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[2.2]Paracyclophane-Bis(triazole) Systems: Synthesis and Photochemical Behavior

Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday

Lucian G. Bahrin,[a] Laura G. Sarbu,[a,b] Peter G. Jones,[c] Lucian M. Birsa*[a,b] and Henning Hopf*[a]

Abstract: 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.

Introduction

Since its discovery in 1949 by Brown and Farthing,[1] [2.2]paracyclophane 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. Both the parent hydrocarbon and its derivatives have been used in asymmetric catalysis,[2] optoelectronics[3] and polymer synthesis.[4]

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. Figure 1 presents seven acetylene-subtituted paracyclophanes, namely 4-ethynyl[2.2]paracyclophane **1**, *pseudo-gem* bis(ethynyl)[2.2]paracyclophane **2**, *pseudo-ortho* bis(ethynyl)[2.2]paracyclophane **3**, *pseudo-meta* bis(ethynyl)[2.2]paracyclophane **4**, *pseudo-para* bis(ethynyl)[2.2]paracyclophane **5**, 4,5-bis(ethynyl)-[2.2]paracyclophane **6** and the cross-tetrasubstituted derivative 4,7,13,16-tetraethynyl[2.2]paracyclophane **7**, which have all been prepared from the corresponding brominated and/or formylated derivatives.[5] Since then, these compounds have been used in coupling reactions,[6] addition reactions,[7] synthesis of polymers [8] and of luminescent compounds.[9]

Azido-subtituted paracyclophanes have been far less studied than their ethynyl counterparts. Figure 2 displays three examples, two of them previously reported in the literature, namely 4-azido[2.2]paracyclophane, **8**,[10] used in the synthesis of some imidazole-[10] and triazole-[11] bearing [2.2]paracyclophanes, and *pseudo-gem* bis(azido)[2.2]paracyclophane, **9**.[12]

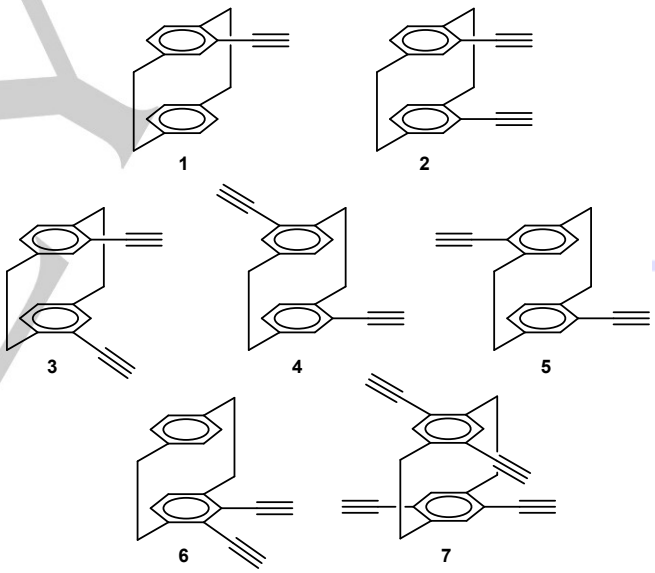

Figure 1. Ethynyl[2.2]paracyclophane derivatives.

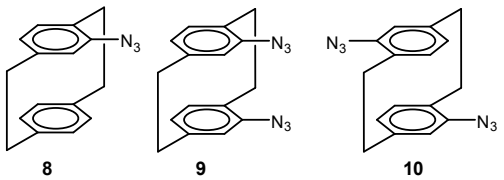

Figure 2. Azido-substituted paracyclophanes.

In a previous paper,[13] we studied the synthesis and properties of some [2.2]paracyclophane derivatives in which two triazole rings were bound to a [2.2]paracyclophane core by methylene units. In an attempt to extend the study to triazole-bearing [2.2]paracyclophanes, this paper presents the synthesis

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of some new triazole[2.2]paracyclophane hybrids, and describes their behavior when exposed to UV radiation.

Results and Discussion

Mono(triazolyl)[2.2]paracyclophanes

The first addition experiment was performed using 4-ethynyl[2.2]paracyclophane **1** and 4-azido[2.2]paracyclophane **8**, with 5 mol % $CuSO_4$/ascorbic acid as a catalyst. The two derivatives were dissolved in dichloromethane, while the catalyst was dissolved in an ethanol/water mixture. The two resulting solutions were then combined and vigorously stirred. After several hours, however, TLC monitoring displayed no change. We thus replaced the catalyst by $Cu(PPh_3)_3Br$, a compound that is soluble in dichloromethane. Again, acetylene **1** and azide **8** were dissolved in dichloromethane, along with 5 mol % of the catalyst system, and the reaction was monitored by TLC analysis. After several hours at room temperature, however, again no change was observed and the situation remained unchanged even when the temperature was raised to 40 °C. For our third attempt, we decided to employ a different Cu(I) catalyst, $[Cu(phen)(PPh_3)_2]NO_3$ **I** (Figure 3), previously reported to yield good results,[14] as well as raise the temperature of the reaction mixture. The catalyst was synthesized according to a literature procedure.[15]

