

## Direct evidence of the existence of organic derivatives of pentacoordinated silicon with the $\text{Si} \leftarrow \text{Cl}$ coordinate bond. Molecular structure of chloro[1-{1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazonium)methyl] dimethylsilane

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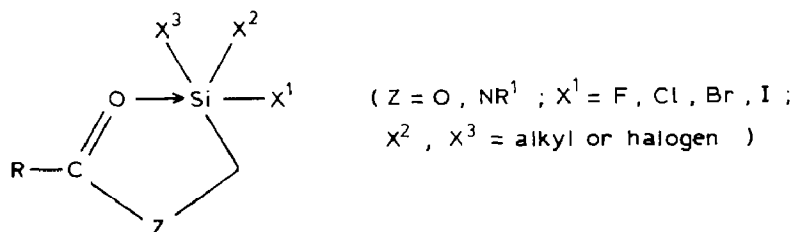
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### Abstract

An X-ray study of chloro[1-{1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazonium)methyl]dimethylsilane (I) has been carried out ( $R = 0.035$  for 2800 reflections). The Si atom, which has a trigonal-bipyramidal [4 + 1] coordination with the O and Cl atoms in axial positions ( $\text{Si}-\text{O}$  1.788(1) Å,  $\text{Si}-\text{Cl}$  2.624(1) Å), is markedly displaced from the equatorial plane towards the oxygen atom ( $\Delta_{\text{Si}}$  0.178 Å), which confirms that there is a coordinate bond between the silicon atom and chloride ion.

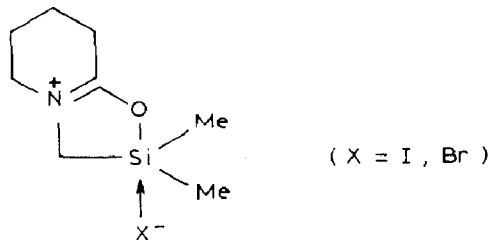
### Introduction

The pentacoordinated silicon in some (O–Si)-chelate derivatives, has trigonal-bipyramidal coordination and is displaced from the equatorial plane towards the axial substituent  $\text{X}^1$  [1], as was indicated by X-ray data. In terms of the Bürgi and Dunitz



approach [2] this means that in the axial moiety the Si-X<sup>1</sup> bond order ( $n$ ) is higher than that of Si-O. The stronger Si-X<sup>1</sup> ( $n > 0.5$ ) and the weaker Si-O ( $n < 0.5$ ) bonds may be regarded, although somewhat arbitrarily, as "covalent" and "coordinate" bonds respectively\*.

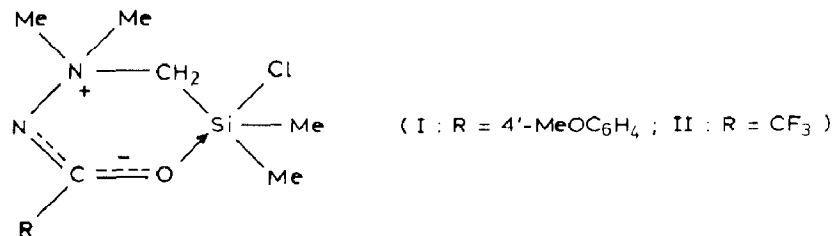
Our recent structural studies [5,6] of the iodo- and bromo-(*N*-piperidone-methyl)dimethylsilanes prove that in these molecules the Si-X rather than the Si-O



bond exhibits the donor-acceptor character. In this case the trigonal-bipyramidal silicon atom is displaced from the equatorial plane of the three carbon atoms towards the oxygen atom and consequently  $n(\text{Si-O}) > n(\text{Si-X})$ . According to the conductometric and NMR data [5,7] the Si-X bonds dissociate appreciably on dissolution, the ionization being more pronounced on cooling. Naturally, in the ionized species the Si atom is four-coordinated.

