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Preposition for a different reaction pathway for the structural transformation mechanism of the oligo–enediyne molecule $C_{26}H_{14}$ T > 90 °C

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Abstract

The researches of the groups lead by Dimas G. de Oteyza published their work - Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions – in the Science 21 June 2013: 1434-1437. The same work was published online on 30th May 2013 in the edition of *Science Express* [DOI:10.1126/science.1238187]

The authors are the teams of Felix Fischer (Department of Chemistry at Berkeley), Michael Crommie (Department of Physics at the same university) and Ángel Rubio (Professor at the UPV/EHU and researcher at the CSIC-UPV/EHU Centre for Physics of Materials and at the Donostia International Physics Center). The leading author of the article is Mr. Dimas Oteyza.

They have taken, for the first time, images of individual molecules (oligo–enediyne molecule $C_{26}H_{14}$ T > 90 °C) as they transform from one condition to another after a complex organic reaction. The images were made by a noncontact Atomic Force Microscope (nc-AFM).

Without this detailed images of the structural transformation of the oligo–enediyne molecule $C_{26}H_{14}$ T > 90 °C it is very hard to predict the unexpected products they got from the reactant. So in their work they propose a transformation pathway from reactant to products.

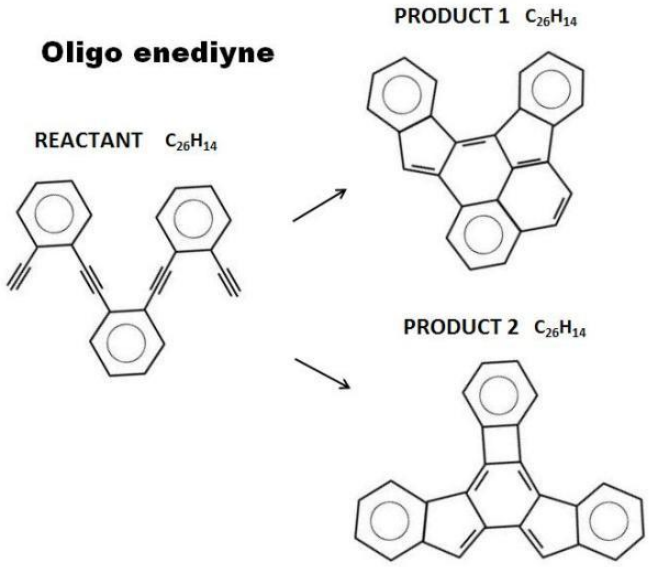
But if we look carefully to the images from the proposed transformation pathway from the reactant to the products, we will find several difficulties. Because of that, it is more useful to make a probe to show a microscopic structural transformation mechanism different than the proposed reaction pathway for the cyclization of the reactant into product 1 and 2 on Ag(100), presented in the original work of this groups. The pathway models presented here may not be real but it is worth to present it as a possible solution. This may help for a better understanding of the microscopic processes.

Keywords: oligo enediyne, $C_{26}H_{14}$, images, bond, transformation, mechanism, single molecule, chemical reaction

Introduction

The following illustration presents an image of the individual oligo–enediyne molecule $C_{26}H_{14}$ on an oriented silver Ag(100) surface, induced thermally with T > 90 °C, as they transform from a reactant into different products with same chemical formula but with different structures.

Here is the image of the molecular structure of the reactant and the products 1 and 2,



and also the real images of the oligo enedyine transformation from reactant to product 1 and 2 got with noncontact Atomic Force Microscope (nc-AFM).

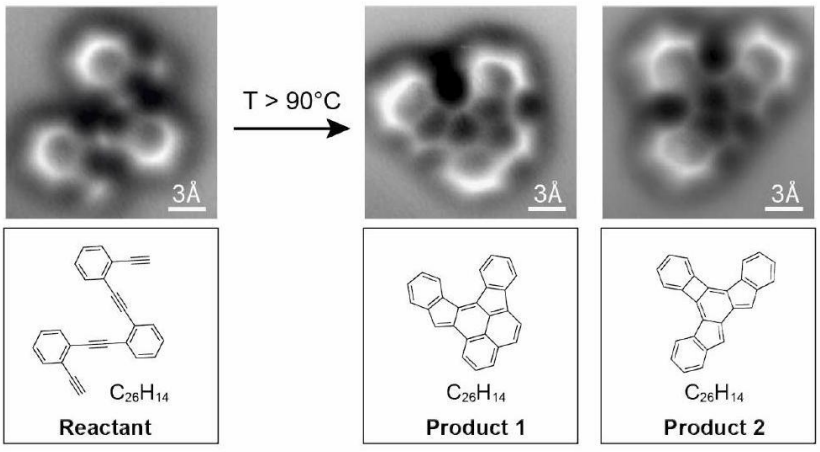


Image credit: Lawrence Berkeley National Laboratory and University of California at Berkeley

