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Synthesis and structure of [2.2]paracyclophanes incorporating alkyne units in the extended linear chain

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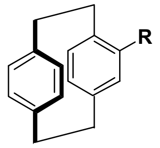
Abstract—The novel [2.2]paracyclophanes **4**–**7** with an extended π-conjugation due to the presence of a linear arylethynyl chain have been synthesized by the Pd-catalyzed Sonogashira coupling reaction.

As a continuation of our interest in [2.2]paracyclophane chemistry,[1] we have undertaken a research project on the synthesis of new cyclophane derivatives containing ethynyl groups. Linear arylethynyl molecules with extended π-conjugation are of considerable interest due to their potential applications in electroluminescence,[2] liquid crystallinity,[3] optoelectronics,[4] and organic semiconductors.[5] The aim of the project is that of using [2.2]paracyclophane (PCP), which has a unique structure with two strained and facing benzene rings, as building block for the construction of extended π-systems containing three-dimensional (PCP)-, linear (acetylene triple bond)-, and planar (benzene rings)-π-electron systems. The triple bonds are employed as conjugation bridges, and phenyl groups and [2.2]paracyclophane as π-centers.

In this article, we report the preliminary results of a study on the synthesis of [2.2]paracyclophane derivatives containing one or two *para*-connected carbon–carbon triple bonds. These molecules have a three-dimensional π-system comparable to that of fullerene.

4-Ethynyl-[2.2]paracyclophane (**3**) was the starting material used to synthesize the target compounds **4**–**7**. It was prepared by coupling trimethylsilylacetylene with 4-bromo[2.2]paracyclophane (**1**) followed by the removal of the alkyne-protecting group[6a] (TMS) (Scheme 1). Compound **3** had been previously prepared by Hopf and co-workers[6b] by another route starting from 4-formyl[2.2]paracyclophane. Compounds **4**–**7** were obtained by Pd-catalyzed Sonogashira[8] reaction between the commercially available aryliodides **8** and **9** and the diaryliodides[9] **12** and **13** (Scheme 2).



1, R = Br; **2**, R = $-C{\equiv}C-SiMe_3$; **3**, R = $-C{\equiv}CH$

Scheme 1.

Whereas the couplings of **3** with aryliodides **8** and **9** were carried out[12] at 75 °C for 20 h, the reactions between **3** and diaryliodides **12** and **13** occurred under milder conditions,[12] at 25 °C for 18 h. All attempts to carry out the Sonogashira reaction of 4-bromo[2.2]paracyclophane (**1**) with *p*-ethynylaniline (**10**) and *p*-ethynylanisole (**11**) gave worse results: only a 37% yield was obtained in the former case and no reaction occurred in the latter. The well-known relative reactivity of aryl halides, Ar-I ≫ Ar-Br > Ar-Cl, might explain these results. The structures of the [2.2]paracyclophanes **4**–**7** were proved unambiguously by analysis of their NMR spectra (^{1}H and ^{13}C) and elemental analysis.

Keywords: [2.2]Paracyclophanes; Sonogashira reaction; Diarylacetylenes; NMR spectroscopy.