In chloro(*N*-piperidonemethyl)dimethylsilane the Si-Cl bond is "covalent" ( $n = 0.53$ ) and the Si-O bond has "coordinate" character ( $n = 0.47$ ) [8,9]. It seems quite natural that in such chelate complexes with the same carbofunctional substituent the decrease in atomic number of the halogen results in a stronger Si-X bond and a weaker coordination of the O atom in the second axial position [10,11]. It is one of the consequences of the hypervalency theory [3]. The weakening of the Si-Cl bond in the OSi(C<sub>3</sub>)Cl group and its transformation into the "coordinate" bond would require the strengthening of the bonding between the Si and O atoms.

We had the opportunity to observe this effect in the structure of the pentacoordinated silicon derivatives of a new type: chloro[1-(1,1-dimethyl-2-acylhydrazonium) methyl]dimethylsilanes I and II [12,13].



Even in the molecule of the 2-trifluoroacetyl derivative (II), in spite of high electron-accepting properties of the CF<sub>3</sub> group, the Si-O and Si-Cl bonds turned out to be the shortest and the longest, respectively, of those found in the derivatives

\* The inadequacy of these terms lies in the fact that the axial atoms are bonded to the Si atom not by a two-center (covalent and donor-acceptor), but by a hypervalent three-center four-electron bond [3]. The total bond order of the two components of the hypervalent bond (Si-X<sup>1</sup> and Si-O) is close to 1 [4].

of pentacoordinated silicon with trigonal-bipyramidal  $\text{OSiC}_3\text{Cl}$ , studied up to now by X-ray crystallography [14]. Analogues of II with less electronegative 2-acyl and 2-aroyl substituents should have even shorter Si–O and as a consequence longer Si–Cl bonds [13,14]. The coordinate nature of the Si–Cl bond was confirmed by NMR spectroscopy which also indicated the ready dissociation of 2-acetyl [12] and 2-aroyl [14] derivatives in solution.

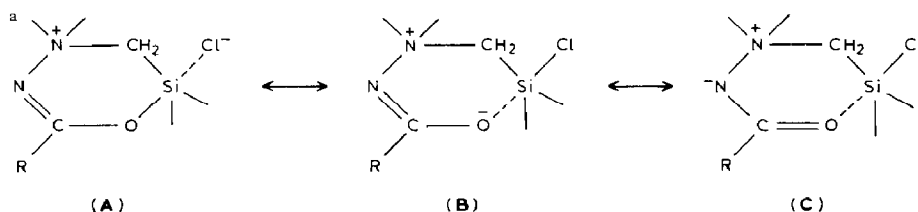
The “coordinate” character of the Si–Cl bond in one such compound, chloro[1-(1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazonium)methyl]dimethylsilane (I), was confirmed directly by the X-ray diffraction study described below.

## Results and discussion

The comparison of main molecular parameters of compounds I and II (Table 1) fully confirms the earlier assumptions [13,14] concerning the influence of the acyl substituent on the character of the coordinate interaction in molecules of chloro[1-(1,1-dimethyl-1-acylhydrazonium)methyl]dimethylsilanes. The silicon atom in I has a markedly distorted trigonal-bipyramidal geometry (Fig. 1, Tables 2–4): the O(1) and Cl atoms are located in axial positions and the three carbon atoms C(1), C(2) and C(6) are located in the equatorial plane. The O(1)SiCl angle  $173.80(5)^\circ$  differs significantly from the ideal value of  $180^\circ$ , whereas the equatorial angles CSiC ( $119.6(1)^\circ$ ,  $119.0(9)^\circ$  and  $118.6(9)^\circ$ ) are closer to the expected value of  $120^\circ$ . The