Why preposition for the new transformation pathway

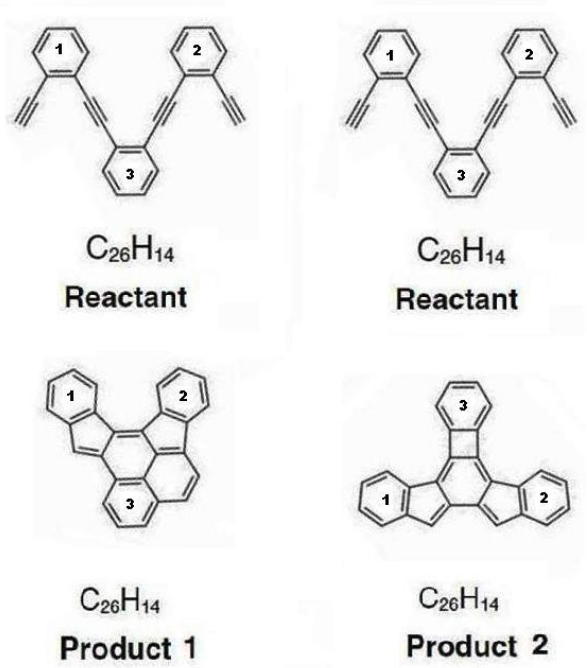
The analysis of the microscopic structural transformation pathway of the oligo–enediyne molecule $C_{26}H_{14}$ T > 90 °C from a reactant to its products, proposed from research groups will show that some proposed reactions are questionable.

For example, in product 1 and product 2 there are proposed rotation of part of molecule with nine Carbon atoms, on silver surface round, so told, exocyclic <u>double</u> Carbon-Carbon bond. It is hard to believe that this reaction is possible, because the Carbon atom with this double bond has also two other fixed single bonds and the rotation is disabled.

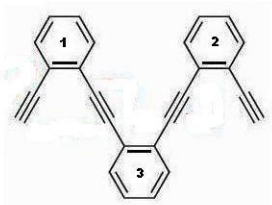
Second, in product 1, there is no explanation how the electron, without a Hydrogen atom, will move almost ten Angstroms, round the benzene ring with four Hydrogen atoms, to connect with another electron without a Hydrogen atom. The similar problem exists in the reaction pathway for product 2.

And finally there is the orientation problem. On the final image of product 1 the newly formed side benzene ring is positioned left in the image and does not correspond to the position on the image got from the AF Microscope, because it is rotated about 180 degrees! The same problem is also present in the product 2 images.

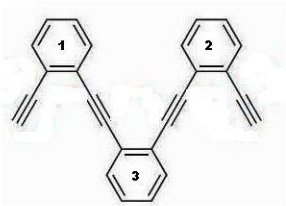
So, instead of this product images, taken with the nc-AF Microscope,



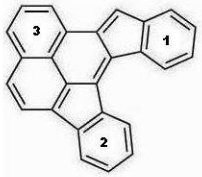
these images are presented as possible products solutions.



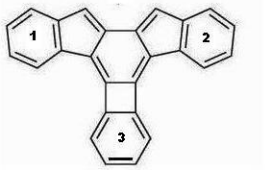
$C_{26}H_{14}$
Reactant



$C_{26}H_{14}$
Reactant

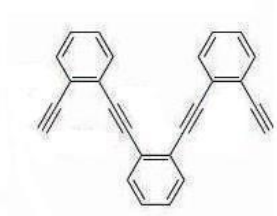


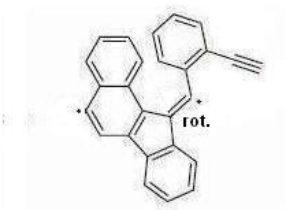
$C_{26}H_{14}$
Product 1

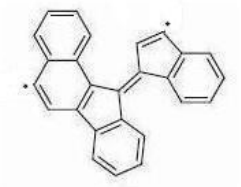


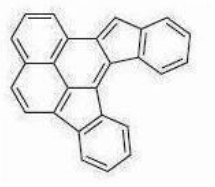
$C_{26}H_{14}$
Product 2

or the same product images presented with the transformation pathways.

