DOI: 10.1002/ejoc.200900138

Transferring Sondheimer's Annulene Chemistry into Three-Dimensional Space[‡]

Christian Werner,[a] Henning Hopf,*[a] Jörg Grunenberg,[a] Ludger Ernst,[b] Peter G. Jones,[c] Felix Köhler,[d] and Rainer Herges[d]

Dedicated to Prof. Dr. Armin de Meijere on the occasion of his 70th birthday

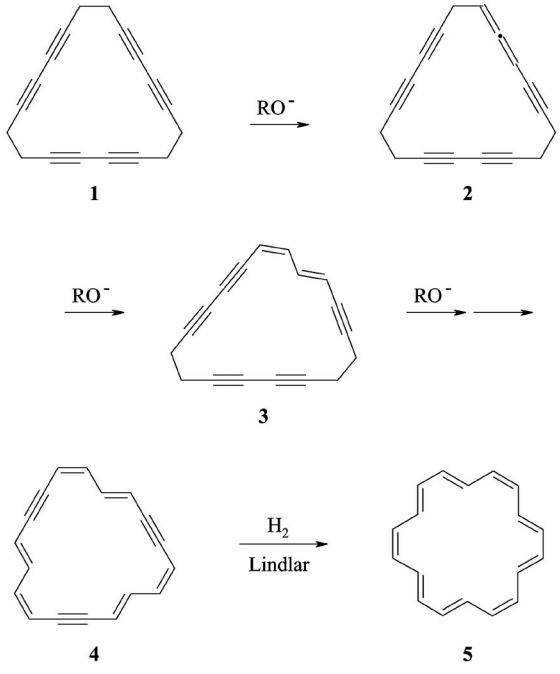
Keywords: Annulene chemistry / Isomerization / Cyclophanes / Nonplanar aromatics / Möbius systems

On treatment with potassium *tert*-butoxide in *tert*-butyl alcohol the two hydrocarbons **10** and **11** isomerize to the [6.6]paracyclophanes **12** and **13**, respectively, with fully conjugated bridges, thus transferring the Sondheimer annulene chemistry to three-dimensional space. The structures of the new hydrocarbons were established by spectroscopic data (**12**, **13**) and X-ray structural analysis (**13**) as well as by computational methods. According to ACID calculations these three-dimensional aromatics are not Möbius systems.

Introduction

In 1959 Sondheimer and Wolovsky published a paper that changed aromatic chemistry forever: on treating cyclooctadeca-1,3,7,9,13,15-hexayne (**1**) with potassium *tert*-butoxide in *tert*-butyl alcohol (90 °C, 25 min) the eighteen-membered hydrocarbon isomerized into the fully conjugated isomer **4** (cyclooctadeca-1,3,7,9,13,15-hexaene-5,11,17-triyne, Scheme 1), which was formed as the main product in 50% yield (see below).[2]

When, as shown in a later publication,[3] the triple bonds of **4** were partially hydrogenated over palladium on charcoal, [18]annulene (**5**) resulted, the ^{1}H NMR spectrum of which displayed the expected shift of its external hydrogen atoms to lower field (δ = 9.28 ppm at –60 °C) and of its internal protons to higher field (δ = –2.99 ppm), stunningly proving the predictions based on Hückel's [4*n* + 2] rule and magnetic anisotropy of **5**.[4] After this feat, which had a strong impact on our thinking about the aromaticity concept, nonbenzenoid aromatic chemistry became one of the most actively studied areas of organic chemistry for several



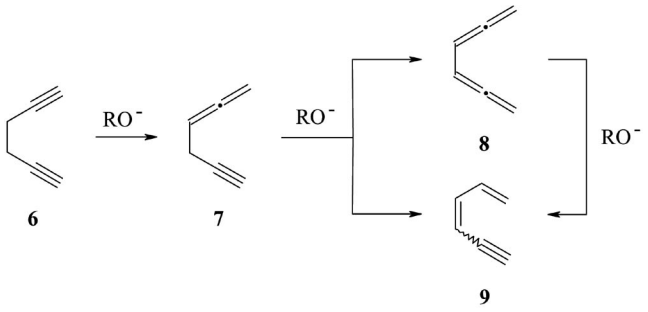
Scheme 1. The Sondheimer synthesis of [18]annulene (**5**).

