

# Towards $\pi$ -wires on a semiconductor surface: Benzyne on Si(001)

T. Glaser,<sup>[a]</sup> M. Tripp,<sup>[b]</sup> J.-N. Luy,<sup>[c]</sup> R. Tonner-Zech,<sup>\*,[c]</sup> U. Koert,<sup>\*,[b]</sup> and M. Dürr<sup>\*,[a]</sup>

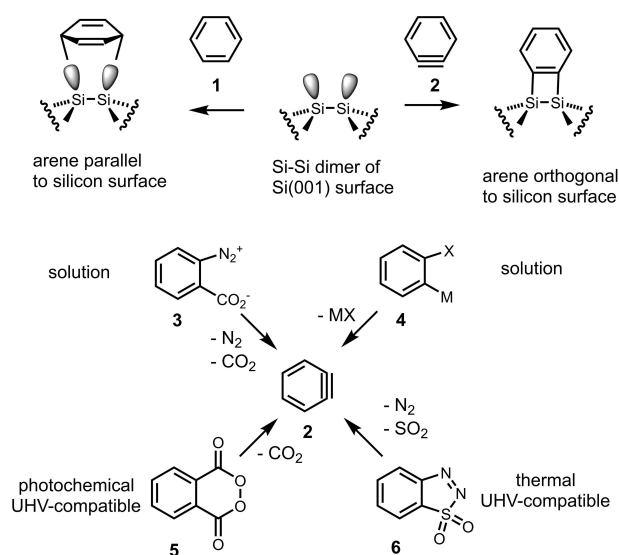
Towards the goal of covalently bound molecular wires on silicon, the adsorption of benzyne on Si(001) was studied by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and density functional calculations (DFT). The benzyne molecule is found to adsorb preferentially via the

strained triple bond on one dimer of the Si(001) surface which results in an intact  $\pi$  system covalently bound to the surface. With increasing coverage, the molecules primarily adsorb along the dimer rows; on stepped surfaces, these molecular wires are all oriented in the same direction.

## Introduction

Ortho-arynes are reactive species which have significance in organic chemistry as reactive intermediates with respect to mechanistic questions and as synthon in organic synthesis.<sup>[1–5]</sup> Benzyne, the simplest ortho-aryne, can be considered as strained alkyne positioned at a benzene, the prototype of an aromatic organic molecule.

The functionalization of semiconductor surfaces with such aromatic organic molecules is of interest in the context of molecular electronics,<sup>[6]</sup> in particular with respect to the technologically most important Si(001) surface. The Si(001) surface consists of rows of Si-dimer units (Figure 1), each Si-dimer can undergo [2+2]-type cycloaddition reactions with C–C double and triple bonds.<sup>[7]</sup> Benzene **1** binds to the silicon surface in a parallel mode,<sup>[8,9]</sup> losing its aromatic properties. Assumed that benzyne **2** could be added via [2+2] cycloaddition to the Si-dimers,<sup>[10–13]</sup> a row of covalently fixed benzene-analogue molecules, each orthogonal to the semiconductor surface, would be the result. If such a row of benzene-like molecules exhibits some type of  $\pi$ -stacking, it



**Figure 1.** Top: Benzene **1** binds on the Si dimer, which represents the basic unit of the Si(001) surface, parallel to the surface (only the “standard butterfly” configuration is shown<sup>[9]</sup>). Adsorption of benzyne **2** via a [2+2] reaction of the strained triple bond would lead to a covalently attached, aromatic benzene molecule on Si(001). Bottom: Different synthetic routes to benzyne. The precursor molecule benzoethiadiazaldioxide **6** decomposes into benzyne **2**, N<sub>2</sub>, and SO<sub>2</sub> when the temperature is increased to values above 0°C; the gas phase benzyne is then led into the UHV chamber for adsorption on the Si(001) surface.

represents a  $\pi$ -wire on the silicon surface which might be employed for charge transport in molecular electronics.