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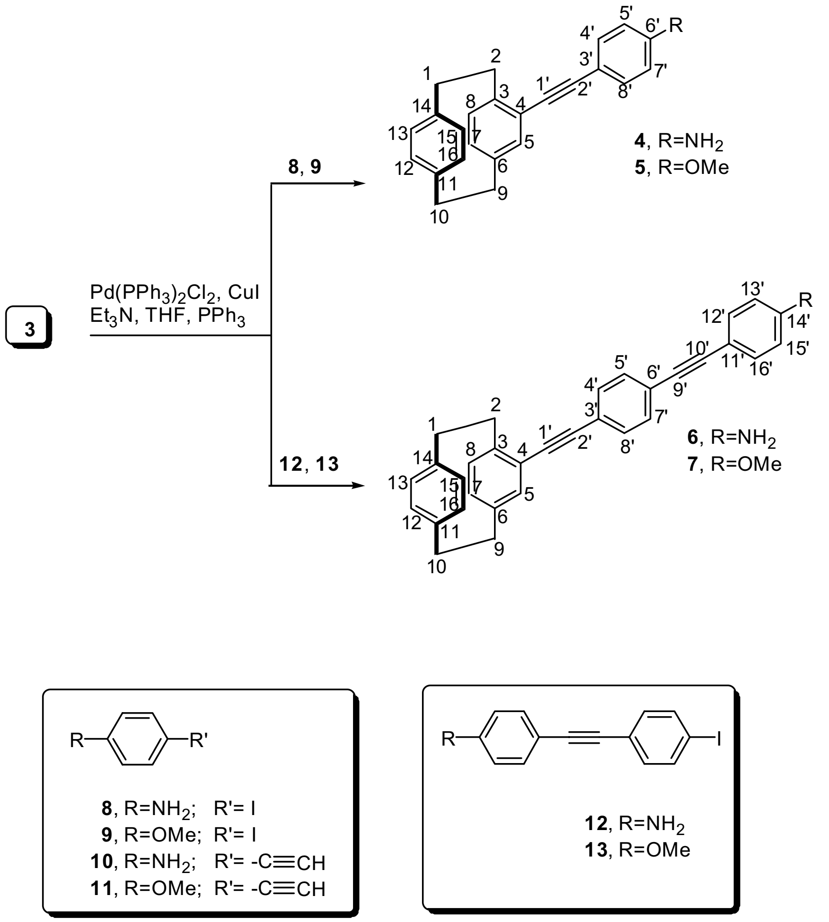

Scheme 2.

In conclusion, a synthetic route to prepare a new series of molecules based on [2.2]paracyclophane moiety as the key building block and containing an extended π-delocalization has been established. The synthesis of new linearly functionalized [2.2]paracyclophanes containing aromatic carbocycles and/or heterocycles as π-centers connected by acetylenic triple bonds, as well as the study of their properties, is currently in progress.

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6. (a) Trimethylsilyl[2.2]paracyclophane (**2**) was prepared in 90% yield starting from 4-bromo[2.2]paracyclophane (**1**)[7a] according to a previously described[7b] procedure used to prepare a diethynyl[2.2]paracyclophane. Data for compound **2**: white crystals; mp 138–139 °C (MeOH); ^{1}H NMR δ 0.34 (s, 9H, SiMe$_3$), 2.84 (ddd, 1H, J = 13.0, 10.5, 5.6 Hz, H-2), 2.9–3.15 (m, 5H, H-1, H$_s$-9, H$_s$-10), 3.22 (m, 1H, H-1), 3.60 (ddd, 1H, J = 13.0, 10.2, 2.6 Hz, H-2), 6.45 (d, 1H, J = 8.0 Hz, H-8), 6.47–6.54 (m, 5H, H$_s$-12, H$_s$-13, H-16), 6.50 (dd, 1H, J = 8.0, 1.7 Hz, H-7), 6.51 (d, 1H, J = 1.7 Hz, H-5), 7.02 (dd, 1H, J = 7.8, 1.7 Hz, H-15); ^{13}C NMR δ 0.36 (SiMe$_3$), 34.2 (C-2), 34.7 (C-1), 35.3, 35.7 (C9, C-10), 97.8 (C-1′), 106.0 (C-2′), 125.1 (C-4), 129.9 (C-15), 132.6, 132.9, 133.1, 133.6, 134.0 (C-7, C-8, C-12, C-13, C-16), 137.4 (C-5), 139.6 (C-6), 139.7, 139.8 (C-11, C-14),

143.2 (C-3); MS *m*/*e* (rel. int.) 104 (38), 141 (15), 185 (61), 200 (100), 304 (M^+, 53); UV–vis ($CHCl_3$) [λ_{max} nm ($\log\varepsilon$)]: 284 (2.76); Anal. Calcd for $C_{21}H_{24}Si$: C, 82.83; H, 7.94. Found: C, 82.81; H, 7.95.(b) Bondarenko, L.; Dix, I.; Hinrichs, H.; Hopf, H. *Synthesis* **2004**, 2751–2759.

