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Molecular Structures of Enantiomerically-Pure (*S*)-2-(Triphenylsilyl)- and (*S*)-2-(Methyldiphenylsilyl)pyrrolidinium Salts

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Abstract: Silyl-substituted pyrrolidines have gained increased interest for the design of new catalyst scaffolds. The molecular structures of four enantiomerically-pure 2-silylpyrrolidinium salts are reported. The perchlorate salts of (*S*)-2-(triphenylsilyl)pyrrolidine [(*S*)-**1**·$HClO_4$] and (*S*)-2-(methyldiphenylsilyl)pyrrolidine [(*S*)-**2**·$HClO_4$], the trifluoroacetate (*S*)-**2**·TFA, and the methanol-including hydrochloride (*S*)-**1**·HCl·MeOH were elucidated by X-ray crystallography and discussed in terms of hydrogen-bond interactions.

Keywords: hydrogen bonds; silicon; 2-silylpyrrolidines; stereochemistry; X-ray crystallography

1. Introduction

In 2010, we and others reported on the enantioselective synthesis of 2-silylpyrrolidines as organocatalysts for the asymmetric Michael addition of aldehydes to nitroolefines [1,2]. Since then, some impressive developments in the catalyst design have been achieved, overcoming synthetic challenges and introducing pyrrolidinylsilanols as bifunctional hydrogen bond-directing organocatalysts [3,4]. The stereochemical information of 2-substituted silylpyrrolidines was introduced by asymmetric deprotonation of *N*-(*tert*-butoxycarbonyl)pyrrolidine (*N*-Boc-pyrrolidine) with *sec*-butyllithium in the presence of (–)-sparteine [5,6], followed by a substitution reaction with a silyl halide or methoxide as the electrophile. Concerning the first successful preparation of enantiomerically-pure (*S*)-2-(triphenylsilyl)pyrrolidine [(*S*)-**1**], we established an indirect synthetic route via intermediate formation of 2-(methoxydiphenylsilyl)-*N*-Boc-pyrrolidine [1]. Recently, a detailed structural and kinetic investigation gave new insight into the structure-reactivity relation in enamines and iminium ions derived from 2-tritylpyrrolidine [7] and 2-(triphenylsilyl)pyrrolidine [8]. (*S*)-2-(Triphenylsilyl)pyrrolidine [(*S*)-**1**] and (*S*)-2-(methyldiphenylsilyl)pyrrolidine [(*S*)-**2**] have already been structurally characterized in the form of their hydrochloride [1,2] and their hydrobromide salts [3] (Figure 1).

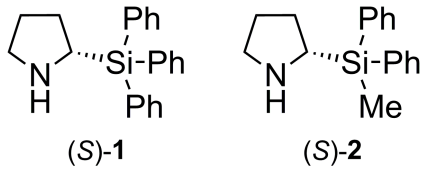

Figure 1. (*S*)-2-(triphenylsilyl)- [(*S*)-**1**] and (*S*)-2-(methyldiphenylsilyl)pyrrolidine [(*S*)-**2**].

Herein, we present the molecular structures of enantiomerically-pure (*S*)-2-(triphenylsilyl)-[(*S*)-**1**·$HClO_4$] and (*S*)-2-(methyldiphenylsilyl)pyrrolidinium perchlorate [(*S*)-**2**·$HClO_4$], which were obtained from the respective optically-pure chloride salts [1] by treatment with perchloric acid. In addition, we report on hydrogen-bonding motifs in the new enantiomerically-pure methanol inclusion compound (*S*)-**1**·HCl·MeOH and in the enantiomerically-pure trifluoroacetate (*S*)-**2**·TFA. Hydrogen bonding in enantiomerically-pure pyrrolidines is worth studying in order to explore new activation modes in organocatalytic transformations.