Here we address the synthetic challenge to add benzyne to the Si(001) surface. In such an approach, the generation of benzyne has to be compatible with ultra-high vacuum (UHV) conditions necessary for the preparation of atomically flat and clean Si substrates and the characterization of the surface chemistry by means of XPS and STM. Therefore, solution-based routes to benzyne **2** such as the decomposition of benzenediazonium-2-carboxylates **3**<sup>[14]</sup> or MX-eliminations from ortho-metallated halobenzenes **4**<sup>[15]</sup> as indicated in Figure 1 are not suitable. On the other hand, the photochemical decomposition of phthaloylperoxide **5**<sup>[16]</sup> or the thermal treatment of

[a] T. Glaser, M. Dürr  
Institut für Angewandte Physik und Zentrum für Materialforschung,  
Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen,  
Germany

[b] M. Tripp, U. Koert  
Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße  
4, D-35032 Marburg, Germany  
E-mail: koert@chemie.uni-marburg.de

[c] J.-N. Luy, R. Tonner-Zech  
Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Uni-  
versität Leipzig, Linnéstraße 2, D-04103 Leipzig, Germany  
E-mail: ralf.tonner@uni-leipzig.de

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1,2,3-Benzothiadiazol-1,1-dioxide  $\mathbf{6}^{[17]}$  should be compatible with experiments in UHV.

## Experimental and Theoretical Methods

STM and XPS experiments, as well as sample preparation were performed in a UHV chamber with a base pressure  $<1 \times 10^{-10}$  mbar. Si(001) samples were prepared by degassing at 700 K and repeated direct current heating cycles up to 1450 K. With cooling rates of about 1 K/s, a well ordered  $2 \times 1$  reconstruction was obtained.<sup>[18,19]</sup>

Benzothiadiazoldioxide was used as precursor of benzyne. It was synthesized according to Wittig and Hoffmann<sup>[17]</sup> (experimental and spectroscopic details are given in the Supporting Information) and stored at  $-25^\circ\text{C}$ . For the adsorption from gas phase, the temperature of the glass vessel, in which 25 mg of the precursor were stored, was increased to  $0^\circ\text{C}$ . The formed benzyne and byproducts were introduced into the UHV chamber via a short stainless steel tube and a precision leak valve.

STM experiments were performed with a variable temperature STM (Omicron VT-STM). XPS measurements were performed using an Al  $K_\alpha$  X-ray source with a monochromator (Omicron XM1000) and a hemispherical energy analyser (Omicron EA125). All XPS spectra were referenced to the Si  $2p_{3/2}$  peak at 99.4 eV.<sup>[20]</sup> For fitting the XPS data, Voigt-profiles were used; they are composed of 90% Gaußfunction and 10% Lorentzfunction. Full width at half maximum (FWHM) was set to approximately 0.9 eV in case of the single components of the C1s signal, a typical value for single lines measured in this setup.<sup>[21–23]</sup> UPS spectra were taken with a He I gas discharge source.

DFT-based calculations were performed with the Vienna Ab Initio Simulation Package (VASP 5.4.4)<sup>[24–26]</sup> using the PBE exchange correlation functional<sup>[27]</sup> and setting the plane wave energy cutoff to 400 eV. A total energy difference of  $10^{-6}$  eV and “accurate” precision is used for SCF convergence. For structural optimization, the force convergence criterion was set to  $10^{-2}$  eV/Å. Standard PAW-pseudopotentials<sup>[28]</sup> PBE.54 with a large core configuration are used to speed up the calculations. A  $\Gamma$ -centered  $2 \times 2 \times 1$   $k$ -mesh was chosen together with a setup of Si(001) slabs (six layers, two bottom layers frozen and terminated with hydrogen atoms) as determined in previous work.<sup>[29]</sup> All structures were optimized at the PBE level while dispersion effects were considered via the DFT–D3 scheme including an improved damping function.<sup>[30]</sup> Adsorption energies ( $E_{\text{ads}}$ ) are computed as difference (Equation 1):

$$E_{\text{ads}} = E_{\text{adsorbate@surface}} - E_{\text{free molecule}} - E_{\text{surface}} \quad (1)$$