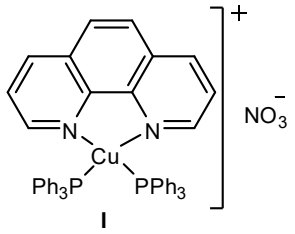
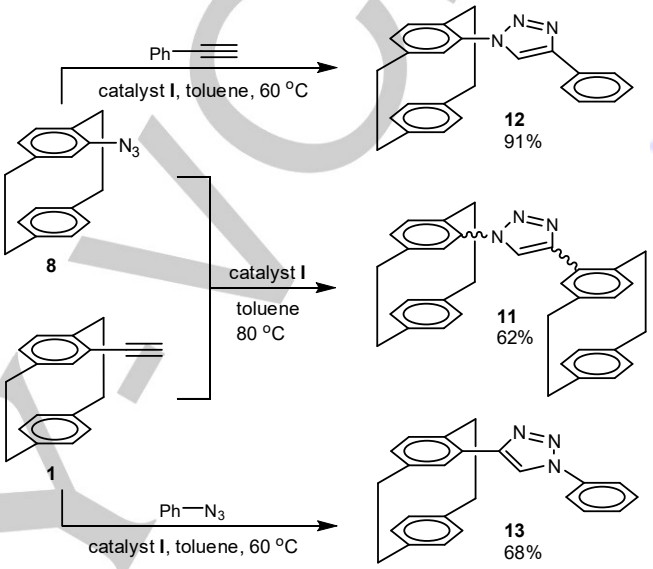


Figure 3. CuAAC reaction catalyst **I**

Acetylene **1,** azide **8**, and 2 mol % catalyst **I** were then stirred in toluene at 80 °C. After 24 h, no more starting material was detected by TLC. The solvent was removed in vacuo and the resulting residue was separated by flash chromatography on silica gel, yielding triazole **11** (Scheme 1). By replacing acetylene **1** by phenylacetylene, or azide **8** by phenylazide, and lowering the reaction temperature to 60 °C, previously described derivative **12**[11b] and triazole **13** were synthesized (Scheme 1). The most prominent signal in the ^{1}H NMR spectra of compounds **11-13** belongs to the triazole proton, which appears as a sharp singlet, around 8.00 ppm. Most of the other aromatic proton signals overlap, resulting in multiplets. The aliphatic protons belonging to the ethano bridges can be found between 2.60 and 4.10 ppm. Further proof of the newly formed triazole ring is a signal at about 148.0 ppm in the ^{13}C NMR spectra of compounds **11-13**, which belongs to the C4 carbon atom of the heterocyclic ring.

The stereochemical outcome of this cycloaddition is complicated (see below), so we decided to get an unambiguous structure assignment first. This was achieved by X-ray structural analysis. Upon slow diffusion of pentane into a chloroform solution of **12** or **13**, single crystals suitable for X-ray diffraction were obtained (Figure 4).[16] The molecules of **12** and **13** show the usual symptoms of strain in [2.2]paracyclophanes, namely bridges with lengthened C–C bonds and widened angles, and rings with a flattened boat conformation and narrow angles at the bridgehead carbons. The same is valid for the other cyclophane structures presented here. For compound **13**, the two independent molecules differ in the orientation of the phenyl rings (torsion angles C5–N1–C22–C23 –33.2, +21.1°); a least-squares fit of the other non-H atoms gave an r.m.s. deviation of 0.08 Å. N.B. Packing diagrams are presented and discussed in the Supplementary Material.



Scheme 1. Synthesis of mono(triazole)[2.2]paracyclophanes.

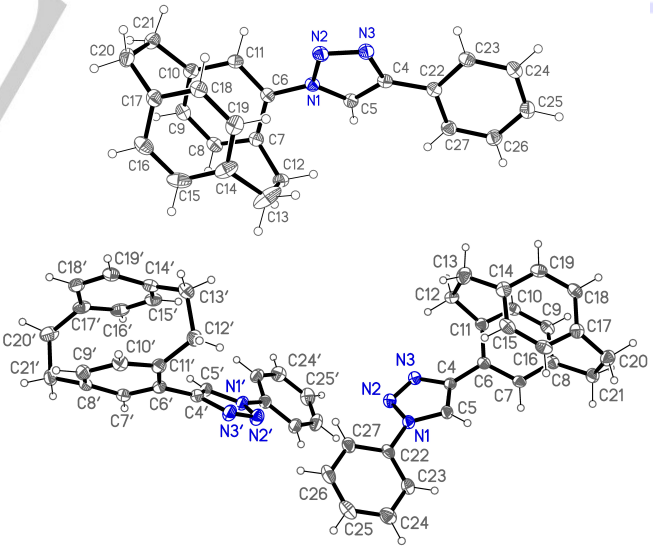


Figure 4. Molecular structure of compounds **12** (above) and **13** (below, two independent molecules). Ellipsoids represent 50% probability levels.[16]

As can be seen from Figure 4 only one regioisomer is generated in both cases. From closer inspection of the structures it can be inferred that the route leading to these isomers avoids steric interactions between the aromatic parts of both substrate

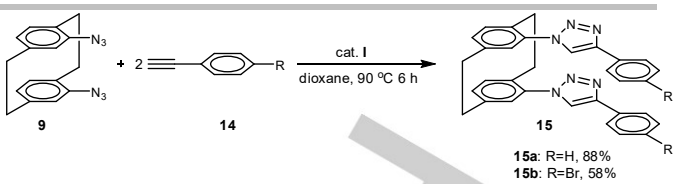
molecules: one obtains the shown "stretched" regioisomers, rather than the (not shown) "congested" forms.