Table 1

Compound	I	II
Si–Cl bond length (Å) and bond order	2.624(1), 0.14	2.432(1), 0.33
Si–O bond length (Å) and bond order	1.788(1), 0.86	1.879(1), 0.61
OSiCl angle ( $^\circ$ )	173.80(5)	172.20(5)
C=O bond length (Å) and bond order	1.321(2), 1.16	1.289(2), 1.31
C=N bond length (Å) and bond order	1.289(2), 1.68	1.283(2), 1.72
Predominant resonance form <sup>a</sup> and coordination of Si atom	A, (4+1)	A + B (3+2)
Six-membered heterocycle conformation	boat: $\Delta(\text{O}(1))$ 0.378(1) Å $\Delta(\text{N}(2))$ 0.615(1) Å	boat: $\Delta(\text{O})$ 0.340(1) Å $\Delta(\text{N}(2))$ 0.677(2) Å
References	this work	1



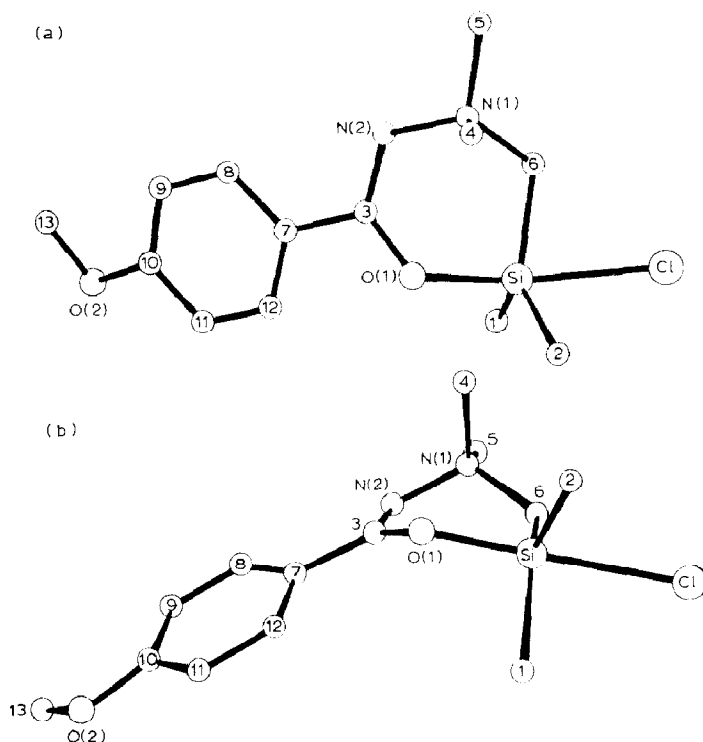


Fig. 1. The structure of chloro[1-{1,1-dimethyl-2-(4'-methoxybenzoyl)hydrazone}methyl]dimethylsilane (I) (H atoms are not shown): (a) projection onto the mean molecular plane, (b) projection, onto the plane perpendicular to the mean molecular plane, passing through the mid-points of the C(3)–N(2) and Si–C(6) bonds.

silicon atom is displaced from being in the plane of its neighbouring carbon atoms towards the O atom by 0.178(1) Å.

The Si–Cl bond length (2.624(1) Å) in I is substantially larger than the standard value (2.048 Å [15]) and is only smaller by 0.6 Å than the sum of the Van der Waals radii of the Si and Cl atoms, which indicates the “coordinate” character of the Si–Cl bond. The Si–O bond is only 0.1 Å longer than the standard Si–O bond (1.68 Å [16]) characteristic of the covalent compounds of the tetrahedral silicon atom. The Si–Cl bonds are longer by 0.192(2) Å and the Si–O bonds are shorter by 0.09(2) Å than in molecule II [14]. In line with suggestions by Pauling [17] this difference reflects the significant inequality of the Si–Cl and Si–O bond orders in molecule I (0.14 and 0.86, respectively, Table 1) which considerably exceeds the difference of the corresponding values in molecule II (0.33 and 0.61, respectively) in which the trigonal-bipyramidal Si atom [3 + 2] coordination of the Si atom is only slightly distorted ( $\Delta(\text{Si})$  0.078 Å) [14].