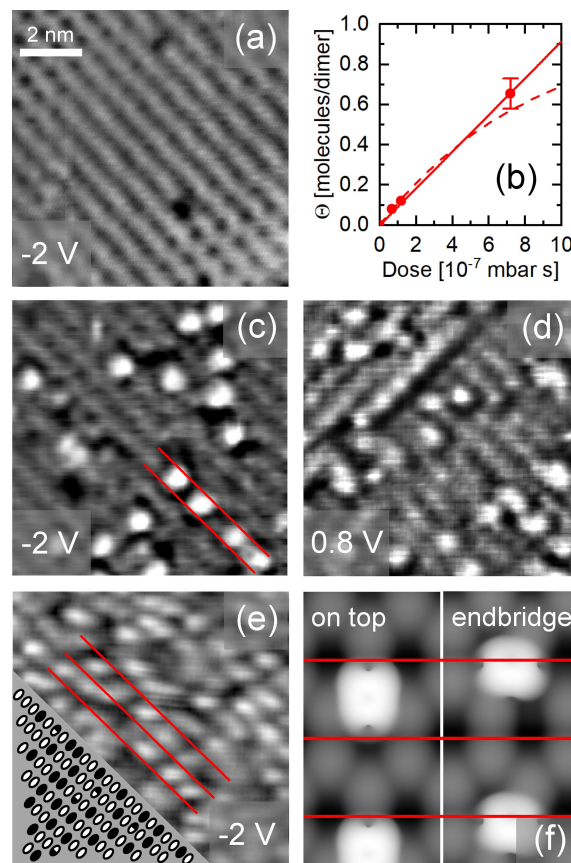
This energy is split up in contributions from the exchange-correlation functional ( $\Delta E_{\text{elec}}$ ) and the dispersion contribution from DFT–D3 ( $\Delta E_{\text{disp}}$ ).

The band structure of the benzyne molecules in on-top adsorption mode has been calculated at full surface coverage with PBE. As we are interested in the bands resulting from the organic layer, the Si-slab has been removed from the optimized surface-adsorbate structure and dangling C-bonds were saturated with hydrogen atoms. A constrained reoptimization of H positions has been carried out.

The density of states (DOS) of a structure with coverage  $\theta = 0.5$  has been calculated with the range-separated hybrid functional HSE06<sup>[31]</sup> based on the PBE–D3 optimized structure. In order to compare to experimental UPS data, a uniform Gaussian broadening of 0.5 eV and a shift of the Fermi-level by 1.73 eV has been applied to the raw peaks.

## Results and Discussion

As a first step, the adsorption of benzyne on a clean Si(001) surface at low and medium coverage was studied by means of STM. In Figure 2(a), (c) and (d), STM images of the clean Si(001) surface as well as after adsorption of benzyne at low coverage (0.08 molecules per dimer) are shown. Both at negative bias ( $U = -2$  V, Figure 2(c)) as well as at positive sample bias ( $U = +0.8$  V, Figure 2(d)), bright features are observed in the STM images. They are directly associated with the adsorbed molecules; more than 90% (out of more than 400 features counted) are symmetric with respect to the dimer rows, indicating that the single benzyne molecules adsorb preferentially on top of one dimer (“on top” or “one dimer” adsorption configuration). In previous experiments with cyclooctynes, the strained triple bond was shown to exhibit a high reactivity which leads to selective



**Figure 2.** (a), (c) to (e): STM images (sample bias  $U = -2$  V in (a), (c) and (e),  $U = +0.8$  V in (d)) of (a) a clean Si(001) surface and (c) to (e) benzyne adsorbed on Si(001). Adsorption and measurement temperature was 300 K. Bright features are assigned to adsorbed benzyne molecules. In (c) and (e), red lines are drawn between selected dimer rows. In the bottom left corner of (e), the adsorption pattern is shown schematically. Oval features shown in black represent unreacted silicon dimers; white ovals represent benzyne molecules adsorbed on top of one dimer. Half-filled ovals represent defects or benzyne molecules in endbridge configuration. (b) Adsorbed molecules per dimer vs. dosage of benzyne molecules. Connected line: linear fit. Dashed line: Langmuir-type adsorption behavior. If not separately indicated, error bars are within symbol size. (f) Calculated STM images at  $U = -2$  V for on-top (left) and endbridge configuration (right) based on surfaces of constant charge density of approx.  $0.27 e^-/\text{\AA}^2$ . Red lines separate dimer rows.