[‡] Cyclophanes, LXIIII. Part LXIII: Ref.[1]

[a] Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-(0)531-391-5388
E-mail: H.Hopf@tu-bs.de
[b] NMR-Laboratorium der Chemischen Institute der Technischen Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-(0)531-391 8192
E-mail: L.Ernst@tu-bs.de
[c] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany
Fax: +49-(0)531-391 5387
E-mail: P.Jones@tu-bs.de
[d] Otto-Diels-Institut für Organische Chemie, Universität Kiel,
Otto-Hahn-Platz 4, 24118 Kiel

decades. Later, the reactivity of **5** was studied[5] and the hydrocarbon was shown to be almost planar by X-ray structural analysis.[6]

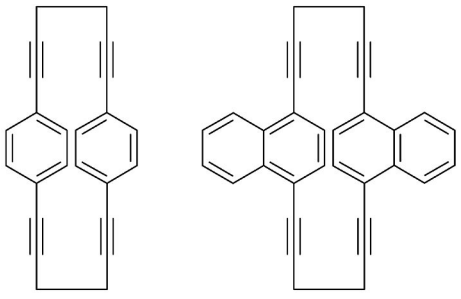
The mechanism of the **1**→**4** isomerization was never investigated in detail, but Sondheimer had previously shown that the "building-block" of **1**, 1,5-hexadiyne (**6**), isomerized to 1,3-hexadien-5-yne (**9**) on base treatment.[7] Still later, we demonstrated[8] that **6** under the influence of different bases (inter alia, potassium *tert*-butoxide or sodium ethoxide) isomerizes initially to 1,2-hexadien-5-yne (**7**) which can either undergo a second propargyl rearrangement to 1,2,4,5-hexatetraene (**8**) or to **9** (Scheme 2).[9]



Scheme 2. Base-catalyzed isomerization of 1,5-hexadiyne (**6**) to 1,3-hexadien-5-yne (**9**).

It is hence likely that the rearrangement of **1** begins with its isomerization to **2** followed by rearrangement to **3**, in which one of the 1,5-hexadiyne moieties has been converted into a conjugated subsystem. Twofold repetition of this sequence ultimately furnishes **4**. As mentioned above, **4**, with its three *E*- and its three *Z*-configured double bonds, is the major isomer of the cyclooctadeca-hexaene-triynes produced.[10] Since at the time of Sondheimer's experiments high performance chromatography techniques were not available, it might be worthwhile to repeat the original studies.

In our studies concerning "extended" or "stretched" 1,*j*-eliminations we recently reported the preparation of several cyclophane systems containing 1,5-hexadiyne units as molecular bridges, among them the hydrocarbons **10** and **11** (Scheme 3).[11]