Because of the chiral plane of **1** and **6** the adducts **12** and **13** are produced as racemates. The case of the hybrid material **11**, of which we unfortunately could not get single crystals suitable for X-ray diffraction measurements is stereochemically more complex. Assuming again that one regioisomer is formed preferentially (the one shown in Scheme 1) we now have two chiral planes and thus could form a mixture of two pairs of diastereomers (one is *RS* and *SR*, the other is *RR* and *SS).* Indeed, the careful analyses of the ^{1}H NMR spectrum confirms this: two different sets of signals were identified in a 1:11 ratio. Because of the size of the paracyclophanyl groups, the major product probably corresponds to an interaction of **8** with **1**, where both bulky substituents are in a mutual *anti* orientation. This approach avoids steric interference to the greatest extent.

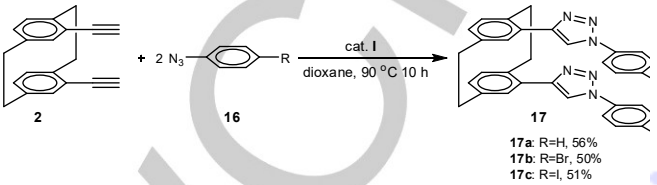
Bis(pseudo-gem triazolyl)[2.2]paracyclophanes

In an attempt to decrease the reaction times, we decided to identify a more suitable solvent for the synthesis of triazole-bearing [2.2]paracyclophane units. Trials were conducted in acetonitrile, cyclohexane and ethanol at 70 °C and in dioxane, DMSO and toluene at 90 °C. Each trial was performed with 0.1 mmol of both acetylene **1** and azide **8**, with 2.4 mol% cat. **I**, in 2 mL of solvent. TLC monitoring revealed that the shortest reaction time of 3 h was achieved for dioxane. After 5 h, the reaction in toluene was complete, whereas the remaining four runs showed only traces of triazole **11**, at which point the reactions were terminated.

Having identified a suitable catalyst and solvent, we next investigated the synthesis of triazoles in which two heterocyclic rings are bound to a [2.2]paracyclophane core in the *pseudo-gem* positions. This was achieved by reacting azide **9** or acetylene **2** with the appropriate acetylenes or azides, as presented below (Scheme 2 and 3). As above, the difference between products **15** and **17** consists in the way the paracyclophane unit is bound to the triazole rings; thus, in compounds **15a,b** the [2.2]paracyclophane moiety is connected to the N1 atoms of the triazole rings, but in compounds **17a-c** to the C4 atoms of the triazole rings. These copper-catalyzed cycloaddition reactions provided the corresponding *pseudo-geminal* bis(1,2,3-triazoles) in a regioselective manner in yields between 50 and 88%. Possibly the bis(azide) prefers an orientation in solution in which the two functional groups are oriented in a parallel fashion. In the cycloaddition step, the incoming dipolarophile clearly prefers an orientation which tends to minimize steric interaction with the cyclophane scaffold, similarly as observed above. In the two-step click process, the monoadduct, formed as a probable intermediate, clearly does not undergo an intramolecular cycloaddition of the remaining azide function to the newly formed triazole ring. This simplifies the process and makes multiple 1,3-dipolar cycloadditions of appropriately substituted [2.2]paracyclophanes preparatively and stereochemically more attractive.



Scheme 2. Reaction of bis(*pseudo-gem* triazole) **9** with acetylenes.



Scheme 3. Reaction of bis(*pseudo-gem* acetylene) **2** with azides.

Despite these structural differences, the spectra of these two types of triazoles present similar characteristics. The signals belonging to the triazole protons appear in the ^{1}H NMR spectra of compounds **15a,b** and **17a** (in $CDCl_3$) as singlets around 7.90 ppm. For triazoles **17b,c** (in DMSO-*d*6), the same signals can be found around 8.60 ppm. The ^{13}C NMR spectra of all five triazoles display the signals belonging to the heterocyclic C4 carbon atom at about 147.0-148.0 ppm. Single crystals suitable for X-ray diffraction were obtained for compounds **15a,b** (Figure 5)[17] and **17b** (Figure 6)[18] through the diffusion of pentane into a chloroform solution (**15a,b**) or recrystallization from DMF (**17b**). Compound **15b** crystallizes as a deuteriochloroform solvate.

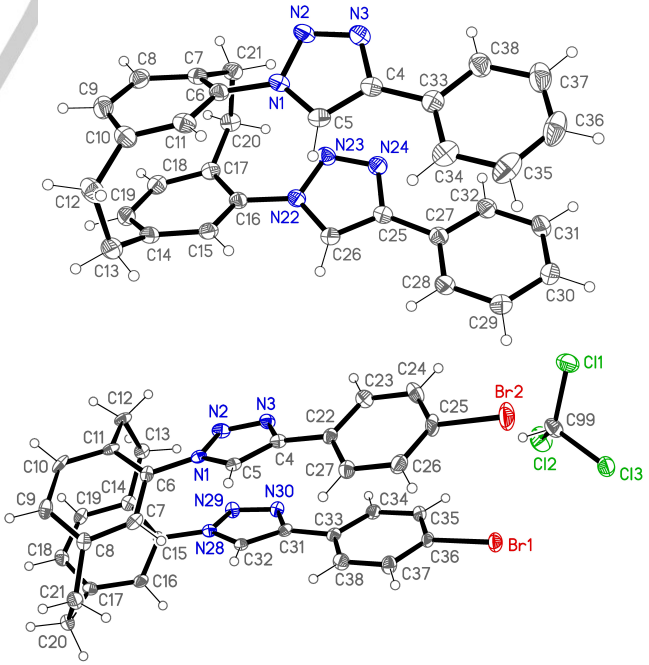


Figure 5. Molecular structure of compounds **15a** (above) and **15b** (below, deuteriochloroform solvate). Ellipsoids represent 50% probability levels.[17]