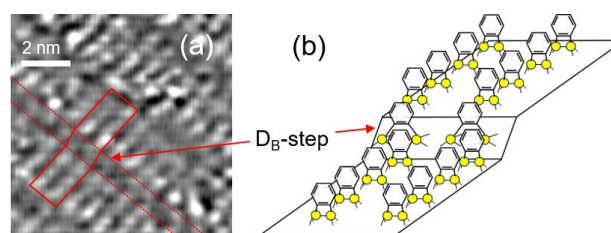
adsorption on top of one dimer even in the case a second functional group is present in the molecule.<sup>[11–13]</sup> If this is also applicable to benzyne, i.e., the molecules adsorb via the strained triple bond of the molecule, it results in a symmetric adsorption configuration of the molecules with an intact  $\pi$ -system, in accordance with the symmetric bright features observed in the STM images. Comparison with calculated STM-images (Figure 2(f), details on calculations see below) also indicate that the on-top configuration can be clearly distinguished from molecules which adsorb over two dimers ("endbridge" configuration). Quantitative evaluation of line scans through the symmetric features along the dimer rows (Figure S1 in the Supporting Information) indicate that they are less than two dimers in width, in good agreement with the calculated images of the on-top configuration (Figure 2(f)).

We can exclude a major contribution of  $\text{SO}_2$  and  $\text{N}_2$ , the byproducts of the reaction leading to benzyne, to the observed adsorption features as we do not detect an N 1s or an S 2s signal in the XPS spectra, neither at low nor at higher coverage. There are some additional dark features in the STM images and a few of the bright features deviate in size or shape; they might be defects of the Si(001) surface, additional adsorbates (see below), or, in the latter case, adsorbed benzyne molecules in the endbridge configuration.

In Figure 2(e), an STM image of Si(001) with a higher coverage of benzyne molecules (0.66 molecules per dimer) is shown. Also at increased coverage, the main adsorption motive known from low coverage, i.e., bright features following the dimer row structure, is predominantly observed. The resulting adsorption pattern is shown schematically in the bottom left corner of Figure 2(e). Some of the bright features appear between the dimers rows, they might be attributed to a low contribution of endbridge configurations or defects. In Figure 2(b), the ratio of molecules per dimer as a function of applied dose of benzyne molecules is shown for three coverages. Within the error bars, the data are compatible with a Langmuir-type of adsorption. However, they can be also described with a linear relationship. Such a deviation from strict Langmuir-type adsorption behavior would point towards an extrinsic precursor state on top of already saturated adsorption sites<sup>[32,33]</sup> or at least some steering of incoming molecules from an occupied to an unoccupied adsorption site as observed previously for cyclooctyne.<sup>[10,34]</sup>

In order to investigate the adsorption at full surface coverage, benzyne was adsorbed on a Si(001) surface miscut by  $5.5^\circ$  towards the [110] orientation. These miscut surfaces form double atomic height  $D_B$ -steps and the dimer rows are all aligned in one direction.<sup>[35,36]</sup> In Figure 3(a), an STM image of such a surface which is completely covered with benzyne molecules is shown. Besides some defects (black features in Figure 3(a)), only bright features are observed, indicating that almost all dangling bonds on the surface were reacted with benzyne molecules. Within each terrace, clear lines which are associated with the dimer rows, are observed thus indicating ordered arrangements of the adsorbed benzyne molecules. The situation is schematically shown in Figure 3(b).

