

Monolayers of 1-Alkynes on the H-Terminated Si(100) Surface

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Monolayers of a series of 1-alkynes, from 1-dodecyne to 1-octadecyne, have been prepared on the hydrogen-terminated Si(100) surface via a thermal reaction of the organic compound with this Si surface. An efficient procedure is presented for the synthesis of 1-alkynes from the corresponding 1-alkenes. The resulting monolayers were characterized by water contact angle measurements, ATR infrared spectroscopy, and X-ray reflectivity. The results show that these 1-alkynes give well-ordered, covalently bonded monolayers, which are at least as ordered as those of the corresponding 1-alkenes. The exact binding geometry of the 1-alkyne to the Si surface was investigated. The results from IR spectroscopy and X-ray reflectivity measurements indicate that the 1-alkynes form two Si–C bonds to the surface per reacting molecule. Quantum mechanical calculations confirm that this formation of two Si–C bonds is not only chemically possible but also energetically much more favorable than formation of only one Si–C bond per reacting molecule.

Introduction

Covalently attached, organic monolayers on silicon surfaces, without the interfacial silicon oxide layer, are an interesting new class of monolayers on solid substrates.^{1,2} These monolayers can be prepared by different routes.² Probably the easiest and technologically most promising method is the hydrosilylation reaction of 1-alkenes with hydrogen-terminated (H-terminated) Si surfaces (Figure 1). This reaction has been successfully performed on both H-terminated Si(111)^{3,4,5} and Si(100)^{6,7,8} surfaces and on porous silicon.^{9–13} It results in the

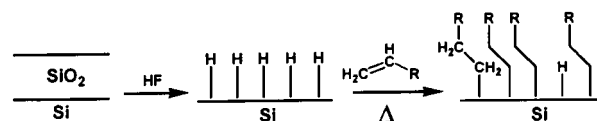


Figure 1. Schematic representation of the reaction of 1-alkenes with a H-terminated silicon surface.

formation of a covalently bonded,¹⁴ stable, and well-ordered monolayer on the Si surface. The advantages of this procedure compared to other available routes are that special equipment, like a high-vacuum chamber, is not required and that 1-alkenes are relatively harmless compounds compared to other reagents, like PCl_5 and Grignard reagents, that are to be used in other wet-chemical procedures.¹⁵ Recently, it was shown that the monolayers can also be prepared with dilute solutions of the 1-alkene in organic (aromatic) solvents. This eliminates the previously required use of neat 1-alkenes and yields a 20–40-fold reduction of the required amount of the organic reagent.¹⁶

Although most of the research on the hydrosilylation of Si surfaces has been done on 1-alkenes, the reaction works equally well for 1-alkynes.^{3,5,9–13} However, so far no systematic investigations have been done on surface modifications with this latter class of compounds. Besides, the monolayers that are reported were also almost all prepared under different conditions. This has resulted in a remarkable observation: the alkyne $\text{C}\equiv\text{C}$ bond has been found to react either once^{3,5,9–12} or twice¹³ with a surface

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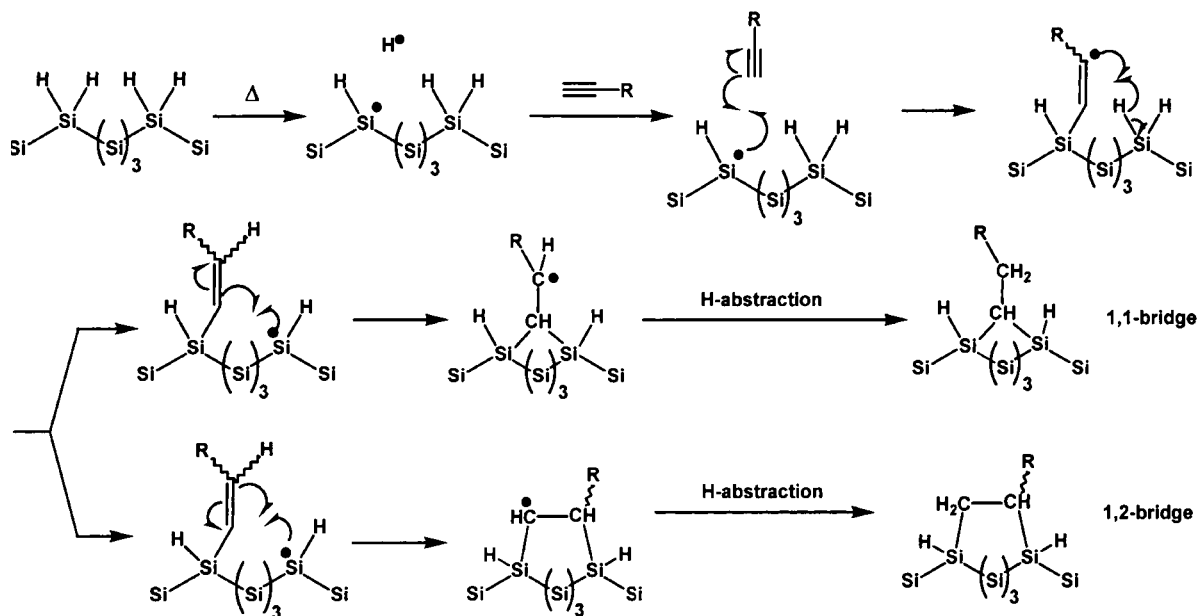


Figure 2. Mechanism of the reaction of a 1-alkyne with a H-terminated Si surface, depicting the possible formation of 2 Si–C bonds per reacting organic molecule.

Si–H group, depending on the reaction conditions used. On the H-terminated Si(111) surface, on which each Si surface atom bears only one hydrogen atom, the peroxide-catalyzed thermal reaction of 1-hexadecyne³ and the photochemical reaction of 1-octyne and phenylacetylene⁵ resulted in alkenyl groups bound to the surface. A weak C=C stretch vibration was observed with infrared spectroscopy, which was interpreted to indicate the formation of only one Si–C bond per alkyne molecule. The same reactivity of 1-alkynes was reported for porous silicon, if the reaction was induced with an Al catalyst,^{9,10,11} with a transition metal catalyst,¹⁰ or with white light.¹² For all these reactions of 1-alkynes on porous silicon a C=C vibration was clearly visible in the IR spectrum of the modified silicon material.

In contrast, the thermal reaction of 1-octyne with porous silicon, this time without any catalyst, has been reported to give two Si–C bonds per molecule, as no alkene vibration was visible with IR spectroscopy.¹³ The formation of a certain amount of such doubly bonded structures has also been suggested to occur in the case of the Rh^I-catalyzed reaction of 1-alkynes with porous silicon.¹⁰ This “double reaction” of the C≡C bond is not unlikely, as porous silicon has many SiH₂ and SiH₃ groups, which could easily react twice with the alkyne, especially because of the proposed radical mechanism of the thermal reaction (Figure 2).³

The reason for this difference in reactivity of 1-alkynes is not clear. In the case of the H-terminated Si(111) surface, the second Si–C bond has to be formed to the next-nearest Si surface atom, which would give rise to a five-membered ring structure, in which considerable deformation of the Si–C bonds is required. This can prohibit the formation of two Si–C bonds per molecule on this surface. However, the reaction of porous silicon with a 1-alkyne can evidently give rise to the formation of two Si–C bonds per reacting 1-alkyne molecule. Thus, such structures can be formed if the reaction proceeds by a mechanism similar to that depicted in Figure 2. The reason such reactivity is observed in the thermal reaction, but is not observed with the light-induced and Lewis acid-catalyzed reactions, is unknown.²

There are no reports on the reaction of 1-alkynes with the H-terminated Si(100) surface. This is somewhat surprising, as this surface consists mainly of SiH₂ groups,

with small amounts of SiH and SiH₃ groups present,¹⁷ which makes the reactivity of this H-terminated Si(100) surface comparable to that of porous silicon. Thus, it could well serve as a model surface to study the reaction of 1-alkynes under more controlled conditions. In addition, the structure of the H-terminated Si(100) surface is relatively well-known compared to that of porous silicon,² which facilitates the interpretation of experimental results.