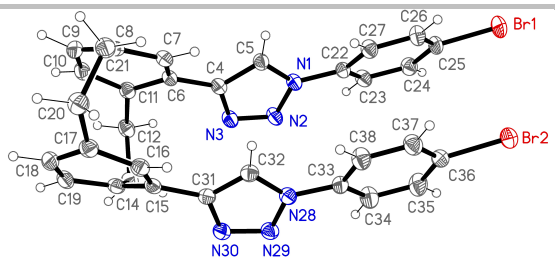
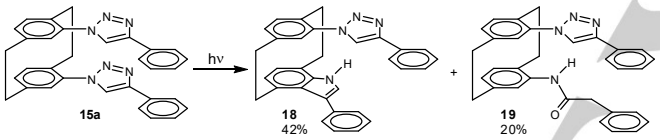


Figure 6. Molecular structure of compound **17b**. Ellipsoids represent 50% probability levels.[18]

Because in the solid state of compound **15a** the distance between the two triazole rings is less than 3.8 Å, we decided to investigate how the two heterocyclic rings interact with each other under both thermal and photochemical conditions. On refluxing a solution of triazole **15a** in toluene (b. p. 110 °C) for several hours, no change could be observed. When *p*-xylene (b. p. 138 °C) was used, the starting material decomposed completely and no defined products could be isolated. Next, we examined intramolecular interactions under photochemical conditions. A 1.1×10^{-3} M solution of **15a** in toluene, under a constant flow of nitrogen gas, was irradiated for 2 h using a TQ150 high pressure mercury lamp. The solvent was then removed under vacuum and the remaining residue was separated using flash chromatography on silica gel, yielding unreacted starting material and two new products (Scheme 4).



Scheme 4. Photolysis of bis(*pseudo-gem* triazole) **15a**.

The isolated yields were 42% for indole **18** and 20% for amide **19**, the remaining 38% consisting of a mixture of unreacted material along with traces of amide **19**. The ^{1}H NMR spectrum of indole **18** displays the signal of the H1 hydrogen atom of the indole ring as a singlet at 8.28 ppm, while the triazole proton appears as a singlet at 7.74 ppm. The ^{13}C NMR spectrum of the same compound shows the signal of the C4 carbon atom of the triazole ring at 146.9 ppm. The ^{1}H NMR spectrum of amide **19** displays the signal of the triazole proton at 7.94 ppm, while the amide proton displays a signal at 7.90 ppm. The two hydrogen atoms α to the carbonyl group are registered as an AB-quartet system at 3.42 and 3.30 (^{2}J=14.3 Hz). The ^{13}C NMR spectrum shows a signal at 168.3 ppm, belonging to the carbonyl carbon atom, while the C4 carbon atom of the triazole ring appears at 148.1 ppm. Single crystals suitable for X-ray diffraction were obtained for **18** and **19** by slow diffusion of pentane into a chloroform solution of the corresponding derivative (Figure 7).[19] The annelated indole ring of **18** does not significantly alter the flattened boat form of the cyclophane ring to which it is attached (the same is true for the other fused-ring derivatives presented below). The molecule of **19** contains an intramolecular N–HΛN hydrogen bond from the amide group to a triazole nitrogen.

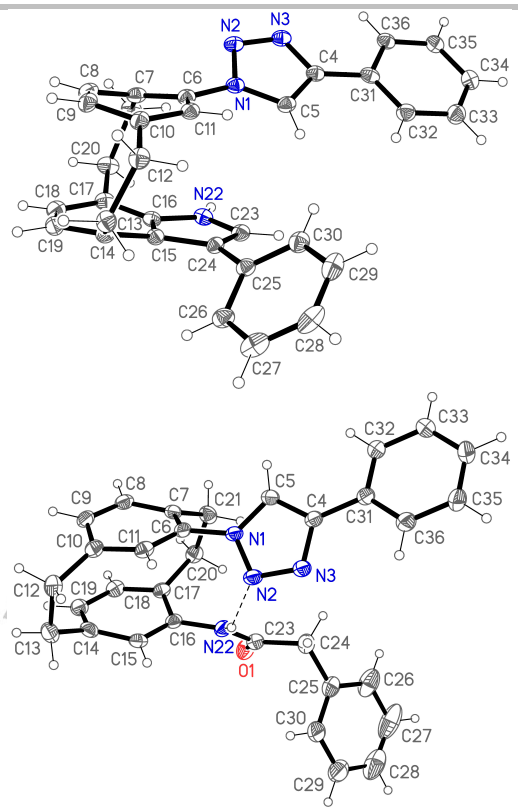
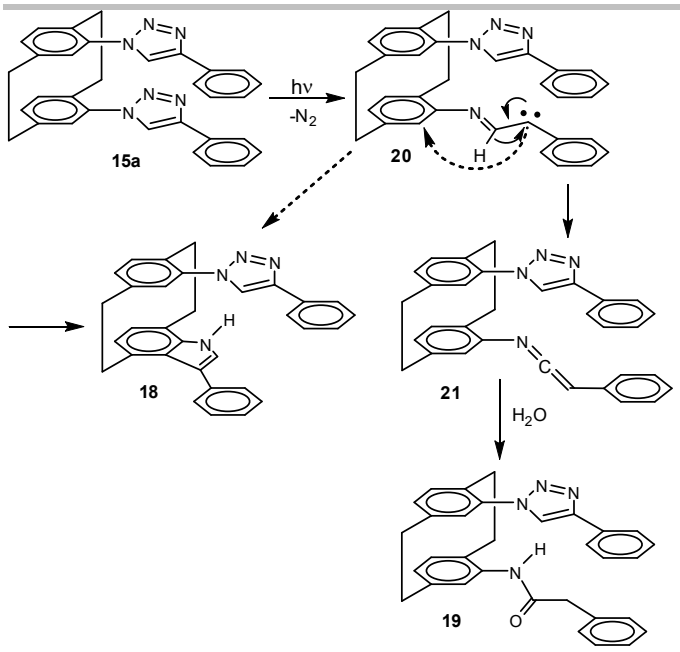