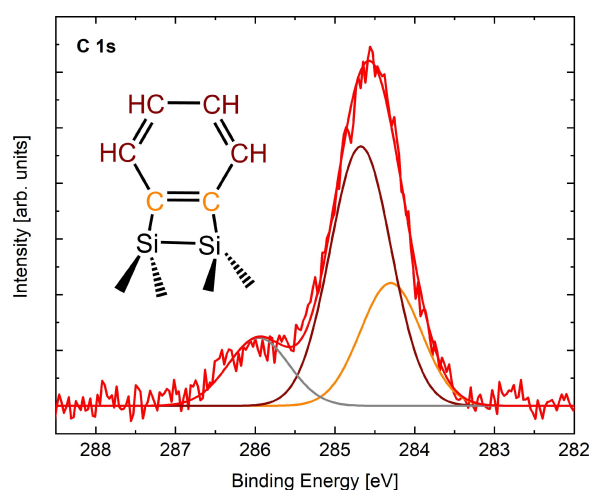
Further information on the chemical bonding of benzyne on Si(001) was obtained by means of XPS. The C 1s spectrum in



**Figure 3.** (a) STM image of a Si(001) surface miscut by  $5.5^\circ$  towards the [110] orientation ( $U = -2$  V,  $I = 0.5$  nA). The sample is completely covered with benzyne molecules. A schematic view of the area indicated by the red frame is shown in (b) with the adsorption of benzyne on Si(001) along the dimer rows of the stepped, single-domain surface.

Figure 4 was taken after a benzyne dosage of  $5 \times 10^{-7}$  mbar-s at room temperature which results in about 0.5 adsorbed molecules per dimer. The main peak in Figure 4 is too broad for one single component and can be divided into two contributions. If we keep the width of these two components constant at 0.9 eV, the main peak can be represented by a smaller component at a binding energy of 284.3 eV (orange) and a larger contribution at 284.7 eV (dark red).

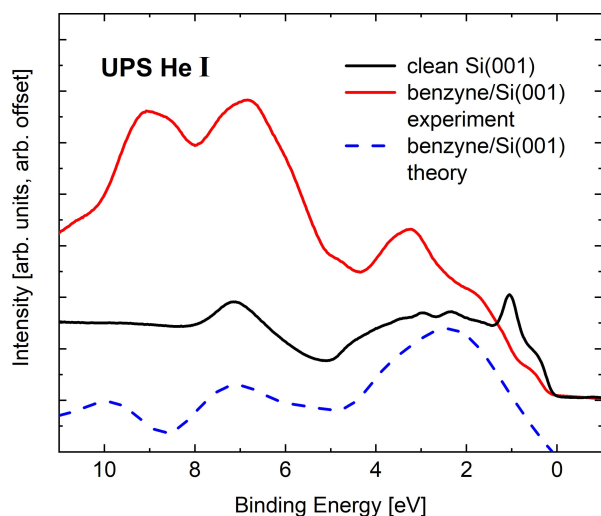
The peak at 284.3 eV is assigned to the two carbon atoms of the benzyne molecule binding to the Si(001) surface;<sup>[11,20,37]</sup> the second peak at a binding energy of 284.7 eV is assigned to the further 4 carbon atoms in the benzyne molecule. The obtained value for the binding energy is typical for carbon atoms in molecules containing C=C double bonds or aromatic systems.<sup>[22,37,38]</sup> The intensity ratio of these two peaks is 1:2 as expected for the ratio of carbon atoms in the adsorbed benzyne molecule which is shown in the inset of Figure 4. The peak at highest binding energy in the C 1s spectrum at 286.0 eV (grey)



