Journal of Organometallic Chemistry, 327 (1987) 167–172
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Crystal and molecular structure of 1-(iododimethylsilylmethyl)piperidone-2

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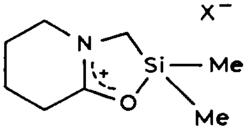
(Received December 25th, 1986)

Abstract

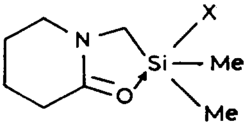
Crystal structure study of 1-(iododimethylsilylmethyl)piperidone-2 ($R = 0.018$ from 1665 reflections) was performed. A donor-acceptor Si ← I interaction, at a distance of 3.734(1) Å, was detected for the first time. The Si atom is distinguished by a distorted trigonal-bipyramidal coordination with O and I atoms in the axial positions.

Introduction

The crystal structure study of the representatives of a new class of penta-coordinated silicon derivatives recently synthesized by us [1], namely the 1-(halogenodimethylsilylmethyl)-piperidones-2, indicates that the corresponding bromide and chloride differ significantly in coordination of a Si atom. In chloride I the Si atom is penta-coordinated and its coordination can be described as [3 + 2] [2], whereas in the bromine derivative (II), Si coordination in the crystal is best described as [4 + 1] with an additional Si ← Br interaction [3].



(a)



(b)

(I : X = Cl ; II : X = Br ; III : X = I)

0022-328X/87/$03.50

There was uncertainty as to the form which the iodine derivative (III) could take in the crystal; either (a) ionic, with a tetrahedral Si or (b) neutral with a penta-coordinated silicon. Clarification of this necessitated an X-ray diffraction study of III.

Note that at present there is little or no data on Si derivatives containing a Si–I bond (except for the geometric parameters of trimethyliodosilane, obtained by microwave spectroscopy [4]).

Experimental

The colourless crystals of III are orthorombic: *a* 12.633(5), *b* 8.189(3), *c* 10.874(5) Å, *V* 1124.9(9) Å^3, d_{calc} 1.755 g.cm^{-3}, $Z = 4$ $C_8H_{16}INOSi$, space group $Pna2_1$. Cell parameters and intensities of 1712 independent reflections were measured on a four-circle automatic Syntex $P2_1$ diffractometer at −120 °C (Mo-K_α radiation, $\theta/2\theta$ scan, θ_{max} 30.5 °). Absorption effects were corrected for by the DIFABS program [5]. The structure was solved by a direct method (MULTAN) and refined by a block-diagonal least-squares method in an anisotropic approximation for non-hydrogen atoms. The positions of all the hydrogen atoms were found by difference synthesis and refined anisotropically. The final divergence factors $R = 0.018$, $R_w = 0.027$ for 1665 reflections with $I \geqslant 2\sigma$. All the computations were carried out on an Eclipse S/200 computer using the INEXTL programs [6]. Coordinates and temperature parameters of the atoms are listed in Table 1. The geometry of the molecule and the bond lengths are presented in Fig. 1 and bond angles are given in Table 2.

Results and discussion

The Si atom in the structure of III has a strongly distorted trigonal-bipyramidal coordination, with the C(1), C(2), and C(3) atoms in equatorial and O and I atoms in axial positions. Table 3 compares the main geometrical parameters of molecules

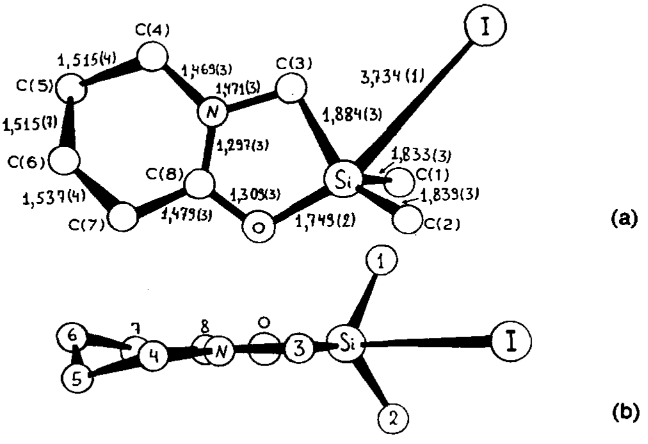


Fig. 1. Projection of molecule I (a) perpendicular to and (b) down the C(3)–N–C(8)–O plane.

TABLE 1

ATOMIC COORDINATES ($\times 10^5$ FOR I AND Si; $\times 10^4$ FOR O, N, AND C; $\times 10^3$ FOR H) AND THEIR EQUIVALENT ISOTROPIC (FOR H ATOMS ISOTROPIC) TEMPERATURE PARAMETERS

