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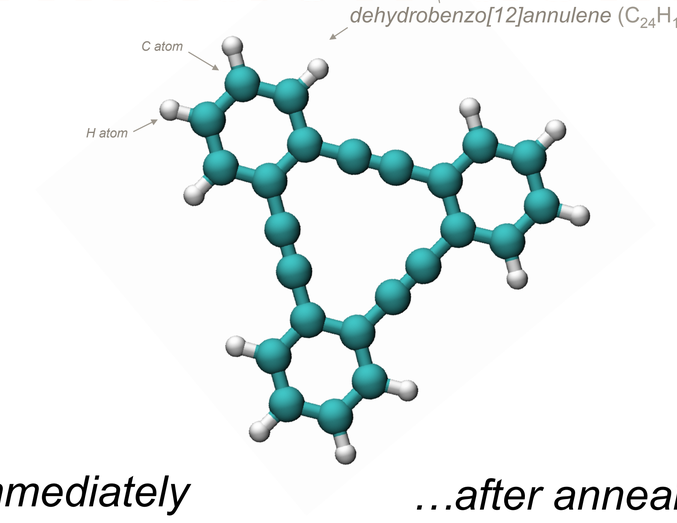
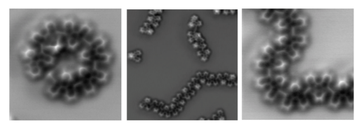
Exploring *the sequential* on-surface structural transformation *of a hydrocarbon molecule* using DFT



Throw this molecule on Cu(111) surface…

…and interesting things happen

- it undergoes *several* on-surface reactions, changing its structure considerably
- final and intermediate structures show self-assembly!

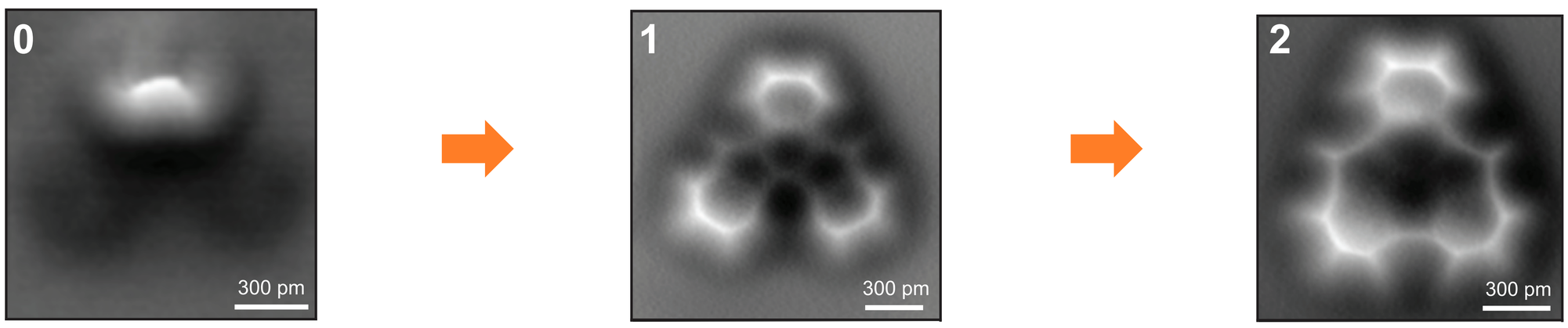


Once deposited, the molecule reacts immediately with the copper surface…

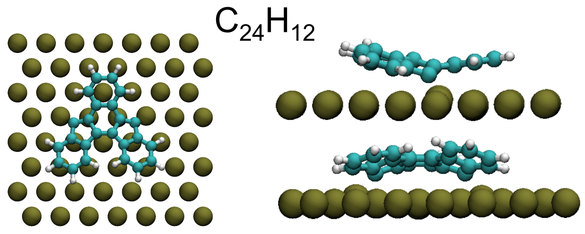
…after annealing at 200°C, first stable transformation happens…

…further annealing at 400°C yields the final structure.