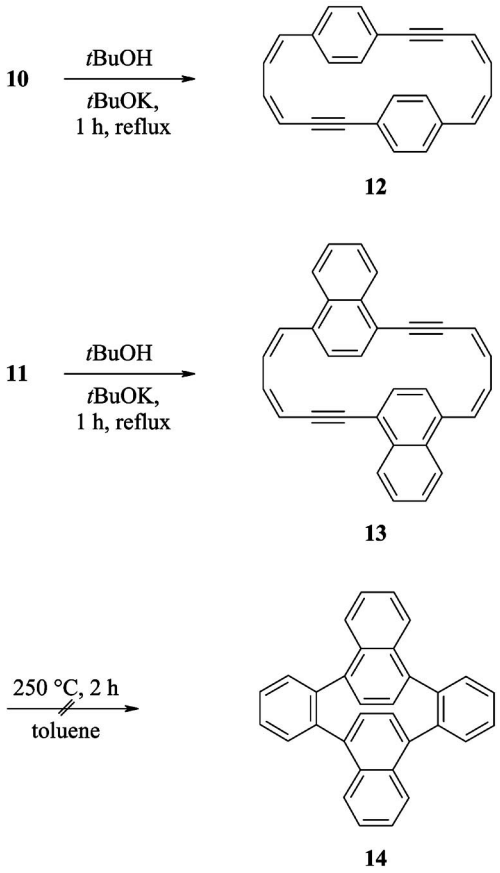


Scheme 3. Two 1,5-hexadiyne-bridged paracyclophanes: **10** and **11**.

Since **10** and **11** are layered hydrocarbons the question arose whether their base-catalyzed isomerization could yield three-dimensional analogs of Sondheimer's planar dehydroannulenes.

Results and Discussion

Heating a solution of **10** in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide under reflux for 1 h results in the quantitative formation (96%) of a new, now yellow, hydrocarbon to which we assign structure **12** (Scheme 4).



Scheme 4. Base-catalyzed isomerization of the [6.6]cyclophanes **10** and **11**.

Hydrocarbon **12** is a surprisingly stable compound: its solutions in dichloromethane or acetonitrile can be exposed to sunlight for several weeks without any change, and the crystalline material is not oxidized when exposed to air for extended periods of time.

The ^{1}H and ^{13}C NMR spectra of **12** were fully assigned by the use of 2D chemical shift correlation techniques. The ^{1}H NMR spectrum contains six and the ^{13}C NMR spectrum ten different chemical shifts, i.e. there is effective twofold molecular symmetry. The *p*-phenylene rings display a common AA′XX′-type proton spectrum. This may cause the impression that the phenylene rings are rotating rapidly about their C1–C4 axes at room temperature, which would be somewhat surprising in view of the steric congestion that is suggested by Dreiding molecular models. As theoretical

calculation show, however, the effectively symmetrical environment of the phenylene rings is caused by rapid conformational rearrangement of the [6.6]bridges (see below). According to the H,H coupling constants of the olefinic hydrogen atoms (12.1 and 12.9 Hz) the double bonds all possess *cis* configuration. Both carbon nuclei of the C≡C triple bonds are deshielded (δ = 102.8 and 91.5 ppm) by ca. 5 ppm relative to the open-chain reference compound **15** for which $\delta_{C\equiv C}$ = 97.2 and 86.7 ppm[12] (**15**: *cis*,*cis*-Ph–C≡C–CH=CH–CH=CH–Ph).

Such deshielding of *sp*-hybridized carbon is usually caused by C≡C–C angle strain as has been demonstrated convincingly by a series of cycloalkynes with decreasing ring size.[13,14] Hence it seems likely that strain also is the cause of the deshielding of the acetylenic carbon nuclei in **12** and **13**.

The mass and the electronic spectra, given in the experimental section, support this structural assignment. Unfortunately we were unable to grow crystals of **12** suitable for an X-ray structural analysis. We therefore resorted to theoretical calculations in order to elucidate the possible three-dimensional structure of the [6.6]paracyclophane. Our simulation was based on a the following strategy: first, we performed a conformational analysis of **12** based on the empirical OPLS-AA force field,[15] followed by a more rigorous calculation of the electronic structure using modern density functional theory. In the case of cyclophanes, as pointed out by Grimme[16] it is important to assure a reliable description of all noncovalent contacts in view of possible π–π interactions. We therefore used the M05–2X hybrid meta functional[17] in combination with a 6-311+G(d,p) basis set for our electronic structure calculations. Two possible low energy all-cis conformers could be identified (see Figure 1): the global minimum is chiral (C_2 symmetry) while the second minimum shows a center of inversion (C_i symmetry). In order to determine possible pathways of the racemization and the interconversion of the two minima, we – in a second step – carried out several MD simulations, each 100 ns long, at 400 K using again the OPLS-AA force field. Analyzing the trajectories the following mechanism could be concluded: The racemization of **12** occurs in a two step manner. Starting from the chiral C_2 symmetric global minimum, the second (C_i symmetric) minimum is reached by a shearing movement of one 1,3-hexadien-5-yne bridge. The transition of the C_i symmetric conformer to the second enantiomer of the global minimum **12**, then occurs via an "inversion" of the second 1,3-hexadien-5-yne moiety.