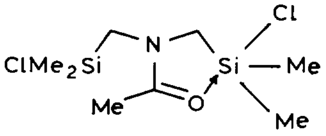
Atom	x	y	z	$B_{\mathrm{iso}}^{\mathrm{eq}}$ (Å^2)	Atom	x	y	z	$B_{\mathrm{iso}}^{\mathrm{eq}}$ (Å^2)
I	39132(1)	27195(2)	10000	1.30(0)	H(1.3)	703(3)	410(6)	−46(5)	3(1)
Si	60137(5)	20413(11)	−13612(9)	1.00(1)	H(2.1)	503(6)	42(7)	−259(7)	8(2)
O	7120(1)	1261(2)	−2129(2)	1.19(4)	H(2.2)	493(6)	264(5)	−314(7)	4(1)
N	7073(2)	−528(2)	−583(2)	0.89(4)	H(2.3)	428(5)	187(8)	−185(8)	4(1)
C(1)	6349(2)	4153(3)	−960(3)	1.42(5)	H(3.1)	627(3)	84(5)	60(4)	1.1(7)
C(2)	4883(2)	1758(4)	−2405(3)	1.49(5)	H(3.2)	549(3)	−58(5)	−3(4)	1.9(8)
C(3)	6166(2)	432(4)	−136(3)	0.98(5)	H(4.1)	744(3)	−152(5)	92(5)	2.7(8)
C(4)	7440(2)	−1920(3)	154(3)	1.26(5)	H(4.2)	686(3)	−284(4)	7(4)	0.9(7)
C(5)	8527(3)	−2505(3)	−238(4)	1.65(7)	H(5.1)	859(3)	−363(5)	10(4)	1.6(7)
C(6)	8615(3)	−2568(3)	−1626(4)	1.59(7)	H(5.2)	911(3)	−179(7)	6(5)	2.0(9)
C(7)	8433(2)	−856(3)	−2167(3)	1.24(5)	H(6.1)	799(3)	−341(6)	−195(4)	1.5(8)
C(8)	7514(2)	−36(3)	−1594(2)	0.80(4)	H(6.2)	941(7)	−324(10)	−215(8)	10(2)
H(1.1)	635(3)	492(5)	−177(4)	1.1(6)	H(7.1)	828(3)	−94(5)	−311(5)	2.7(9)
H(1.2)	580(4)	453(8)	−29(6)	6(2)	H(7.2)	908(3)	−9(7)	−196(4)	2.3(9)

TABLE 2

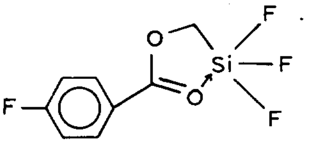
BOND ANGLES φ (°)

Angle	φ	Angle	φ
I-Si-O	161.90(7)	C(3)-N-C(4)	118.7(2)
I-Si-C(1)	82.99(9)	C(3)-N-C(8)	116.6(2)
I-Si-C(2)	83.7(1)	C(4)-N-C(8)	124.6(2)
I-Si-C(3)	71.97(9)	Si-C(3)-N	102.7(2)
O-Si-C(1)	105.9(1)	N-C(4)-C(5)	112.2(2)
O-Si-C(2)	106.3(1)	C(4)-C(5)-C(6)	111.0(3)
O-Si-C(3)	90.0(1)	C(5)-C(6)-C(7)	109.8(3)
C(1)-Si-C(2)	116.4(1)	C(6)-C(7)-C(8)	111.8(2)
C(1)-Si-C(3)	117.9(1)	O-C(8)-N	117.7(2)
C(2)-Si-C(3)	115.3(1)	O-C(8)-C(7)	111.7(2)
Si-O-C(8)	112.9(2)	N-C(8)-C(7)	123.6(2)

I-III with those of chloro-[(*N*-chlorodimethylsilylacetamido)methyl]dimethylsilane (IV) [11] and (4-fluorobenzoyloxymethyl)trifluorosilane (V) [12].



(IV)



(V)

That Si ← I interaction, if any, will be the weakest of the Si ← X interactions in compounds I-V, i.e., X = I, Br, Cl, F [13] is borne out by the fact that the Si ← I coordination bond in III (3.734(1) Å) exceeds the length of the covalent Si-I bond (2.46 Å in Me$_3$SiI [4]) by 51.8% and is only 0.3 Å smaller than the sum of the Van der Waals radii of the Si and I atoms (4.08 Å [14]).

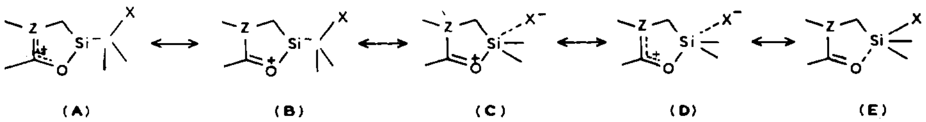
A weakening of the Si ← X interactions in the order V → I → IV, and a change from a strongly distorted trigonal-bipyramidal [4 + 1] coordination (V) to an almost undistorted [3 + 2] coordination (IV) of the Si atom is observed (Table 3). The transition IV → II → III involves further weakening of the Si ← X interaction and distortion of a nearly ideal trigonal-bipyramidal coordination of the Si atom to the "reverse" side to attain a [4 + 1] coordination in III. Accordingly, in the transition V → I → IV → II → III "a displacement" of the Si atom relative to the equatorial plane from X to O is observed (values of Δ are shown in Table 3). Weakening of the coordinative Si ← X interaction, consistent with hypervalent bonding considerations [13], involves a strengthening (contraction) of the second axial bond (Si-O). In fact, the Si-O bond in the crystal of III is the shortest (1.749(2) Å) of the Si-O bonds in compounds I-V. The bond angle (ω) between the axial substituents, shows a progressive decrease from 180° (and, accordingly, a progressive deviation from trigonal-bipyramidal geometry) on going from V → III. Also noteworthy is the appreciable deviation from 180° of ω in IV, where the Si atom has the least distorted trigonal-bipyramidal geometry. This deviation, and the inequality of the XSiC bond angles, is likely to be due to the different volumes of the equatorial Si atom substituents.