If 1-alkynes can indeed form two Si–C bonds per molecule, this would also be relevant for an interesting application of monolayers of these compounds. It has been shown that monolayers of 1-alkenes on Si surfaces can be used for surface passivation.¹⁸ Formation of two stable Si–C bonds per molecule, instead of only one as in the case of alkenes, will reduce the number of available surface sites for further reactions and is therefore expected to improve the passivation properties.

In this paper, we present the first investigation of the thermal reaction of 1-alkynes with the H-terminated Si(100) surface. Four nonfunctionalized 1-alkynes of various lengths were used: 1-octadecyne (**I**), 1-hexadecyne (**II**), 1-tetradecyne (**III**), and 1-dodecyne (**IV**). The properties of the resulting monolayers are compared to those of monolayers of the corresponding 1-alkenes, which are also prepared and investigated. All reactions were performed in refluxing mesitylene, which has been shown to be the solvent of choice for the thermal modification of H-terminated Si surfaces with 1-alkenes.¹⁶ The monolayers were characterized by water contact angle measurements, attenuated total reflection (ATR) infrared spectroscopy, and X-ray reflectivity. To get more insight into the way in which the 1-alkynes are bound to the Si(100) surface, several possible binding structures were also investigated with molecular mechanics and quantum mechanical calculations.

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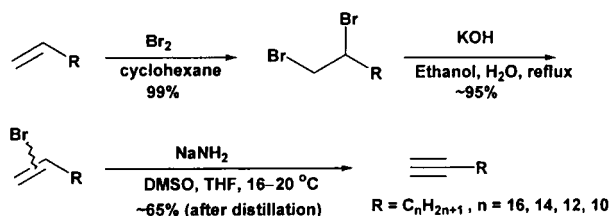


Figure 3. General route for the synthesis of the 1-alkynes.

Experimental Section

General Information. The 1-alkynes I–IV were synthesized according to the procedure described below. All 1-alkynes and 1-alkenes used for monolayer preparations were distilled under reduced pressure and stored at $-20\text{ }^{\circ}\text{C}$, except for 1-octadecyne, which was recrystallized from methanol and stored at room temperature under vacuum.¹⁹ Mesitylene (Acros, 99%, or Fluka, 99%) was distilled at atmospheric pressure and stored on CaCl_2 .²⁰ All glassware for the distillations and the monolayer preparations was cleaned with distilled solvents only. All other chemicals are commercially available and were used as received, unless noted otherwise. The silicon substrates were either pieces of double-polished silicon (Si(100), n-type, $250\text{ }\mu\text{m}$ thickness), shards ($\sim 1 \times 3\text{ cm}$) of single-polished silicon (Si(100), n-type, $500\text{ }\mu\text{m}$ thickness), or Si(100) parallelogram plates (ATR-plates) designed for multiple internal reflection spectroscopy (Harrick Scientific, 45° , $50 \times 10 \times 1\text{ mm}^3$, 50 reflections).

¹H NMR spectra were recorded in CDCl_3 at 200 MHz on a Bruker AC200 FT-NMR spectrophotometer at ambient temperature; ¹³C NMR spectra were measured in CDCl_3 at 50 MHz. Chemical shifts are in ppm relative to tetramethylsilane. To obtain more reliable integrations of the ¹³C NMR signals, pulse sequences with a longer relaxation time ($T_1 = 12\text{ s}$) were used. Infrared spectra of the synthesized compounds were recorded on a Biorad FTS-7 infrared spectrometer. IR measurements of fluids were performed between NaCl windows, while all solids were measured as solutions in CCl_4 . Melting points were determined on a Mettler FP80 HT melting point apparatus. Mass spectra were recorded on a Mat95 GC/MS mass spectrometer. The measurement conditions for the investigation of the monolayers are described below.

1-Alkyne Synthesis. All 1-alkynes were synthesized by the route depicted in Figure 3.²¹ The synthesis of 1-hexadecyne (II) is described here as an example; the analogous syntheses of the other 1-alkynes are described in the Supporting Information.

1,2-Dibromohexadecane. A solution of 44.8 g (0.20 mol) of 1-hexadecene in 200 mL of dry cyclohexane was cooled to $0\text{ }^{\circ}\text{C}$. Subsequently, 11.2 mL (35.2 g, 0.22 mol) of bromine was added dropwise at this temperature over 30 min. The resulting dark red mixture was allowed to warm to room temperature and stirred overnight. The solution was washed with 200 mL of a 2% NaHSO_3 solution, to remove excess bromine, and with brine and dried over MgSO_4 . Evaporation of the solvent yielded the desired 1,2-dibromohexadecane as a yellow oil in 100% isolated yield.

¹H NMR: δ 4.25–4.12 (m, 1H), 3.87 (dd, 1H, $J = 4.4\text{ Hz}$, $J = 10.2\text{ Hz}$), 3.64 (dd, appears as t, 1H, $J = 10.0\text{ Hz}$ ($2\times$)), 2.20–2.07 (m, 1H), 1.86–1.70 (m, 1H), 1.70–1.25 (br m, 24H), 0.90 (t, 3H, $J = 6.4\text{ Hz}$). ¹³C NMR: δ 53.10, 36.31, 35.99, 31.92, 29.65 (5C), 29.61, 29.53, 29.37, 28.81, 26.74, 22.69, 14.13. IR (cm^{-1}): 2923 (m), 2852 (m), 1465 (m), 1436 (m). MS: m/z (relative intensity)

(19) The purity of the 1-alkynes obtained from the synthesis was found to be insufficient for the preparation of monolayers, as this reaction is very sensitive to small amounts of impurities in the reagents. Therefore, a second distillation step was always performed. No change in boiling points was observed.

(20) In some cases, mesitylene that was stored on NaOH became turbid after several weeks. Storage on CaCl_2 did not give this problem.

(21) (a) The original procedure^{21b} lead—in contrast with claims by the authors—to the formation of large amounts of 2-alkynes (even over 50%) rather than 1-alkynes. The mistake in the interpretation of their data was most likely caused by insufficient resolution in the high-field NMR spectroscopy (60 MHz). Our modified procedure (see Experimental Section) yields only 2–3% of the 2-alkyne (GC analysis) and 97–98% of the desired 1-alkyne. (b) Klein, J.; Gurfinkel, E. *Tetrahedron* **1970**, *26*, 2127–2131.

41 (44.0), 43 (67.7), 55 (50.6), 57 (100), 69 (39.9), 71 (68.7), 83 (39.8), 85 (47.3), 97 (15.2), 111 (17.7), 226 (12.6), 303 (11.0), 305 (11.1). Exact mass: 303.1687 for $\text{C}_{16}\text{H}_{32}\text{Br}^+$; found 303.1687. No peak corresponding to the M^+ of $\text{C}_{16}\text{H}_{32}\text{Br}_2$ was observed.

1/2-Bromo-1-hexadecene (Mixture of Isomers). A mixture of 77.5 g (0.20 mol) of 1,2-dibromohexadecane, 200 mL of ethanol, 16.8 g (0.30 mol) of KOH, and 20 mL of water was refluxed for 3 h. The reaction mixture was cooled to $\sim 40\text{ }^{\circ}\text{C}$, and the ethanol was removed by evaporation in vacuo. Subsequently, 50 mL of water and 10 mL of brine were added to the residue. The aqueous layer was extracted with subsequently 200 mL of ether, a mixture of 100 mL of ether and 50 mL of petroleum ether ($40\text{--}60\text{ }^{\circ}\text{C}$), and 100 mL of petroleum ether ($40\text{--}60\text{ }^{\circ}\text{C}$). The combined organic layers were washed with 50 mL of water and with 50 mL of brine and dried over MgSO_4 . Evaporation of the organic solvents gave 56.2 g (0.186 mol, 93%) of 1/2-bromo-1-hexadecene (mixture of the three isomers) as a yellow oil.