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9. Diarylacetylenes **12** and **13** were prepared according to a previously described procedure[10] by Sonogashira coupling between *p*-diiodobenzene and the commercially available *p*-ethynylaniline (**10**) and *p*-ethynylanisole (**11**).[8b,11] It is noteworthy that in the case of **13** the reaction yield was improved from 65% to 90% by employing $Pd(PPh_3)_2Cl_2$ and Et_2NH.
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12. General procedure for the Sonogashira reaction of 4-ethynyl[2.2]paracyclophane (**3**) with aryliodides **8**, **9** and diaryliodides **12** and **13**. The following discussion of the **3**–**8** reaction is a typical procedure used for all coupling reactions. Dry THF (6 ml), 4-ethynyl[2.2]paracyclophane (**3**) (0.189 g, 0.81 mmol), triphenylphosphine (0.021 g, 0.08 mmol), CuI (0.008 g, 0.04 mmol), 4-iodoaniline (**8**) (0.118 g, 0.54 mmol) and the palladium catalyst (0.028 g, 0.04 mmol) were placed in a flask and degassed with Ar. The mixture was heated at 75 °C for 20 h. Then, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with petroleum ether/dichloromethane 1:2 afforded 0.145 g (83% yield) of **4** as pale orange crystals; mp 173–174 °C (MeOH); ^{1}H NMR δ 2.85 (m, 1H, H-2), 2.9–3.15 (m, 5H, H-1, H_s-9, H_s-10), 3.25 (m, 1H, H-1), 3.65 (m, 1H, H-2), 3.81 (br s, 2H, $-NH_2$), 6.42 (d, 1H, *J* = 7.9 Hz, H-8), 6.44–6.54 (m, 4H, H-7, H-12, H-13, H-16), 6.52 (d, 1H, *J* = 1.7 Hz, H-5), 6.68 (m, 2H, H-5′, H-7′), 7.05 (dd, 1H, *J* = 7.7, 1.9 Hz, H-15), 7.40 (m, 2H, H-4′, H-8′); ^{13}C NMR δ 34.5 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 87.9 (C-1′), 93.8 (C-2′), 113.6 (C-3′), 115.1 (C-5′, C-7′), 125.8 (C-4), 130.2 (C-15), 132.4, 132.9 (C-7, C-12), 133.0, 133.5 (C-13, C-16, C-4′, C-8′), 134.0 (C-8), 137.0 (C-5), 139.6 (C-11), 139.8 (C-6, C-14), 142.3 (C-3), 146.8 (C-6′); MS *m*/*e* (rel. int.) 103 (5), 147 (4), 165 (4), 189 (8), 219 (100), 323 (M^+, 36); UV–vis ($CHCl_3$) [λ_{max} nm ($\log\varepsilon$)]: 276 (3.49); Anal. Calcd for $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33. Found: C, 89.34; H, 6.53; N, 4.34. **5**: white crystals (95% yield); mp 148–149 °C (MeOH); ^{1}H NMR δ 2.80 (ddd, 1H, *J* = 13.0, 10.4, 5.5 Hz, H-2), 2.90–3.10 (m, 5H, H-1, H_s-9, H_s-10), 3.20 (m, 1H, H-1), 3.80 (s, 3H, OMe), 3.58 (ddd, 1H, *J* = 13.0, 10.1, 2.7 Hz, H-2), 6.45–6.55 (m, 3H, H-12, H-13, H-16), 6.47 (d, 1H, *J* = 7.9 Hz, H-8), 6.52 (dd, 1H, *J* = 7.9, 1.9 Hz, H-7), 6.53 (d, 1H, *J* = 1.8 Hz, H-5), 6.86 (m, 2H, H-5′, H-7′), 6.95 (dd, 1H, *J* = 7.7, 1.8 Hz, H-15), 7.42 (m, 2H, H-4′, H-8′); ^{13}C NMR δ 34.6 (C-2), 34.8 (C-1), 