TABLE 3

MAIN GEOMETRIC PARAMETERS OF THE PENTACOORDINATED Si DERIVATIVES I–V WITH THE AXIAL X–Si–O FRAGMENT

Compound	III	II	IV	I	V
L [a]	1.749(2)	1.800(4)	1.918(3)	1.954(2)	2.029(2)
r [b]	3.734(1)	3.122(2)	2.348(2)	2.307(2)	1.606(2)
ΔL [c]	7.3	10.4	17.7	19.9	24.5
Δr [c]	51.8	41.3	15.7	13.3	3.6
ω [d]	161.90(7)	162.6(3)	170.3(2)	171.16(5)	176.0(1)
Δ [e]	0.348(1)	0.218(2)	−0.029	−0.058(2)	−0.199
Conformation of 5-membered cycle	Strongly flattened envelope	Envelope	Planar	Strongly flattened envelope	Planar
$d_1$max [f]	Si by 0.058(1)	C(8) by 0.20(2)	0.007	Si by 0.15(2)	C(8) by 0.058
Conformation of 6--membered cycle	Half-chair	Chair	–	Half-chair	–
$d_2$max [f]	C(5) by −0.34 C(8) by 0.40	(C5) by −0.81 C(8) by 0.28	–	C(5) by 0.42 C(6) by −0.36	–
m [g]	1.884(3)	1.862(9)	1.888(4)	1.890(3)	1.869(3)
n [g]	1.297(3)	1.342(8)	1.323(4)	1.315(2)	–
p [g]	1.309(3)	1.296(6)	1.266(4)	1.269(2)	–
Main canonical forms [h]	**A+D**	**A+D**	**A**	**A+E**	**B+E**
Refs.	This work	3	11	2	12

[a] L is the Si ← O bond length (Å). [b] r is the Si–X bond length (Å). [c] ΔL and Δr are increases in the Si–O and Si–X distances relative to those observed in the tetrahedral Si derivatives, respectively (%) [4,7–10]. [d] ω is the O–Si–X angle (degr); [e] Δ is the deviation of the Si atom from the plane of the equatorial atoms towards the O atom (Å). [f] $d_1$max and $d_2$max are the maximum deviations of the atoms from the planes of the 5- and 6-membered cycles, respectively (Å). [g] m, n, and p are the *endo*-Si–C, *endo*-C(8)–N, and C=O bond lengths, respectively (Å). [h] Canonical forms describing the structure of molecules I–V:



Z = O, N; X = F, Cl, Br, I (in V two equatorial positions are occupied by the F atoms)

Generally, the geometry of molecule III indicates that its structure, and that of molecule II, is best described as the resonance hybrid of the canonical forms **A** and **C** (when Z = N) with a partial positive charge on the N⩦C⩦O fragment and an additional Si ← X bond (see Table 3).

The five-membered "chelate" cycle $\overline{\mathrm{SiOC(8)NC(3)}}$ in III has a strongly flattened envelope conformation (the puckering parameters [15] Q 0.038 Å and ψ 303.8°). The Si atom deviates from the plane of the remaining four atoms of the cycle by 0.058(1) Å, which corresponds to the bend in the cycle along C(3)...O by only 2.6°. The five-membered cycle in molecules I and II also have an envelope conformation: in I the Si atom deviates from the plane of the remaining four atoms by 0.15 (2) Å and in II the C(8) atom deviates by 0.20(2) Å. In molecule V the cycle is planar and in V it has a flattened envelope conformation with maximum deviation of the C(8) atom of 0.058 Å.

The puckering parameters of the six-membered lactam cycle in III (Q 0.749 Å, θ 143.1°, ψ 242.2°) indicate that its conformation can be described as a half-chair, the C(5) and C(6) atoms deviate by -0.34 and 0.40 Å, respectively from the NC(4)C(7)C(8) plane (the maximum deviation of these atoms being 0.008 Å). In molecule II the lactam cycle is distorted more (Q 0.963 Å) and has a chair conformation. In molecule I the conformation and degree of distortion ($Q = 0.788$ Å) of the lactam cycle are very much the same as those in III.

No shortening of the intermolecular contacts in the crystal of III, as in the other structures I–V, is observed. The shortest distance between the I atom and the partial-charge bearing fragment NC(8)O of the adjacent molecule is I...C(8) $(\frac{1}{2}-x;\ -\frac{1}{2}+y;\ \frac{1}{2}+z)$ of 3.863(2) Å as compared with the sum of the Van der Waal's radii of 3.68 Å [14].

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