cyclopropane C–H bonds associated with the introduction of a trigonal center is largely responsible for destabilization of the molecule. The formation of **2** may be facilitated by an entropic factor (juxtaposition of the 5′-CH_2 group with the heterocyclic base in **1** owing to the presence of a rigid methylenecyclopropane system) and by incorporation of the methylenecyclopropane moiety into a multiring system.

The reaction of **1** with less reactive phosphorylating agents, such as chlorophosphoramidates,[10] leads to 5′-*O*-phosphorylation products without formation of **2**. There is also evidence[11] that intracellular phosphorylation of **1** forms the phosphates **4** and **5** necessary for antiviral activity (Scheme 1). Like other nucleoside analogues, **1** is thus a prodrug of the corresponding triphosphate **5**, which is the final product of the phosphorylation cascade. Anhydrosynadenol (**2**) lacks two features important for the biological activity per se: 1) the 5′-hydroxyl group necessary for phosphorylation and 2) the *anti* conformation of the base as in **1**. The triphosphate group of **5** is a better leaving group than the monophosphate residue of **4**. Nucleophilic displacement of this functional group in ATP is an important feature of some enzyme-catalyzed transformations.[12] Whether a similar intramolecular reaction (Scheme 1) can play a role in the inactivation of **5** remains to be established.

The ^{1}H NMR spectrum of **2** exhibits a strong downfield shift of the signals of all cyclopropane protons. The H-5′ protons are nonequivalent; one of them is strongly shielded. Models indicate that this shielding is possibly due to the double bond of the methylenecyclopropane unit in an *exo* conformer[13] of **2**. The formation of **2** is unambiguous proof of the *Z* configuration of **1**. This configuration is important for the antiviral activity of **1** and its analogues.[1, 2] In addition, the structure of **2** is a novel polycyclic system containing a methylenecyclopropane moiety.

Experimental Section

2: $POCl_3$ (86 μL, 0.92 mmol) was added to a suspension of **1** (100 mg, 0.46 mmol) in $PO(OMe)_3$ (16 mL) with stirring at 0°C. The clear solution was allowed to stand for 19 h at room temperature, and the solvent was then removed in vacuo (bath temperature <47°C). The sirupy residue solidified after addition of THF (20 mL) and sonication. The solvent was decanted to leave a hygroscopic solid, which was washed with THF (5 mL) and dissolved in water (50 mL). The aqueous phase was washed with CH_2Cl_2 (5 × 20 mL) and then lyophilized. The residue was stirred with Dowex 2 (X-8, 100–200 mesh, acetate, 7 g) in water (20 mL) for 0.5 h. Filtration and lyophilization of the filtrate gave **2** (112 mg, 87 %), m.p. > 300°C. Paper electrophoresis (Whatman No. 1 paper, 0.02 M Na_2HPO_4, pH 7.0, 40 V cm^{-1}, 1 h): Mobility −1.33 of AMP, identical with that of 2′,3′-*O*-isopropylidene-3,5′-anhydroadenosine.[14] UV (ethanol): λ_{max} (ε) = 274 (16700), 238 (14100); (H_2O, pH 7): 272 (16400), 240 (13400). ^{1}H NMR (D_2O): δ = 8.47, 8.37 (2 s, 2 H, H-2, H-8), 7.47 (s, 1 H, H-1′), 5.05 (dd, 1 H) and 3.60 (dd, 1 H, H-5′), 2.50 (q, 1 H), 2.38–2.50 (m, 1 H) and 1.82 (dd, 1 H, H-3′, H-4′); ^{13}C NMR: δ = 181.05 (CO), 157.16, 148.88, 141.86, 138.74, 124.30, 120.22, 115.22 (adenine, C-1′ and C-2′), 58.05 (C-5′), 23.16 (CH_3), 15.89 (C-4′), 14.24 (C-3′). FAB-MS (thioglycerol matrix): *m*/*z* (%): 308 [*M*+H − AcOH+thioglycerol] (100), 260 [*M*+H] (22), 200 [*M*+H − AcOH] (41.0), 136 [adenine+H] (59.5); elemental analysis calcd for $C_{10}H_9N_5 \cdot 0.95\,CH_3CO_2H \cdot 1.35\,H_2O$: C 50.94, H 5.57, N 24.96; found: C 50.67, H 5.37, N 25.24.

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Perchloropolysilane: X-Ray Structure, Solid-State ^{29}Si NMR Spectroscopy, and Reactions of $[SiCl_2]_n$**

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We have succeeded in the preparation of perchloropolysilane, $[SiCl_2]_n$ (**1**) as very pale yellow, highly moisture-sensitive single crystals and obtained the X-ray structure. This is the first example of a single crystal X-ray structure analysis of a polysilane. We also report solid-state ^{29}Si NMR data.[1]

Since the investigations by Schwarz and co-workers[2a, b] of the higher silicon halides (described as viscous liquids or

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glassy solids), there have been few reports in this area, save for discussions[2c, 3, 4] on the small cyclic species $[SiCl_2]_n$ where $n = 4$, 5, and 6. Continuing our investigations[5] of cyclic and linear polysilanes, we sublimed Si_4Cl_8[2c] and obtained crystals of **1** in yields of about 27% upon condensation onto a cold finger ($-10^\circ C$). This phenomenon was apparently not observed during the purification of Si_4Cl_8 by sublimation described in earlier reports.[2c] We postulate that **1** is formed by the ring-opening of Si_4Cl_8 molecules after sublimation to give diradical species which could couple by radical recombination to yield the observed linear perchloropolysilane.