35.4, 35.7 (C-9, C-10), 55.6 (OMe), 85.7 (C-1′), 93.1 (C-2′), 114.3 (C-5′, C-7′), 116.3 (C-3′), 125.5 (C-4), 130.2 (C-15), 132.6, 132.9, 133.1, 133.5, 134.1 (C-7, C-8, C-12, C-13, C-16, C-4′, C-8′), 137.1 (C-5), 139.6 (C-6), 139.8, 139.9 (C-11, C-14), 142.5 (C-3), 159.8 (C-6′); MS *m*/*e* (rel. int.) 189 (17), 219 (15), 234 (100), 338 (M^+, 38); UV–vis ($CHCl_3$) [λ_{max} nm($\log\varepsilon$)]: 335 (4.92); Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 89.35; H, 6.58. **6**: orange crystals (95% yield); mp 80–81 °C (MeOH); ^{1}H NMR δ 2.89 (ddd, 1H, *J* = 13.3, 10.4, 5.3 Hz, H-2), 2.95–3.16 (m, 5H, H-1, H_s-9, H_s-10), 3.26 (m, 1H, H-1), 3.66 (ddd, 1H, *J* = 13.3, 10.2, 2.6 Hz, H-2), 3.85 (br s, 2H, NH_2), 6.48 (d, 1H, *J* = 7.8 Hz, H-8), 6.51 (dd, 1H, *J* = 7.8, 2.0 Hz, H-7), 6.48–6.55 (m, 3H, H-12, H-13, H-16), 6.58 (d, 1H, *J* = 2.0 Hz, H-5), 6.64 (m, 2H, H-13′, H-15′), 7.01 (dd, 1H, *J* = 7.8, 1.9 Hz, H-15), 7.35 (m, 2H, H-12′, H-16′), 7.50–7.53 (m, 4H, H-4′, H-5′, H-7′, H-8′); ^{13}C NMR δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 87.5 (C-9′), 91.6 (C-1′), 92.4 (C-10′), 93.0 (C-2′), 112.7 (C-11′), 115.0 (C-13′, C-15′), 123.2, 123.9 (C-3′, C-6′), 125.0 (C-4), 130.4 (C-15), 131.5 (C-4′, C-5′, C-7′, C-8′), 132.7, 132.9, 133.0, 133.5 (C-12, C-13, C-16), 133.1 (C-7), 133.3 (C-12′, C-16′), 134.1 (C-8), 137.2 (C-5), 139.6 (C-11), 139.7 (C-6), 140.0 (C-14), 142.7 (C-3), 147.1 (C-14′); UV–vis ($CHCl_3$) [λ_{max} nm ($\log\varepsilon$)]: 347 (2.99); Anal. Calcd for $C_{32}H_{25}N$: C, 90.74; H, 5.95; N, 3.31. Found: C, 90.92; H, 5.93; N, 3.27. **7**: pale yellow crystals (90% yield); mp 179–180 °C (MeOH); ^{1}H NMR δ 2.90 (ddd, 1H, *J* = 13.2, 10.4, 5.4 Hz, H-2), 2.92–3.15 (m, 5H, H-1, H_s-9, H_s-10), 3.25 (m, 1H, H-1), 3.66 (ddd, 1H, *J* = 13.2, 10.3, 2.8 Hz, H-2), 3.84 (s, 3H, OCH_3), 6.49 (d, 1H, *J* = 7.8 Hz, H-8), 6.48–6.56 (m, 3H, H-12, H-13, H-16), 6.53 (dd, 1H, *J* = 7.8, 1.9 Hz, H-7), 6.58 (d, 1H, *J* = 1.9 Hz, H-5), 6.89 (m, 2H, H-13′, H-15′), 7.02 (dd, 1H, *J* = 7.8, 1.8 Hz, H-15), 7.49 (m, 2H, H-12′, H-16′), 7.51–7.55 (m, 4H, H-4′, H-5′, H-7′, H-8′); ^{13}C NMR δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 55.5 (OCH_3), 88.2 (C-9′), 91.5 (C-1′), 91.7 (C-2′), 92.9 (C-10′), 114.3 (C-13′, C-15′), 115.5 (C-11′), 123.5 (C-6′), 124.9 (C-4, C-3′), 130.4 (C-15), 131.6, 131.7 (C-4′, C-5′, C-7′, C-8′), 132.7, 132.9 (C-12, C-16), 133.2 (C-7), 133.3 (C-12′, C-16′), 133.5 (C-13), 134.1 (C-8), 137.2 (C-5), 139.6 (C-11), 139.7 (C-6), 140.0 (C-14), 142.7 (C-3), 160.1 (C-14′); UV–vis ($CHCl_3$) [λ_{max} nm ($\log\varepsilon$)]: 336 (4.65); Anal. Calcd for $C_{33}H_{26}O$: C, 90.38; H, 5.98. Found: C, 90.82; H,5.94.