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## Intramolecular interactions in [2.2]paracyclophanes

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Since its discovery in 1949 by Brown and Farthing, [2.2]para-cyclophane has been intensely studied by chemists. Consisting of two benzene rings bound together by two ethano bridges, the [2.2]paracyclophane core can undergo chemical transformations specific to both aliphatic and aromatic compounds, resulting in a wide variety of functionalized [2.2]paracyclophanes. Thus, cyclophanes are ideal model systems to investigate whether and how functionalized groups can interact and react with each other. Because of the rigid molecular framework provided by the paracyclophane moiety and its short interannular distance, functional groups in pseudo-geminally substituted [2.2]paracyclophanes are often held in such a position as to allow highly specific reactions to take place between them. Both the parent hydrocarbon and its derivatives have been used in asymmetric catalysis, optoelectronics<sup>3</sup> and polymer synthesis.<sup>4</sup> Acetylene-substituted paracyclophanes are important because of the ability of the acetylene moiety to easily undergo coupling and addition reactions, leading to new derivatives that contain one or more units of the [2.2]paracyclophane core. Orthogonal  $\pi$ -bridges have been introduced into [2.2]paracyclophanes by the reaction of the pseudo-geminal bisacetylene with various monoacetylenes and nitriles. The reactions with bistrimethylsilylacetylene and dimethylacetylenedicarboxylate take place even in the absence of a catalyst. This procedure can incorporate not only aromatic but also heteroaromatic bridges, as in pyridine-annulated cyclophane. Mono, pseudo-gem and pseudo-para ethynylcyclophanes and bis(azides) have been employed as addition partners in CuAAC reactions to design and build complex extended molecular scaffolds. The reactivity of the resulting triazoles was investigated under photochemical conditions. A variety of newly substituted [2.2]paracyclophanes were identified; deazotization of pseudo-gem and pseudo-para adducts provided indolophane derivatives. An intramolecular stabilization effect was observed in the case of pseudo-gem derivatives. A photochemical rearrangement from a pseudo-para adduct to a pseudo-ortho product was identified.

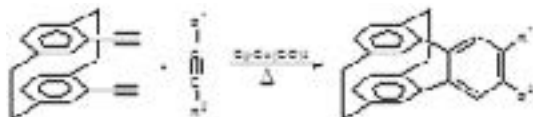


Figure 1: Description

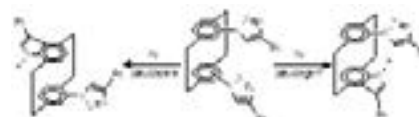


Figure 2: Description

## Recent publications

1. Brown CJ, Farthing AC (1949) Nature 164: 915-916.
2. Modern Cyclophane Chemistry (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, 2004.
3. Bartholomew GP, Bazan GC (2001) Acc. Chem. Res. 34: 30-39.
4. Hopf H (2008) Angew. Chem. Int. Ed. 47: 9808-9812.
5. Birsa ML, Jones PG, Hopf H (2011) Synlett: 259-261.
6. Bahrin LG, Sarbu LG, Jones PG, Birsa ML, Hopf H (2017) Chem. Eur. J. 23: 12338-12345.

## Biography

Lucian M Birsa is currently a Professor in the Department of Chemistry at the Alexandru Ioan Cuza University of Iasi, Romania. He received a Bachelor of Science Degree in Chemistry from the same university in 1995. He joined the Master's Program at Alexandru Ioan Cuza University of Iasi in 1995, and in 2000 was awarded a PhD Degree in Organic Chemistry. From 2000 to 2002, he was a Postdoctoral Fellow under the mentorship of Professor Samuel Braverman at Bar-Ilan University, Israel. In 2003 he was selected as a member of the Alexander von Humboldt Foundation, working with Professor Henning Hopf in TU Braunschweig-Germany. Since then numerous return fellowships were granted by the Alexander von Humboldt Foundation.

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