

The Crystal and Molecular Structure of [2-(Dimethylamino)ethylthiomethyl]diphenylsilanol

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[2-(Dimethylamino)ethylthiomethyl]diphenylsilanol, $C_{17}H_{23}NOSSi$, $M_r=317.5$, monoclinic, space group $P2_1/c$ (No 14), $a=6.121(3)$ Å, $b=15.956(5)$ Å, $c=18.348(5)$ Å, $\beta=93.09(2)^\circ$, $V=1789.4$ Å³, $Z=4$, $D_x=1.18$ Mg m⁻³, $\mu(MoK\alpha)=0.196$ mm⁻¹, $F(000)=680$.

The intensities of 4234 unique reflexions were measured on an automatic diffractometer. The structure was solved by direct methods and refined by least-squares procedures. The final R -value was 0.068 based on 1925 reflexions. The angle between the phenyl rings is $86.9(6)^\circ$ and the aminoethylthiomethyl chain is maximally extended. The molecules are held together by intermolecular O—H...N hydrogen bonds forming cyclic dimers.

The present structure determination forms part of a research project on organosilicon compounds. The title compound is related to a class of diphenylsilanols which exhibits anticholinergic activity.¹ The material was kindly supplied by Dr Reinhold Tacke, *der Technischen Universität, Braunschweig*.

EXPERIMENTAL

A preliminary investigation of the crystals was made by oscillation and Weissenberg techniques. The systematic absences were: $0k0$ when k is odd and $h0l$ when l is odd which uniquely indicated the centrosymmetric space group $P2_1/c$. Unit cell parameters: $a=6.121(3)$ Å, $b=15.956(5)$ Å, $c=18.348(5)$ Å, $\beta=93.09(2)^\circ$. A crystal with the dimensions $0.25 \times 0.25 \times 0.30$ mm was mounted about b in an automatic diffractometer (Philips PAILRED). Integrated intensities were collected using graphite monochromatized $MoK\alpha$ radia-

tion ($\lambda=0.7107$ Å) for the layers $h0l$ through $h20l$ within $\sin \theta/\lambda \leq 0.66$ Å⁻¹, scan range $\pm 1.8 - \pm 2.2^\circ$, scan speed 2.5° min⁻¹. The fainter reflexions were measured two or three times and the background was measured for 60 s at the beginning and the end of each scan. Reference reflexions measured after each layer showed no significant changes in their intensities. Out of a total of 4234 unique reflexions, 1925 with $I > 3(\sigma I)$ were considered observed. The intensities were corrected for Lorentz and polarization factors using our own program system.² No absorption correction was made owing to the low μ -value. An Amdahl 470V/7A computer was employed for all calculations in this study.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods and Fourier synthesis using the program systems MULTAN 80³ and SHELX⁴. From the E -maps the positions of 12 non-hydrogen atoms were established. In the subsequent Fourier synthesis the remaining non-hydrogen atoms were located. The non-hydrogen atoms were first isotropically refined to an R -value of 0.16 and then anisotropically refined yielding an R -value of 0.085. A difference Fourier synthesis indicated the positions of all hydrogen atoms. Weights were applied to F_o according to $w=0.9628/(\sigma^2(F_o)+0.0003F_o^2)$. The non-hydrogen atoms were refined anisotropically and the positional parameters of the hydrogen atoms were refined with fixed isotropic thermal parameters ($U=0.05$ Å²) until the shifts were all below the esd's. The final $R_w=\sum w^{1/2}||F_o|-|F_c||/\sum w^{1/2}|F_o|$ was 0.065 with a conventional $R=\sum ||F_o|-|F_c||/\sum |F_o|$ of 0.068. A

