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The molecular structure of 1-phenylsilatranone

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Abstract

The crystal structure of 1-phenylsilatranone ($C_6H_5\overset{\leftarrow}{Si}(OCOCH_2)(OCH_2CH_2)_2\vec{N}$) was determined from X-ray diffraction studies. The asymmetric unit (space group $Pna2_1$) is built up of two molecules ($Z = 8$) with different Si←N dative bonds of 2.126(3) and 2.111(3) Å. A CNDO/2 calculation was performed with *spd* base and the results were compared with those obtained for other silatrane and silatranone molecules. Wiberg indices for the transannular donor–acceptor bonds are in linear correlation with the Si←N distances and they fall in the range of 0.33–0.45.

Introduction

Structural studies on silatrane molecules substituted by CO groups in the silatrane skeleton (2,8,9-trioxa-5-aza-1-sila-tricyclo[3.3.3.0^{1,5}]undecane-3-ones, silatranones) involved five X-ray structure determinations (Table 1). Comparison of the molecular geometries with those of the analogous silatranes, showed that the Si←N dative bond had been shortened. This shortening was attributable to the electron-withdrawing effect of the carbonyl groups.

Here we report on the molecular structure of the simplest aryl-substituted silatranone to investigate the effect of the carbonyl group on the molecular geometry by comparison with those of the analogous silatranes [8–10]. CNDO/2 calculations revealed variations in the partial charges.

Experimental

Synthesis

The compound was synthesized by a published method [11]. KOH was used as catalyst. The compound was recrystallized from ethanol.

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Table 1

Some geometrical data of silatranones, $RSi(OCOCH_2)(OCH_2CH_2)_2N$ (Å)

R	Si←N	Si←N [a]	Si–C	Si–O(C=O)	O–C(=O)	Ref.
p-FC_6H_4	2.129(3)	–	1.885(3)	1.718(2)	1.329(4)	[1]
m-$CF_3C_6H_4$	2.106(3)	–	1.884(4)	1.722(4)	1.336(5)	[1]
$ClCH_2$	2.085(3)	2.120 [5]	1.881(5)	1.707(3)	1.330(5)	[2]
$Cl(CH_2)_3$	2.149(5)	2.181 [6]	1.863(7)	1.718(4)	1.320(7)	[3]
CH_3 [b]	2.146(7)	2.175 [7]	1.84	1.702	1.335	[4]
				1.699	1.330	

[a] Si←N distance in the analogous silatrane molecule. [b] Silatrane-dione.

Table 2

Atomic coordinates for the non-hydrogen atoms (second lines refer to molecule 2) B_{eq} (Å^2) is defined as $B_{eq} = 4/3(\text{trace } B \cdot G)$ where B is the thermal motion tensor and G is the direct metric tensor