In the last part of our simulation strategy, the force field minima and the relevant snapshots from our MD trajectories were used as starting points for the downhill search and transition state optimizations at the DFT level, respectively. We thereby were able to estimate the barrier of racemization based on electronic structure calculations. Our calculated gas phase barrier of only 7.42 kcal/mol at the M05-2X/6-311+G(d,p) level of theory points to a rapid racemization at room temperature in the solvent phase as well. We assume the same mechanism and a similar barrier of racemization for the hydrocarbon **13**.

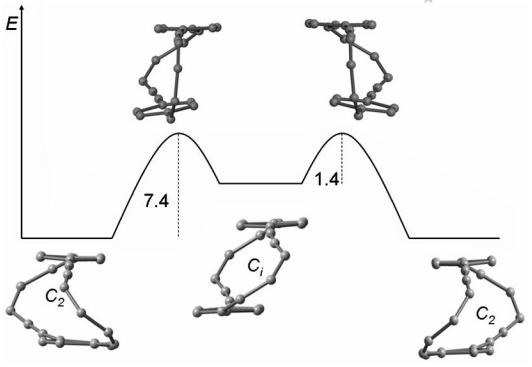


Figure 1. M05-2X-optimized stationary points on the energy surface of **12** using a 6-311+G(d,p) basis set. The racemization of the C_2 symmetric conformer occurs via a two step mechanism inverting each 1,3-hexadien-5-yne bridge one by one and running through the C_i symmetric minimum. The energy barriers are given in kcal mol^{-1}.

More detailed structural information could be obtained for **13**, the benzolog of **12** (Scheme 4), formed in 98% yield as an orange-yellow compound, when **11** was treated under the same conditions as above. At room temperature the ^{1}H and ^{13}C NMR spectra of **13** show no reduction of the number of resonances due to symmetry. For example, one observes 29 ^{13}C signals for the molecule's 32 carbon atoms, so there are three accidental chemical shift degeneracies, see the Exp. Section. Hence in solution the molecule exists in a conformation of C_1 symmetry. Heavy overlap of the aromatic proton resonances unfortunately precluded spectral assignments in much detail. The other analytical data of **13** are also given in the experimental section.

Recrystallization from dichloromethane/cyclohexane yielded orange needles of the naphthalenophane and allowed to establish its structure by X-ray diffraction.

The molecule of compound **13**, which displays no imposed symmetry, is shown in Figure 2 (a), with selected bond lengths and angles in Table 1 (see Exp. Section). Bond lengths may be regarded as normal. Strain in the molecule is indicated by the systematic distortion of bond angles in the regions C1 to C6 and C17 to C22, whereby the angles at *sp* carbon are narrowed by 4–8° and those at sp^2 carbon widened by 8–13° from ideal values. The torsion angles about the double bonds do not differ greatly from zero, whereas significant torsion is observed about the formally single bonds C4–C5 and C20–C21 (torsion angles –34.3 and –30.6°, respectively). Some further distortion involves the naphthalene ring substituents, whereby the atoms C6, C17 and C1 lie 0.15, 0.20 and 0.23 Å out of the plane of their respective rings. The naphthalene ring systems are planar (r.m.s. deviation 0.033 Å for the ring system C7–C16 and 0.025 Å for C23–C32) with an interplanar angle of 7.8°.