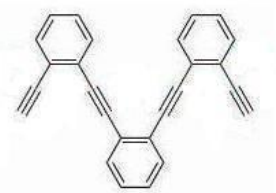


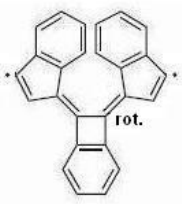


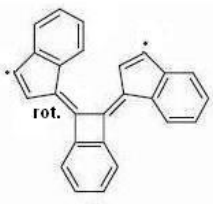


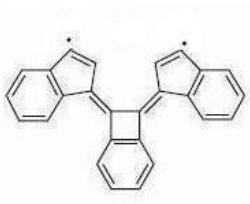


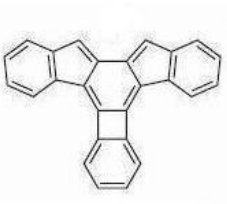
reactant **product 1**







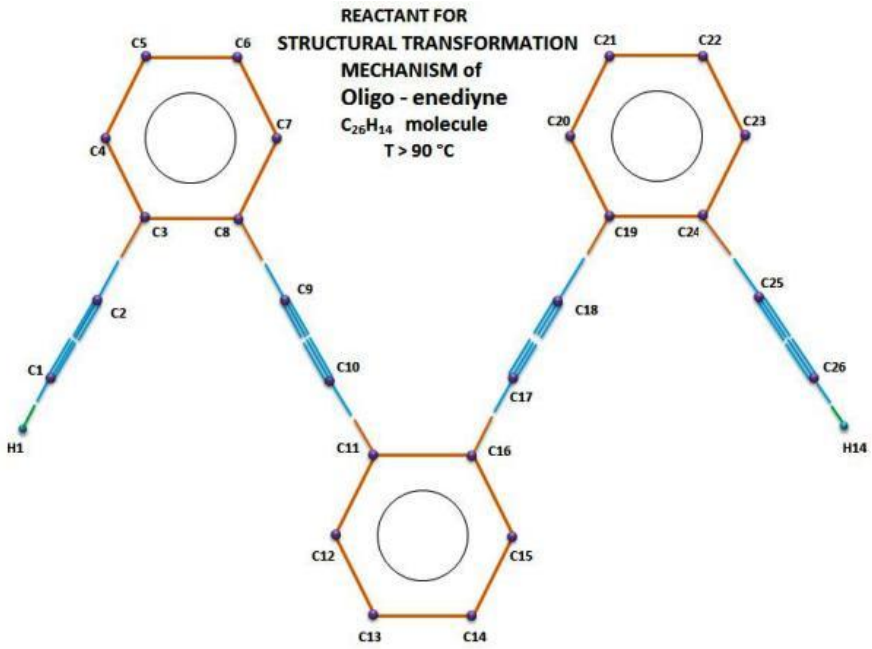




reactant * dot mark - free electrons rot. - rotation round double bond ??? **product 2**

