**On-Surface Reactivity Hot Paper**

**Aromatic Azide Transformation on the Ag(111) Surface Studied by Scanning Probe Microscopy**

Jack Hellerstedt*, Aleš Cahlík†, Oleksander Stetsovich, Martin Švec, Tomoko K. Shimizu, Pingo Mutombo, Jiří Klívar, Irena G. Stará, Pavel Jelínek,* and Ivo Starý*

**Abstract:** Chemical transformation of 9-azidophenanthrene on the Ag(111) surface was studied by nc-AFM in UHV. High-resolution imaging supported by first-principle calculations revealed the structure of the final products that originated from a common and elusive 9-phenanthryl nitrenoid intermediate chemisorbed on the Ag(111) surface. A formal nitrene insertion into the C–H bond along with its dimerisation and hydrogenation were identified as main reaction channels. Thus, the ability of aryl azides to form covalent α- and π-bonds between their transformation products on a solid surface was demonstrated at a single-molecule level.

Organic azides are attractive not only for synthetic chemistry[1] but also for their applicability to biosciences[2] and materials chemistry.[3] Importantly, copper(I)-catalysed azide–alkyne cycloaddition yielding 1,2,3-triazoles has gained enormous popularity across various branches of science constituting click chemistry.[4] Organic azides are widely employed in transition-metal-catalysed (Fe, Mn, Rh, Ru, Ir, Cu, Ag, Au) nitrene transfer reactions (for example, amination and aziridination).[5] The essential mechanism is that organic azides generate free nitrene intermediates under the influence of heat or UV light. Their high reactivity can be utilised in the photoaffinity labelling of biomolecules[6] or synthesis of N-heterocycles.[7,8] Indeed, the reactivity of nitrenes is “wonderfully complex”[9] and has been extensively documented in predominantly solution-based studies[1,9] as well as gas phase (utilising flash vacuum thermolysis, FVT).[10]

and the solid state (in a frozen matrix).[8,11] Reaction channels that nitrenes undergo are typically insertion into the C–H bond, 1,2-rearrangement to imines, addition across the adjacent C–C bond forming azirine, ring expansion/opening, and dimerisation to azo compounds. Despite accomplishments in azide chemistry, azides and nitrenes in a dimensionally confined space, namely on a solid surface under ultrahigh vacuum (UHV) have not been systematically studied so far except for azide–alkyne cycloaddition reactions.[12]

In the context of an emerging field of on-surface chemistry at the nanoscale,[13] there is an urgent need for developing a wider portfolio of building blocks and synthetic methodologies for the construction of complex molecular 2D architectures by connecting them through covalent bonds. It can be exemplified by the UHV bottom-up synthesis of uniform graphene nanoribbons (GNR)[14] where Ullmann coupling accompanied by cyclodehydrogenation dominates. These reactions are usually assisted by coinage metals[14a,15] and due to the catalytic effect of the single crystal surface, transferring such processes to semiconducting or insulating surfaces is difficult. It is therefore unsurprising that there are only scattered examples of an on-surface synthesis on nonmetals.[16]

In the quest for identifying other useful on-surface reactions triggered by heat (or light), we turned our attention to 9-azidophenanthrene[16,17] (Figure 1) whose transformation on the Ag(111) surface was studied by UHV scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (nc-AFM). High-resolution imaging supported by first-principle calculations revealed the structure of the prevalent products 2–5 that pointed to their origin in a common and elusive 9-phenanthryl nitrenoid intermediate chemisorbed on the Ag(111) surface. The distribution of the

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**Figure 1.** 9-Azidophenanthrene[16,17] whose transformation to the products 2–5 on the Ag(111) surface was studied by UHV STM/nc-AFM.

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[1] Dr. J. Hellerstedt,[10] A. Cahlík,[1] Dr. O. Stetsovich, Dr. M. Švec, Dr. P. Mutombo, Dr. P. Jelínek
Institute of Physics, Academy of Sciences of the Czech Republic
Cukrovarnická 10, 16200 Prague 6 (Czech Republic)
E-mail: jelinekp@fzu.cz

Regional Centre of Advanced Technologies and Materials
Faculty of Science, Palacký University
Šlepčitelá 27, 78371 Olomouc (Czech Republic)

[3] J. Klívar, Dr. I. G. Stará, Dr. I. Stary
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
Flemingoovo nám. 2, 16610 Prague 6 (Czech Republic)
E-mail: stary@uochb.cas.cz

[4] Dr. O. Stetsovich, Dr. T. K. Shimizu
National Institute for Materials Science (NIMS)
1-2-1 Sengen, Tsukuba 305-0047 (Japan)

[5] These authors contributed equally to this work.