The packing (Figure 2, b) involves hexagonally packed layers of molecules parallel to the **bc** plane. There are no especially short intermolecular contacts, but two types of weak interaction are observed: (i) π-stacking of the rings C(7–11,16) and C(23–27,32) via **b** translation (interplanar

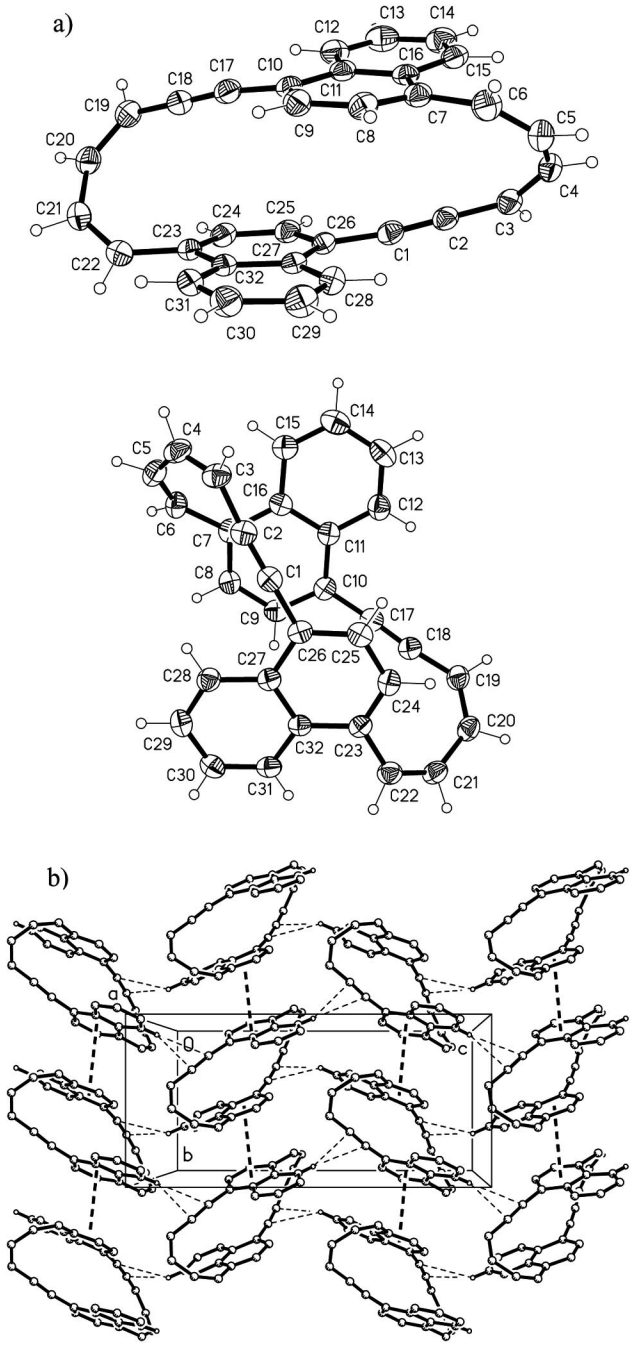


Figure 2. a) Two ellipsoid representations (50% level) of compound **13** in the crystal. b) Packing diagram of compound **13** viewed perpendicular to the *bc* plane in the region $x \approx 1/4$; interactions C–H···(C≡C) are indicated by thin dashed lines and π-stacking by thick dashed lines. Hydrogen atoms not involved in weak interactions are omitted.

angle 6°, centroid-to-centroid distance 3.72 Å, perpendicular distance ca. 3.5 Å, offset ca. 1.3 Å) and (ii) C–H···(C≡C) contacts from H14 to C17≡C18 (normalised H···midpoint 2.70 Å, angle 136°) and from H31 to C1≡C2 (normalised H···midpoint 2.73 Å, angle 145°), both via the glide planes.

