Cyclotrimerization of Benzobarrelene: Synthesis of New Isomeric Barrelene Architectures

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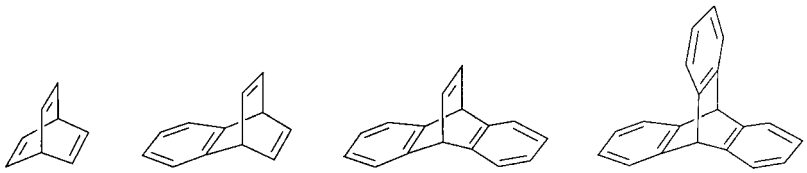
The cyclotrimerization reaction of benzobarrelene derivatives was investigated. Dibromobenzobarrelene **10** was converted to the bromostannyl derivative **11**, which was used as the substrate of the cyclotrimerization reaction. Thus, reaction of **11**, with copper(I) thiophene-2-carboxylate (CuTC) gave a mixture of the isomeric cyclotrimers **5** and **6** and the dimers **12** and **13**, in addition to a trace of protodestannylated bromoalkene **14** (*Scheme 2*).

Introduction. – In general, the class of molecules headed by barrelene (**1**) and constituted by its benzo derivatives **2**–**4** offers the possibility of several mechanistically interesting investigations. For example, these compounds exhibit a unique behavior in the photochemical di-π-methane rearrangement [1], in the cationic *Wagner–Meerwein* rearrangement [2], and in other instances [3]. In addition, they recently have raised interest as molecules related to fullerenes, and the polycyclic [2.2.2] system is often observed in fullerene derivatives [4]. From a different viewpoint, benzocyclotrimers of polycyclic systems are interesting compounds in view of the long-standing topic of aromaticity [5] and because they represent fullerene substructures or even subunits of new, hitherto unobserved carbon allotropes [6].

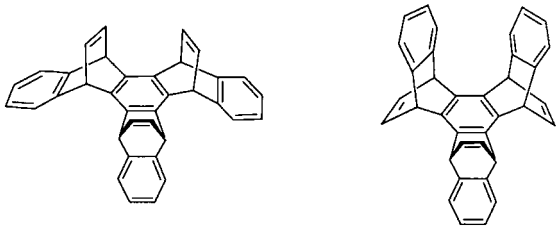


1 **2** **3** **4**

In this work, we present the cyclotrimerization of benzobarrelene that led to the new benzocyclotrimers **5** and **6** and gave also the opportunity to observe dimers whose symmetric and chiral structures were defined by chemical methods.

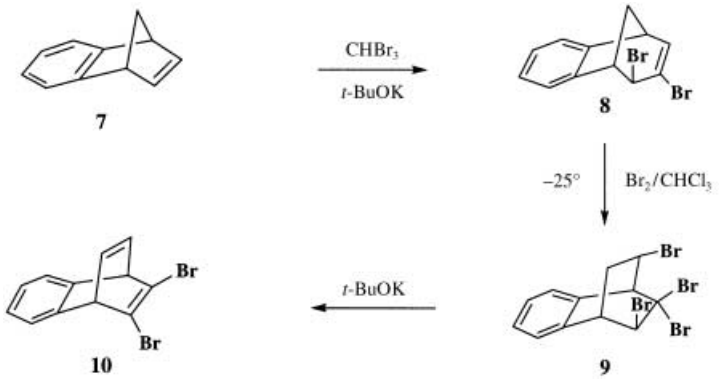
Results and Discussion. – The 2,3-dibromobenzobarrelene **10** was prepared by published methods [7] starting from benzonorbornadiene **7** *via* **8** and **9** (*Scheme 1*).

The reaction of dibromide **10** with BuLi followed by quenching with chlorotrimethylstannane afforded **11** in nearly quantitative yields. For the cyclotrimerization