Figure 7. Molecular structure of compounds **18** (above) and **19** (below). Ellipsoids represent 30% probability levels for **18** and 50% for **19**.[19]

Photolysis or pyrolysis of the 1,4-diaryl-1,2,3-triazole ring can lead to the formation of carbene intermediates. These may in turn lead to indoles, or undergo Wolff rearrangements, to give ketenimines.[20] Scheme 5 presents a tentative sequence of these transformations for compound **15a**.

When subjected to UV radiation, triazole **15a** eliminates a molecule of nitrogen, with the formation of carbene **20**. This can then either form indole **18** by C-H-insertion into the neighboring benzene ring, or ketenimine **21** via a Wolff rearrangement. Subsequently, **21** could add one molecule of water during workup, leading to the formation of amide **19**.

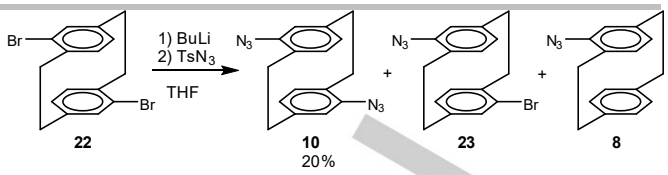


Scheme 5. Plausible mechanism for the formation of the photolysis products **18** (dashed arrows) and **19** (full arrows).

In an attempt to photolyse both triazole rings, we raised the irradiation time from 2 to 7 h. However, only indole **18** (31%) and amide **19** (28%) were recovered. By changing the solvent to acetonitrile and irradiating the solution for 2.5 h, we isolated indole **18** (19%), amide **19** (7%) and unreacted starting material (35%). In a further attempt, we added benzophenone as a sensitizer to a toluene solution of **15a** and irradiated the reaction mixture for 2 h. However, again only indole **18**, amide **19** and unreacted starting material were recovered. The fractions containing the two reaction products also displayed considerable amounts of decomposed material and no further purification was attempted. Using diacetyl as a sensitizer led to the decomposition of triazole **15a**, with possible traces of indole **18** and amide **19** being identified by TLC. Irradiation of a pure sample of indole **18** in toluene for 4 h was also performed, however no new products were identified by TLC and therefore, no workup was performed for this attempt.

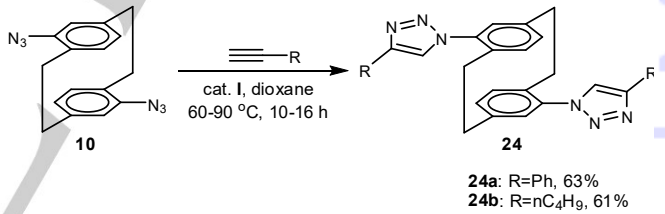
***Pseudo-para* bis(triazole)[2.2]paracyclophanes**

Because the second triazole ring did not react in any of the conditions reported above, we assumed it might be stabilized by the indole/amide function in the *pseudo-geminal* position. To test this hypothesis, we decided to synthesize a new [2.2]paracyclophane bis(triazole), where the two heterocyclic rings occupied the *pseudo-para* positions, thus limiting the possible interactions between them. Toward this end, we first prepared *pseudo-para* bis(azido)[2.2]paracyclophane **10** by reacting *pseudo-para* bis(bromo)[2.2]paracyclophane with *n*-butyllithium, followed by tosyl azide treatment, according to a previously described procedure (Scheme 6).[10]



Scheme 6. Synthesis of *pseudo-para* bis(azido)[2.2]paracyclophane **10**.