2. Results and Discussion

Compound (*S*)-**1**·$HClO_4$ crystallized in the monoclinic crystal system, space group $P2_1$, as colorless plates (Figure 2 and Table 1). The pyrrolidinyl nitrogen atom of (*S*)-**1**·$HClO_4$ has been protonated by perchloric acid and is involved in hydrogen bonds to two perchlorate anions via H(1N) and H(2N). The hydrogen bond N–H(1N)···O(1) is slightly stronger [N–H(1N) 0.911 Å, H(1N)···O(1) 1.966 Å, N···O(1) 2.845 Å, N–H(1N)···O(1) 161.79°] than the interaction between H(2N) and O(2) [N–H(2N) 0.773 Å, H(2N)···O(2) 2.230 Å, N···O(2) 2.940 Å, N–H(2N)···O(2) 152.82°]. The C–Si bond lengths of the triphenylsilyl moiety are comparable to those found in the hydrochloride species (*S*)-**1**·HCl [1] and in other triphenyl-substituted silanes [9,10]. The C(19)–Si bond between silicon and the heterocyclic carbon atom amounts to 1.9111(15) Å and is in the characteristic range for 2-(triphenylsilyl)pyrrolidines [1] (Figure 2). This significantly longer bond compared to the respective C–C bond in the carbon analogue 2-tritylpyrrolidine was considered a crucial parameter for the higher reactivity of (*S*)-**1** in enamine catalysis [1].

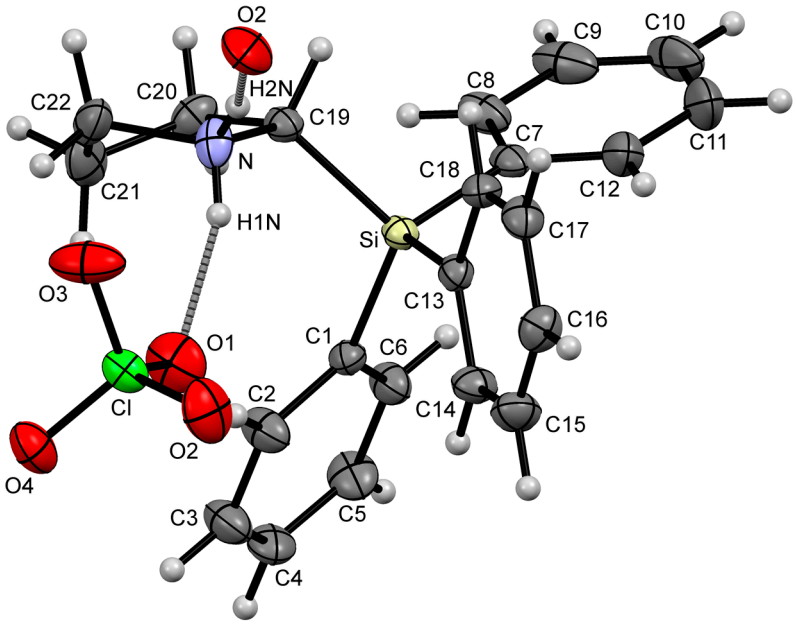

Figure 2. Part of the crystal structure (ORTEP plot) of compound (*S*)-**1**·$HClO_4$ in the crystal, with the displacement ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–Si 1.8727(15), C(7)–Si 1.8724(15), C(13)–Si 1.8595(15), C(19)–Si 1.9111(15), C(19)–N 1.5229(19), C(22)–N 1.4999(19), Cl–O(1) 1.4376(12), Cl–O(2) 1.4305(13), Cl–O(3) 1.4316(13), Cl–O(4) 1.4217(12), C(13)–Si–C(7) 111.31(7), C(13)–Si–C(1) 111.55(7), C(7)–Si–C(1) 108.77(7), C(13)–Si–C(19) 108.01(6), C(7)–Si–C(19) 105.67(7), C(1)–Si–C(19) 111.39(6). Hydrogen bond N–H(1N)···O(1): N–H(1N) 0.911, H(1N)···O(1) 1.966, N···O(1) 2.845, N–H(1N)···O(1) 161.79. Hydrogen bond N–H(2N)···O(2): N–H(2N) 0.773, H(2N)···O(2) 2.230, N···O(2) 2.940, N–H(2N)···O(2) 152.82. Symmetry transformations used to generate the equivalent atom O(2), hydrogen-bonded to H(2N): $1 - x, \frac{1}{2} + y, -z$.