Table 1. Selected bond lengths [Å] and angles [°] for compound **13**.

C(1)–C(2)	1.201(3)	C(22)–C(23)	1.465(3)
C(1)–C(26)	1.431(3)	C(2)–C(1)–C(26)	173.8(2)
C(2)–C(3)	1.414(3)	C(1)–C(2)–C(3)	175.5(2)
C(3)–C(4)	1.341(3)	C(4)–C(3)–C(2)	127.7(2)
C(4)–C(5)	1.449(3)	C(3)–C(4)–C(5)	130.4(2)
C(5)–C(6)	1.338(3)	C(6)–C(5)–C(4)	132.5(2)
C(6)–C(7)	1.472(3)	C(5)–C(6)–C(7)	133.0(2)
C(10)–C(17)	1.434(3)	C(18)–C(17)–C(10)	171.9(2)
C(17)–C(18)	1.206(3)	C(17)–C(18)–C(19)	174.8(2)
C(18)–C(19)	1.416(3)	C(20)–C(19)–C(18)	129.3(2)
C(19)–C(20)	1.341(3)	C(19)–C(20)–C(21)	133.1(2)
C(20)–C(21)	1.457(3)	C(22)–C(21)–C(20)	132.7(2)
C(21)–C(22)	1.339(3)	C(21)–C(22)–C(23)	130.1(2)

Just like **12**, hydrocarbon **13** is air-stable and can be kept in solution for many weeks. Since its bridges are made of 1,3-hexadien-5-yne units and the latter are known to cyclize to benzene on heating[18,19] we pyrolyzed **13** in toluene solution at 250 °C (2 h, sealed heavy-walled ampoule). However, besides insoluble brown-black material, we could not isolate any characterizable compound(s). Certainly, the intended product, the doubly benzo-bridged naphthalenophane **14** (Scheme 4), was not generated under these conditions in detectable amounts.

Whenever working with formally fully conjugated systems such as **12** and **13** the question arises whether the respective compounds could possess Möbius topology.[20] Both **12** and **13** are doubly twisted annulenes. As in most large ring annulenes and particularly in extended porphyrins[21] the twist is mainly projected into writhe[22] or in other words: the molecule adopts a figure-eight shape to reduce strain. Thus, the double twist notwithstanding, the largest deviation of the 20-electron π system from planarity (defined by the dihedral angle C3–C4–C5–C6) is only 39.6°. Hydrocarbons **12** and **13** belong to the group of belt-shape conjugated compounds. In contrast to "normal" aromatic compounds the p-orbitals are not orthogonal with respect to the ring plane but perpendicular to the surface of a deformed cylinder (except for the second set of p orbitals at the sp-hybridized carbons). The inner phases of the p orbit-

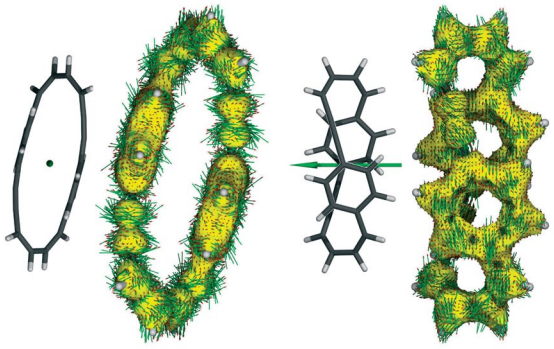


Figure 3. ACID plot (yellow surface, isosurface value: 0.05) of **12** based on the M05-2X/6-311+G(d,p) optimized structure. The induced current is plotted onto the isosurface (small green arrows with red arrow head). The direction of the magnetic field is indicated by the large green arrow in the structure plot.