The X-ray data for the structure analysis of **1** was collected at $-140^\circ C$ with a charge-coupled device (CCD) area detector, which enabled rapid analysis (ca. 12 h); speed is important because of the great sensitivity of **1** towards moisture (many attempts were required to find a crystal that diffracted satisfactorily). The final R value (18%) is high and reflects the poor sample quality by crystallographic standards. This poor crystallinity, which may be due to hydrolysis, chain length inhomogeneity, or the presence of terminal groups, is revealed by very broad peak profiles of 3–8 degrees. Such broad peaks could not have been measured on routine instruments with point detectors, but required an area detector to collect the intensity data. Nevertheless, a chemically reasonable structure solution could be refined and produced the arrangement of atoms shown in Figure 1.[6]

The polysilane **1** consists of infinite parallel-aligned all-*trans* chains of $SiCl_2$ repeat units. It is interesting that the Si–Si bond length (2.414(8) Å) is unusually long (typical value 2.34 Å) and even longer than that in the strained precursor to **1**, Si_4Cl_8 (2.372(2) Å).[5] The Si-Si-Si and Cl-Si-Cl angles (114.4(6) and 111.0(4)°, respectively) are both slightly larger than the ideal tetrahedral angle.

The polymer is virtually insoluble in all solvents, but is nevertheless chemically reactive, and substitution of the Cl atoms by nucleophiles is possible. In the presence of excess 2-propanol, the diisopropoxypolysilane (**2**)[7] is formed as a white powder. Size exclusion chromatography indicated a degree of polymerization (DP) for **2** of about 35. This may be taken as an approximate guide to the DP of **1**, and hence the average molecular weight of **1** may be estimated as approximately 3500. Exposure of **1** to moist air resulted in the evolution of HCl gas and a color change of the solid from off-white to bright yellow. Infrared analysis of this material indicated both Si–OH (3400 cm^{-1}) and Si-OSi (1016 cm^{-1}) moieties. Exposure for a further 24 h afforded a very pale yellow material, analysis of which showed a decrease in the Si–OH absorption and an increase in the Si-OSi peak. This indicates the formation, initially, of a partially hydroxy-substituted polysilane (bright yellow), which becomes gradually cross-linked to give a network-type, polysiloxy-cross-linked polysilane (pale yellow). The polysilane **1** also reacts with dialkylamines and amide salts to yield low molecular weight aminopolysilanes.

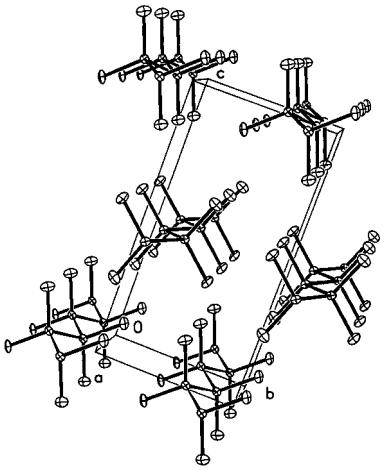

Figure 1. Unit cell and molecular structure of $[SiCl_2]_n$ **1** in the crystal (50% probability displacement ellipsoids). Selected interatomic distances (Å) and angles (°): Si(1)–Cl(1) 2.120(9), Si(1)–Cl(2) 2.088(9), Si(1)–Si(1)^a 2.414(8), Si(1)–Si(1)^b 2.414(7) Si(1)^a-Si(1)-Si(1)^b 114.4(6), Cl(1)-Si(1)-Cl(2) 111.0(4). a and b indicate symmetrically equivalent atoms generated by the symmetry transfomations $x-0.5$, $-y+0.5$, $-z+1$, and $x+0.5$, $-y+0.5$, $-z+1$.

It seems evident that **1** will prove to be a valuable synthon for the preparation of new kinds of polysilanes that cannot be synthesized by current methods. Further work to clarify the mechanism of formation and chemistry of this unique compound is underway.

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[6] Crystallographic data for **1**: $(Cl_2Si)_n$: $M = 98.99$, orthorhombic, $P2_12_12_1$, $a = 4.0569(10)$, $b = 6.783(2)$, $c = 13.346(3)$ Å; $V = 367.3(2)$ Å^3, $Z = 4$, $\rho_c = 1.790$ g cm^{-3}; graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; absorption coefficient = 1.814 mm^{-1}; $F(000) = 192$; $T = 133(2)$ K; pale yellow transparent prisms; crystal dimensions: $0.48 \times 0.32 \times 0.18$ mm; Siemens P4/CCD diffractometer, measurement range $3.05 \le \theta \le 24.99^\circ$; $-5 \le h \le 4$, $-3 \le k \le 8$, $-13 \le l \le 16$. Of 1540 intensity data, 646 were independent ($R_{int} = 0.0823$) and 602 observed [$I > 2\sigma(I)$]. Structure solution by direct methods; refinement by full-matrix least-squares on F^2 (SHELXTL V. 5, 1994). Neutral atom scattering factors were taken from ref. [8]. $R_1 = 0.1859$ [$I > 2\sigma(I)$], w$R_2 = 0.4148$ (all data); GOF(F^2) = 1.303, Flack = 0 (2). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-59448.

[7] Analytical data for **2**: UV/Vis (THF): $\lambda_{max} = 288$ nm (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.40$ (6H), 4.76 (1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.12, 70.93; ^{29}Si NMR (99.36 MHz): $\delta = -11.2$. All the peaks in the NMR spectra were broad.

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