Table 1. Crystal data and structure refinement of compounds (*S*)-**1**·$HClO_4$, (*S*)-**1**·HCl·MeOH, (*S*)-**2**·$HClO_4$, and (*S*)-**2**·TFA.

Compound	**(*S*)-1·$HClO_4$**	**(*S*)-1·HCl·MeOH**	**(*S*)-2·$HClO_4$**	**(*S*)-2·TFA**
Empirical formula	$C_{22}H_{24}ClNO_4Si$	$C_{23}H_{28}ClNOSi$	$C_{17}H_{22}ClNO_4Si$	$C_{19}H_{22}F_3NO_2Si$
Formula weight [g·mol^{-1}]	429.96	398.00	367.90	381.47
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1\ 2_1\ 2_1$	$P2_1$	$P2_1\ 2_1\ 2_1$
a [Å]	8.1535(2)	7.2981(3)	9.6006(6)	9.5760(14)
b [Å]	7.8737(2)	11.7818(5)	14.2054(8)	9.7100(17)
c [Å]	16.9410(4)	25.1513(11)	13.3890(8)	41.176(4)
β [°]	100.780(2)	90	91.537(6)	90
Volume [Å^3]	1068.39(5)	2162.63(16)	1825.34(19)	3828.7(9)
Z	2	4	4	8
Density (calculated) .9ρ [g·cm^{-3}]	1.337	1.222	1.339	1.324
Absorption coefficient μ [mm^{-1}]	0.263	0.245	0.295	0.163
F(000)	452	848	776	1600
Crystal size [mm^3]	0.20 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.10	0.40 × 0.20 × 0.10
Theta range for data collection θ [°]	2.45–25.99	2.37–26.00	2.56–26.00	2.18–25.00
Index ranges	–10 ≤ *h* ≤ 10	–9 ≤ *h* ≤ 9	–11 ≤ *h* ≤ 11	–11 ≤ *h* ≤ 11
	−9 ≤ *k* ≤ 9	−14 ≤ *k* ≤ 14	−17 ≤ *k* ≤ 17	−11 ≤ *k* ≤ 10
	−20 ≤ *l* ≤ 20	−31 ≤ *l* ≤ 30	−16 ≤ *l* ≤ 16	−47 ≤ *l* ≤ 48
Reflections collected	46,918	16,132	28,993	41,441
Independent reflections	4181 (R_{int} = 0.0369)	4244 (R_{int} = 0.0388)	7177 (R_{int} = 0.0540)	6661 (R_{int} = 0.0425)
Completeness to θ	100.0% (θ = 25.99°)	99.9% (θ = 26.00°)	99.9% (θ = 26.00°)	99.3% (θ = 25.00°)
Max. and min. transmission	0.9742 and 0.9493	0.9527 and 0.9085	0.9711 and 0.9433	0.9681 and 0.9376
Data/restraints/parameters	4181/1/270	4244/0/254	7177/1/435	6661/0/566
Goodness-of-fit on F^2	1.000	1.000	1.000	1.000
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0237, w*R*2 = 0.0620	*R*1 = 0.0337, w*R*2 = 0.0682	*R*1 = 0.0596, w*R*2 = 0.1683	*R*1 = 0.0340, w*R*2 = 0.0572
R indices (all data)	*R*1 = 0.0257, w*R*2 = 0.0624	*R*1 = 0.0459, w*R*2 = 0.0700	*R*1 = 0.0809, w*R*2 = 0.1745	*R*1 = 0.0539, w*R*2 = 0.0592
Absolute structure parameter (Flack parameter)	0.01(4)	0.01(6)	0.08(9)	0.02(8)
Largest diff. peak and hole [e·Å^{-3}]	0.207 and −0.228	0.424 and −0.252	0.447 and −0.309	0.260 and −0.197