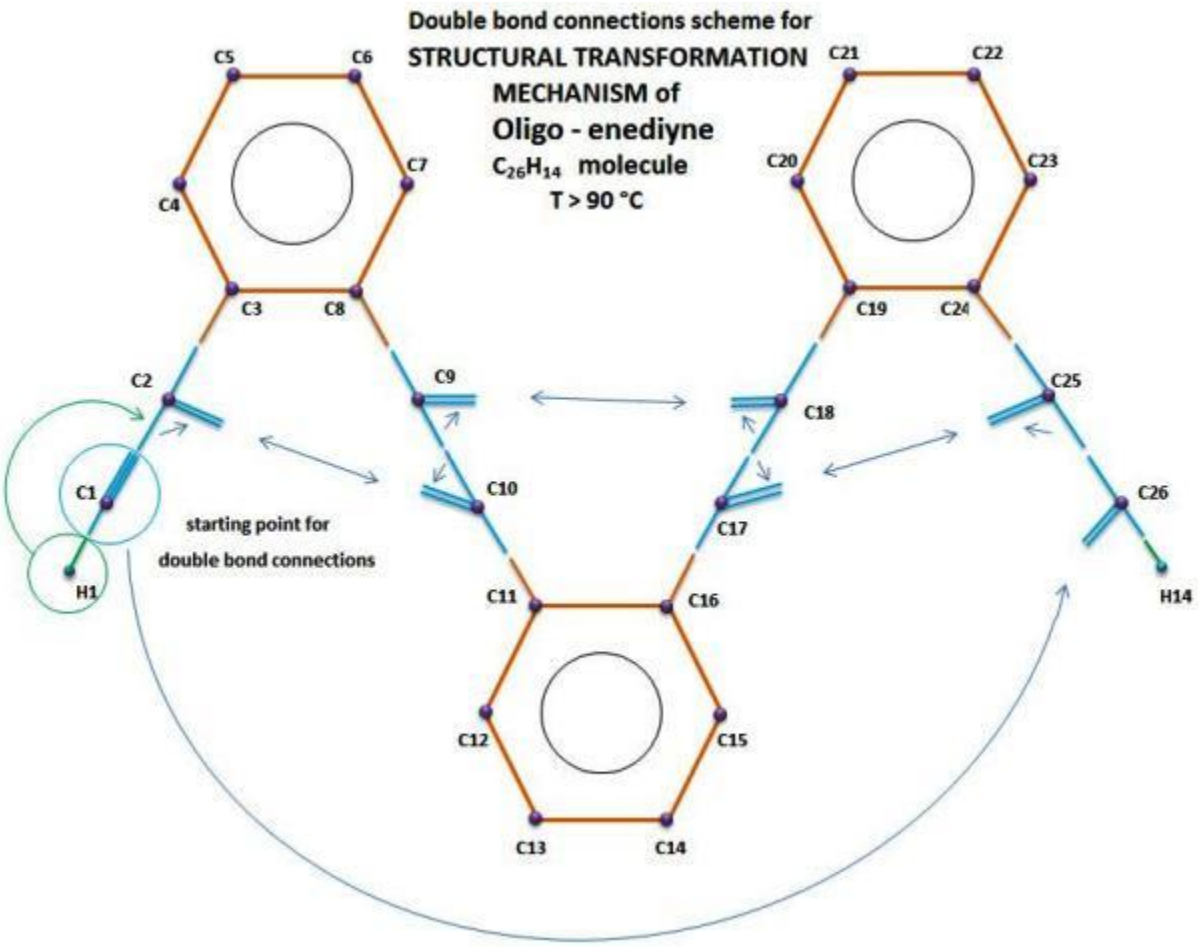
PRODUCT 1

At first, the new proposed atomic changes in an oligo enediyne molecule during the transformation pocesses from reactant to product 1 will be presented. Oligo enedyne is a simple molecule composed of three benzene rings linked by carbon atoms with triple bonds. The number of the Carbon atoms is 26 while the number of the Hydrogen atoms is 14 – as in the picture below. The benzene rings in all reaction prosesses will maintain their benzene aromatic ring structure.



First reaction pathway - Image 1

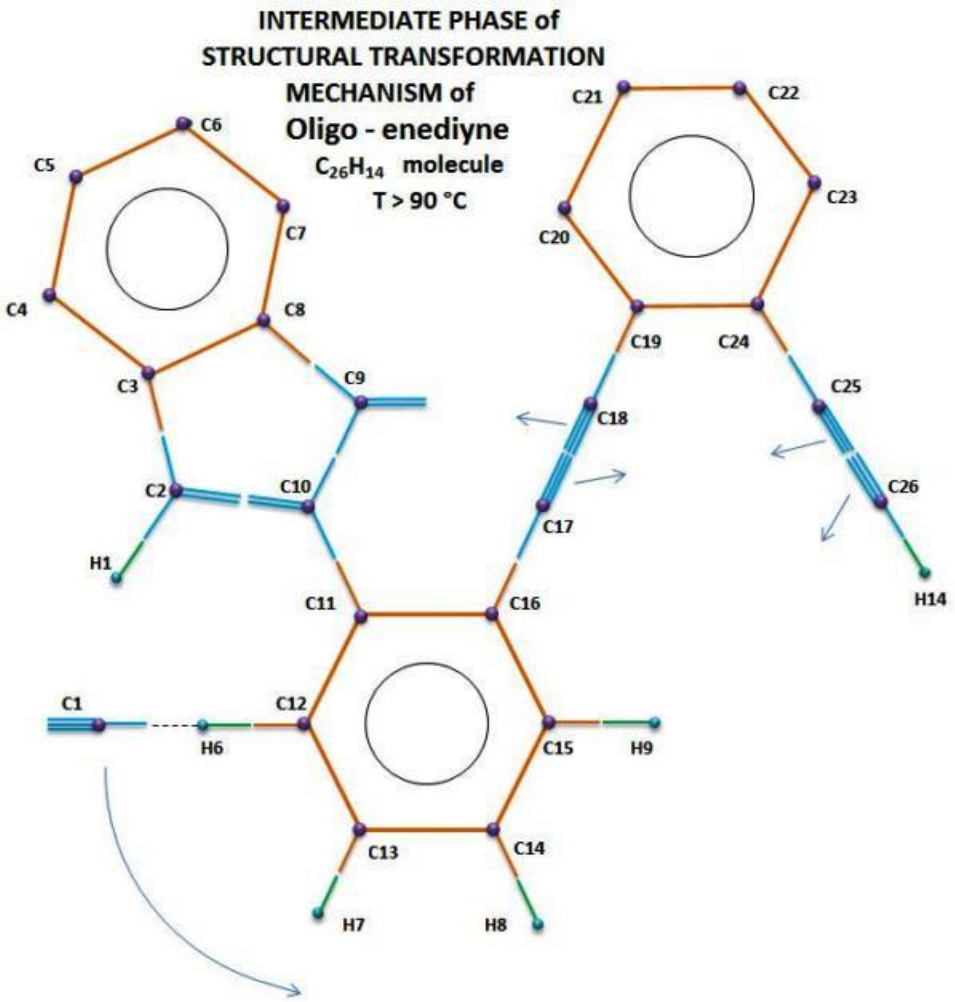
By heating the silver (Ag), as supporting surface, the molecule will change the structure forming new chemical bonds and getting a new structure. The triple bond will open and will form new double bond connections. The image of this new proposed double connection scheme is presented below.