als point towards the axis of the cylinder. With 20 p-electrons in the conjugated periphery and a double twist in its π system one would expect antiaromatic behaviour. However, the molecule escapes antiaromatic destabilization by localization of the double bonds. The ACID analysis[23] (anisotropy of the induced current density, Figure 3) confirms this view. There is no contiguous isosurface of delocalized electrons (at an isosurface value of 0.05) and only local ring currents are induced (no ring current within the 20-electron periphery). Another way of escaping antiaromaticity in **12** and **13** would be reducing the double twist to a single twist and thus adopting Möbius topology, which would lead to an aromatic system. However, the two benzene rings (in **12** or naphthalene rings in **13**) would then have to be twisted orthogonal to each other, which is unfavourable for steric reasons.

Experimental Section

1. General Remarks: DSC: Commercial DC plates, type Polygram Sil G/UV$_{254}$, were purchased from Macherey–Nagel & Co. (Düren, Germany). Column chromatography: Merck kieselgel 60 (70–230 mesh) (Darmstadt). Melting points: Büchi 530 melting point apparatus, uncorrected values. NMR: Bruker AM-400. ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz). Internal references: tetramethylsilane (δ_H = 0.00 ppm), $CDCl_3$ (δ_C = 77.05 ppm). IR: Nicolet 320 FT-IR; KBr pellets. UV/Vis: Beckman UV 5230 and HP 8452 A Diode Array. EI-MS: Finnigan MAT 8430 (70 eV). The two cyclophanetetraynes **10** and **11** were prepared according to the procedure given in ref.[9]

2. Base-Catalyzed Isomerization of [6.6]Paracyclophane-1,5,13,17-tetrayne (10): To a solution of **10** (25.0 mg, 0.082 mmol) in *tert*-butyl alcohol (50 mL) was added potassium *tert*-butoxide (1 g, 8.9 mmol). The mixture was heated to reflux for 1 h, cooled to room temp., and hydrolyzed with saturated aqueous sodium hydrogen carbonate solution (100 mL). After thorough extraction with dichloromethane, the organic fractions were combined, the dried (sodium sulfate) solution filtered through a pad of silica gel, and the solvent removed by rotary evaporation. The remaining yellow solid was purified by column chromatography (silica gel, cyclohexane/dichloromethane, 9:1, v/v); yield 24.0 mg (96%) of **[6.6]paracyclophane-1,3,11,13-tetraene-5,15-diyne** (**12**), m.p. 130 °C (tiny yellow needles, methanol/dichloromethane). ^{1}H NMR: δ = 5.73 (d, J = 12.1 Hz, 2 H, 4-, 16-H), 5.99 (dd, J = 12.9, 6.3 Hz, 2 H, 2-, 14-H), 6.37 (dd, J = 12.1, 6.3 Hz, 2 H, 3-, 15-H), 6.57 (d, J = 12.9 Hz, 2 H, 1-, 13-H), 6.85, 7.16 (AA′XX′, N = 8.2 Hz, 4 H each, 8-, 12-, 20-, 24-H and 9-, 11-, 21-, 23-H, respectively) ppm. ^{13}C NMR: δ = 91.5 (C$_q$, C-5,-17), 102.8 (C$_q$, C-6,-18), 110.0 (CH, C-4,-16), 121.6 (C$_q$, C-7,-19), 125.0 (CH, C-2,-14), 128.7 (CH, C-9,-11,-21, -23), 130.8 (CH, C-8,-12,-20,-24), 132.4 (CH, C-1,-13), 135.7 (CH, C-3,-15), 137.6 (C$_q$, C-10,-22) ppm. IR (KBr): $\tilde{\nu}$ = 3002 (m), 2950 (w), 2189 (w), 1500 (m), 840 (s), 736 (s), 683 (s). UV (acetonitrile): λ_{max} (lg ε) = 196 (4.68), 240 (4.33), 290 (4.63), 348 nm (3.95). MS (EI, 70 eV): m/z (%) = 304 (100) [M$^+$], 288 (21), 276 (28), 150 (18). HRMS: $C_{24}H_{16}$: calcd. 304.1252, found 304.125 ± 3 ppm.