Previously-known single-crystal X-ray diffraction data of compound (*S*)-**1**·HCl correspond to the chloroform adduct (*S*)-**1**·HCl·$CHCl_3$ [1]. After recrystallization of compound (*S*)-**1**·HCl from methanol, single crystals of the methanol including compound (*S*)-**1**·HCl·MeOH were obtained (Figure 3 and Table 1). Compound (*S*)-**1**·HCl·MeOH crystallized in the orthorhombic crystal system, space group $P2_1\ 2_1\ 2_1$, as colorless needles. The chloride ion is involved in hydrogen bond interactions with H(1N), H(2N), and the methanol hydroxyl group, with the O–H(1O)···Cl hydrogen-bond [O–H(1O) 1.034 Å, H(1O)···Cl 2.071 Å, O···Cl 3.086 Å, O–H(1O)···Cl 166.42°] being essential for the formation of a defined inclusion compound. In addition, a short distance of 3.651 Å between chloride and the phenyl carbon atom C(14) gives a hint for a weak C(14)–H(14)···Cl interaction within the crystal structure of (*S*)-**1**·HCl·MeOH (Figure 3).

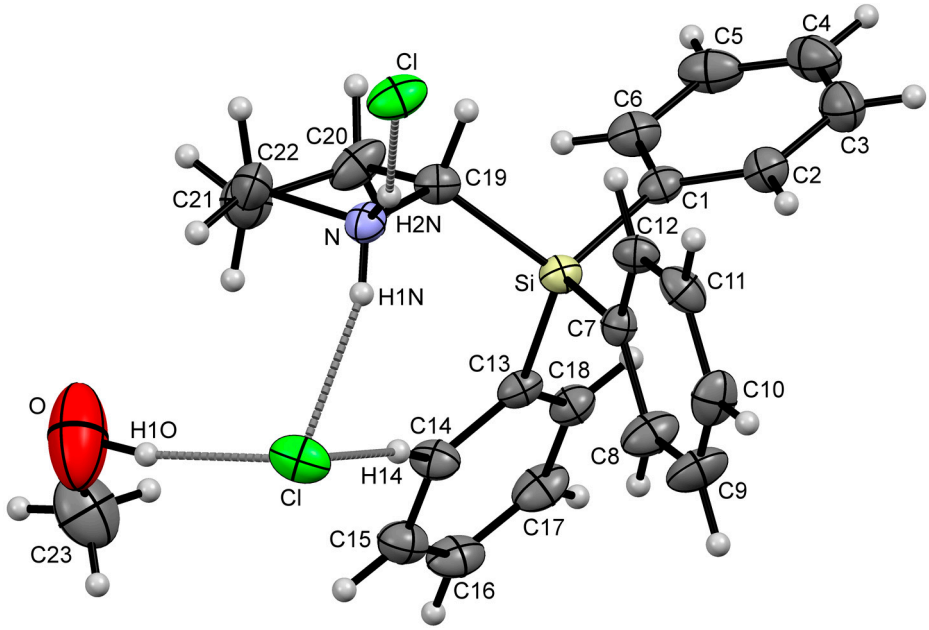

Figure 3. Part of the crystal structure (ORTEP plot) of compound (*S*)-**1**·HCl·MeOH in the crystal, with the displacement ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–Si 1.863(2), C(7)–Si 1.870(2), C(13)–Si 1.873(2), C(19)–Si 1.905(2), C(19)–N 1.498(3), C(22)–N 1.494(3), O–C(23) 1.385(3), C(13)–Si–C(7) 112.48(9), C(13)–Si–C(1) 108.46(9), C(7)–Si–C(1) 110.86(9), C(13)–Si–C(19) 110.34(9), C(7)–Si–C(19) 108.18(9), C(1)–Si–C(19) 106.34(9). Hydrogen bond N–H(1N)···Cl: N–H(1N) 0.870, H(1N)···Cl 2.310, N···Cl 3.125, N–H(1N)···Cl 155.93. Hydrogen bond N–H(2N)···Cl: N–H(2N) 0.913, H(2N)···Cl 2.184, N···Cl 3.062, N–H(2N)···Cl 160.99. Hydrogen bond O–H(1O)···Cl: O–H(1O) 1.034, H(1O)···Cl 2.071, O···Cl 3.086, O–H(1O)···Cl 166.42. C(14)–H(14)···Cl interaction: C(14)···Cl 3.651, C(14)–H(14)···Cl 171.50. Symmetry transformations used to generate the equivalent methanol molecule: x, $1 + y$, $1 + z$. Symmetry transformations used to generate the equivalent atom Cl, hydrogen-bonded to H(2N): $\frac{1}{2} + x$, $1.5 - y$, $2 - z$.