Upon separation of the reaction mixture, bisazide **10** was obtained in 20% isolated yield and 6% was unreacted starting material, the remaining 74% being a mixture of bis(azide) **10**, monoazide **8** and bromoazide **23** (as identified by ^{1}H NMR analysis), the latter probably being the result of an incomplete bromometal exchange of **22**. The next step consisted of reacting bis(azide) **10** with phenylacetylene, as depicted in Scheme 7. This led to the formation of triazole **24a** as a colorless solid, poorly soluble in all common solvents. Because we wished to record an X-ray structure, we decided to synthesize another *pseudo-para* bis(triazole), using 1-hexyne instead of phenylacetylene as a trapping reagent, in order to increase the solubility of the product. Indeed, triazole **24b** exhibited a much higher solubility in solvents such as dichloromethane or chloroform. The ^{1}H NMR spectra of triazoles **24a, b** confirm the formation of the triazole rings. The triazole protons are found at 9.15 ppm for **24a** and 7.27 ppm for **24b**. In the ^{13}C NMR spectra, the C4 carbon atoms of the newly formed heterocyclic rings absorb at 146.9 ppm for **24a** and 148.3 ppm for **24b**.



Scheme 7. Synthesis of *pseudo-para* bis(triazoles) **24**.

Single crystals suitable for X-ray diffraction were obtained for both bis(azide) **10** and triazole **24b**, by slow diffusion of pentane into a chloroform solution. For the poorly soluble triazole **24a**, an NMR tube containing a dilute chloroform solution was set aside until all the solvent had evaporated, leaving single crystals (Fig. S7) suitable for X-ray diffraction. The three structures are presented in Figures 8 and 9.[21,22] The molecule of **10** displays non-crystallographic inversion symmetry with an r.m.s. deviation of 0.03 Å.

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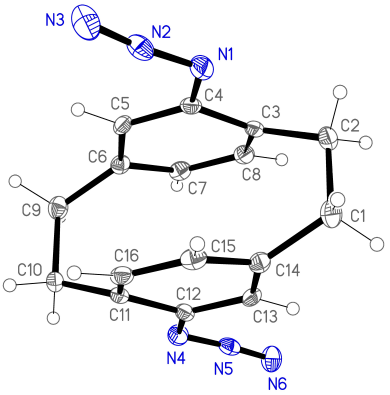


Figure 8. Molecular structure of compound **10**. Ellipsoids represent 50% probability levels.[21]

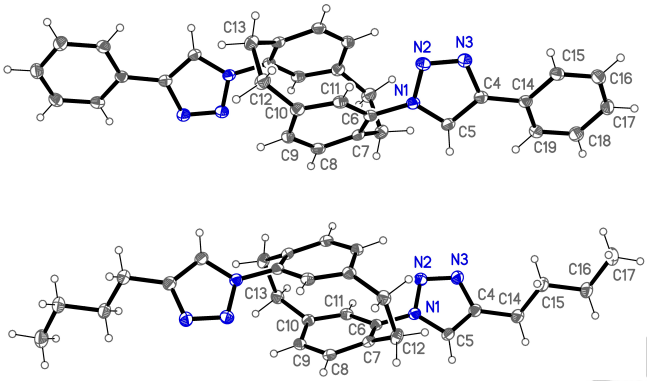
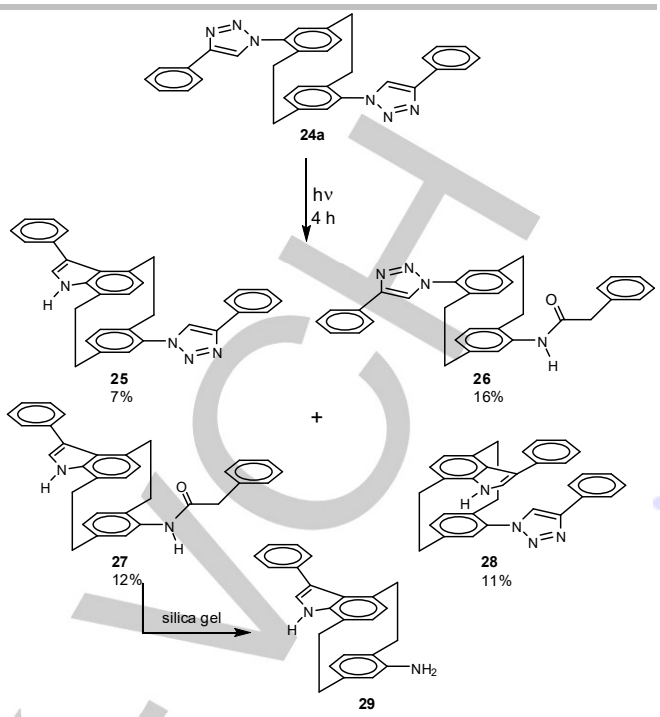


Figure 9. Molecular structure of compounds **24a** (above) and **24b** (below). Ellipsoids represent 50% probability levels.[22]

Compounds **24a** and **24b** both crystallize with imposed inversion symmetry in space group $P2_1/c$ with similar cell constants; they are effectively isotypic.

Once *pseudo-para* bis(triazole) **24a** was available, we submitted a suspension of it in toluene to UV radiation. We performed several experiments that lasted 4, 5, 6 and 10 h, using the same TQ150 high pressure mercury vapor lamp. Each time, the solvent was removed in vacuo. TLC analysis of the reaction mixtures indicated the presence of some unreacted substrate, together with five new compounds, as shown in Scheme 8.



Scheme 8. Photolysis of bis(*pseudo-para* triazole) **24a**.