Atom	x/a	y/b	z/c	B_{eq}
Si(1)	0.28906(3)	0.16562(8)	0.7354(0)	3.17(3)
	0.53576(3)	0.27639(7)	0.0151(1)	3.03(3)
O(2)	0.25492(7)	0.0504(1)	0.6571(2)	3.8(1)
	0.51271(7)	0.1406(1)	0.0679(2)	3.39(9)
O(8)	0.26264(8)	0.2979(1)	0.7199(3)	4.3(1)
	0.50101(8)	0.3922(1)	0.0707(3)	4.2(1)
O(9)	0.33206(7)	0.1334(2)	0.8731(2)	3.91(9)
	0.57666(7)	0.2834(2)	−0.1313(2)	3.83(9)
O(12)	0.18392(9)	−0.0622(2)	0.6435(3)	5.7(1)
	0.46076(8)	−0.0140(2)	0.0309(3)	5.4(1)
N(5)	0.23356(9)	0.1444(2)	0.9169(3)	3.5(1)
	0.47800(9)	0.2583(2)	−0.1581(3)	3.3(1)
C(3)	0.2086(1)	0.0132(3)	0.7090(4)	4.0(1)
	0.4784(1)	0.0773(2)	−0.0153(4)	3.7(1)
C(4)	0.1900(4)	0.0773(3)	0.8508(4)	4.4(1)
	0.4649(1)	0.1321(3)	−0.1678(4)	3.4(1)
C(6)	0.2193(1)	0.2660(3)	0.9622(4)	4.3(1)
	0.4339(1)	0.3295(3)	−0.1009(4)	4.4(1)
C(7)	0.2204(1)	0.3378(3)	0.8153(5)	5.0(1)
	0.4574(1)	0.4339(3)	−0.0162(5)	5.3(1)
C(10)	0.3182(1)	0.1201(3)	1.0327(4)	4.7(1)
	0.5603(1)	0.2705(3)	−0.2903(4)	4.6(1)
C(11)	0.2618(1)	0.0771(3)	1.0381(4)	4.5(1)
	0.5029(1)	0.3054(3)	−0.3001(4)	4.5(1)
C(13)	0.3380(1)	0.1777(2)	0.5769(4)	3.4(1)
	0.5867(1)	0.2859(2)	0.1729(4)	3.2(1)
C(14)	0.3567(1)	0.2845(3)	0.5234(5)	4.5(1)
	0.6115(1)	0.3936(2)	0.2038(4)	3.7(1)
C(15)	0.3958(1)	0.2932(3)	0.4128(4)	5.7(1)
	0.6522(1)	0.4038(3)	0.3089(4)	4.5(1)
C(16)	0.4174(1)	0.1928(4)	0.3522(4)	6.1(1)
	0.6697(1)	0.3044(3)	0.3866(4)	5.0(1)
C(17)	0.3998(1)	0.0850(3)	0.4002(4)	5.6(1)
	0.6461(1)	0.1986(3)	0.3605(5)	5.2(1)
C(18)	0.3606(1)	0.0768(3)	0.5090(4)	4.4(1)
	0.6046(1)	0.1895(3)	0.2572(4)	4.1(1)

X-ray structure analysis

Crystal data. $C_{12}H_{15}NO_4Si$, Fwt.: 265.3 a.m.u., a 25.578(3), b 11.304(2), c 8.623(1) Å (from single crystal diffractometry), V 2493.2(10) Å^3, space group $Pna2_1$ (from systematic absences), $Z = 8$, $F(000) = 1120$, D_{calc} 1.414 g cm^{-3}, μ(Cu-$K_{\bar{\alpha}}$) 17.3 cm^{-1} (λ 1.5418 Å).

Data collection, structure determination and refinement. A colourless needle-shaped crystal of approx. 0.08 × 0.13 × 0.28 mm was used for the measurement of intensity data. The intensity data collection was performed on an Enraf–Nonius CAD-4 computer-controlled four-circle single crystal diffractometer with graphite-monochromated Cu-$K_{\bar{\alpha}}$ radiation. 2352 non-zero reflections were measured in the range $3 < 2\theta < 150°$ using θ—2θ scan technique.

The structure was solved by direct methods (MULTAN, [12]) and Fourier techniques. Non-hydrogen atomic parameters were refined by full-matrix anisotropic least-squares. Positions of hydrogen atoms were generated from assumed geometries (C–H 0.95 Å). Hydrogen atoms were included in structure factor calculations with isotropic temperature factors derived from the B_{eq} values of the

Table 3

Atomic coordinates and isotropic B values (Å^2) for the hydrogen atoms (second lines refer to molecule 2)