Compound (*S*)-**2**·$HClO_4$ crystallized in the monoclinic crystal system, space group $P2_1$, as colorless plates (Figure 4 and Table 1). The asymmetric unit of compound (*S*)-**2**·$HClO_4$ contains two independent molecules [(*S*)-**2**·$HClO_4$-**A** and (*S*)-**2**·$HClO_4$-**B**]. The bond lengths between the silyl group and the heterocycle with 1.878(5) Å [C(14)–Si(1), molecule **A**] and 1.889(5) Å [C(31)–Si(2), molecule **B**] differ slightly from each other, but are considerably shorter than the respective bond in the 2-triphenylsilyl derivative (*S*)-**1**·$HClO_4$ (compare Figures 2 and 4). The C–Si–C angles are in both independent molecules very close to the ideal tetrahedral angle (Figure 4).

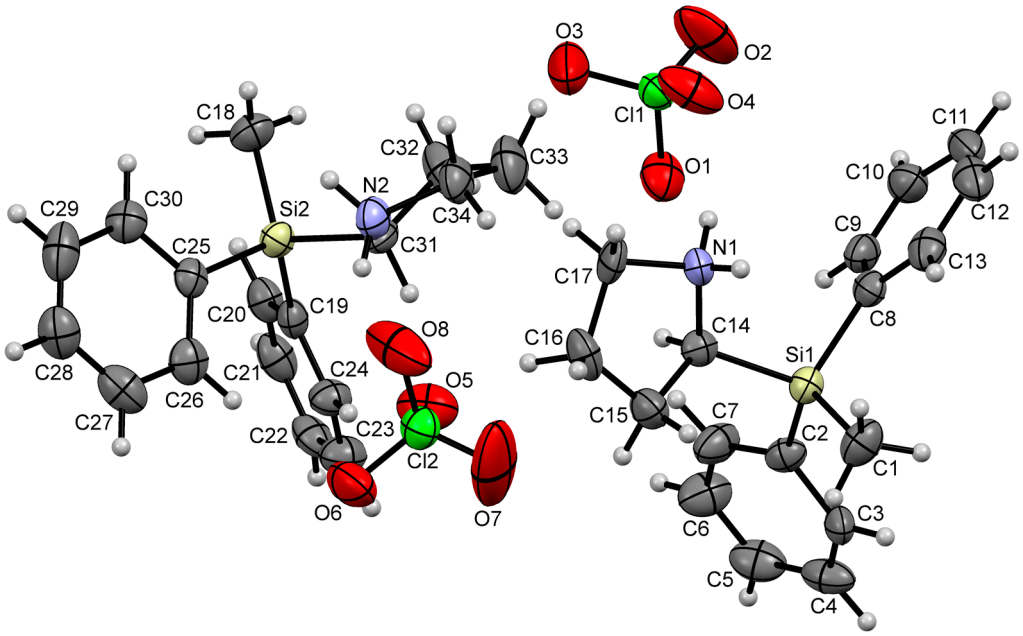

Figure 4. Molecular structure (ORTEP plot) of compound (*S*)-**2**·$HClO_4$ in the crystal, with the displacement ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (°): Molecule (*S*)-**2**·$HClO_4$-**A**: C(1)–Si(1) 1.852(6), C(2)–Si(1) 1.855(6), C(8)–Si(1) 1.871(5), C(14)–Si(1) 1.878(5), C(14)–N(1) 1.508(7), C(17)–N(1) 1.508(6), Cl(1)–O(1) 1.416(4), Cl(1)–O(2) 1.413(5), Cl(1)–O(3) 1.426(5), Cl(1)–O(4) 1.413(5), C(1)–Si(1)–C(2) 112.5(3), C(1)–Si(1)–C(8) 109.7(3), C(2)–Si(1)–C(8) 110.6(2), C(1)–Si(1)–C(14) 109.4(3), C(2)–Si(1)–C(14) 106.4(2), C(8)–Si(1)–C(14) 108.1(2). Molecule (*S*)-**2**·$HClO_4$-**B**: C(18)–Si(2) 1.856(6), C(19)–Si(2) 1.875(6), C(25)–Si(2) 1.884(5), C(31)–Si(2) 1.889(5), C(31)–N(2) 1.509(7), C(34)–N(2) 