¹H NMR: δ [6.19–5.98 (m) + 5.56–5.55 (m) + 5.39–5.38 (m); total of 2H, relative integral height = $\sim 1.5:1:1$], [2.45–2.39 (m) + 2.26–2.16 (m) + 2.09–2.00 (m); total of 2H, relative integral height = $\sim 1.5:1:1$], 1.60–1.22 (br m, 24H), 0.90 (t, 3H, $J = 6.5\text{ Hz}$). IR (cm^{-1}): 3078 (w), 2925 (m), 2851 (m), 1630 (m), 1464 (m).

1-Hexadecyne (II). In a large, three-necked flask fitted with a mechanical stirrer was placed 23.4 g of sodium amide (0.60 mol). This was dissolved in 120 mL of dry DMSO by stirring the suspension at $60\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere for 1 h. The resulting bluish solution was cooled to room temperature, and the flask was placed in a large water bath of $\sim 15\text{ }^{\circ}\text{C}$. Subsequently, a solution of 56.2 g (0.186 mol) of 1/2-bromo-1-hexadecene (mixture of isomers) in 30 mL of dry THF was added dropwise over 45 min, maintaining the temperature of the water bath between 16 and $20\text{ }^{\circ}\text{C}$. After the addition was complete, the resulting viscous brown suspension was stirred at $20\text{ }^{\circ}\text{C}$ for another 2 h.

The reaction mixture was mixed with 400 mL of ice water, and the aqueous layer was extracted four times with 100 mL of ether. The combined organic layers were washed twice with brine and dried over MgSO_4 . Evaporation of the solvent gave the crude 1-alkyne as a dark oil. Subsequent distillation gave 29.8 g (0.134 mol, 72%) of 1-hexadecyne (bp $144\text{--}145\text{ }^{\circ}\text{C}$ at 12 mmHg; lit. $144\text{ }^{\circ}\text{C}$ at 10 mmHg)²² as a colorless liquid.

¹H NMR: δ 2.18 (dt, 2H, $J = 2.6\text{ Hz}$, $J = 6.9\text{ Hz}$ ($2\times$)), 1.93 (t, 1H, $J = 2.6\text{ Hz}$), 1.63–1.20 (br m, 24H), 0.89 (t, 3H, $J = 6.4\text{ Hz}$). ¹³C NMR: δ 84.67, 68.00, 31.94, 29.68 (3C), 29.64, 29.53, 29.39, 29.14, 28.93, 28.78, 28.51, 22.71, 18.39, 14.11. IR (cm^{-1}): 3315 (s), 2924 (m), 2853 (m), 2120 (w), 1464 (m). MS: m/z (relative intensity) 41 (52.6), 43 (49.9), 55 (48.7), 57 (27.7), 67 (63.8), 69 (26.9), 81 (100), 82 (73.8), 95 (52.3), 96 (57.4). No M^+ was observed.

Monolayer Preparation. For the water contact angle measurements, the monolayers were prepared as described previously.¹⁶ In short, 10 mL of a 0.2 M solution of 1-alkyne or 1-alkene in mesitylene was placed in a small, three-necked flask fitted with a nitrogen inlet, a thermometer, and a reflux condenser with a CaCl_2 tube. The solution was deoxygenated with dry nitrogen for at least 1 h. Subsequently, a piece of double-polished silicon was etched in 2.5% HF for 2 min and immediately placed in the solution. The flask was immersed in an oil bath of $210\text{ }^{\circ}\text{C}$ and refluxed for 2 h, while maintaining a slow N_2 flow. Subsequently, the sample was removed from the solution and cleaned.^{6,16}

A specially designed flask allowed for full immersion of the ATR crystal in combination with a short time ($< 60\text{ s}$) between immersion of the crystal and refluxing of the solution. This latter aspect is required to obtain well-ordered monolayers. Additional details of the flask and procedure used can be found in the Supporting Information.

The ATR crystals were recycled by oxidative removal of the monolayer in “piranha solution” ($30\% \text{H}_2\text{O}_2/\text{H}_2\text{SO}_4 = 1:2\text{ (v/v)}$) at $85\text{ }^{\circ}\text{C}$ for 60 min.^{23,24} *Caution: The acidic solutions of hydrogen peroxide described in this procedure are dangerous, strong oxidants, and should be handled with great care.* The crystal was removed from the solution and rinsed extensively with water. After this cleaning, drops of water spread completely on the surface, and IR spectroscopy showed the complete absence of

any C–H vibrations. This indicates that the monolayer was completely removed.

Contact Angle Measurements. Water contact angles were determined by the Wilhelmy plate method as described previously.^{6,16} All samples were prepared in triplicate, and for each sample at least seven measurements were made for both advancing and receding contact angles. The reported values are the averages of the three samples. The reproducibility of the advancing contact angles is $\pm 1^\circ$, and that of the receding angles is $\pm 1-2^\circ$.

Infrared Spectroscopy. Infrared spectra of the monolayers were recorded on a Perkin-Elmer 1725X FT-IR spectrophotometer, equipped with a liquid nitrogen-cooled MCT detector, using a fixed angle multiple reflection attachment (Harrick Scientific). The infrared light was incident on one of the 45° bevels of the ATR crystal. Spectra of the monolayers were recorded with s- and p-polarized light. Measurement conditions were as follows: resolution 0.25 cm^{-1} , with 512 scans. A clean, untreated Si ATR crystal was used as a background. All crystals were cleaned with chloroform before mounting. The reproducibility of the peak positions in different measurements of the same samples, for example, after repositioning of the sample or cleaning of the monolayer-modified crystal, was $\pm 0.25\text{ cm}^{-1}$. From the measurements of the independent s- and p-polarized spectra an average tilt angle with respect to the surface normal can be calculated. This procedure has been described previously.⁶

X-ray Reflectivity. X-ray reflectivity measurements were performed using a rotating anode Rigaku RU-300H generator having a maximum power of 18 kW and a two-circle diffractometer. The incident beam was monochromatized (Cu K α , $\lambda = 1.54\text{ \AA}$) and converted into a parallel beam by a W/B₄C graded multilayer monochromator, which had an inherent divergence of 5.23×10^{-4} . Additionally, the incoming and outgoing divergences were given by the slit widths, which resulted in an in-plane resolution of $\Delta q_z = 4.3 \times 10^{-3}\text{ \AA}^{-1}$ and $\Delta q_x = (5.3 \times 10^{-3})q_z$.

Before starting a measurement, the samples were rinsed in chloroform. During the measurement they were kept in a cell which was continuously evacuated in order to avoid contamination through air exposure. The X-ray reflectivity data were corrected for the sample size effects at small incidence angles, as well as for the background scattering, and were normalized to unit incident intensity. They were analyzed according to an iterative matrix formalism derived from the Fresnel equations by taking into account the deviation from the ideal decay of the reflectivity for a perfectly smooth surface due to the presence of roughness.^{25,26} The calculated reflectivity profiles were convoluted with the experimental resolution, which is assumed to be of Gaussian statistics.