Table 1. Final positional and thermal parameters for non-hydrogen atoms ($\times 10^4$). The esd'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	y	z	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	8403(2)	1639(1)	3582(1)	486(5)	345(8)	6(6)	12(6)	30(7)
O	6158(6)	1138(2)	3681(2)	562(15)	531(22)	-41(15)	47(18)	37(17)
N	14174(7)	503(2)	6758(2)	580(20)	384(25)	0(18)	-53(22)	-22(22)
S	10496(3)	1415(1)	5093(1)	1148(12)	380(9)	-48(8)	-35(9)	490(11)
C1	10734(9)	1187(2)	4148(3)	515(20)	366(27)	-6(20)	40(25)	-27(24)
C2	12815(10)	896(3)	5515(3)	654(26)	571(38)	79(25)	-160(33)	15(28)
C3	12686(11)	1023(3)	6355(3)	784(30)	718(45)	-128(29)	-188(36)	189(33)
C4	16427(12)	755(3)	6703(4)	758(31)	1089(62)	-47(35)	-210(47)	4(39)
C5	13836(12)	544(4)	7539(3)	1038(41)	452(40)	-19(33)	-137(42)	-1(43)
C6	7853(9)	2743(2)	3882(2)	575(22)	291(26)	35(21)	22(24)	48(25)
C7	9345(9)	3367(3)	3782(3)	507(21)	722(39)	-1(26)	74(31)	-9(29)
C8	8964(13)	4170(3)	4009(4)	580(27)	821(49)	-76(29)	86(44)	-99(34)
C9	7185(14)	4371(3)	4334(3)	508(26)	663(47)	-236(29)	-133(45)	227(39)
C10	5642(11)	3756(4)	4450(3)	865(35)	657(42)	-183(31)	-23(36)	273(38)
C11	6016(10)	2950(3)	4226(3)	596(26)	498(35)	-41(25)	49(32)	-32(30)
C12	9151(9)	1634(2)	2606(2)	492(19)	351(27)	-31(22)	-6(25)	48(26)
C13	11139(11)	1450(3)	2368(3)	862(34)	364(31)	1(27)	-29(31)	93(32)
C14	11587(12)	1439(4)	1628(4)	1066(41)	581(43)	-135(35)	233(39)	92(39)
C15	9923(14)	1612(3)	1123(3)	797(32)	337(34)	33(29)	72(37)	-45(43)
C16	7948(13)	1819(4)	1337(4)	1296(52)	515(45)	55(36)	-68(40)	315(48)
C17	7572(10)	1834(3)	2070(3)	1050(39)	502(39)	19(31)	-23(33)	318(36)

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

	x	y	z
HO1	630(6)	76(2)	353(2)
H1A	1216(7)	141(2)	402(2)
H1B	1089(7)	66(2)	407(2)
H2A	1430(6)	110(2)	539(2)
H2B	1279(7)	38(2)	535(2)
H3A	1125(7)	84(2)	663(2)
H3B	1288(6)	169(2)	649(2)
H4A	1675(6)	69(2)	610(2)
H4B	1758(7)	34(2)	700(2)
H4C	1665(7)	134(2)	684(2)
H5A	1225(7)	34(2)	763(2)
H5B	1416(7)	112(2)	774(2)
H5C	1506(7)	13(2)	776(2)
H7	1081(6)	330(2)	352(2)
H8	996(6)	448(2)	392(2)
H9	715(7)	481(2)	452(2)
H10	433(7)	384(2)	456(2)
H11	490(6)	260(2)	430(2)
H13	1203(6)	128(2)	266(2)
H14	1288(7)	128(2)	150(2)
H15	1054(6)	172(2)	60(2)
H16	672(6)	197(2)	101(2)
H17	602(7)	203(2)	222(2)

difference Fourier synthesis based on the final parameters of all atoms (Tables 1 and 2) showed no peak higher than 0.36 e \AA^{-3} . The atomic