1.510(7), Cl(2)–O(5) 1.400(5), Cl(2)–O(6) 1.405(5), Cl(2)–O(7) 1.365(6), Cl(2)–O(8) 1.431(5), C(18)–Si(2)–C(19) 109.9(3), C(18)–Si(2)–C(25) 111.5(3), C(19)–Si(2)–C(25) 110.1(2), C(18)–Si(2)–C(31) 110.4(3), C(19)–Si(2)–C(31) 106.0(2), C(25)–Si(2)–C(31) 108.8(2).

Treatment of enantiomerically-enriched (*S*)-2-(methyldiphenylsilyl)pyrrolidine [(*S*)-**2**] with trifluoroacetic acid in dichloromethane resulted in the formation of the trifluoroacetate (*S*)-**2**·TFA. Enantiomerically-pure single crystals of (*S*)-**2**·TFA were obtained after recrystallization from acetonitrile. Compound (*S*)-**2**·TFA crystallized in the orthorhombic crystal system, space group $P2_1\ 2_1\ 2_1$, as colorless needles (Figure 5 and Table 1). Like in the perchlorate (*S*)-**2**·$HClO_4$ (see Figure 4) and in the hydrochloride (*S*)-**2**·HCl [1], the asymmetric unit of compound (*S*)-**2**·TFA contains two independent molecules [(*S*)-**2**·TFA-**A** and (*S*)-**2**·TFA-**B**]. The fluorine atoms of the trifluoroacetate anions and the pyrrolidine carbon atom C(35) of molecule (*S*)-**2**·TFA-**B** are disordered. Each trifluoroacetate is hydrogen-bonded to two silylpyrrolidinium cations via an N–H···O interaction. The parameters of the found hydrogen-bonds differ from each other, with the N–H distances ranging from 0.847 Å [N(2)–H(4N)] to 1.082 Å [N(2)–H(3N)], and the N–H···O angles ranging from 159.48° [N(1)–H(2N)···O(2)] to 172.31° [N(2)–H(3N)···O(3)], although the N···O distances are quite similar (Figure 5).