Molecular Mechanics Calculations. All calculations were performed with the MSI program Cerius² (version 3.5).²⁷ The

(23) (a) The following procedure was used: In a high, small cylinder (volume of 25 mL) was placed 7 mL of H₂O₂ (30% solution in H₂O). This was cooled to 0 °C, and 14 mL of H₂SO₄ was added. *Caution: This addition is strongly exothermic.* The crystal was placed in the now hot (~85 °C) solution, and the cylinder was immersed in an oil bath of 105–110 °C, thus maintaining the temperature of the oxidizing solution around 85 °C. The solution was occasionally stirred with a glass rod. After 1 h the oil bath was removed and the crystal was taken from the solution using Teflon tweezers. (b) Based on: Pintchovski, F.; Price, J. B.; Tobin, P. J.; Peavey, J.; Kobold, K. *J. Electrochem. Soc.* **1979**, *26*, 1428–1430.

(24) In a previous publication⁶ a UV/ozone oxidation was used for recycling of the ATR crystals. Though this is an easier procedure compared to the piranha oxidation method, it was observed that in some cases the surface of the ATR crystals gets a brownish, matte appearance after the UV oxidation. Such crystals were found to be no longer suitable for monolayer preparations, as only monolayers of poor quality could be prepared on these surfaces. This could happen at any time; that is, some crystals showed this effect after their first UV/ozone oxidation, whereas others could be recycled many times. The current oxidation procedure, though more elaborate, does not give any such problems, and the crystals can be recycled many times without any effect on the quality of the new monolayer that is prepared.

(25) See, for example: (a) Tolan, M. *X-ray Scattering from Soft-Matter Thin Films*; Springer Tracts in Modern Physics, Vol. 148; Springer-Verlag: Berlin, Germany, 1999. (b) Holý, V.; Pietsch, U.; Baumbach, T. *High-Resolution X-ray Scattering from Films and Multilayers*; Springer Tracts in Modern Physics, Vol. 149; Springer-Verlag: Berlin, Germany, 1999.

(26) Fitting program REFGR by I. Samoilenco.

structures were optimized using the “Smart Minimizer” minimization routine with “high-convergence” criteria.²⁸ Two different force fields were used: the Universal Force Field (UFF)²⁹ and the Polymer Consistent Force Field (PCFF),³⁰ both as implemented in Cerius.² A cluster of 32 Si atoms was prepared from an enlarged Si crystal unit cell, which is available in the database of Cerius.² This cluster was terminated with hydrogen atoms, which gave a cluster with four surface SiH₂ groups, which represents the H-terminated Si(100) surface. The 1-butyne or 1-butene molecule was bound to this surface in such a way that the aliphatic tail of the organic molecule was above the Si crystal surface, to include the interactions between the alkyl chain and the Si surface in an optimal fashion. In all calculations, only the top two layers of Si atoms were allowed to move, whereas the remaining atoms were fixed at their positions. In this way the underlying Si crystal structure is properly represented, as the Si cluster was directly prepared from the Si crystal unit cell.

Ab Initio Calculations. The optimized structures obtained from the molecular mechanics calculations (vide supra) were investigated with B3LYP/6-31G(d) computations. The Gaussian 98 suite of programs was used, with the functional and basis set as implemented in there.³¹ All structures were fully optimized. Natural population analysis (NPA) charges were obtained using the NBO program as implemented in Gaussian,³² since the computations using the 6-31G(d) basis set involve the use of 752 basis functions, which is larger than the maximum of allowed basis functions in the NBO module in Gaussian 98, we used the LANL2DZ basis set for silicon in the NPA computations. Test calculations on smaller systems in which both the LANL2DZ and 6-31G(d) basis sets could be used showed only negligible differences between the resulting NPA charges.

Results and Discussion

Structure of the Monolayers. Information about the packing density of the molecules in the monolayers can be obtained from a combination of water contact angle and infrared spectroscopy measurements. In Table 1 the water contact angles as determined for the 1-alkyne and 1-alkene monolayers are listed (columns 2 and 3, respectively). From these results it is evident that all four 1-alkynes I–IV give ordered monolayers on the Si(100) surface (column 2). The advancing contact angles ($\Theta_a = 108-110^\circ$) are indicative of ordered monolayers that are terminated with methyl groups, as they are well compa-

(27) (a) Cerius², version 3.5, Molecular Simulations Inc., September 1997. (b) Terms that are specific to the Cerius² program have in the text been put between quotes.

(28) Criteria for the “high-convergence” minimizations: atom root-mean-square force $1 \times 10^{-3}\text{ kcal mol}^{-1}\text{ \AA}^{-1}$; atom maximum force $5 \times 10^{-3}\text{ kcal mol}^{-1}\text{ \AA}^{-1}$; energy difference $1 \times 10^{-4}\text{ kcal mol}^{-1}$; root-mean-square displacement $1 \times 10^{-5}\text{ \AA}$; maximum displacement $5 \times 10^{-5}\text{ \AA}$.

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Table 1. Water Contact Angles for the 1-Alkyne and 1-Alkene Monolayers (Columns 2 and 3, Respectively)

compound, R =	Θ_a/Θ_r (H ₂ O) ^a (deg)	
	HC≡C-R	H ₂ C=CH-R
C ₁₆ H ₃₃	110/98	109/96
C ₁₄ H ₂₉	110/101	109/97
C ₁₂ H ₂₅	110/100	108/98
C ₁₀ H ₂₁	108/98	108/97

^a Advancing and receding contact angles for water.

Table 2. Infrared Absorptions (in cm⁻¹) for the Antisymmetric (ν_a) and Symmetric (ν_s) Methylene Stretching Vibrations of the Monolayers of I–IV, Using p-Polarized Light

monolayer	ν_a	ν_s
HC≡C–C ₁₆ H ₃₃ (I)	2921.1	2851.9
HC≡C–C ₁₄ H ₂₉ (II)	2921.4	2852.2
HC≡C–C ₁₂ H ₂₅ (III)	2921.9	2852.4
HC≡C–C ₁₀ H ₂₁ (IV)	2921.5	2852.2

table to the values reported for thiols on gold.^{33,34} The same holds for the receding angles ($\Theta_r = 98$ – 101°).

The values for the 1-alkene monolayers prepared with our recently developed solution procedure¹⁶ (column 3) are all comparable to the values reported earlier for the well-ordered monolayers prepared on the Si(100) surface using neat 1-alkenes.⁶ Comparing the results from the monolayers of the 1-alkynes to those of the 1-alkenes shows that the average values for both the advancing and the receding contact angles as observed for the monolayers of 1-alkynes are slightly higher than those of the corresponding 1-alkenes ($\Theta_a = 108$ – 110° vs 108 – 109° ; $\Theta_r = 98$ – 101° vs 96 – 98°). They are also the highest values reported so far for any methyl-terminated alkyl monolayer on the Si(100) surface. This indicates that the monolayers of 1-alkynes are at least as well-ordered as these 1-alkene monolayers. The difference between the receding contact angles of the monolayers of the 1-alkynes and the 1-alkenes might be caused by differences in the orientation of the methyl groups.^{35,36}

The results from the infrared spectroscopy measurements on the monolayers of the 1-alkynes I–IV are shown in Table 2. The antisymmetric methylene stretching vibrations appear near 2921 cm^{-1} , and the symmetric vibrations are near 2852 cm^{-1} . The antisymmetric CH₃ vibration is visible at 2960 cm^{-1} . As an example, the spectrum of a monolayer of II is shown in Figure 4. It is known that shifts occur for these vibrations on going from the liquid to the solid state. In long, linear *n*-alkanes the antisymmetric vibration shifts from approximately 2928 to 2920 cm^{-1} and the symmetric vibration from 2856 to 2850 cm^{-1} .³⁷ Consequently, the packing of the 1-alkyne molecules in the monolayers resembles that of the solid state of *n*-alkanes. This indicates that the molecules are closely packed and form a well-ordered monolayer.