Atom	x/a	y/b	z/c	B
H(4a)	0.163	0.130	0.823	5.4
	0.485	0.096	−0.248	4.4
H(4b)	0.178	0.022	0.925	5.4
	0.429	0.123	−0.188	4.4
H(6a)	0.244	0.296	1.035	5.3
	0.413	0.284	−0.032	5.4
H(6b)	0.185	0.267	1.007	5.3
	0.413	0.356	−0.185	5.4
H(7a)	0.225	0.419	0.840	6.0
	0.432	0.468	0.052	6.3
H(7b)	0.188	0.328	0.761	6.0
	0.469	0.492	−0.089	6.3
H(10a)	0.321	0.194	1.085	5.7
	0.565	0.191	−0.322	5.6
H(10b)	0.341	0.064	1.081	5.7
	0.581	0.321	−0.355	5.6
H(11a)	0.247	0.092	1.137	5.5
	0.500	0.389	−0.304	5.5
H(11b)	0.260	−0.005	1.017	5.5
	0.487	0.272	−0.390	5.5
H(14)	0.342	0.355	0.564	4.4
	0.600	0.462	0.151	4.2
H(15)	0.407	0.369	0.379	4.4
	0.668	0.479	0.328	4.2
H(16)	0.445	0.198	0.277	4.4
	0.698	0.310	0.458	4.2
H(17)	0.415	0.015	0.358	4.4
	0.658	0.130	0.414	4.2
H(18)	0.348	0.001	0.539	4.4
	0.588	0.115	0.244	4.2

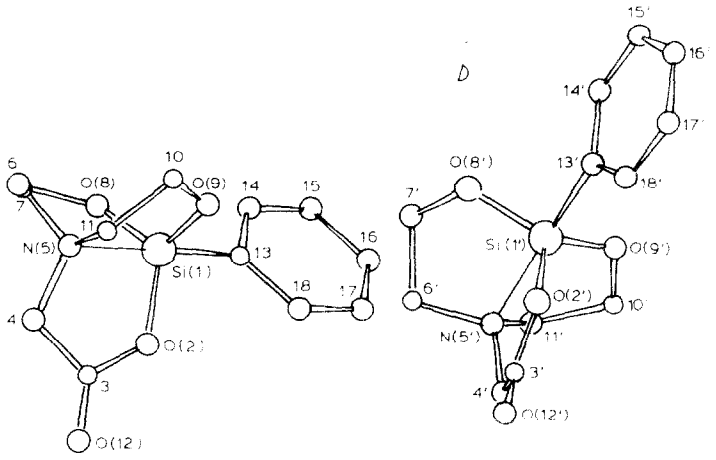

Fig. 1. A diagram of the 1-phenylsilatranone molecule.

carbon atoms to which they are bonded ($B_H = B_{eq(o)} + 1$ (Å^2)). No hydrogen atomic parameters were refined. 2291 observarions ($F_o^2 \geq 3\sigma(F_o^2)$) were used in least-squares. At the end of the isotropic refinement an empirical absorption correction [13] was applied (the minimum, maximum and average absorption corrections were 0.84, 2.25 and 1.00 respectively). Final atomic coordinates for the non-hydrogen atoms are listed in Tables 2 and 3 *. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 14.

Discussion

The asymmetric unit consists of two independent molecules (Fig. 1). The dative Si←N bond lengths in the two molecules differ by more than the 3σ limit (2.126(3) and 2.111(3), Δ 0.015 Å, Table 4), their mean value is 2.119(8) Å. This might be a consequence of the slight conformational differences in the silatranone skeletons due to the intramolecular motion (ring inversion) of the fused N–C–C–O–Si five-membered rings. Ring inversion sometimes results in different isolable crystallographic modifications such as those of 1-phenylsilatrane [8–10].

The Si–O(C=O) bonds (1.707(2) Å, 2 ×) are 0.157 Å longer than the average of Si–O(C–C) bond (1.650(4) Å) and is a typical feature of the silatranones [1–4]. The mean O–C bond distances for the two kinds of O–C bond are 1.338(4) Å (O–C(=O)) and 1.431(4) Å (O–C(–C)).

There is a significant difference in the Si–C_{Ar} bond lengths (Δ 0.027 Å), the shorter bond (1.859(3) Å) belongs to the molecule with the weaker Si←N interaction (Si←N 2.126(3) Å). A strong donor–acceptor interaction presumably reduces the multiple-bond character of the Si–C_{Ar} bond.