First reaction pathway - Image 2

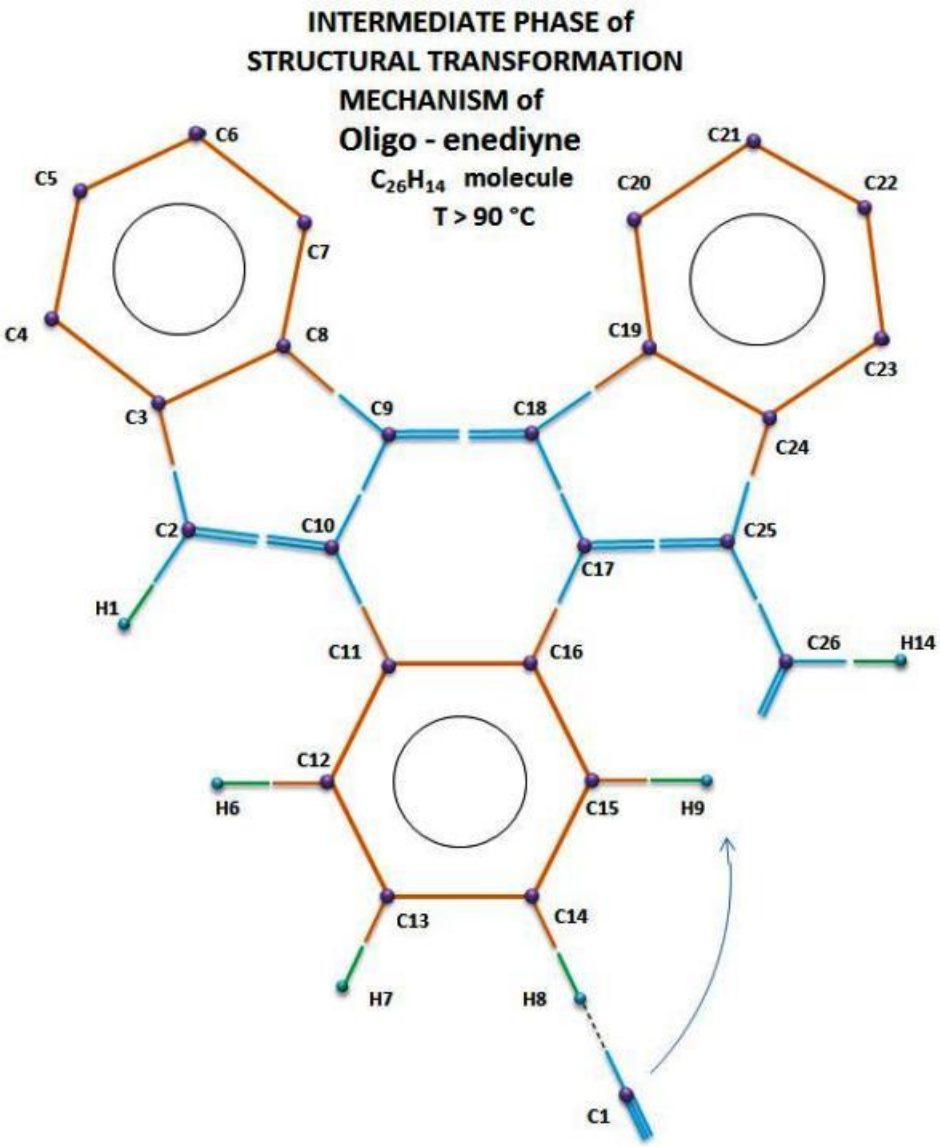
The key event here is the Carbon atom with number one (C1) bound with the Hydrogen atom (H1). By increasing the temperature, this CH group will split in two parts. The Hydrogen atom (H1) from this group will connect to the Carbon atom number two (C2), while Carbon atom one (C1) as free radical will move in a distant place to be connected with Carbon atom 15 and 26.

The free Carbon atom one (C1) will move or roll over the Hydrogen atoms from the lower benzene ring (C12H6, C13H7 and C14H8) until its final position. The gliding of this C1 Carbon atom is enabled by the presence of the Ag surface atoms. The connection between Carbon atom C1 and H atoms will be through a type of Hydrogen bonding - scheme below.