The reaction mixture was submitted to flash chromatography, allowing isolation of the different products. The detailed NMR analysis of compound **25** indicated that it was an indole derivative. The H1 hydrogen atom of the indole ring absorbs as a singlet at 8.36 ppm in the ^{1}H NMR spectrum of **25**, while the triazole proton can be found as a singlet at 8.09 ppm (2D NMR analysis). ESI-MS analysis indicated the mass of **25** to be 466.2150 (calcd. 466.2157). 2D NMR analysis confirms that the two nitrogen atoms directly bound to the [2.2]paracyclophane unit of **25** are disposed in a *pseudo-para* fashion. Unfortunately, indole **25** proved to be unstable and we were not able to perform any more analyses on it before it decomposed.

Compound **26** was identified as an amide. The ^{1}H NMR spectrum reveals the amide proton at 6.99 ppm, in the form of a broad singlet. 2D NMR analysis, especially NOESY experiments pointed towards a *pseudo-para* substituted [2.2]paracyclophane. It appears to be a stable compound that does not hydrolyze during purification on silica gel.

When attempting to isolate derivative **27** using flash chromatography on silica gel, we always obtained it as part of a mixture with a different compound. However, when basic alumina was employed, a pure sample of **27** was obtained. Single crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane into a chloroform solution of **27**. The results are presented in Figure 10.[23] The structure involves two independent but closely similar molecules (a least-squares fit of all non-H atoms led to an r.m.s. deviation of 0.15 Å). It seems that compound **27** is hydrolyzed on contact with silica gel. TLC-MS analysis indicated a compound with a molecular mass corresponding to amine **29**.

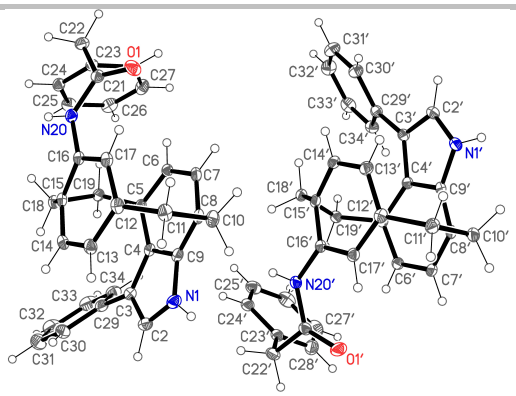
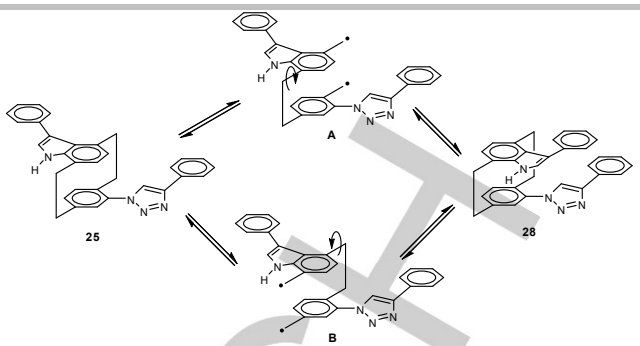


Figure 10. Molecular structure of compound **27** (two independent molecules). Ellipsoids represent 30% probability levels.[23]

The mechanism for the formation of derivatives **25-27** could be similar to the one presented in Scheme 5. Triazole **24a** first loses a molecule of nitrogen under UV-light, leading to the formation of a carbene similar to structure **20**. This, in turn, can lead to the formation of an indole ring (derivatives **25** and **27**), or rearrange to a ketenimine which, upon workup hydrolyzes, forming an amide (derivatives **26** and **27**). It is worth noting that for the indole-amide derivative **27,** both initial triazole rings suffered photolysis. As mentioned above, this was not observed for *pseudo-gem* derivatives **18** and **19**. This suggests that the triazole ring in compounds **18** and **19** is stabilized by the indole ring or amide function found in its proximity. This is no longer the case for derivatives **25** and **26**, where the photolysis of the triazole ring clearly takes place, as evidenced by the formation of indole-amide derivative **27**.

The structure of indole **28** was also established through X-ray analysis, after obtaining suitable single crystals by slow diffusion of pentane into a chloroform solution of **28**. Examination of the crystals under the microscope (Fig. 11) showed two strikingly different types of crystal, large blocks and fine needles; these proved to be two polymorphs of **28**, one monoclinic and one orthorhombic (Figure 12).[24] Both molecules are closely similar except for the orientation of the phenyl rings; a least-squares fit of all other atoms gave an r.m.s. deviation of 0.11 Å. The structure determinations show that the starting triazole **24a** has not only lost a molecule of nitrogen to form an indole ring, but has also undergone conversion to the *pseudo-ortho* isomer. It is known that under thermal[25,26] or photochemical[27,28] conditions, one of the ethano bridges of the [2.2]paracyclophane core can suffer homolysis, leading to the formation of a diradical. By bond rotation of a benzene ring and radical recombination, *pseudo-para* and *pseudo-ortho* isomers, and also *pseudo-gem* and *pseudo-meta* isomers, are interconvertible.[25] Thus, derivative **28** was probably formed from indole **25** via one or both diradicals **A**, **B** presented in Scheme 9. The presence of indole **28** in the reaction mixture supports the theory that an indole ring in close proximity to a triazole ring stabilizes the latter. While *pseudo-para* indole **25** is unstable and decomposes, its isomer, *pseudo-ortho* indole **28** is a stable compound.



Scheme 9. The formation of **28** from **25**, via diradicals **A** and/or **B**.