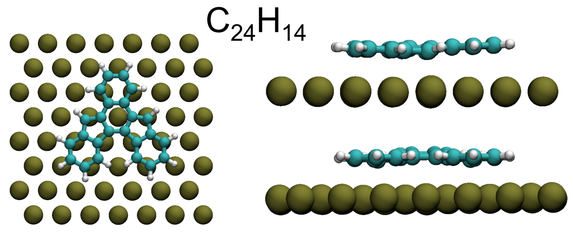
Atomic force microscopy images at T = 4.8 K



1 ***H or no H?*** Although the low-temperature AFM images reveal the molecular geometries with high precision, hydrogen atoms are difficult to identify.
We used DFT calculations to investigate the problem:



the structures without…

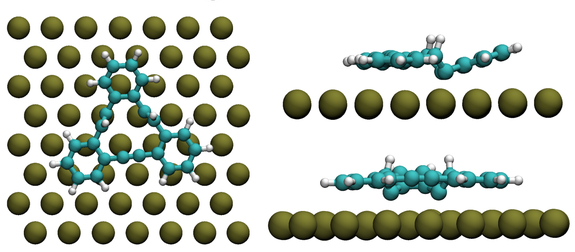


…and with "extra" H atoms clearly differ in geometry…

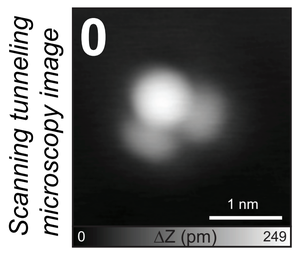
…the structure with two "extra" hydrogen atoms ($C_{24}H_{14}$) matches the experiments!

0 ***H or no H? – prequel*** Perhaps the "extra" hydrogen atoms are already present in the first reaction?

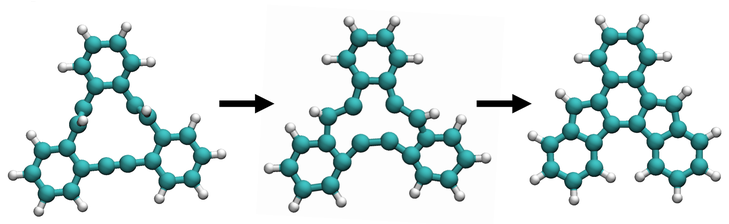
According to DFT calculations this is indeed plausible:



the geometry is stable enough to exist…



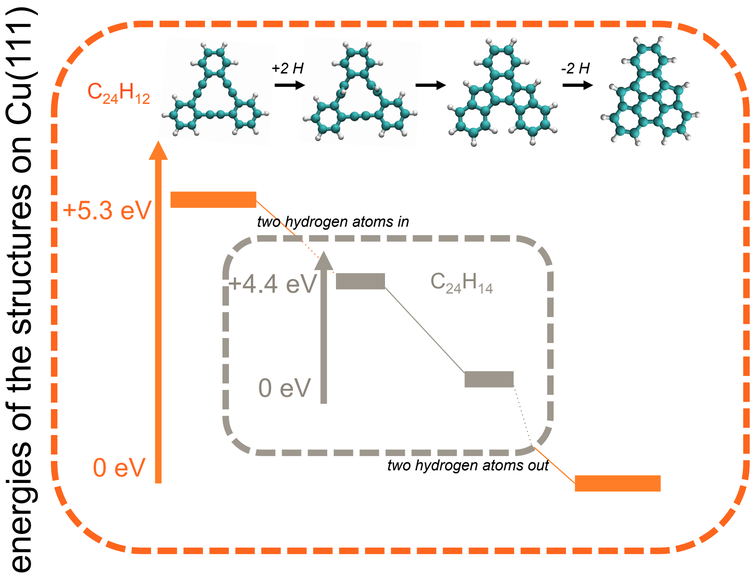
…it fits both to AFM and STM characteristics…



…and it suggest a realistic pathway leading to the first stable structure

experimental details
non-contact AFM with a CO tip
measurements performed at T = 4.8 K
oscillation frequency 24.768 × 10^3 Hz
oscillation amplitude 53 pm
spring constant 1800 N/m

2 ***H or no H? – sequel*** To obtain the final structure, two hydrogen atoms need to be removed.
Experimentally this is observed after annealing at 400°C, in accordance with DFT energetics.



These results demonstrate the potential of on-surface reactions as a route for chemical synthesis – and the necessity of computations.

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computational details
PBE-D3/DZVP/500 Ry
17.8 × 17.7 × 25.0 Å^3
(six layers of Cu)
optimizations at T = 0 K
www.CP2K.org

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