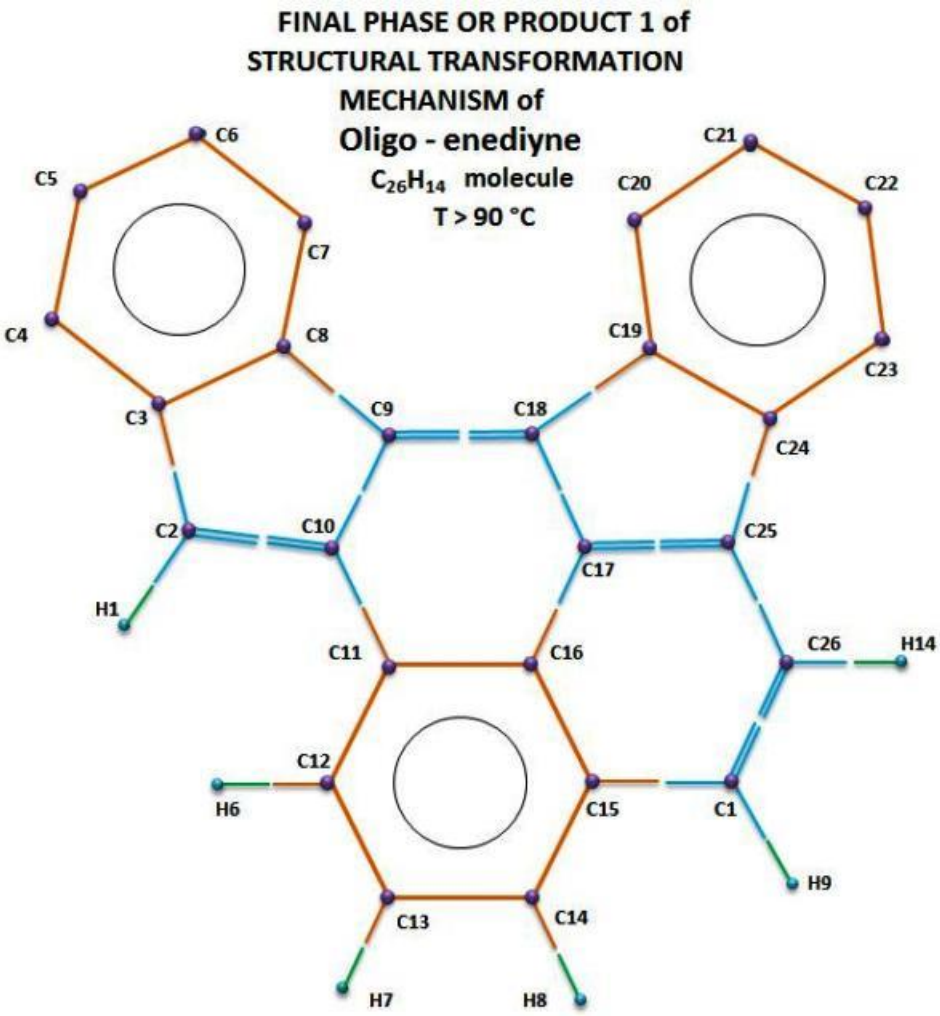
First reaction pathway - Image 3

Now the Hydrogen atom 9 bound with Carbon atom 15 will slip from this bond connection and connect with Carbon atom one.



First reaction pathway - Image 4

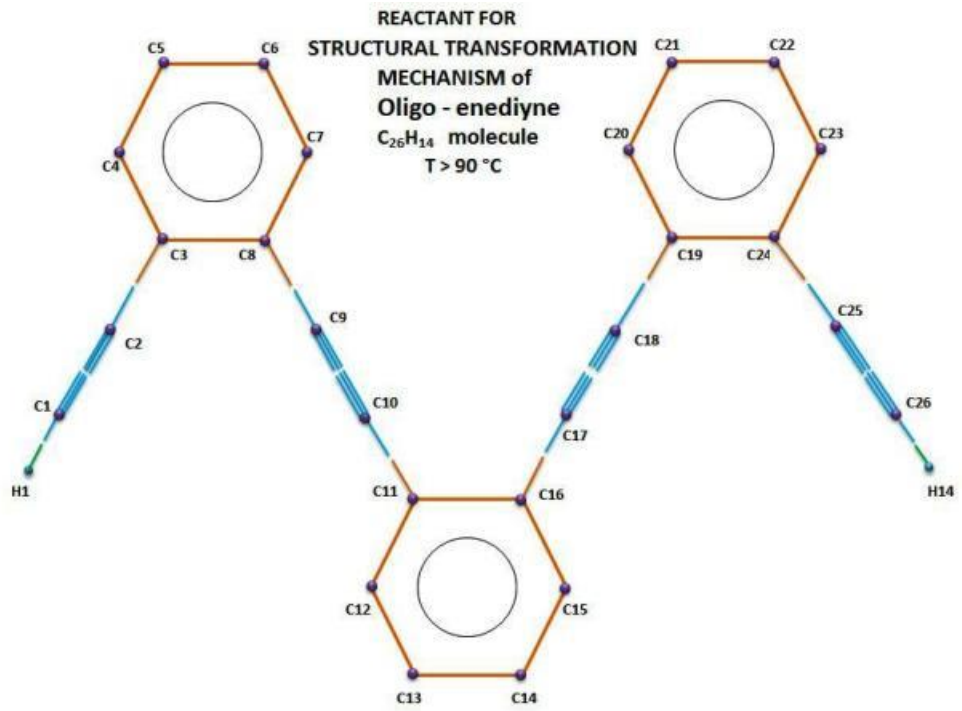
The final product of this structural transformation is also an oligo enediyene (C_{26} H_{14}) with 26 Carbon and 14 Hydrogen atoms, but with a totally different arrangement, same as image of product 1 got by researches with the nc-AFM.



