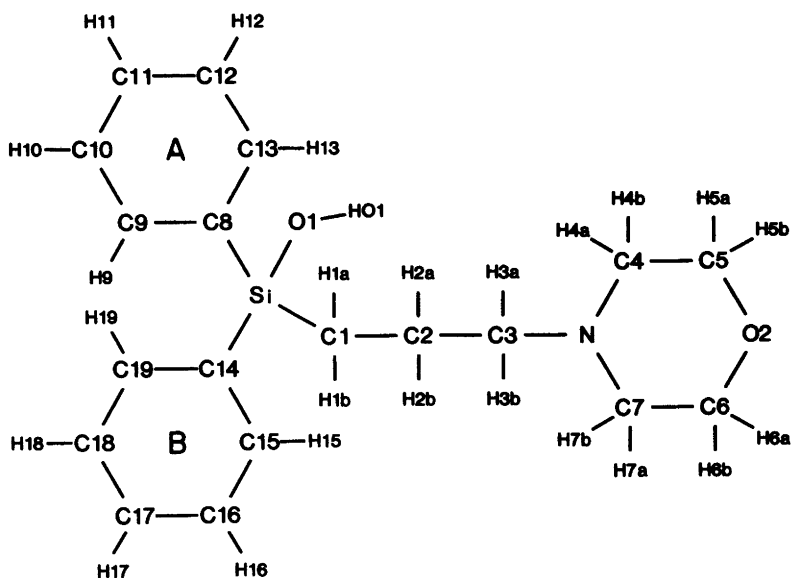
Fig. 1. Schematic drawing of the (3-morpholinopropyl)diphenylsilanol molecule, showing the numbering scheme of the atoms.
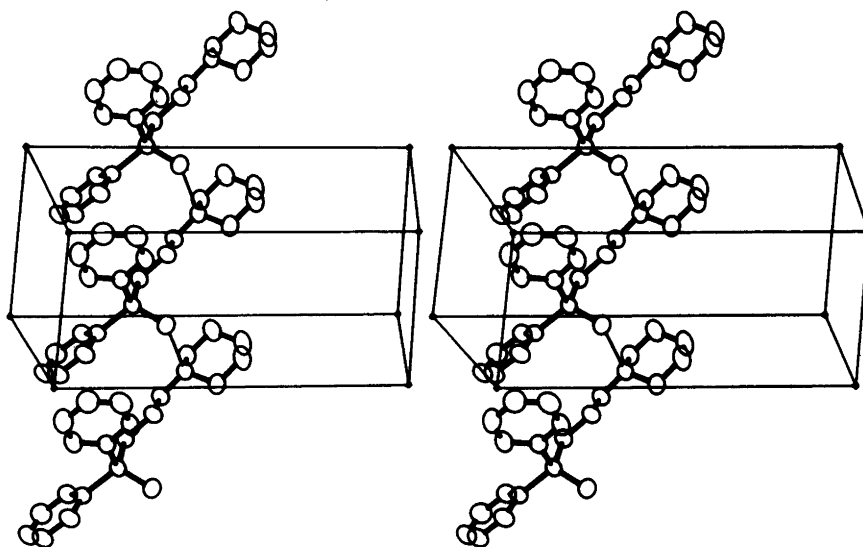
Fig. 2. Stereoview (ORTEP[11]) of the molecular packing showing the hydrogen bonding system. For clarity only half the content of the cell is shown.

The crystal structure is built up by infinite chains of intermolecular hydrogen bonded molecules. These chains are running in the c-axis direction which is illustrated in Fig. 2. Each molecule is linked to another by the hydrogen bond $O1-HO1\cdots N$ where the symmetry code for the N atom is $x, y, 1+z$. The geometry of this bond is characterized by an $O\cdots N$ distance of 2.840(3) Å, an $O-H$ distance of 0.67(3) Å, and an $O-H\cdots N$ angle of 174(3)°. The hydrogen bonding system described above is very similar to that of (2-morpholinoethyl)diphenylsilanol where the molecules also form intermolecular $O-H\cdots N$ hydrogen bonds ($O\cdots N$ distance 2.78 Å)[7] but it differs completely from that of sila-difenidol where there is a strong intramolecular $O-H\cdots N$ hydrogen bond (2.69 Å).[2]

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