[6] Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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final products showed that the main reaction channels were formal nitrene insertion into the C–H bond along with its dimerisation and hydrogenation.

The design of the aryl azide 1 stemmed from two contradictory requirements: 1) It has to be volatile enough not to decompose during thermal evaporation under UHV conditions and 2) it needs to interact sufficiently with the substrate to enable both imaging of molecule adsorbates (by reducing their mobility) and allow for the thermal generation of a “nitrene” intermediate (see below) without desorbing from the surface. Indeed, it was possible to deposit native azide 1 directly onto the cold Ag(111) surface (15 K, coverage: ca. 35 molecules per 30 × 30 nm²). A flat structure of the molecular adsorbate allowed for the acquisition of high-resolution nc-AFM images with submolecular detail at 4.5 K (Figure 2). As can be seen, the experimental image of 1 was in full accord with the corresponding simulation based on the chemical structure.

Remarkably, the result completely changed upon depositing the azide 1 onto an ambient temperature Ag(111) substrate (300 K, coverage: ca. 145 molecules per 80 × 80 nm²): Under such conditions, azide 1 was no longer present on the surface but new molecular architectures arose (Figure 3). Further heating up to the desorption temperature (ca. 620 K) did not lead to significant changes in the structure, self-assembly or distribution of molecular adsorbates. By utilising high-resolution STM/nc-AFM imaging supported by ab initio density functional theory (DFT) calculations to optimise the structure of molecular adsorbates and simulate their nc-AFM images, we could sort out, based on their appearance, the manifold molecular architectures into 1) large clusters, 2) dominating dimers or dimer-like species, and 3) rare individual molecules.

The clusters of a complex and variable composition appeared to consist of circa 2–4 molecular subunits (comparable in size to the phenanthrene core), the structure and mutual interaction (covalent vs. noncovalent) of which were not possible to elucidate. The non-planar structure of the clusters on the surface made nc-AFM submolecular resolution imaging and subsequent structural assignment impossible. Based on the large-area images, we estimated that they encompassed circa 35% of all adsorbed molecular materials being randomly distributed on the Ag(111) surface.

Dimers and dimer-like species were the most abundant molecular architectures we identified (Figure 3). In the large area STM images, they represented circa 65% of all adsorbed molecular materials. Evidently, the dimeric structures contained two phenanthrene subunits but the nature of their linkage appeared to be manifold as can be seen from the diverse nature of shapes observed (Figure 4). The planar nature of these species is particularly well suited to study via submolecular nc-AFM imaging. The images are compared directly with simulations, revealing both covalent (in 2, 3, 4a and 4b, Figures 4a–d) and noncovalent (in dimers of 5, Figures 4e, f) dimeric structures. The covalent character of the bonding interaction between the two adjacent phenanthrene units can be determined in the data by a comparatively short distance (Figures 4a–d) or even by displaying interconnecting covalent bonds (Figure 4a). On the other hand, larger distances between the phenanthrene units indicate a non-covalent bonding interaction. This is further supported by the absence of any covalent interlinks between them in the experimental images (Figures 4e, f).