scattering factors used were those of International Tables for X-ray Crystallography.⁵ Lists of the final structure factors are available 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 thermal motion are given in Table 3. The C–H distances are in the range of 0.78–1.14 Å. The interatomic distances and angles are on the whole quite acceptable. However, the C2–C3 bond is somewhat too long and the bonds to the nitrogen atom are too short. Especially the C3–N distance (1.411 Å) deviates as much as 0.06 Å from the standard value.⁶ Because of these discrepancies as well as some rather short C–C distances in the phenyl rings a redetermination of the structure was performed. A new crystal was selected and the intensities were collected on another automatic diffractometer (Philips PW1100). In spite of this effort no improvement was achieved, on the contrary the abnormal dimensions were exaggerated and the *R*-value could not be brought below 0.095. No good explanation to the above mentioned inconsistencies has been found. An increased diffuse scatter around intense reflexions in the Weissenberg diagrams may indicate some kind of disorder in the crystals.

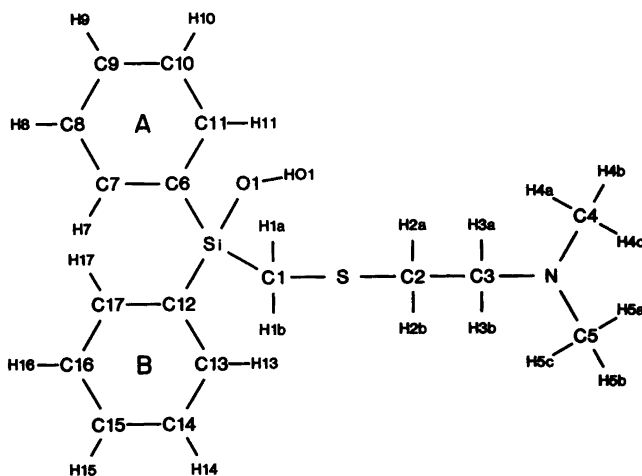


Fig. 1. The [2-(dimethylamino)ethylthiomethyl]diphenylsilanol molecule, showing the numbering scheme of the atoms.

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

Si-O1	1.609(3)	C7-C8	1.371(7)
Si-C1	1.865(5)	C8-C9	1.310(9)
Si-C6	1.881(4)	C9-C10	1.386(8)
Si-C12	1.872(5)	C10-C11	1.374(6)
C1-S	1.785(5)	C11-C6	1.360(7)
S-C2	1.784(6)	C12-C13	1.347(7)
C2-C3	1.561(7)	C13-C14	1.399(8)
C3-N	1.411(6)	C14-C15	1.369(9)
N-C4	1.445(7)	C15-C16	1.333(9)
N-C5	1.462(6)	C16-C17	1.376(8)
C6-C7	1.370(6)	C17-C12	1.378(7)
O1-Si-C1	112.1(2)	C6-C7-C8	120.9(6)
O1-Si-C6	105.4(2)	C7-C8-C9	121.8(6)
O1-Si-C12	111.1(2)	C8-C9-C10	119.2(5)
C1-Si-C6	110.1(2)	C9-C10-C11	119.4(6)
C1-Si-C12	108.2(2)	C10-C11-C6	121.4(5)
C6-Si-C12	110.0(2)	C11-C6-C7	117.4(4)
Si-C1-S	111.2(3)	Si-C12-C13	125.6(4)
C1-S-C2	102.8(3)	Si-C12-C17	118.9(4)
S-C2-C3	106.7(4)	C12-C13-C14	123.0(5)
C2-C3-N	112.0(4)	C13-C14-C15	118.5(6)
C3-N-C4	113.1(4)	C14-C15-C16	120.2(5)
C3-N-C5	111.4(5)	C15-C16-C17	119.7(6)
C4-N-C5	104.0(5)	C16-C17-C12	123.0(6)
Si-C6-C7	120.7(4)	C17-C12-C13	115.5(5)
Si-C6-C11	121.9(4)		