The values for the monolayers of 1-octadecyne (I) and 1-hexadecyne (II) are also similar to those previously reported for the corresponding 1-octadecene and 1-hexadecene monolayers on the Si(100) surface, which gave values of 2920 – 2921 and 2851 – 2852 cm^{-1} , respectively.⁶

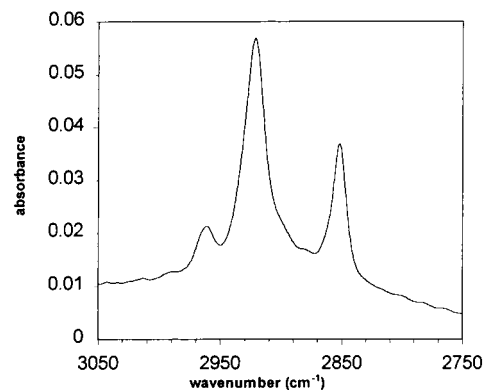
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**Figure 4.** Infrared spectrum (C–H stretching region) of a monolayer of II on Si(100).**Table 3. Tilt Angles for the Monolayers of 1-Alkynes I–IV^a**

monolayer	A_a^{s-pol}	α_a (deg)	A_s^{s-pol}	α_s (deg)	Θ_{IR} (deg)
I	0.064	70	0.035	66	33
	0.062		0.035		
II	0.047	71	0.027	71	27
	0.045		0.026		
III	0.035	60	0.018	66	40
	0.037		0.018		
IV	0.059	64	0.035	62	40
	0.060		0.036		

^a $A_a^{s-pol,p-pol}$, absorbance of the antisymmetric methylene stretch vibration using polarized light. $A_s^{s-pol,p-pol}$, absorbance of the symmetric methylene stretch vibration using polarized light. α , angle between the surface normal and the (anti)symmetric CH₂ dipole moment. Θ_{IR} , calculated tilt angle from IR-dichroism (see also Experimental Section).

As values for a monolayer of 1-tetradecene were not available and the values previously reported for 1-dodecene are less reliable,⁶ these monolayers were prepared by the same procedure as that for the 1-alkyne monolayers. The methylene stretch vibrations of these monolayers of 1-tetradecene and 1-dodecene showed absorptions at $\nu_a/\nu_s = 2922.2/2852.6\text{ cm}^{-1}$ and $\nu_a/\nu_s = 2922.1/2852.5\text{ cm}^{-1}$, respectively, again indicative of ordered monolayers in which the alkyl chains will adopt an all-trans conformation. In general, the absorptions of these methylene stretching vibrations shift to slightly higher values for shorter molecules.³⁸ The absorption values for the monolayers of 1-tetradecyne (III) and 1-dodecyne (IV) (Table 2) are well comparable to these values, which confirms that also the shorter 1-alkynes give well-ordered monolayers. Thus, on the basis of the results from the water contact angle measurements and IR spectroscopy it is concluded that all four 1-alkynes I–IV give well-ordered monolayers on the Si(100) surface and that the ordering of the alkyl chains in these monolayers is similar to, if not better than, that of the monolayers of the corresponding 1-alkenes.

The separate measurement of s- and p-polarized IR spectra of the 1-alkyne monolayers allows for an estimate of the tilt angle of the alkyl chains with respect to the surface normal. The differences between the absolute absorbances of the antisymmetric and symmetric methylene vibrations can be used for this purpose.⁶ The results are listed in Table 3. The calculated average tilt angle of the four 1-alkynes is $35 \pm 5^\circ$, which agrees with the value of $30 \pm 9^\circ$ that was previously found for the 1-alkene

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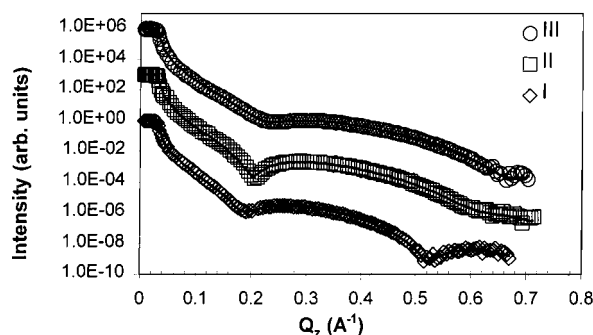


Figure 5. X-ray reflectivity profiles and fit curves for the monolayers of I–III.

monolayers by the same method.⁶ This again confirms a high similarity between the structures of monolayers of 1-alkynes and 1-alkenes on the Si(100) surface.

X-ray Reflectivity. Further information about the packing of the molecules in the monolayers is obtained by X-ray reflectivity.³⁹ This technique is based on the condition that the resulting wave vector transfer Q is parallel to the surface normal of the sample. Thus, X-ray reflectivity probes changes in the electron density perpendicular to the monolayer surface, which are used to determine the following sample parameters: the layer thickness, the electron density of the layer, and the interfacial roughness of the monolayer.³⁹

Three of the monolayers, that is, of compounds I–III, were studied with X-ray reflectivity. The results are depicted in Figure 5, which shows the reflectivity profiles of the monolayers as a function of momentum transfer Q_z . The shape of the reflectivity curve is determined by two characteristic regions.²⁵ An intensity plateau is typical for incident angles smaller than the critical angle for external total reflection ($Q < Q_{\text{crit}}$, with $Q = 4\pi/\lambda \sin \alpha_i$, with α_i the incident angle). From the position of the critical angle of total reflection the electron density of the layers is deduced. For angles beyond this critical angle the curve is characterized by a rapid decrease of the intensity ($\sim Q^{-4}$). Superimposed to this decay a low-frequency oscillation is obtained due to interference of the reflected X-ray waves at the air–monolayer and monolayer–Si interfaces. From its period ΔQ the layer thickness may be estimated using the Bragg equation $d = 2\pi/\Delta Q$. Due to the small thickness of the monolayers the curves show in fact only one maximum and two minima, which is, however, sufficient to obtain a precise fit of the monolayer thickness. Only for the monolayer of III, where the smallest thickness is expected, the second minimum could not be seen, because the background at high Q_z limits the analyzable range of the measurement. This gives less accurate results for the monolayer thickness, and therefore, the monolayer of IV, which will be even thinner, was not investigated with this technique.

The solid lines in Figure 5 are the best fit curves, using a two-layer model for the organic monolayer (vide infra). In all three cases there is a good agreement between the experimental data and the fit curve, which is not the case for fits using a single-layer model. The calculated electron density, the layer thickness, and the interfacial roughness of the various layers as obtained from these fit curves are listed in Table 4.

Table 4. Film Properties As Obtained from Two-Layer Fits to the X-ray Reflectivity Measurements

layer (air = 1)	prop- erty ^a	I	II	III
monolayer	t_2	18.3 ± 0.1	16.2 ± 0.2	15.8 ± 0.6
	ρ_2	0.31 ± 0.01	0.32 ± 0.01	0.27 ± 0.01
	σ_{12}	3.0 ± 0.1	2.7 ± 0.1	3.1 ± 0.1
intermediate layer	t_3	1.3 ± 0.7	0.2 ± 0.1	1.1 ± 0.4
	ρ_3	1.21 ± 0.02	1.21 ± 0.02	1.21 ± 0.02
silicon substrate ^b	σ_{23}	4.2 ± 0.1	2.4 ± 0.2	3.5 ± 0.3
	σ_{34}	5.0 ± 0.3	1.9 ± 0.2	3.1 ± 0.2

^a t_x = thickness (in Å) of layer x , ρ_x = electron density (in $e^{-}/\text{Å}^3$) of layer x , σ_{yx} = roughness (in Å) between layers y ($=x-1$) and x .
^b In all fits, a value of $\rho = 0.71 e^{-}/\text{Å}^3$ was used for the electron density of Si, as well as an absorption of 1.727×10^{-7} .