From the above data the pentacoordinated Si atom in I can be assigned the trigonal-bipyramidal [4 + 1] coordination. To our knowledge molecule I is the first compound with a coordinate Si←Cl bond to be structurally characterised.

Each of the corresponding bond lengths in the six-membered heterocycles of molecules I and II are quite close. Apart from the Si–O bond, the only other bond lengths with some differences are those in the NCO fragment. The most significant

Table 2

Atomic coordinates ( $\times 10^5$  for Cl, Si;  $\times 10^4$  for O, N, C; and  $\times 10^3$  for H) and equivalent isotropic (isotropic for H) temperature factors  $B(\text{\AA}^2)$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
Cl	18841(8)	79371(6)	45765(2)	3.18(2)
Si	27999(8)	101969(6)	39534(2)	1.69(2)
O(1)	3500(2)	11851(1)	3590(0)	2.17(5)
O(2)	946(2)	4856(2)	2581(1)	2.27(6)
N(1)	2744(2)	13004(2)	4537(1)	1.68(6)
N(2)	4389(2)	13603(2)	4236(1)	1.84(6)
C(1)	4979(3)	9019(2)	3795(1)	2.62(9)
C(2)	454(3)	9956(3)	3606(1)	2.57(9)
C(3)	4570(2)	12976(2)	3787(1)	1.69(7)
C(4)	838(3)	13567(2)	4308(1)	1.93(8)
C(5)	3005(3)	13703(2)	5064(1)	2.66(9)
C(6)	2757(3)	11262(2)	4588(1)	2.16(8)
C(7)	6160(2)	13571(2)	3455(1)	1.64(7)
C(8)	-2861(3)	4926(2)	3575(1)	2.43(8)
C(9)	-1270(3)	5408(2)	3289(1)	2.36(8)
C(10)	-657(2)	4532(2)	2874(1)	1.72(7)
C(11)	-1691(3)	3218(2)	2733(1)	2.48(8)
C(12)	6741(3)	12741(2)	3023(1)	2.21(8)
C(13)	2227(3)	6050(3)	2760(1)	2.9(1)
H(1.1)	555(3)	933(2)	348(1)	5.4(6)
H(1.2)	466(3)	795(3)	379(1)	6.1(6)
H(1.3)	601(3)	920(3)	406(1)	6.3(6)
H(2.1)	-11(3)	1070(3)	346(1)	0.3(7)
H(2.2)	-27(3)	912(3)	376(1)	0.3(7)
H(2.2)	-27(3)	912(3)	376(1)	8.3(7)
H(2.3)	60(3)	945(3)	331(1)	8.8(8)
H(3.1)	152(2)	1103(2)	480(1)	2.4(4)
H(3.2)	389(2)	1102(2)	479(1)	2.8(5)
H(4.1)	25(2)	678(2)	546(1)	2.4(4)
H(4.2)	90(2)	1466(2)	431(1)	2.9(5)
H(13.3)	333(3)	607(3)	251(1)	7.1(6)
H(4.3)	63(2)	1316(2)	394(1)	2.4(4)
H(5.1)	296(2)	1488(2)	502(1)	3.3(5)
H(5.2)	190(2)	1330(2)	527(1)	2.7(4)
H(5.3)	434(2)	1337(2)	521(1)	2.8(4)
H(8)	668(2)	1550(2)	386(1)	2.6(4)
H(9)	-63(3)	633(2)	338(1)	3.6(5)
H(11)	-129(3)	267(2)	245(1)	2.9(5)
H(12)	606(2)	1178(2)	293(1)	2.5(4)
H(13.1)	150(3)	715(2)	274(1)	5.8(6)
H(13.2)	268(3)	592(2)	313(1)	4.8(5)

difference is observed between the C(3)=O(1) bond lengths (1.321(2) Å in I and 1.289(2) Å in II), however that of I is only 0.039 Å smaller than the standard C( $sp^2$ )-O bond length [18]. The N=C bond lengths (1.289(2) Å in I and 1.283(2) Å in II) are in fact equal. These bonds are markedly shorter than the single N-C( $sp^2$ ) bonds (1.43 Å [19]). The C=O and N=C bond orders, which were calculated by use of a method taken from ref. 20, are equal to 1.16 and 1.68 in molecule I and 1.31 and 1.72 in molecule II, respectively.