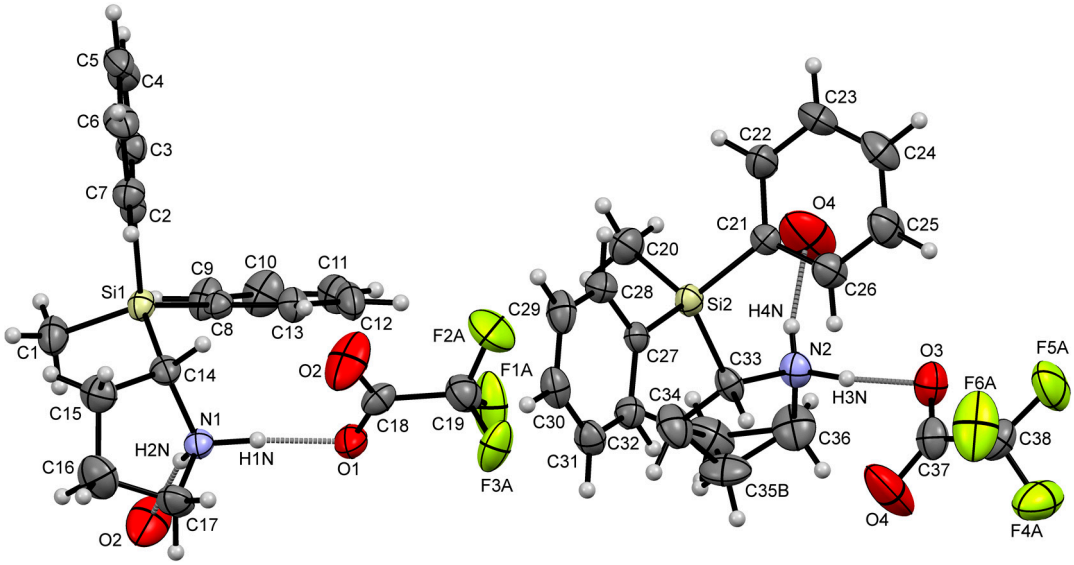

Figure 5. Part of the crystal structure (ORTEP plot) of compound (*S*)-**2**·TFA in the crystal, with the displacement ellipsoids set at the 50% probability level. The ellipsoids F(1B), F(2B), and F(3B) of molecule (*S*)-**2**·TFA-**A**, and the ellipsoids F(4B), F(5B), and F(6B) of (*S*)-**2**·TFA-**B** are omitted for clarity. Selected bond lengths (Å) and angles (°): Molecule (*S*)-**2**·TFA-**A**: C(1)–Si(1) 1.849(2), C(2)–Si(1) 1.863(2), C(8)–Si(1) 1.857(2), C(14)–Si(1) 1.889(2), C(14)–N(1) 1.505(2), C(17)–N(1) 1.491(3), C(18)–C(19) 1.520(3), C(18)–O(1) 1.225(3), C(18)–O(2) 1.206(3), C(1)–Si(1)–C(2) 111.77(10), C(1)–Si(1)–C(8) 110.07(10), C(2)–Si(1)–C(8) 108.11(9), C(1)–Si(1)–C(14) 109.69(10), C(2)–Si(1)–C(14) 107.16(10), C(8)–Si(1)–C(14) 109.98(9). Hydrogen bond N(1)–H(1N)···O(1): N(1)–H(1N) 1.050, H(1N)···O(1) 1.680, N(1)···O(1) 2.716, N(1)–H(1N)···O(1) 167.81. Hydrogen bond N(1)–H(2N)···O(2): N(1)–H(2N) 1.010, H(2N)···O(2) 1.769, N(1)···O(2) 2.738, N(1)–H(2N)···O(2) 159.48. Symmetry transformations used to generate the equivalent atom O(2), hydrogen-bonded to H(2N): $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$. Molecule (*S*)-**2**·TFA-**B**: C(20)–Si(2) 1.845(2), C(21)–Si(2) 1.850(2), C(27)–Si(2) 1.851(2), C(33)–Si(2) 1.884(2), C(33)–N(2) 1.507(3), C(36)–N(2) 1.491(3), C(37)–C(38) 1.522(3), C(37)–O(3) 1.220(3), C(37)–O(4) 1.205(3), C(20)–Si(2)–C(21) 110.03(11), C(20)–Si(2)–C(27) 110.46(10), C(21)–Si(2)–C(27) 108.38(9), C(20)–Si(2)–C(33) 111.26(11), C(21)–Si(2)–C(33) 110.30(9), C(27)–Si(2)–C(33) 106.30(10). Hydrogen bond N(2)–H(3N)···O(3): N(2)–H(3N) 1.082, H(3N)···O(3) 1.665, N(2)···O(3) 2.740, N(2)–H(3N)···O(3) 172.31. Hydrogen bond N(2)–H(4N)···O(4): N(2)–H(4N) 0.847, H(4N)···O(4) 1.903, N(2)···O(4) 2.728, N(2)–H(4N)···O(4) 164.58. Symmetry transformations used to generate the equivalent trifluoroacetate anion, hydrogen-bonded to H(3N): $\frac{1}{2} + x, 1.5 - y, 1 - z$. Symmetry transformations used to generate the equivalent atom O(4), hydrogen-bonded to H(4N): $1 + x, y, z$.