First reaction pathway - Image 5

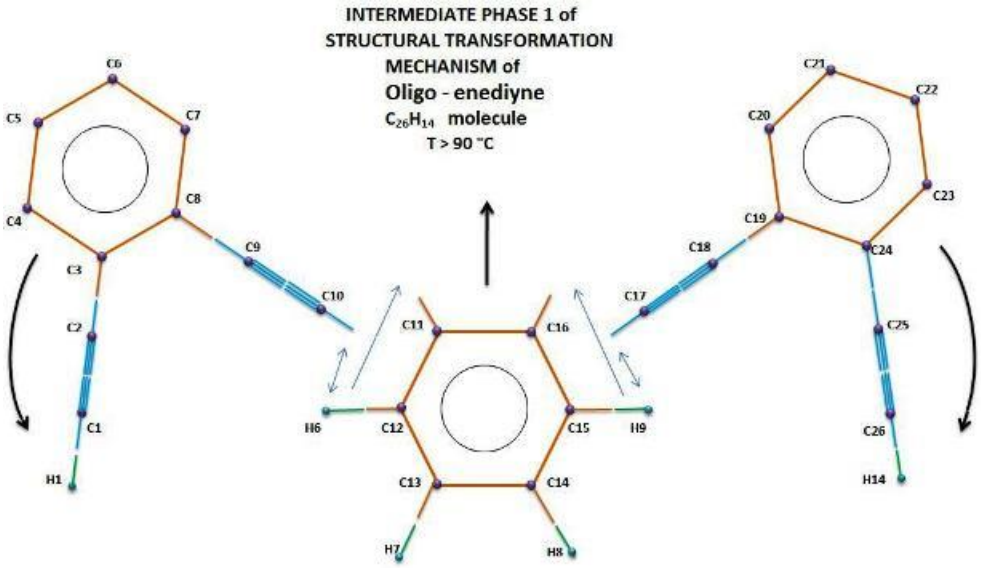
PRODUCT 2

The starting molecule for product 2 is the same as for product 1 - image below.



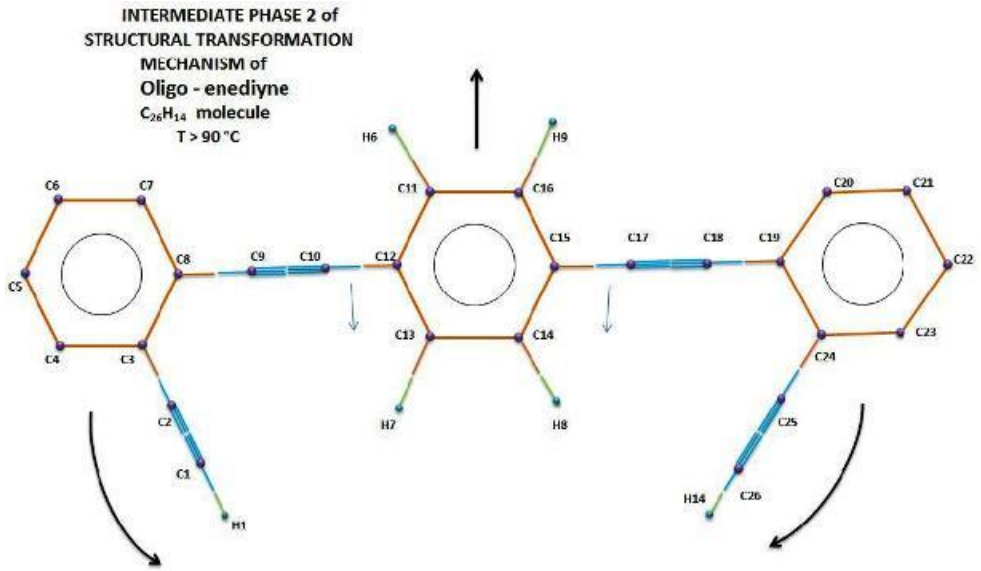
Second reaction pathway - Image 1

In this case, the new proposed reaction pathway has a different connections scheme. Heated silver surface T > 90 induces a moving of the two side benzene rings round the middle benzene ring, together with the triple bound carbon atoms. This can happen because the two of the weakest connections in this oligo-enediyne molecule are the single bonds between carbon atoms C11 and C16 from the middle benzene ring and carbon atoms C10 and C17 - image below.