5 **6**

Scheme 1



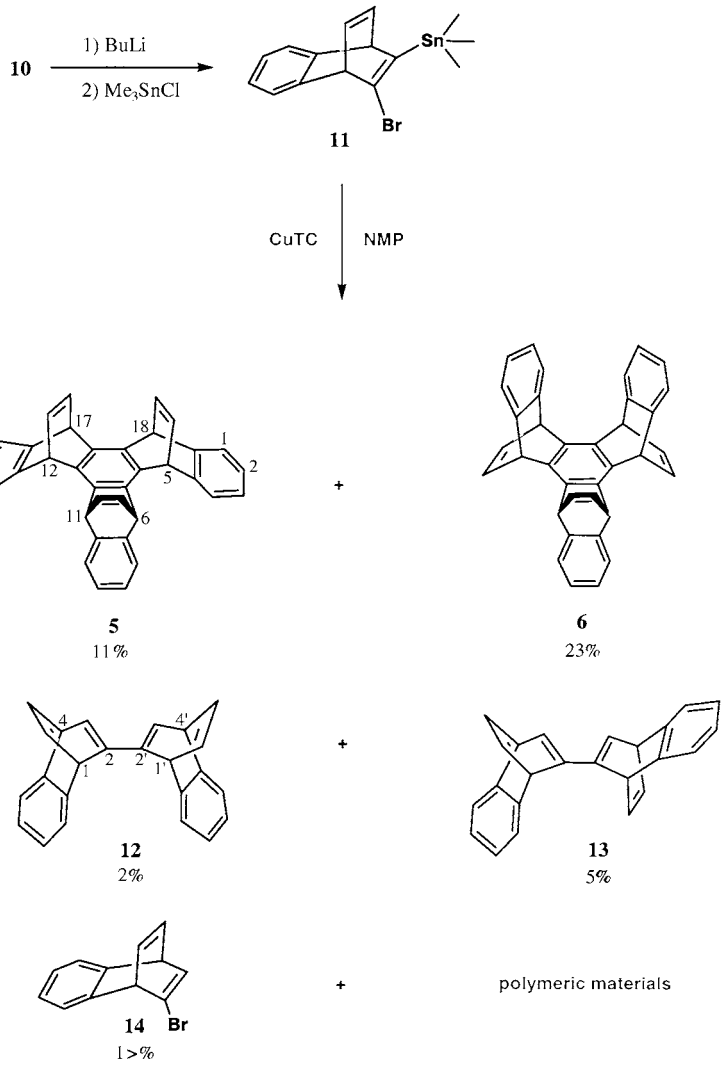
reaction, the latter was treated with copper(I) thiophene-2-carboxylate (CuTC) in 1-methylpyrrolidin-2-one as solvent at $-20°$ to provide the cyclotrimers **5** and **6** in a total yield of 34% ('*syn*'/'*anti*' ratio[1]) of 1:2; *Scheme 2*). Recently, we have demonstrated with different systems that this copper reagent provided the highest yield in the cyclotrimerization reactions [5d–g]. In the same reaction, protodebrominated dimers **12** and **13** were also detected in 7% yield in a '*syn*'/'*anti*' ratio[1]) of 2:5, in addition to protodestannylated product **14**.

At variance with the present reaction, where the trimers **5** and **6** were produced in a 34% total yield, the same reaction performed with vicinal bromostannyl derivatives of the norbornene system generally gave exclusively benzocyclotrimers in very high yields [5d–e]. We assumed that the reason for this observation may reside in the benzobarrelene system, *i.e.*, in both the presence of the extra C=C bond and in the diminished strain of the [2.2.2] with respect to the [2.2.1] system that cause a higher propensity to form an acetylenic intermediate, which eventually leads to polymers or undesired products. Differently, the cyclotrimerization in the [2.2.1] system proceeds *via* consecutive couplings between the functionalized C-atoms as the acetylene intermediate does not form because of its excessive strain.

The structure analyses of the trimers **5** and **6** was performed by ^{1}H- and ^{13}C-NMR spectroscopy. Because the '*syn*'- and '*anti*'-isomers present different symmetry and

[1]) The descriptors '*syn*'/'*anti*' refer to the relative position of the etheno bridges.

Scheme 2

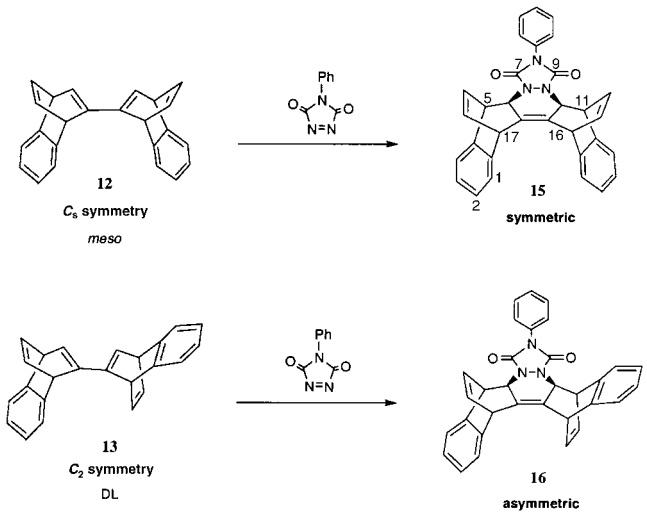


rigid structures, the NMR spectra were quite indicative, and the assignment was straightforward.