Combining outcomes of the detailed analysis of the nc-AFM images along with the possible and manifold reactivity of organic azides upon heating (or, optionally, under UV light irradiation) documented in the literature (see above), we came to conclusions about the chemical structure of the molecular species 2–5 (Figure 4). The bow-tie-like adsorbate shown in Figure 4a was identified as a fully aromatic flat tetrabenzo derivative of phenazine (2).18 These products were absorbed in the vicinity of non-planar clusters of an unknown structure, which is why the molecule is not centred in the experimental image. The related adsorbate 3 (not yet known) shown in Figure 4b was identified as a dihydro congener of 2. Here, the presence of a pseudoxaflial hydrogen atom located on the carbon atom of the central 1,2-dihydropyrazine ring caused repulsion in the nc-AFM scanning mode, which was reflected by a localised bright protrusion in the corresponding image. Furthermore, the slightly distorted or almost symmetric butterfly-like flat
adsorbates shown in Figures 4c and d, respectively, were described as conformational isomers 4a and 4b of (E)-di(phenanthren-9-yl)diazene.\textsuperscript{10} They differ in the orientation of one of the phenanthren-9-yl groups being rotated by 180° around the respective C-N bond (Figures 4c,d). Finally, the similar butterfly-like adsorbates shown in Figures 4e,f, the wings of which are more separated than those found in 4a, 4b, were interpreted as noncovalent dimers of phenanthren-9-amine 5.\textsuperscript{10} They form a chiral adsorbate and, therefore, both the homochiral (Figure 4e) and heterochiral pairs (Figure 4f) could be identified. The spatial distribution of the molecular adsorbates 2-5 on Ag(111) was found to be random with hints of preferential alignment along the surface lattice vectors (011, 101, 110).

Individual molecules containing a single phenanthrene core unit, spatially separated from other molecular adsorbates by a distance beyond any noncovalent interaction, were rarely found as they occupied only about 1% of all adsorbed molecular materials. Based on the nc-AFM imaging and respective simulations, we assigned them the structure of phenanthren-9-amine 5 (Supporting Information, Figure S2).

To explain the transformation of the starting azide 1 into the products 2-5 observed on the Ag(111) surface, we propose the following scenarios: The chemical reactions take place either on the Ag(111) surface (most likely) or during the deposition process (less likely). With respect to the first scenario, azide 1, once adsorbed on Ag(111) at ambient temperature, forms a reactive nitrenoid intermediate by the release of dinitrogen. We did not directly observe this elusive species in the STM/nc-AFM imaging at 4.5 K since we saw either the native azide 1 (deposited at 15 K) or already the products 2-5 (depositing azide 1 at ambient temperature). Owing to the generally high reactivity of nitrenes, they are not expected to be physisorbed but chemically bound to the Ag(111) surface. This raises a question about the nature of the bonding interaction in the key metal-nitrenoid couple (Figure 5A): It can be formally expressed as a Lewis pair in the singlet (A) or triplet (B) state, o-bonded nitrene radical (C), o- or o\textpi-bonded imido complex (D and E, respectively) and aziridine-like complex (F).\textsuperscript{5,20} However, there is a variety of data available on the structure of nitrenoid complexes/products (inferred from spectroscopy, DFT calculations, and stereochemical reaction outcomes) as documented, for example, by a triplet state phenylnitrene at the Ge(100)-2×1 surface being covalently bonded via a single Ge-N bond,\textsuperscript{21} triplet state tosylimido bonded to complexed Ag\textsuperscript{+} via a single Ag-N bond,\textsuperscript{22} or metal-nitrenoid intermediates represented by tosylimido complexes of Ru.\textsuperscript{23} Owing to such structural and mechanistic manifold and lack of relevant studies on nitrenes on a silver surface, the structure of 9-phenanthryl nitrenoid intermediate 6 bound to Ag(111) was calculated (Figure 5B). Total energy DFT calculations predict strong covalent coupling of the transient nitrene to Ag(111).

Figure 4. Left column: High-resolution nc-AFM images of various dimer products, measured in constant height mode. Scale bars: 500 pm. Middle: Proposed molecule structures obtained from DFT simulations (Ag atoms not plotted for clarity). Right: Simulated nc-AFM images from the proposed molecule structures. The respective STM images are shown in the Supporting Information, Figure S3.

Figure 5. Possible bonding interactions in the proposed metal-nitrenoid couple (A) and the electrostatic potential map of the optimised structure of phenanthren-9-nitrene 6 on Ag(111) (isosurface 0.05 Å\textsuperscript{-3}) adopting non-planar configuration due to the formation of a strong covalent bond between the nitrogen atom and metal surface (B).
surface via its nitrogen atom forming an ionic complex (N is negatively charged). It quenches a possible biradical state of nitrene, as DFT shows a zero spin density for the given configuration. However, the complex 6, which exhibits a strong distortion, was never observed in the experiments. This suggests a very short lifetime of this intermediate. Stemming from the DFT calculations, we propose to describe the 9-phenanthryl nitrenoid intermediate 6 as a coordinately bonded imido complex (Scheme 1).