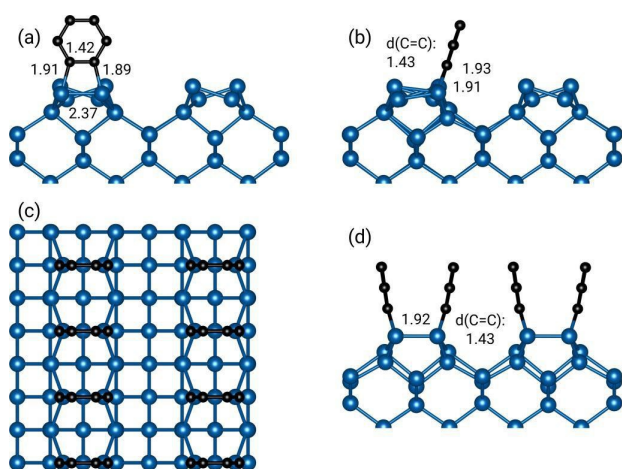
**Figure 4.** C 1s spectrum after the adsorption of benzyne on the Si(001) surface at room temperature. The expected reaction product is shown as inset. The main peak can be decomposed into two contributions: The peak shown in orange is assigned to carbon atoms binding to the silicon surface. The peak shown in dark red is assigned to the remaining 4 atoms of the benzyne molecule. The peak at highest binding energy is assigned to a small amount of contaminations on the surface with carbon bound to oxygen.

component) is assigned to some contamination on the surface, e.g., some oxygen containing species as we observe a small signal in the O1s region. They might be associated with the black and/or additional bright signatures in the STM images and are a possible origin for the deviation from a perfect ordering at increased coverage.

In Figure 5, the UPS spectrum taken from a clean silicon surface (black) is compared to a spectrum taken after adsorption of benzyne. In the spectrum from the clean surface, the dangling bond surface states show up as a dominant peak



**Figure 5.** UPS spectra of the clean (black) and benzyne-covered (red) Si(001) sample. For the clean surface, the characteristic peak of the dangling bonds is observed at low binding energy. For the spectrum of the benzyne-covered Si(001) surface, adsorption and measurement were performed at room temperature, coverage was approximately 0.65 molecules per dimer. The intensity of the dangling bond peak is strongly reduced; in the range of higher binding energy, molecular peaks are observed. Qualitatively, the peak positions are in good agreement with the calculated UPS spectrum ( $\theta_{\text{theory}} = 0.5$ , the corresponding charge distributions are shown in Figure S2 in the Supporting Information).



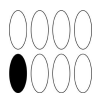
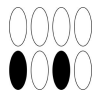
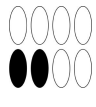
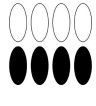

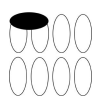
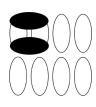
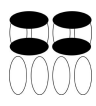
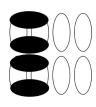

**Figure 6.** Computed (PBE–D3) adsorption structures for benzyne on Si(001)- $(4 \times 2)$ . (a) on-top and (b) bridge adsorption modes for lowest coverage ( $\theta = 0.125$ ) considered. Molecular arrangement for full coverage ( $\theta = 1$ ) for (c) on-top in top view and (d) bridge in side view. Bond lengths are given in Å.

at low binding energy. After the adsorption of benzyne, this peak is strongly reduced in intensity, indicating that adsorption takes place via the dangling bonds. Additional peaks at higher binding energy are observed after adsorption, they are attributed to molecular states of the adsorbed benzyne molecules (compare Figure S2 in the Supporting Information).

To shed further light on the adsorption configuration and electronic states of the adsorbed benzyne molecules on Si(001), we have performed DFT calculations. The investigation of adsorption structures resulted in stable configurations for adsorption in on-top and bridge modes shown in Figure 6. We investigated coverages (calculated as molecules/dimer, see Figure 2) from  $\theta = 0.125$  (Figures 6(a) and (b)) to  $\theta = 1$  (Figures 6(c) and (d)). Adsorption energies ( $E_{\text{ads}}$ ) for a series of surface coverages and molecular arrangements are shown in Table 1. Further adsorption configurations in analogy to the adsorption of benzene<sup>[8,9]</sup> have been investigated but all these structures were found to be significantly less stable (compare Figure S3 in the Supporting Information).