3. Experimental Details

3.1. Synthetic Methods

Synthesis and characterization data of compounds (*S*)-**1**·HCl and (*S*)-**2**·HCl were previously reported by our group [1]. The perchlorate salts (*S*)-**1**·$HClO_4$ and (*S*)-**2**·$HClO_4$ were prepared by treatment of (*S*)-**1**·HCl and (*S*)-**2**·HCl, respectively, with excess perchloric acid (60 wt %). Colorless single-crystals were formed overnight under normal atmosphere at room temperature within the remaining solvent. Single crystals of the inclusion compound (*S*)-**1**·HCl·MeOH were obtained after recrystallization of (*S*)-**1**·HCl from methanol. (*S*)-**2**·TFA was prepared by treatment of 800 mg (2.99 mmol) enantiomerically-enriched (*S*)-2-(methyldiphenylsilyl)pyrrolidine [(*S*)-**2**, e.r. = 89:11] with 341 mg (2.99 mmol) trifluoroacetic acid in 10 mL dichloromethane at room temperature. After removing of all volatiles in vacuo, the residue was dissolved in acetonitrile. Enantiomerically-pure single crystals of (*S*)-**2**·TFA were formed under normal atmosphere at room temperature within three months.

3.2. X-ray Crystallography

Single-crystal X-ray diffraction analyses were performed on an Oxford Diffraction Xcalibur S diffractometer (Oxford Diffraction Ltd. (Abingdon, UK)) at 173(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were mounted at room temperature. The crystal structures were solved with direct methods (*SHELXS*-97 [11]) and refined against F^2 with the full-matrix least-squares method (*SHELXL*-97 [12,13]). A multi-scan absorption correction using the implemented CrysAlis RED program (Version 1.171.32.37, Oxford Diffraction Ltd.) was employed. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms H(1N) and H(2N) in compound (*S*)-**1**·$HClO_4$, H(1N), H(2N), and H(1O) in compound (*S*)-**1**·HCl·MeOH, and H(1N), H(2N), H(3N), H(4N), H(34A), H(34B), H(36A), and H(36B) in compound (*S*)-**2**·TFA were located on the difference Fourier map and refined independently. All other hydrogen atoms were placed in geometrically-calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding model. The fluorine atoms F(1)–F(6) and the carbon atom C(35) in (*S*)-**2**·TFA are disordered. The absolute configuration of (*S*)-**1**·$HClO_4$, (*S*)-**1**·HCl·MeOH, (*S*)-**2**·$HClO_4$, and (*S*)-**2**·TFA was determined by Flack's method based on resonant scattering [14]. Figures 2–5 were created using Mercury (Version 3.3). Crystal and refinement data are collected in Table 1. Crystallographic data of enantiomerically-pure 2-silylpyrrolidinium salts (*S*)-**1**·$HClO_4$, (*S*)-**2**·$HClO_4$, (*S*)-**1**·HCl·MeOH, and (*S*)-**2**·TFA have been deposited with The Cambridge Crystallographic Data Centre. CCDC 1582443 [(*S*)-**1**·HCl·MeOH], CCDC 1582444 [(*S*)-**2**·TFA], CCDC 1582445 [(*S*)-**1**·$HClO_4$], and CCDC 1582446 [(*S*)-**2**·$HClO_4$] contain the supplementary crystallographic data for this paper (see Supplementary Materials). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

In the context of studies concerning the effect of the counter anion in organocatalytic reactions with polar species involved, we were interested to synthesize salts of optically-pure 2-silylpyrrolidines with different counter anions for further reactivity studies, which might be of interest in terms of hydrogen-bond activation in the initial enamine formation step. By studying the hydrogen-bonding behavior of 2-silylpyrrolidines, interesting information about silicon-specific effects on the basicity of the pyrrolidine nitrogen center may be provided. Future studies will also address the respective salts of the carbon analogue 2-tritylpyrrolidine for comparison.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/5/4/88/s1. Cif and cif-checked files.

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Author Contributions: Jonathan O. Bauer performed the experiments and wrote the manuscript. Carsten Strohmann was coordinating the project and performed the XRD analyses.

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