Table 3

Bond lengths  $d$  (Å)

Bond	$d$	Bond	$d$
Cl–Si	2.6241(8)	N(1)–C(6)	1.523(2)
Si–O(1)	1.788(1)	N(2)–N(1)	1.470(2)
Si–C(1)	1.856(2)	N(2)–C(3)	1.289(2)
Si–C(2)	1.849(2)	C(3)–C(7)	1.487(2)
Si–C(6)	1.885(2)	C(7)–C(8)	1.390(2)
O(1)–C(3)	1.321(2)	C(7)–C(12)	1.392(3)
O(2)–C(10)	1.366(2)	C(8)–C(9)	1.387(3)
O(2)–C(13)	1.432(3)	C(9)–C(10)	1.386(3)
N(1)–C(4)	1.504(2)	C(10)–C(11)	1.391(3)
N(1)–C(5)	1.500(2)	C(11)–C(12)	1.378(3)

Although the N=C=O fragment bonded to the aryl group is almost coplanar with it (the angle is  $15.14^\circ$ ) there is little to indicate  $\pi$ -electron conjugation between them. The C(3)–C(7) bond length (1.487(2) Å) is close to the standard value for the single C( $sp^2$ )–C( $sp^2$ ) bond (1.476 Å) [21]. The endocyclic angle at the C(3) atom is  $127.1(2)^\circ$  in I and  $131.3(2)^\circ$  in II.

Thus the obtained data show that the lower electron-accepting ability of aryl substituent in molecule I compared with trifluoromethyl group in II ensures a more pronounced localization of  $\pi$ -electrons on the N=C bond, and hence an increase in the  $\sigma$ -donor ability of the O atom, and therefore its stronger bonding with the Si atom in molecule I than in molecule II. As a result the transfer of the electron density from the O to the Si atom in the axial fragment of molecule I becomes more pronounced, the Si–Cl bond becomes weaker and acquires more distinct “coordinate” character.

The bond length distribution in molecule I (Table 1) suggests that its structure may be represented as the canonical forms **A** and **B**, but tending more to **A** than to **B**. The geometry of molecule II is best represented as three forms, **A**, **B** and **C**, with the hybrid tending to lie between **A** and **B**, and less so between **B** and **C**.

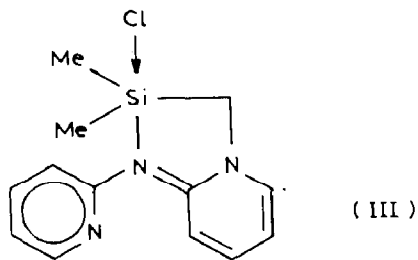
The puckering parameters [22] of the six-membered heterocycle in I ( $Q$  0.797 Å,  $\theta$   $103.1^\circ$ ,  $\psi$   $202.5^\circ$ ) suggest a somewhat distorted boat conformation with a displacement of the O(1) and N(2) atoms from the N(1)C(6)SiC(3) plane by 0.378(1) and 0.615(1) Å respectively. The planes N(1)N(2)C(3) and C(6)O(1)Si, are at dihedral angles of  $48.19$  and  $32.06^\circ$ , respectively, to the plane of the bottom of the boat. The folding angle of the six-membered cycle along the N(2)...O(1) line is  $42.1^\circ$ . In general the bond lengths in the N(2)–N(1)–C(6)–Si moiety of I, within experimental error, are equal to the corresponding bond lengths in molecule II.