The results in Table 4 show that there is an approximately linear correlation between the calculated layer thickness and the length of the organic molecule, as can be expected for ordered alkyl layers on solid substrates. The monolayer of III is somewhat too thick compared to the length of the 1-tetradecyne molecule but still agrees with this linearity within experimental error, as this error is much larger in this case than that for the monolayers of I and II, because the second minimum in the reflectivity profile could not be observed. The layers of compounds I and II have an electron density of 0.31 and 0.32 $e^{-}/\text{Å}^3$, respectively, which is well comparable to the previously found value of 0.30–0.32 $e^{-}/\text{Å}^3$ for the monolayers of the corresponding 1-alkenes on the Si(100) surface. When compared to the electron density of crystalline alkanes of 0.35 $e^{-}/\text{Å}^3$,⁴⁰ the electron density of the alkyl chains in the monolayers shows that they are closely packed, as was already found with IR spectroscopy. The electron density of 0.27 $e^{-}/\text{Å}^3$ for the monolayer of III is somewhat lower compared to these values. This may indicate that this monolayer is slightly less densely packed, although the larger experimental error in this measurement compared to those of monolayers of I and II precludes definitive conclusions.

For all three monolayers the roughness of ~ 4 Å of the Si surface is comparable to the roughness of ~ 3 Å of the air–monolayer interface. This shows that a smooth, densely packed film has been formed on the Si surface. These values are also similar to those measured for the corresponding 1-alkene monolayers on the Si(100) surface,⁶ which confirms the high similarity between the monolayers of 1-alkenes and of 1-alkynes on this Si surface, as already observed with contact angle measurements and IR spectroscopy.

As mentioned above, the fitting of the reflectivity profiles as measured for the monolayers of the 1-alkynes I–III required the introduction of a second layer, that is, an intermediate layer between the organic layer and the Si surface. Such a layer was not necessary for the corresponding 1-alkene monolayers, which indicates that there is an important difference between the structure of the two layers. The calculated electron density of 1.21 $e^{-}/\text{Å}^3$ of this intermediate layer is the same for all three samples. Interestingly, this value is much higher than that of the alkyl layer, and also above that of Si, which has a value of 0.71 $e^{-}/\text{Å}^3$.²⁵ This indicates that there must be a very high density of probably strongly electronegative atoms in this interfacial region between the Si surface and the alkyl chains.

It is known that the Si–H groups that remain unreacted are oxidized to Si–OH groups, but further oxidation of

(39) For an explanation of the analysis of thin organic films on solid substrates by specular X-ray reflectivity see: (a) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852–5861. (b) Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. *Phys. Rev. B* **1990**, *41*, 1111–1128.

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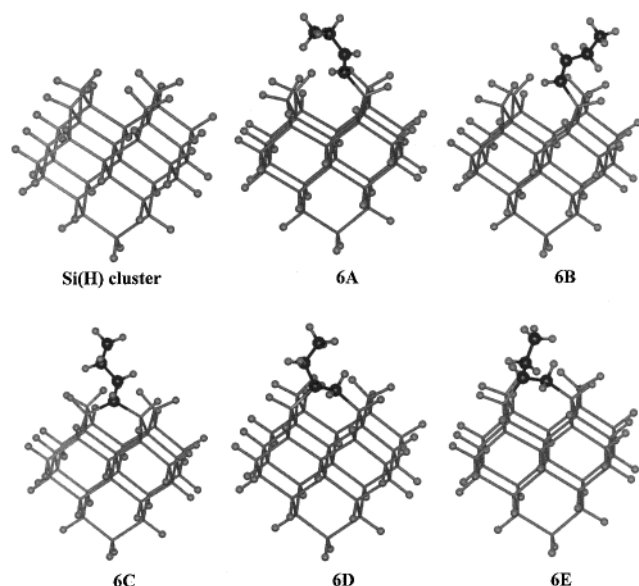


Figure 6. Si cluster with 32 Si atoms, the top of which represents the H-terminated Si(100) surface, and the five lowest-energy optimized structures **6A–6E** of this Si cluster bound to a 1-butyne molecule in various ways. Carbon and hydrogen atoms of these clusters in their fully optimized geometries are shown as balls for reasons of clarity. For more details see text.

the Si surface to SiO₂ does not occur.³ The electron density of SiO₂ is comparable to that of Si itself⁴¹ and thus significantly lower than the calculated value for the intermediate layer. Besides, Si surface oxidation would generate a SiO₂ layer with a thickness of at least several angstroms. Thus, it can be assumed that this interfacial layer is not due to the presence of SiO₂.

A possible explanation for the presence of the intermediate layer is that the 1-alkynes are bound to the Si surface in a different way than that for the 1-alkenes (see Figure 2). The various possible structures, which will be discussed in more detail in the next section, are shown in Figure 6. If each 1-alkyne forms two bonds to the Si surface, there will be an increase in the electron density near this surface when compared to that of the rest of the alkyl chain. If both bonds are formed to the terminal carbon atom of the 1-alkyne (structure **6C**), this carbon atom comes close to the Si surface and will also have a considerable negative charge (vide infra), which implies an increase in the electron density on this atom. A ball-and-stick model shows that the second carbon atom of the former acetylene moiety is in such a bonding situation in a plane not much above this first carbon atom and that it has limited flexibility, whereas the remaining methylene groups are highly flexible. Thus, the alkyl chains can be in an all-trans conformation, as found with IR spectroscopy, except for the first two carbon atoms. Consequently, a thin layer is formed between the Si surface and the alkyl tails, which has a higher electron density compared to that of these alkyl tails. A similar situation occurs when the two Si–C bonds are formed to the two different carbon atoms of the 1-alkyne. In this case these two atoms are both in the same plane and at the same height above the Si surface (structures **6D** and **6E**). If the 1-alkyne makes only one Si–C bond to the Si surface, such an electron-rich layer is not formed, as the two carbon atoms in the

remaining C=C double bond are not in the same plane above the Si surface (structures **6A** and **6B**) and also have on average the same electron density as that of an alkyl chain (vide infra). Thus, this gives a plausible explanation for the presence of an electron-rich intermediate layer between the Si surface and the alkyl chains.

The presence of such an intermediate layer of increased electron density makes it difficult to obtain an accurate value for the tilt angle of the alkyl chains in the monolayers of **I–III**. It can be reasoned that the interfacial region reduces the alkyl chain length by two methylene groups, as the first two carbon atoms of the former 1-alkyne are in this intermediate layer. Consequently, using the same formula as was used for the 1-alkenes⁶ ($\Phi_{\text{xray}} = \cos^{-1}[(d - 0.77)/(2.52(n - 1)/2)]$, with d = layer thickness and n = number of C atoms in the alkyl chain), the tilt angle of the alkyl chains in the monolayer of **I** would be 22°, and the monolayer of **II** would give a tilt angle of 20°. However, both values deviate significantly from the value of $35 \pm 5^\circ$ as determined with IR spectroscopy. It is known that IR dichroism can give large experimental errors in the calculated tilt angles,^{3,6} which suggests that there is probably a significant uncertainty in this latter value. The tilt angles calculated from the X-ray measurements also differ significantly from those obtained for the monolayers of the corresponding 1-alkenes (29° and 26° for monolayers of 1-octadecene and 1-hexadecene, respectively).⁶ This also indicates that it is not realistic to calculate a tilt angle for the monolayer of **III**, because of the large uncertainty in the thickness of that monolayer.

Si–C Interface: One or Two Si–C Bonds per Molecule? The results shown above indicate that 1-alkynes form densely packed, well-ordered monolayers on the H-terminated Si(100) surface. However, although the results from the X-ray reflectivity suggest a significant difference between the monolayers of 1-alkynes and 1-alkenes, so far no experimental evidence has been obtained about the nature of the binding between the 1-alkyne and this Si surface, that is, whether the 1-alkynes form one or two Si–C bonds per reacting molecule (see Figure 2).