At variance, the determination of the structures of dimers **12** and **13** by spectroscopic methods was not as simple, because the C_s symmetry of the '*syn*'-dimer **12**, the C_2 symmetry of the '*anti*'-isomer **13**, and the free rotation around the central σ bond make them indistinguishable. To determine which is which, resort was made to chemical correlation in the determination of the products of a *Diels–Alder* cycloaddition. Reaction of **12** with 1-phenyl-1*H*-1,2,4-triazole-3,5-dione (PTAD) gave a symmetrical *Diels–Alder* addition product **15**, establishing the C_s symmetry of the

starting diene and as a consequence identifying the '*syn*'-structure of **12**. As for the symmetric addition product **15**, it should also be noted that between the two possible *exo*- and *endo*-isomeric cycloadducts, the *exo*-addition product is exclusively formed, as is normally observed in such 'bicyclic' systems. At variance, the other isomer, the '*anti*'-dimer **13**, gave the nonsymmetric addition product **16**, as expected. These addition reactions were followed by ^{1}H-NMR spectroscopy (*Fig.*).

Scheme 3



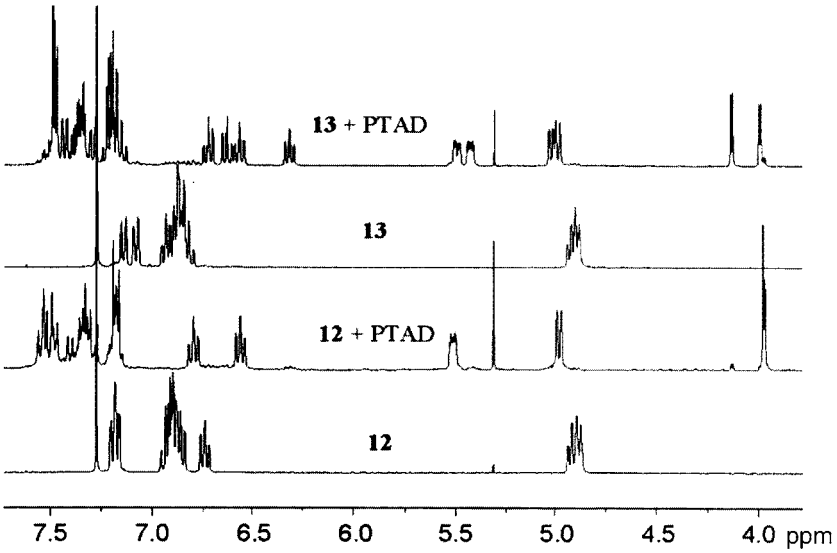


Figure. *Titration experiment of* **12** *and* **13** *with PTAD in* $CDCl_3$

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Experimental Part

General. All substances reported in this paper are in their racemic forms. All reactions were carried out under Ar and monitored by TLC and/or ^{1}H-NMR. All solvents were dried and distilled before use. Flash chromatography (FC): silica gel (60 mesh, *Merck*). TLC: *Merck* 0.2-mm silica gel *60* F_{254} anal. aluminium plates. M.p.: uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Varian-400* and *Bruker-300* spectrometers; apparent splitting is given in all cases. δ in ppm, J in Hz.