In crystal I no shortened intermolecular contacts are observed.

Thus, of all the derivatives having a pentacoordinated Si atom in the OSi(C)<sub>3</sub>Cl moiety [8,9,14,23,24] our molecule I has an unprecedentedly long Si–Cl bond with pronounced “coordinate” character. In addition in molecule I was found to have the second shortest Si–O bond of these compounds. The shortest Si–O bond was observed in iodo[*N*-(piperidone)methyl]dimethylsilane.

Compound I, together with other six-membered heterocyclic chloro [1-(1,1-dimethyl-2-acylhydrazonium)methyl]dimethylsilanes [12,13] and compound III [25]

belong to previously unknown class of derivatives of the penta-coordinated Si atom with a "coordinate" Si ← Cl bond.



## Experimental

Synthesis and physico-chemical characteristics of I have been reported previously [13]. Single crystals suitable for an X-ray diffraction study were isolated by recrystallization from the hexane-chloroform mixture (1/3).

The crystals of I are colourless monoclinic:  $a$  6.821(1),  $b$  8.712(2),  $c$  25.851(6) Å,  $\beta$  90.72(2)°,  $V$  1536.1(2) Å<sup>3</sup>,  $d_{\text{calc}}$  1.240 g cm<sup>-3</sup>,  $Z = 4$  (C<sub>13</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>Si), space group  $P2_1/n$ . Unit cell parameters and intensities of 3217 independent reflections were measured with a four-circle "Syntex P2<sub>1</sub>" automatic diffractometer at 153 K ( $\lambda$  Mo- $K_{\alpha}$ ,  $\theta/2\theta$ -scan,  $\theta_{\text{max}}$  30°). The structure was solved by the direct method using the MULTAN program [26], and refined anisotropically by block-diagonal least squares for non-hydrogen atoms. H atoms located in the difference synthesis were refined isotropically. Final discrepancy factors are  $R = 0.035$  and  $R_w = 0.030$  for a total of 2800 reflections with  $I \geq 2 \sigma(I)$ . All calculations were carried out using INEXTL programs [27] with an "Eclipse S/200" computer. The atomic coordinates and temperature factors are given in Table 2.

Table 4

Bond angles  $\omega$  (°)

Angle	$\omega$	Angle	$\omega$
C1SiO(1)	173.80(5)	C(4)N(1)C(5)	108.5(1)
C1SiC(1)	85.30(7)	N(1)N(2)C(3)	114.1(1)
C1SiC(2)	80.08(7)	SiC(6)N(2)	114.6(1)
C1SiC(6)	80.15(6)	O(1)C(3)N(2)	127.1(2)
O(1)SiC(1)	96.30(8)	N(2)C(3)C(7)	116.9(2)
O(1)SiC(2)	96.28(8)	C(1)C(3)C(7)	116.0(1)
O(1)SiC(6)	93.87(7)	C(3)C(7)C(8)	121.2(2)
C(1)SiC(2)	119.65(9)	C(3)C(7)C(12)	120.0(2)
C(1)SiC(6)	119.02(9)	C(8)C(7)C(12)	118.7(2)
C(2)SiC(6)	118.62(9)	C(7)C(8)C(9)	121.0(2)
SiO(1)C(3)	123.0(1)	C(8)C(9)C(10)	119.5(2)
C(10)O(2)C(13)	117.4(2)	O(2)C(10)C(9)	124.5(2)
N(2)N(1)C(4)	109.7(1)	O(2)C(10)C(11)	115.6(2)
N(2)N(1)C(5)	104.7(1)	C(9)C(10)C(11)	119.9(2)
N(2)N(1)C(6)	113.3(1)	C(10)C(11)C(12)	120.0(2)
C(6)N(1)C(4)	111.3(1)	C(7)C(12)C(11)	120.7(2)
C(6)N(1)C(5)	109.0(1)		

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