The ^{1}H NMR spectrum of **28** displays the nitrogen-bound indole proton as a singlet at 8.48 ppm, while the triazole proton appears as a singlet at 7.54 ppm. HRMS analysis of **28** revealed a molecular mass of 466.2151, virtually identical to the recorded value for indole **25**.

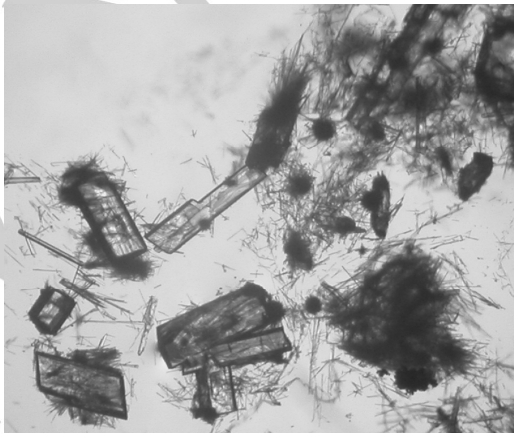


Figure 11. Crystalline sample of compound **28**, showing the monoclinic polymorph (large blocks) and the orthorhombic polymorph (fine needles).

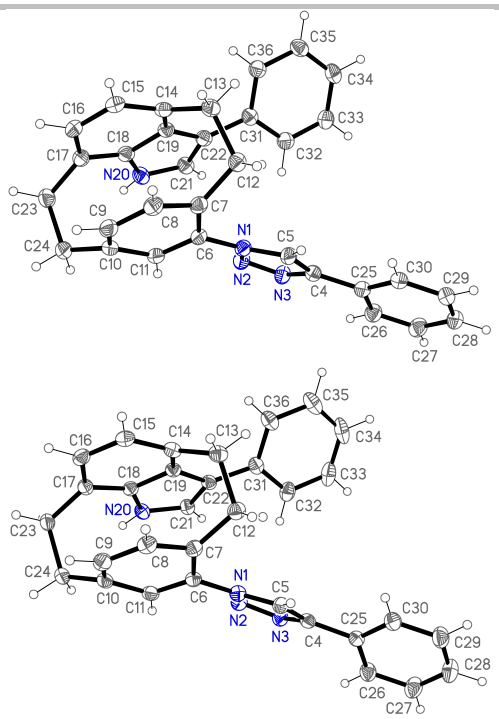


Figure 12. Molecular structure of compound **28**. Above, monoclinic polymorph; below, orthorhombic polymorph. Ellipsoids represent 50% probability levels.[24]

Conclusions

We have demonstrated with the respective model compounds that both mono- and disubstituted ethynylcyclophanes **1**, **2** and **5** and bis(azides) **9** and **10** can be employed as addition partners in CuAAC reactions to design and build complex extended molecular scaffolds. It seems likely that 1,3-dipolar cycloadditions can also be performed with the other oligo ethynyl cyclophanes listed in Fig. 1. Likewise, the oligo azides corresponding to these alkynes should be obtainable by the standard reactions used here.

This may mean that polyethynylated [2.2]paracyclophanes and the corresponding azide derivatives can be used as multivalent "molecular knots" or "superatoms" to construct new molecular scaffolds with designed orientation of functional groups in three-dimensional space. Of particular interest would be cyclophane derivatives with more than four ethynyl or azido substituents; these derivatives are presently unknown.

Once the new adducts have been prepared and characterized, they can be employed in further transformations. Examples given here involve the photochemical deazotization of adducts such as **15a** and **25a**. By these routes hitherto unknown paracyclophane derivatives become available, such as the indolophanes **26**, **28**, **29**.

In summary, we believe that the approach described here, which involves reaction paths starting from the [2.2]paracyclophane nucleus and subsequently "moving out" structurally provides a novel and potentially strongly variable approach to complex molecular objects with a clearly defined orientation of functional groups. In a sense the [2.2]paracyclophane core functions as a "seed crystal" on which the functional groups "grow" in specific orientation.

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Keywords: azides • click chemistry • [2.2]paracyclophane • photochemistry • triazoles

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[18] CCDC-1513386 contains the supplementary crystallographic data for compounds **17b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[19] CCDC-1513387 and -1513388 contain the supplementary crystallographic data for compounds **18** and **19**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[23] CCDC-1513394 contains the supplementary crystallographic data for compounds **27**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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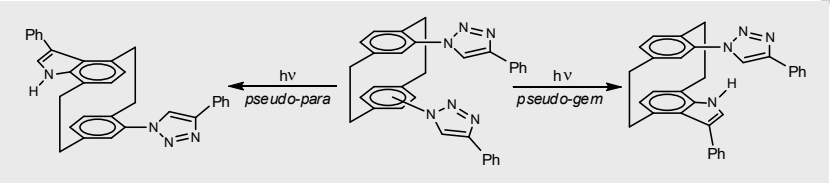

Click reactions: Mono and disubstituted ethynylcyclophanes and azides have been employed as addition partners in CuAAC reactions to build designed complex extended molecular scaffolds. The resulting triazoles were investigated under photochemical conditions. A variety of newly substituted [2.2]paracyclophanes were identified; deazotation of *pseudo-gem* and *pseudo-para* adducts provided indolophane derivatives.

*Lucian G. Bahrin, Laura G. Sarbu, Peter G. Jones, Lucian M. Birsa and Henning Hopf**

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[2.2]Paracyclophane-Bis(triazole) Systems: Synthesis and Photochemical Behavior