We find that for adsorption of the first molecule, the on-top mode is preferred by  $19 \text{ kJ mol}^{-1}$  over the bridge mode which is mainly due to a stronger covalent bonding energy contribution ( $\Delta\Delta E_{\text{elec}} = 26 \text{ kJ mol}^{-1}$ ) while the bridge mode shows a slightly larger stabilization by dispersion interaction ( $\Delta\Delta E_{\text{disp}} = 7 \text{ kJ mol}^{-1}$ ) resulting from the slight bending over the dimer rows (Figure 6(b)). The increase in coverage results in a small preference for the bridge mode already for  $\theta = 0.25$  which is a combination of stronger covalent bonding and increased dispersion interaction. The differences in energy are however small ( $14 \text{ kJ mol}^{-1}$  comparing the structures with the largest  $E_{\text{ads}}$  value for the same surface coverage). More interesting is that the adsorption energy hardly changes upon increasing coverage. The inverse trend of covalent and dispersion bonding contributions for increasing coverage leads to rather constant energies from  $\theta = 0.25$  to  $\theta = 1$  for both adsorption modes. This is very unusual since commonly, adsorption energies for such large organic molecules decreases significantly upon increasing coverage due to intermolecular repulsion.<sup>[29]</sup> The reason here is clearly the adsorption of benzyne in an upright configuration perpendicular to the surface which leads to favorable arrangements in both adsorption modes even at full coverage (Figures 6(c) and (d)). The molecule shows a very large adsorption energy which even by far exceeds the bonding of other strongly bound alkynes on Si(001) like acetylene ( $E_{\text{ads}} = -268 \text{ kJ mol}^{-1}$ ) and cyclooctyne ( $E_{\text{ads}} = -308 \text{ kJ mol}^{-1}$ ).<sup>[34]</sup> The main reason is the very good match of the adsorbate to the surface which requires minimal distortion for bonding (called preparation energy  $\Delta E_{\text{prep}}$  in previous work). As shown previously, acetylene has to distort strongly mainly by rearranging from a linear to a bent form resulting in  $\Delta E_{\text{prep}} = 364 \text{ kJ mol}^{-1}$  for the adsorbate. Even cyclooctyne, which already has a non-linear arrangement of atoms around the triple bond, shows a smaller but still significant  $\Delta E_{\text{prep}} = 313 \text{ kJ mol}^{-1}$ .<sup>[34]</sup> Benzyne nevertheless has a strongly bent triple bond already in the molecular structure and thus shows a significantly smaller value of  $\Delta E_{\text{prep}} = 97 \text{ kJ mol}^{-1}$ . It is thus not surprising that we find barrierless adsorption pathways from the gas phase into both on-top and bridge adsorption modes. This is an indication for a direct adsorption without a stable precursor

**Table 1.** Adsorption energy ( $E_{\text{ads}}$ ) with contributions from electronic ( $E_{\text{elec}}$ ) and dispersion ( $E_{\text{disp}}$ ) effects in  $\text{kJ mol}^{-1}$  for different coverages  $\theta$ .

Adsorption structure	arrangement	$E_{\text{ads}}$	$E_{\text{disp}}$	$E_{\text{elec}}$
<b>on-top</b>				
$\theta = 0.125$		-464	-29	-435
$\theta = 0.25$		-463	-42	-421
$\theta = 0.25$		-470	-47	-423
$\theta = 0.5$		-474	-59	-415
$\theta = 1$		-474	-65	-409
<b>bridge</b>				
$\theta = 0.125$		-445	-36	-409
$\theta = 0.25$		-484	-50	-434
$\theta = 0.5$		-488	-56	-431
$\theta = 0.5$		-484	-64	-419
$\theta = 1$		-488	-69	-419