As seen in Table 3 the phenyl rings deviate from the regular hexagonal geometry of a benzene ring. The distortions of the phenyl rings are most pronounced in the bond angles C7-C6-C11 [117.4(4)°] and C17-C12-C13 [115.5(5)°]. This close up of the endocyclic angle

of the carbon atom which is attached to the silicon atom is a common feature in organosilicon compounds.^{7,8,9,10} Both phenyl rings are almost planar. The maximum deviation from the least-squares plane is -0.007(6) Å for the atom C6 in phenyl ring A and 0.015(9) Å for the atom C15 in

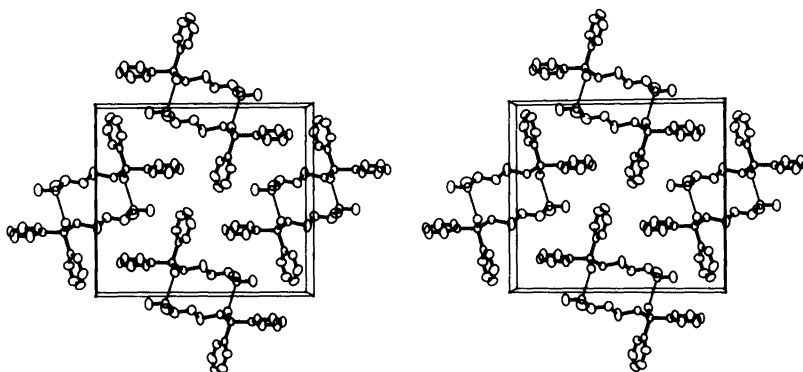


Fig. 2. Stereoview (ORTEP¹²) of the crystal structure. The drawing is essentially seen along *a*. Hydrogen bonds are shown as thin lines and for clarity the hydrogen atoms are omitted.

phenyl ring B. The angle between the phenyl rings is $86.9(6)^\circ$. The C1-S-C2-C3-N fragment is fully extended. The torsion angles Si-C1-S-C2, C1-S-C2-C3 and S-C2-C3-N are $178.1(3)$, $-177.2(3)^\circ$ and $168.0(4)^\circ$ respectively. The distance between the phenyl centre and the nitrogen atom is for rings A 7.9 \AA and for ring B 9.5 \AA . The packing of the molecules is shown in Fig. 2 which is a view down the *a* axis. Centrosymmetrically related molecules form dimers as they are linked to each other by O-H...N hydrogen bonds. The symmetry code for the N atom is $2-x, -y, 1-z$. The geometry of this bond is characterized by an O...N distance of $2.744(6) \text{ \AA}$, an O-H distance of $0.67(4) \text{ \AA}$, and an O-H...N angle of $161(2)^\circ$. The hydrogen bonding system in the present structure is very similar to that of sila-pridinol¹¹ where the molecules also form dimers.

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REFERENCES

1. Tacke, R. and Wannagat, U. *Fortschr. Chem. Forsch.* 84 (1979) 1.
2. Bergin, R. *Internal Report I/71*, Dept. of Medical Biophysics, Karolinska Institutet, Stockholm 1971.
3. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. and Woolfson, M. M. *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Univs. of York, England and Lovain-la-Neuve, Belgium 1980.
4. Sheldrick, G. M. *SHELX. Program for Crystal Structure Determination*, Univ. of Cambridge, England 1975.
5. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
6. Sutton, L. E., Ed., *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Suppl. 1956-1959, Special Publication No. 18, The Chemical Society, London 1965.
7. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr. B* 31 (1975) 221.
8. Párkányi, L. and Bocelli, G. *Cryst. Struct. Commun.* 7 (1978) 335.
9. Söderholm, M. *Acta Chem. Scand.* 38 (1984) 31.
10. Söderholm, M. and Carlström, D. *Acta Chem. Scand. B* 31 (1977) 193.
11. Tacke, R., Strecker, M., Sheldrick, W. S., Ernst, L., Heeg, E., Berndt, B., Knapstein, C.-M. and Niedner, R. *Chem. Ber.* 113 (1980) 1962.
12. Johnson, C. K. *ORTEP. Report ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge 1980.

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