The deviation of the silicon atoms from the plane formed by the three equatorial oxygen atoms (ΔSi) and the distance of the nitrogen atoms from the plane of their

* Lists of observed and calculated structure factors and anisotropic temperature factors may be obtained from the authors.

Table 4

Bond lengths (Å) and angles (°) in the silatranone moiety (second lines refer to molecule 2)

Si(1)–O(2)	1.707(2)	O(2)–C(3)	1.334(4)	N(5)–C(6)	1.474(5)
	1.707(2)		1.341(4)		1.471(4)
Si(1)–O(8)	1.646(2)	O(8)–C(7)	1.431(4)	N(5)–C(11)	1.481(5)
	1.653(2)		1.423(4)		1.479(5)
Si(1)–O(9)	1.659(2)	O(9)–C(10)	1.429(5)	C(3)–C(4)	1.499(6)
	1.641(2)		1.441(4)		1.494(5)
Si(1)–N(5)	2.126(3)	O(12)–C(3)	1.202(4)	C(6)–C(7)	1.505(6)
	2.111(3)		1.194(4)		1.513(6)
Si(1)–C(13)	1.859(3)	N(5)–C(4)	1.463(4)	C(10)–C(11)	1.524(5)
	1.886(3)		1.467(4)		1.522(5)
O(2)–Si(1)–O(8)	116.8(2)	N(5)–Si(1)–C(13)	177.7(2)	C(6)–N(5)–C(11)	114.4(5)
	116.7(2)		177.5(2)		114.2(5)
O(2)–Si(1)–O(9)	117.1(2)	Si(1)–O(2)–C(3)	124.2(4)	O(2)–C(3)–O(12)	122.2(6)
	117.9(2)		124.3(4)		122.0(5)
O(2)–Si(1)–N(5)	82.2(2)	Si(1)–O(8)–C(7)	123.4(4)	O(2)–C(3)–C(4)	113.8(5)
	81.9(2)		122.1(4)		113.6(5)
O(2)–Si(1)–C(13)	96.3(2)	Si(1)–O(9)–C(10)	123.2(4)	O(12)–C(3)–C(4)	124.0(6)
	95.6(2)		122.8(4)		124.4(5)
O(8)–Si(1)–O(9)	122.0(2)	Si(1)–N(5)–C(4)	106.2(4)	N(5)–C(4)–C(3)	109.1(5)
	121.8(2)		107.1(3)		107.5(5)
O(8)–Si(1)–N(5)	83.6(2)	Si(1)–N(5)–C(6)	104.8(3)	N(5)–C(6)–C(7)	106.0(5)
	84.6(2)		104.3(4)		106.5(5)
O(9)–Si(1)–N(5)	83.8(2)	C(4)–N(5)–C(6)	113.5(5)	O(9)–C(10)–C(11)	107.4(5)
	84.6(2)		112.1(5)		107.8(5)
O(9)–Si(1)–C(13)	95.5(2)	C(4)–N(5)–C(11)	112.3(4)	N(5)–C(11)–C(10)	106.0(5)
	96.4(2)		113.6(5)		106.0(5)
O(8)–Si(1)–C(13)	98.6(2)	Si(1)–N(5)–C(11)	104.6(4)	O(8)–C(7)–C(6)	109.1(5)
	96.7(2)		104.4(4)		107.9(5)

substituent carbon atoms (ΔN) are presented below:

Deviation of atom	Molecule 1	Molecule 2
ΔSi (Å)	0.198(1)	0.182(1)
ΔN (Å)	0.386(3)	0.388(3)

Significant differences in the ΔSi values indicate that the stronger the Si←N interaction, the more complete the formal sp^3d hybridization of the silicon atom. The configuration around the nitrogen atom is unchanged showing that the ΔN values are a less better measure of donor–acceptor interaction.