The binding structure of the 1-alkyne at the Si interface was investigated with infrared spectroscopy, as these measurements can reveal the presence of C=C and/or C=C–H vibrations in the monolayer. If the 1-alkyne reacts only once with a Si–H group, forming only one Si–C bond per molecule, such vibrations will be present; if the 1-alkyne reacts with two Si–H groups on the surface and a doubly bonded structure is formed, these vibrations will be absent.⁴²

No vibrations from alkene moieties were observed in any of the IR spectra of the 1-alkynes investigated here. As an example, the spectrum of a monolayer of 1-hexadecyne (**II**) is shown in Figure 7. This observation strongly suggests that alkene moieties are absent in the monolayers of 1-alkynes on the H-terminated Si(100) surface, as the C=C vibration has been detected with IR spectroscopy in the monolayer of a 1-alkyne on the H-terminated Si(111) surface.^{3,5} Thus, the 1-alkynes seem to form two Si–C bonds per molecule to the Si(100) surface. However, it is known that the intensity of infrared absorptions in monolayers on solid substrates can be orientation-de-

(41) The electron density is proportional to the mass density of a material. For Si and SiO₂ these mass densities are 2.33 and 2.23 g/cm³, respectively. This results in $\rho_{\text{el}}(\text{Si}) = 0.71 \text{ e}^-/\text{\AA}^3$ and in $\rho_{\text{el}}(\text{SiO}_2) = 0.68 \text{ e}^-/\text{\AA}^3$. In ref 39 a ratio of $\rho_{\text{el}}(\text{SiO}_2)/\rho_{\text{el}}(\text{Si})$ of 0.96 ± 0.01 has been found experimentally. More information can be found in ref 25.

(42) In principle, the presence or absence of vibrations from the resulting tertiary C–H groups (methyne groups) in the doubly bonded structures could also be investigated with IR spectroscopy. However, these vibrations will most likely be too difficult to detect, as they are usually weak. Besides, the antisymmetric methyne vibration coincides with the much stronger symmetric methyl vibration and will therefore not be visible.

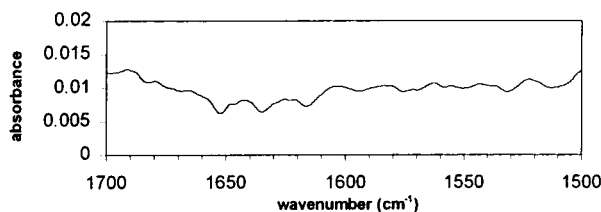


Figure 7. Infrared spectrum (C=C stretching region) of a monolayer of **II** on Si(100).

pendent, as has for example been observed for carboxyl groups in the case of thiol monolayers on gold.⁴³ It is not known to which degree this may also occur for the C=C vibrations in these monolayers, and therefore, the results from IR spectroscopy on their own are not fully conclusive.

Theoretical calculations were therefore performed to obtain further insight in the way the 1-alkynes are bound to the Si(100) surface. The structure of monolayers of 1-alkenes on Si surfaces has been successfully investigated by molecular mechanics calculations, using two-dimensionally repeating boxes to describe the modified Si surface.⁴⁴ Unfortunately, this molecular mechanics approach is not suitable here, as the predominant factor that determines the overall monolayer structure is formed by the long alkyl chains, while the precise binding geometry at the Si surface has only a small influence on the layer thickness.

Therefore, quantum chemical computations were performed on small silicon-alkyl clusters, for which the starting structures were obtained using molecular mechanics computations. As a model system was chosen a Si₃₂ cluster with a single alkyne molecule (1-butyne) bound in all chemically realistic geometries that could be designed on a three-dimensional ball-and-stick model of the surface. This Si cluster had four Si surface atoms that are terminated with two H atoms to describe the structure of the Si(100) surface (Figure 6, Si(H) cluster). The alkyne chain was always oriented above this Si surface.

Several different structures are possible for a 1-alkyne that is bound to the H-terminated Si(100) surface. The results from the molecular mechanics calculations showed that the relative order of stability of the structures depends on the force field that is used (see Supporting Information). Therefore, these molecular mechanics results are only suitable to select the structures that are chemically most realistic. In Figure 6 these structures are presented. If the C=C bond reacts only once with a Si-H group, this leads to the formation of a 1-alkenyl type structure. This leaves two possibilities:^{10,11} structure **6A** with the remaining C=C bond trans, and structure **6B** with the C=C bond cis. If the 1-alkyne forms two Si-C bonds to the surface, only one structure (**6C**) is possible if both bonds are formed to the terminal carbon of the 1-alkyne (1,1-bridge). Several different structures are possible if the two Si-C bonds are formed to the two different carbon atoms of the former 1-alkyne (1,2-bridge), as the second carbon atom of the 1-alkyne can reach any of the surrounding Si surface atoms and form a covalent Si-C bond to it. Only the two most suitable ones of these structures were considered, as these 1,2-bridged structures already have an energy significantly higher than that of **6A-6C**. They differ in the orientation of the remaining ethyl group: upward (axial) in structure **6D** and sideward (equatorial) in structure **6E**. The energy of all the other 1,2-bridged structures was

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Table 5. Relative Energies of the Structures **6A-6E** As Obtained from B3LYP/6-31G(d) Calculations

structure ^a	E_{rel} (kcal mol ⁻¹) ^b
6A	+19.57
6B	+21.82
6C	0
6D	+4.74
6E	+7.33

^a The structures are depicted in Figure 6. ^b Energy of the structures relative to the lowest-energy structure, that is, to structure **6C**.

considerably higher compared to that of **6D** and **6E** (>20 kcal mol⁻¹ difference). Therefore, they were eliminated from the present investigations.

More accurate calculations were performed by quantum mechanical B3LYP/6-31G(d) investigations of the structures **6A-6E**. The PCFF-optimized structures described above were used as starting structures for this purpose.⁴⁵ Quantum mechanical calculations have frequently been used to investigate the binding structure of small molecules adsorbed on Si surfaces under ultrahigh vacuum conditions.⁴⁶ Usually, a small Si cluster of only ~7-15 Si atoms is used to represent the Si surface, to reduce the time required for the computations. In the present calculations, however, a large cluster of 32 Si atoms was used. This has two advantages: (a) the underlying Si crystal structure is much better described by such a large Si cluster, and (b) the use of such a large cluster allows for an estimate of the positions of the valence and conduction bands of the semiconductor. This can be used to investigate possible shifts of these levels as a result of the binding of the organic molecule to the Si surface.

So far, these monolayers of 1-alkenes or 1-alkynes on H-terminated Si surfaces have not been investigated by quantum mechanical calculations, which means that there are no reference values available (e.g., for the binding energy). Therefore, three structures, that is, the H-terminated Si cluster shown in Figure 6, a 1-butene molecule, and a Si surface with a butyl group bound to the surface (i.e., the structure that is formed when 1-butene reacts with the H-terminated Si(100) surface), were also investigated. The results⁴⁷ showed that it is energetically favorable to bind an organic molecule to the Si surface. The binding of a 1-butene molecule to the Si cluster, resulting in the formation of the covalent Si-C bond and rehybridization of the terminal 1-alkene from sp² to sp³, yields 23.4 kcal mol⁻¹.

The results of the calculations on the various 1-alkyne structures are listed in Table 5, which shows the relative energies of the structures **6A-6E**. It is found that the 1,1-bridged structure **C** has the lowest energy. It was calculated that the energy of **6C** is 59.9 kcal mol⁻¹ lower than that of the separate 1-butyne molecule plus the H-terminated Si cluster.⁴⁸ The 1,2-bridged structures **6D**

(45) The choice to use the PCFF results is somewhat arbitrarily, as both force fields give rise to the same structures for the various clusters **A-E**.