![Diagram of the proposed scenario for the formation of the products 2-5 on the Ag(111) surface through manifold reaction channels.](Image)

We cannot rigorously exclude the possibility that azide 1 decomposes into the respective free singlet/triplet nitrene upon contact with materials of the load lock chamber before being deposited on the Ag(111) surface at ambient temperature. Nevertheless, azide 1 exhibits a reasonable thermal and chemical stability. It can be routinely purified by liquid chromatography on silica gel (in the dark), the melting point measured by us) and, when subjected to FVT, no significant reaction takes place below 450°C.\[^{[10]}\]

We finally note that the low-temperature deposition experiments show unchanged precursor molecules on the surface. It provides evidence to decline the hypothesis of chemical changes before adsorption.

Consequently, we propose the following mechanistic scenario of the transformation of azide 1 to the products 2–5 adsorbed on the Ag(111) surface (Scheme 1). The silver nitrenoid intermediate 6 may enter three parallel reaction pathways: In channel 1, 6 undergoes an intermolecular insertion into a C–H bond of either the unreacted azide 1 or another nitrenoid intermediate 6 to yield an azide intermediate 7 or nitrenoid intermediate 8. Then, after conversion of 7 to 8, the second, now intramolecular, nitrenoid insertion into a C–H bond takes place, leading to the 1,4-dihydropyrazine-type intermediate 9. It can follow either dehydrogenation (9→2) or tautomerisation (that is, [1,3] hydrogen shift, 9→3) leading to the final phenazine- and dihydrophenazine-type products 2 and 3. In channel 2a, 6 dimerises directly into the 9,9′-azophenanthrene conformers 4a, b. Alternatively, in channel 2b, 6 attacks the unreacted azide 1 forming the tetraaza intermediate 10 that yields 4a, b by releasing dinitrogen. Finally, in channel 3, 6 is hydrogenated to amine 5 owing to the presence of hydrogen in the UHV environment\[^{[25]}\] or other organic materials serving as a hydrogen donor.\[^{[10]}\]

We can now compare the proposed reaction scheme and identified products to the results of previous studies: Under FVT at 500°C, azide 1 produced 9-cyanofluorene as a main product (73%) along with 4a and 5 (both 10%), bare phenanthrene (7%), and trace amounts (ca. 2.5%) of 1-cyanofluorene and 4-cyanofluorene.\[^{[10]}\] Notably, the phenazine- and 1,4-dihydropyrazine-type products 2 and 3, which we identified, were absent in the FVT study. On the other hand, phenazine derivatives were formed as side products along with major amines and azocompounds by thermalysis of respective aryl azides in solution.\[^{[26]}\]

As far as the relative importance of the reaction channels 1–3 is concerned, we determined the statistical abundance of the most important molecular adsorbates 2–5 by analysing a series of overview images (50×50 nm²) encompassing about 80 structures in question. Accordingly, we could conclude that the nitrenoid intermediate 6 insertion into the C–H bond (channel 1), its dimerisation (channel 2), and hydrogenation (channel 3) are comparably important processes.

In summary, we studied chemical transformations of 9-azidophenanthrene 1 on the Ag(111) surface by STM/nc-AFM high-resolution imaging in UHV supported by first-principles calculations. While azide 1 was found to be stable on cold Ag(111) (15 K), the deposition at ambient temperature led to a manifold of chemical transformations. We propose the silver-nitrenoid species 6 as a transient intermediate that is common for three competitive reaction pathways characterised by the insertion of 6 into a C–H bond, its dimerisation, and hydrogenation. Both covalent and noncovalent dimers encompassing phenazine-, dihydrophenazine-, azo-, and aminoderivatives 2–5 were identified as main products. Importantly, we observed evidence of the ability of aryl azides to form covalent o- and π-bonds between...
their transformation products on a solid surface. Further UHV STM/nc-AFM studies on the photochemical activation of aryl azides on wide-gap surfaces are under way.

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Conflict of interest

The authors declare no conflict of interest.

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