A number of semi-empirical calculations for silatrane molecules has been published. A CNDO/2 calculation with *spd* base was, thus, carried out for the phenylsilatranone molecule using the atomic coordinates of molecule 1. Net atomic charges are listed in Table 5. The experimental Si←N distances and the net atomic charges of Si, N and the carbon atoms in α position to the oxygen atoms were compared with those in other molecules (methylsilatrane, β-phenylsilatrane and methylsilatrane-dione) (Table 6). Both in alkyl- and aryl-substituted silatranes, and in silatranones, the partial positive charge of silicon decreases and the partial negative charge of nitrogen increases with lengthening of the Si←N dative bond.

Table 5

Net atomic charges in phenylsilatranone

Si	0.4591	C(7)	0.1415	C(13)	−0.1076
O(2)	−0.3195	O(8)	−0.2951	C(14)	0.0535
C(3)	0.4082	O(9)	−0.2965	C(15)	−0.0250
C(4)	−0.0068	C(10)	0.1396	C(16)	0.0248
N	−0.0836	C(11)	0.0591	C(17)	0.0206
C(6)	0.0625	O(12)	−0.3266	C(18)	0.0506

Table 6

Net atomic charges of Si, N, and C_α in some silatranones and analogous silatranes

	Si←N (Å)	Si	N	C_α	Ref.
$CH_3Si(OCOCH_2)_2(OCH_2CH_2)N$	2.146	0.51	−0.08	0.41; 0.42	[4]
$CH_3Si(OCH_2CH_2)_3N$	2.175	0.4828	−0.0903	0.1566 [a]	This work
$C_6H_5Si(OCOCH_2)(OCH_2CH_2)_2N$	2.119	0.4591	−0.0836	0.4082	This work
β-$C_6H_5Si(OCH_2CH_2)_3N$	2.156	0.4553	−0.0899	0.1505 [a]	[15]

[a] Mean values.

Introducing the electron-withdrawing C=O group into the silatrane moiety (to give a silatranone), substantially increases the positive charge on the carbonyl carbon atom with respect to the CH_2 carbon of silatranes. The negative partial charge of the oxygen atom linked to the C=O group also increases:
methylsilatrane-dione: −0.29 → −0.32
phenylsilatranone: −0.2965; −0.2951 → −0.3155.

The calculated Wiberg indices (i/Si←N) [16,17] and the experimentally determined Si←N bond distances are in linear correlation ($i = -0.616d + 1.705$, $r = -0.969$) (Table 7, Fig. 2). The Wiberg indices fall in the range 0.33–0.45 and their magnitudes indicate considerable interactions between the silicon and the nitrogen atom.

Table 7

i(Si←N) Wiberg indices of silatranes $RSi(OCH_2CH_2)_3N$

R	d(Si←N) (Å)	i(Si←N)
Cl	2.023	0.453
F	2.042	0.459
2-furyl	2.112	0.402
C_6H_5 [a]	2.119	0.404
$ClCH_2$	2.120	0.376
γ-C_6H_5	2.132	0.394
β-C_6H_5	2.156	0.376
p-$CH_3C_6H_4$	2.169	0.379
CH_3	2.175	0.368
γ-$Cl(CH_2)_3$	2.181	0.368
α-C_6H_5	2.193	0.350
C_2H_5	2.215	0.336

[a] $C_6H_5Si(OCOCH_2)(OCH_2CH_2)_2N$.