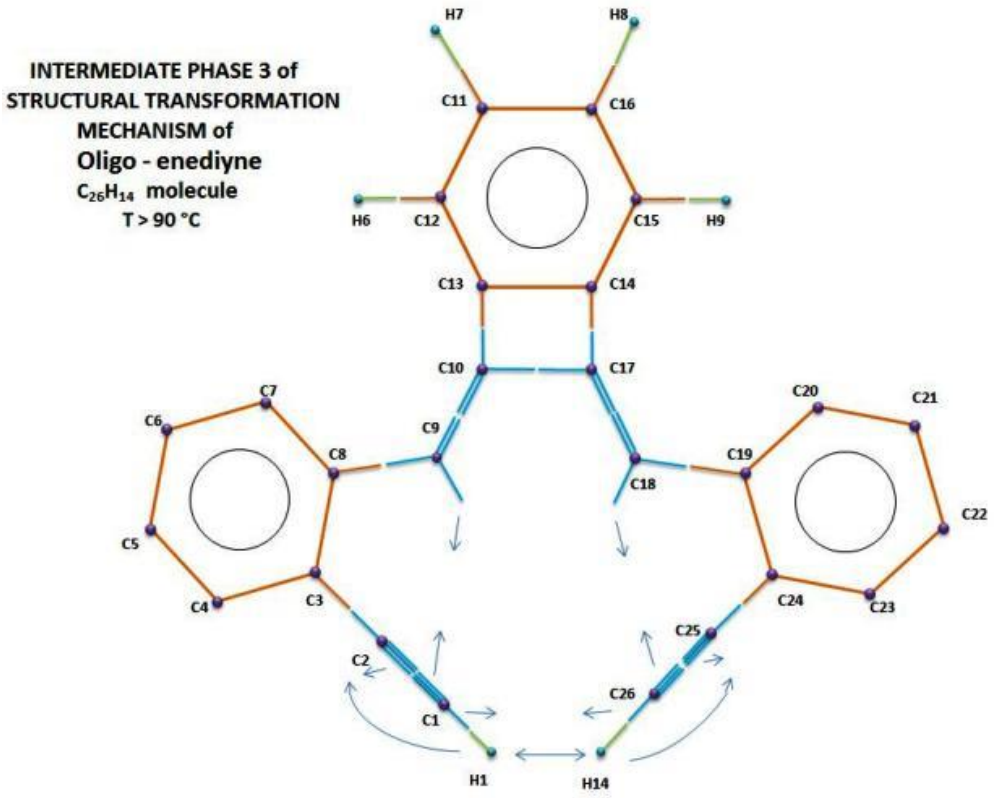
Second reaction pathway - Image 2

In this dynamic processes the Hydrogen atoms H6 and H9, attracted by the electrons from Carbon atoms C10 and C17 will pull apart their connection and move into a new position. The same process will also happen with the next Hydrogen atoms.



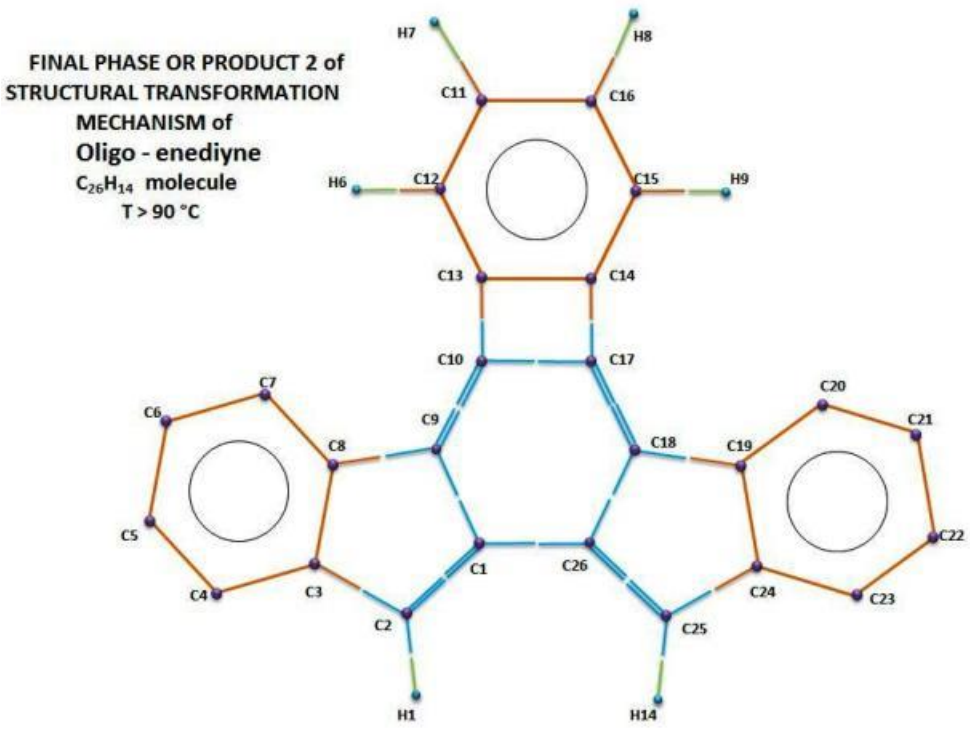
Second reaction pathway - Image 3

When the side benzene rings are in the lower position the triple bound carbon atoms will rearrange their connection making new double connections. At first, a four bound carbon atoms ring will be formed, then a six bound carbon atoms ring and finally the two five benzene carbon atoms rings – image below.



Second reaction pathway - Image 4

The final molecule structure will look the same as the image got with the non-contact Atomic Force Microscope, presented in "Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions" article - image below.



Second reaction pathway - Image 5

Conclusion

To see, visualize and make sharp images of the atoms and molecules with their bonding structure and chemical reaction is something that researches has always dreamed of. The importance of this method is that now the researches and scientist have a new powerful tool to analyze and predict chemical reactions and molecular transformations. Maybe this is only the beginning of some more surprising discoveries.

Link:

http://phys.org/news/2013-05-first-ever-high-resolution-images-molecule-reforms.html

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