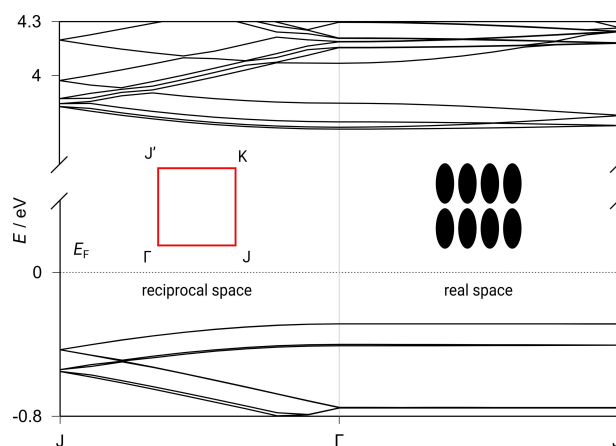
intermediate on the clean surface. Notably, the intrinsic bond strength (calculated as the interaction of deformed adsorbate and surface, thus after considering the preparation energy) is somewhat smaller ( $60\text{--}70 \text{ kJ mol}^{-1}$ ) compared to acetylene and cyclo-octyne. We can thus conclude that the highly strained arrangement of benzyne makes it an ideal match to the Si(001) surface dimer resulting in a very strongly bound structure. The preference of the on-top mode for initial adsorption indicates that this will be the dominant structure also towards full coverage: After a few adsorbates adsorb in on-top mode, less and less surface dimers will be available for bridge adsorption. Furthermore, dispersion-mediated steering of incoming adsorbates could be a valid

mechanism towards preferential adsorption in on-top structures at full coverage.<sup>[39]</sup>

As outlined in the introduction, the creation of  $\pi$  wires is a motivation for the current study. We thus investigated the band structure of the on-top structure with full coverage (Figure 7) which corresponds to the situation shown in Figure 3. We can clearly distinguish between band dispersion along the dimer row (in reciprocal space:  $\Gamma \rightarrow J$ ) and across the dimer rows (in reciprocal space:  $\Gamma \rightarrow J'$ ). While there are flat bands found across the dimer rows, the bands show significant dispersion along the rows indicating stronger electronic interaction between neighboring adsorbates. This effect is more pronounced for the occupied bands but can also be found for the unoccupied bands. This gives a hint that a full layer of benzyne adsorbed on Si(001) can indeed be used as a set of molecular  $\pi$ -wires which could show anisotropic charge transport properties. From this initial findings, hole transport (i.e., removing an electron from the dispersed occupied bands) in the direction along the dimer rows seems the most promising effect to search for in the future.

## Conclusion

In conclusion, benzyne which has been prepared via thermal decomposition of benzothiadiazoldioxide can be used for the functionalization of highly reactive silicon surfaces under UHV conditions. Both experiment and theory suggest upright adsorption of the resulting benzene-like molecule, preferentially on top of one dimer. At increased coverage, the surface-adsorbed molecules arrange in lines along the dimer rows. The calculated band structure indicates much stronger delocalization of the charge carriers along the dimer rows when compared to the direction perpendicular to the rows. The



**Figure 7.** Calculated band structure (PBE) for the on-top adsorption mode at coverage  $\theta = 1$ . Only the organic layer has been considered, see method section for details. The surface unit mesh (shown in red) emphasizes that the reciprocal space path  $\Gamma \rightarrow J$  corresponds to real space direction along the dimer row while  $\Gamma \rightarrow J'$  corresponds to the direction across rows. The Fermi energy ( $E_F$ ) corresponds to an artificial reference level resulting from the computation.

benzyne molecules adsorbed on one dimer row can thus be seen as a molecular  $\pi$ -wire on top of the silicon surface.

## Supporting Information

The Supporting Information includes: description of the synthesis of benzothiadiazoldioxide **6** including general methods and materials; NMR-spectra of all compounds; line scans across the features associated with adsorbed benzyne in STM images; calculated charge distributions of adsorbed benzyne molecules; additional calculated adsorption structures; information on computational raw data.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Raw data underlying the results of the computational section are freely available via the NOMAD database: <https://dx.doi.org/10.17172/NOMAD/2022.05.12-1>. Further data that support the findings of this study are available from the corresponding authors upon reasonable request.

**Keywords:** adsorption · benzyne · molecular wires · organic molecules · silicon surface

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