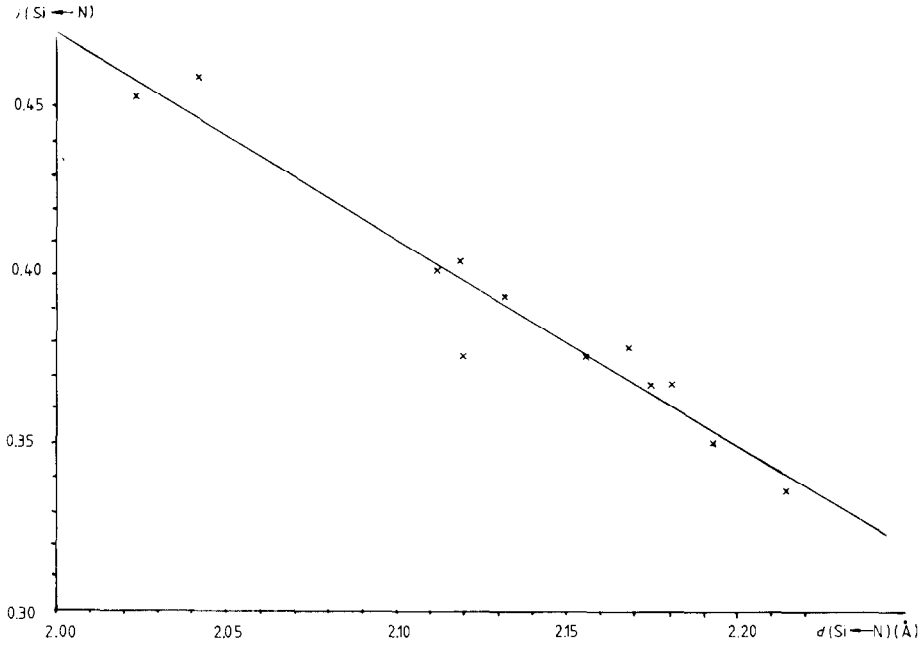

Fig. 2. The correlation of i(Si←N) Wiberg indices to d(Si←N) distances in silatranes.

These calculations also substantiate the fact that the simple bonding model of silatranes based on electron-withdrawing and releasing effects are reasonable and by use of structural correlations, they can be of predictive value.

References

1 L. Párkányi, P. Hencsei and E. Popowski, J. Organomet. Chem., 197 (1980) 275.
2 Dai Jinbi, Zhang Jiping, Wu Yexin and Wu Guanli, Jiegou Huaxue, 2 (1983) 207.
3 Dai Jinbi, Zhang Jiping and Wu Yexin, Jiegou Huaxue, 2 (1983) 107.
4 A. Kemme, J. Bleidelis, A. Lapsina, M. Fleisher, G. Zelčans and E. Lukevics, Latv. PSR Zinát. Akad. Véstis, Kim. Ser., (1985) 242.
5 A.A. Kemme, Ya.Ya. Bleidelis, V.M. Dyakov and M.G. Voronkov, Zhurn. Strukt. Khim., 16 (1975) 914.
6 A.A. Kemme, Ya.Ya. Bleidelis, V.M. Dyakov and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2400.
7 L. Párkányi, L. Bihátsi and P. Hencsei, Cryst. Struct. Comm., 7 (1978) 435.
8 J.W. Turley and F.P. Boer, J. Amer. Chem. Soc., 90 (1968) 4026.
9 L. Párkányi, K. Simon and J. Nagy, Acta Crystallogr., B30 (1974) 2328.
10 L. Párkányi, J. Nagy and K. Simon, J. Organomet. Chem., 101 (1975) 11.
11 E. Popowski, M. Michalik and H. Kelling, J. Organomet. Chem., 88 (1975) 157.
12 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declerq and M.M. Woolfson, MULTAN 78, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data (Universities of York (Great Britain) and Leuven (Belgium)).
13 N. Walker and D. Stuart, Acta Crystallogr., A39 (1983) 158.
14 D.T. Cromer and J.T. Waber, International Tables for X-Ray Crystallography, Vol. IV, Tables 2.2B and 2.3.1, The Kynoch Press, Birmingham, England (1974).
15 P. Hencsei and G. Csonka, Acta Chim. Acad. Sci. Hung., 106 (1981) 285.
16 P. Hencsei and J. Nagy, Proc. 10th Conf. Coord. Chem., Smolenice, 1985, p. 141.
17 Zhu Jin-Chang, Wu Hua-Ju, Li-Chin Chiang, G.J. Martin, Chen Pang-Chin, Wu Guan-Li and Lai Zhu-Gen, J. Chim. Phys., 81 (1984) 407.