(46) Recent examples are: (a) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1997**, *101*, 9581-9585. (b) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098-11099. (c) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 687-692. (d) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Zgierski, M. Z.; Wolkow, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 4532-4533. (e) Ellison, M. D.; Hamers, R. J. *J. Phys. Chem. B* **1999**, *103*, 6243-6251. (f) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. B* **1999**, *103*, 6803-6808. (g) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 11311-11317.

(47) The 6-31G(d) calculations gave the following energies: Si(H) cluster = -9285.887 914 1 Hartree; 1-butene = -157.221 066 9 Hartree; butyl chain bound to Si(H) cluster = -9443.146 197 5 Hartree.

(48) The 6-31G(d) calculations gave the following energies: 1-butyne = -155.966 868 4 Hartree; structure **6C** = -9441.950 328 8 Hartree.

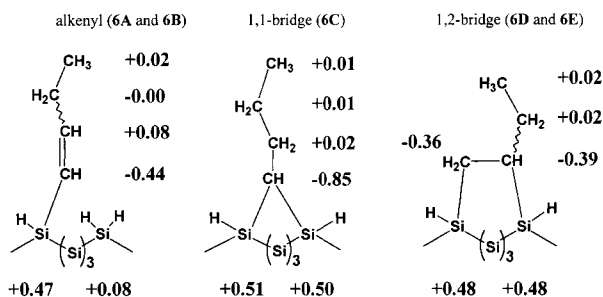


Figure 8. Group charges of selected moieties (sum charges of C and Si with H atoms bonded to them) in the various Si clusters. For the alkenyl-type structures (**6A** and **6B**, left) and the 1,2-bridged structures (**6D** and **6E**, right) the average values are shown, as the differences in the group charges are <0.01 for each pair of structures.

and **6E** are the intermediate situations, with energies that are only 4.7 and 7.3 kcal mol⁻¹ higher than that of **6C**. The two 1-alkenyl structures **6A** and **6B** have the highest energies, being approximately 20 kcal mol⁻¹ less favorable than the 1,1-bridged situation, since the C=C bond is weaker than a Si-C σ -bond. The formation of two Si-C bonds, this time combined with the rehybridization of the carbon atoms of the triple bond from sp to sp³, is not only structurally feasible, as was already found with the molecular mechanics calculations, but is apparently energetically highly favorable, despite the introduction of some ring tension in the resulting structure.

Binding of the organic molecule leads to changes in the charge distribution of the Si atoms in the cluster, especially of those at the surface. Figure 8 shows the charges as calculated for selected atoms from the clusters. Binding of the alkyl chain results in a Si surface atom that is more positively charged compared to the Si surface atoms that are bonded to hydrogen atoms. This is expected on the basis of Pauling's electronegativities for the various atoms: C = 2.5, H = 2.1, and Si = 1.8.⁴⁹ The binding of the organic compound also results in a small change in the difference between the HOMO and the LUMO of the structures, which is reduced by ~ 0.005 eV (0.12 kcal mol⁻¹) compared to that for the hydrogen-terminated cluster.

The results from the quantum mechanical calculations show that it is likely that upon reaction of a 1-alkyne with the H-terminated Si(100) surface two Si-C bonds will be formed per reacting molecule, as shown in Figure 2. The formation of the second Si-C bond is energetically favorable, which suggests that after the reaction no alkenyl-type structures will be left in the monolayer. This is in line with the results from infrared spectroscopy (vide supra), where no C=C vibrations were observed in the resulting monolayers of the 1-alkynes **I-IV**. These calculations also provide an explanation for the intermediate layer between the Si surface and the alkyl chains, as observed with X-ray reflectivity. In the 1,1-bridge structure **6C** as well as in the 1,2-bridged structures **6D** and **6E**, the two carbon atoms closest to the Si surface are (nearly) in the same plane and together have a high negative charge. This generates a thin layer with a relatively high electron density, as found with X-ray reflectivity. The alkenyl-type structures **6A** and **6B** do not give such a layer with high electron density, as for this situation the charges on the C and Si atoms are approximately equal to those found for the above-

mentioned 1-butyl group bound to the Si surface. The energy difference between the 1,1-bridged structure **6C** and the 1,2-bridged structures **6D** and **6E** is small ($\sim 5-7$ kcal mol⁻¹), which does not allow for a definitive conclusion about which structure will be formed. However, because of the high reaction temperature (165 °C), the radical mechanism (Figure 2),³ and the roughness of the Si(100) surface,¹⁷ it is not unlikely that the two situations will also both be present to some degree in the monolayers. Thus, on the basis of the results from IR spectroscopy, the X-ray reflectivity measurements, and the quantum mechanical calculations, it must be concluded that in monolayers of 1-alkynes on the H-terminated Si(100) surface two Si-C bonds are formed to this surface per reacting molecule.

Conclusions

A series of four 1-alkynes, ranging from 1-dodecyne to 1-octadecyne, has been synthesized and used to prepare organic monolayers on the H-terminated Si(100) surface. The properties of these monolayers were compared to those of monolayers of the corresponding 1-alkenes. The monolayers were formed by a thermal reaction of the organic compound with the Si surface. Well-ordered monolayers were obtained for the 1-alkynes in all cases, as became evident from water contact angle measurements, ATR infrared spectroscopy, and X-ray reflectivity measurements. The properties of the monolayers, that is, the hydrophobicity, the tilt angles of the alkyl chains, and the packing density of the alkyl chains in the monolayers, show that they are at least as ordered as the previously investigated monolayers of 1-alkenes on the Si(100) surface.⁶

On the H-terminated Si(100) surface the 1-alkynes can form either one or two Si-C bonds to the Si surface per reacting molecule. The results from IR spectroscopy showed the complete absence of any remaining C=C vibrations in the monolayers, which strongly suggests that the acetylene moiety had reacted twice with the Si-H groups on the surface. The X-ray reflectivity measurements indicated that the monolayers of 1-alkynes were considerably thinner, by $\sim 1.5-2$ Å, compared to the corresponding monolayers of 1-alkenes. However, an intermediate layer was found to be present between the Si surface and the alkyl chains, which showed that there is a significant difference between the binding of 1-alkynes and 1-alkenes to the Si(100) surface. It was inferred that this intermediate layer is the result of the formation of two Si-C bonds per 1-alkyne molecule.

The binding geometry of the 1-alkynes was further investigated by quantum mechanical calculations. These results showed that the formation of two Si-C bonds per 1-alkyne is energetically much more favorable, by $\sim 15-20$ kcal mol⁻¹, than the formation of only one Si-C bond, which would leave C=C groups near the Si surface. The situation in which both bonds are to the former terminal carbon atom of the 1-alkyne (the 1,1-bridged situation **6C**) is more favorable by $\sim 5-7$ kcal mol⁻¹ compared to the 1,2-bridged geometry (structures **6D** and **6E**). Combined with the results from IR spectroscopy and from X-ray reflectivity measurements on the monolayers, it is concluded that 1-alkynes form two Si-C bonds per reacting molecule on the hydrogen-terminated Si(100) surface.

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(49) A table of Pauling's electronegativities for atoms can be found in most organic chemistry textbooks. In this case they were taken from: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*, 3rd ed.; Plenum Press: New York, 1980; p 15.

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Supporting Information Available: A sketch of the flask used in the modification of the ATR crystals, detailed

procedures for the synthesis of 1-octadecyne (**I**), 1-tetradecyne (**III**), and 1-dodecyne (**IV**), and a table of energies from molecular mechanics calculations for the structures **6A–6E** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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