(3-Bromo-1,4-dihydro-1,4-ethenonaphthalen-2-yl)trimethylstannane (**11**). At $-78°$, 2.5M BuLi (2.5 ml, 6.3 mmol) was added dropwise to a soln. of dibromide **10** [7] (1.90 g, 6.1 mmol) in dry THF (20 ml), and the resulting mixture was stirred for 1 h. Chlorotrimethylstannane (1.25 g, 6.3 mmol) was added portionwise, and the mixture was stirred for 2 h at $-78°$ and then allowed to reach r.t. overnight. The crude was taken up with H_2O (50 ml) and extracted with Et_2O (3×40 ml), the combined Et_2O extract dried ($MgSO_4$) and evaporated, and the residue purified by FC: **11** (2.36 g, 98%). Colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.20 (*m*, 1 H); 7.12 (*m*, 1 H); 6.93 (*m*, 2 H); 6.88 (*m*, 1 H); 6.81 (*dt*, $J = 5.6$, 1.5, 1 H); 4.99 (*dd*, $J = 5.6$, 1.5, 1 H); 4.93 (*dd*, $J = 5.6$, 1.0, 1 H); 0.28 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.8; 145.7; 145.4; 143.9; 138.8; 138.0; 124.1; 123.6; 122.3; 121.9; 60.2; 56.1; −8.8.

Reaction of **11** *with CuTC*. To a well-stirred dispersion of copper(I) thiophene-2-carboxylate (CuTC; 1.43 g, 7.50 mmol) in dry 1-methylpyrrolidin-2-one (25 ml) at $-20°$ was added rapidly **11** (1.98 g, 5.0 mmol) *via* syringe, and the slurry was maintained at $-20°$ for 1 h. A 10% aq. NH_3 soln. (20 ml) was added, and the mixture was stirred until the brown solid had disappeared. The resulting mixture was extracted with Et_2O (3×30 ml), the combined Et_2O extract dried ($MgSO_4$) and evaporated, and the crude purified by FC (hexane/Et_2O 99:1): *2-bromo-1,4-dihydro-1,4-ehtenonaphthalone* (**14**) [8] (10 mg, 1 ≥ %), followed by '*anti*'-dimer **13** (38 mg, 5%), '*syn*'-dimer **12** (16 mg, 2%), '*anti*'-trimer **6** (175 mg, 23%), and '*syn*'-trimer **5** (85 mg, 11%). *(1*RS*,1′*RS*,4*SR*,4′*SR*)-1,1′,4,4′-Tetrahydro-2,2′-bi-1,4-ethenonaphthalene* (**13**): Colorless crystals from CH_2Cl_2/hexane 1:4. M.p. 170°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.11 (*dd*, $J = 6.7$, 1.6, 2 arom. H); 7.09 (*dd*, $J = 6.7$, 1.6, 2 arom. H); 6.96–6.80 (*m*, 10 H, arom. H, olef. H); 4.93 (*td*, $J = 6.0$, 1.5, 2 aliph. H); 4.90 (*dt*, $J = 6.0$, 1.5, 2 aliph. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.2; 147.2; 146.3; 140.2; 139.2; 130.5; 123.6; 123.4; 122.4; 121.7; 50.0; 48.6. EI-MS (70 eV): 306 (48, M^+), 291 (30), 276 (11), 178 (100), 152 (67), 128 (56).

*(1*RS*,1′*SR*,4*SR*,4′*RS*)-1,1′,4,4′-Tetrahydro-2,2′-bi-1,4-ethenonaphthalene* (**12**): Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. 225°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.19 (*m*, 4 arom. H); 6.96–6.84 (*m*, 8 H, arom. H, olef. H); 6.74 (*ddd*, $J = 7.5$, 6.0, 1.5, 2 olef. H); 4.91 (*td*, $J = 6.0$, 1.5, 2 aliph. H); 4.89 (*dt*, $J = 5.7$, 1.6, 2 aliph. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.1; 147.4; 146.7; 139.8; 138.9; 130.6; 123.7; 123.5; 122.3; 121.7; 50.0; 48.5. EI-MS (70 eV): 306 (52, M^+), 291 (30), 276 (11), 178 (100), 152 (63), 128 (51).

*(5*RS*,6*RS*,11*SR*,12*SR*,17*RS*,18*SR*)-5,6,11,12,17,18-Hexahydro-5,18:6,11:12,17-triethenotrinaphthalene* (**6**): Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. >310°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 (*AA′* of *AA′XX′*, 2 arom. H); 7.25 (*m*, 4 arom. H); 6.97 (*XX′* of *AA′XX′*, 2 arom. H); 6.93 (*m*, 8 arom. H, olef. H); 6.83 (*AA′* of *AA′XX′*, 2 olef. H); 5.50 (*m*, 6 aliph. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.2; 146.1; 146.1; 139.4; 139.2; 139.2; 134.7; 134.6; 134.5; 124.5; 124.4; 124.4; 123.1; 123.0; 122.9; 46.8; 46.7; 46.7.

