

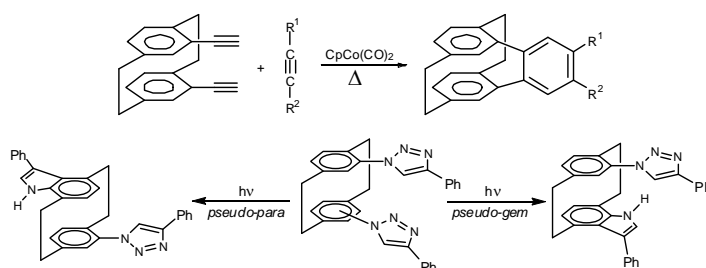
INTRAMOLECULAR INTERACTIONS IN [2.2]PARACYCLOPHANES

Lucian M Birsa and Laura G Sarbu

Alexandru Ioan Cuza University of Iasi, Romania

Since its discovery in 1949 by Brown and Farthing [1], [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 and polymer synthesis.

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 π -bridges have been introduced into [2.2]paracyclophanes by the reaction of the *pseudo-geminal* bisacetylene with various monoacetylenes and nitriles [2]. 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 [3]. 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.



[1] Brown CJ, Farthing AC (1949) Nature 164: 915-916.

[2] Birsa ML, Jones PG, Hopf H (2011) Synlett: 259-261.

[3] Bahrin LG, Sarbu LG, Jones PG, Birsa ML, Hopf H (2017) Chem. Eur. J. 23: 12338-12345.