*(5*RS*,6*SR*,11*RS*,12*SR*,17*RS*,18*SR*)-5,6,11,12,17,18-Hexahydro-5,18:6,11:12,17-triethenotrinaphthalene* (**5**): Colorless crystals from CH_2Cl_2/hexane 1:2. M.p. >310°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.21 (*AA′* of *AA′XX′*, 6 arom. H, 7.01 (*AA′* of *AA′XX′*, 6 olef. H); 6.87 (*XX′* of *AA′XX′*, 6 arom. H); 5.50 (*XX′* of *AA′XX′*, 6 aliph. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.3; 139.9; 135.0; 124.9; 123.3; 47.2.

*(5*RS*,5a*RS*,10a*SR*,11*SR*,16*RS*,17*SR*)-5,5a,10a,11,16,17-Hexahydro-8-phenyl-5,17:11,16-dietheno-7*H*-benzo[*g*]naphtho[2,3-*c*][1,2,4,]triazolo[1,2-*a*]cinnoline-7,9(8*H*)-dione* (**15**). To a stirred soln. of **12** (50 mg, 0.16 mmol) in CH_2Cl_2 (1 ml) at 0°, a soln. of PTAD (30 mg, 0.17 mmol) in CH_2Cl_2 (0.5 ml) was added. The red color of PTAD disappeared immediately. The solvent was evaporated, and the crude was recrystallized from CH_2Cl_2/hexane 1:1: **15** (75 mg, 96%). Colorless crystals. M.p. 208–210° (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54–7.17 (*m*, 13 arom. H); 6.80 (*ddd*, $J = 7.7$, 6.3, 1.6, 2 olef. H); 6.57 (br. *dd*, $J = 7.5$, 6.3, 2 olef. H); 5.51 (*ddd*, $J = 6.3$, 3.2, 1.6, 2 aliph. H); 4.99 (br. *d*, $J = 6.3$, 2 aliph. H); 3.98 (br. *d*, $J = 3.2$, 2 aliph. H). ^{13}C-NMR

(75 MHz, $CDCl_3$): 150.0; 140.4; 140.2; 135.4; 132.5; 131.4; 129.0; 128.8; 128.1; 126.7; 126.5; 125.9; 124.8; 123.6; 57.6; 43.6; 43.5.

*(5*RS*,5a*RS*,10a*SR*,11*RS*,16*SR*,17*SR*)-5,5a,10a,11,16,17-Hexahydro-8-phenyl-5,17:11,16-dietheno-7*H*-benzo[g]naphtho[2,3-*c*][1,2,4]triazolo[1,2-*c*]cinnoline-7,9(8*H*)-dione* (**16**). As described for **15**, with **13** (50 mg, 0.16 mmol) and PTAD (30 mg, 0.17 mmol): **16** (75 mg, 96%). Colorless crystals. M.p. 175–177° (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50–7.13 (*m*, 13 arom. H); 6.73 (*ddd*, *J* = 7.4, 6.0, 1.3, 1 olef. H); 6.64 (*ddd*, *J* = 7.4, 6.5, 1.4, 1 olef. H); 6.58 (*ddd*, *J* = 7.4, 6.4, 1.5, 1 olef. H); 6.33 (br. *dd*, *J* = 7.4, 6.3, 1 olef. H); 5.50 (*ddd*, *J* = 6.5, 2.7, 1.4, 1 aliph. H); 5.43 (*ddd*, *J* = 6.5, 2.7, 1.5, 1 aliph. H); 5.03 (*dd*, *J* = 6.0, 1.3, 1 aliph. H); 4.99 (br. *d*, *J* = 6.4, 1 aliph. H); 4.14 (*d*, *J* = 2.7, 1 aliph. H); 4.00 (*d*, *J* = 2.7, 1 aliph. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.1; 150.1; 142.3; 140.3; 140.3; 138.3; 134.8 (2C); 134.2; 132.3; 131.4; 129.2; 129.0; 128.0; 127.9; 126.63; 126.59; 126.5; 126.3; 126.1; 125.8; 124.8; 123.6; 121.5; 57.5; 56.9; 43.4; 43.4 (2 C); 42.9.

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