3. Base-Catalyzed Isomerization of [6.6](1,4)Naphthalenophane-1,5,17,21-tetrayne (11): As described above for **10**, 48.0 mg (0.119 mmol) of **11** was isomerized to give 47.0 mg (98%) of **[6.6](1,4)naphthalenophane-1,3,11,13-tetraene-5,15-diyne** (**13**), m.p. 197 °C (yellow needles, methanol/dichloromethane). ^{1}H NMR: δ = 5.76 (d, J = 12.1 Hz, 1 H), 5.85 (d, J = 12.5 Hz, 1 H, 4-, 20-H), 6.15 (d, J = 7.5 Hz, 1 H), 6.23–6.43 (m, 4 H), 6.84 (ddd, J = 8.4, 6.6, 1.1 Hz, 1 H), 6.93 (d, J = 8.3 Hz, 1 H), 7.04 (d, J = 7.5 Hz, 1 H), 7.09 (d, J = 12.8 Hz, 1 H), 7.14–7.19 (m, 3 H), 7.40 (d, J = 7.4 Hz, 1 H), 7.47–7.51 (m, 2 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.91–7.95 (m, 2 H) ppm. – ^{13}C NMR: δ = 93.8, 94.8 (C$_q$, C-5,-21), 99.3, 101.3 (C$_q$, C-6,-22), 110.1, 110.4 (CH, C-4,-20), 119.8, 120.0 (C$_q$, C-7,-23), 123.6, 125.5, 125.6 (2 C), 125.8, 125.9, 126.0 (2 C), 126.3 (2 C), 126.7, 126.8, 129.1, 129.7, 130.0, 130.37 (CH, C-1,-2,-9,-10, -11,-12,-15,-16,-17,-18,-25,-26,-27,-28,-31,-32), 134.1, 134.7 (CH, C-3,-19), 130.43, 130.6, 131.6, 132.5, 134.9, 135.5 (C$_q$, C-8,-13,-14, -24,-29, 30) ppm. IR (KBr): $\tilde{\nu}$ = 3059 (vw), 3011 (w), 2952 (vw), 2183 (w), 2177 (w), 1508 (w), 1152 (w), 846 (s), 770 cm^{-1} (vs). UV (acetonitrile): λ_{max} (lg ε) = 196 (4.78), 238 (4.67), 316 (4.45), 392 nm (3.92). MS (EI, 70 eV): m/z (%) = 404 (100) [M$^+$], 387 (26), 200 (30). $C_{32}H_{20}$ (404.51): calcd. C 95.02, H 4.98; found C 95.20, H 4.69.

4. X-ray Structure Determination of Compound 13: Crystal data: $C_{32}H_{20}$, M = 404.48; monoclinic, $P2/c$, a = 16.934(3), b = 7.652(2), c = 16.220(3) Å, β = 92.74(2)°, U = 2099.2 Å^3, Z = 4, T = –130 °C, D_x = 1.280 g cm^{-3}, μ = 0.07 mm^{-1}, F(000) = 848. Data collection: A yellow tablet 0.75 × 0.45 × 0.2 mm was mounted in inert oil and transferred to the cold gas stream of a Stoe STADI-4 diffractometer. Data were recorded to 2θ 50° using Mo-K_α radiation (λ = 0.71073 Å). Of 6087 intensities, 3690 were unique (R_{int} = 0.069). Structure refinement: The structure was refined anisotropically against F^2 using the program SHELXL-97.[24] Hydrogen atoms were included using a riding model. The final $wR2$ for 289 parameters and all reflections was 0.116, with $R1$ = 0.048 for the reflections with $I > 2\sigma(I)$; S = 1.04, max. $\Delta\rho$ 0.15 e Å^{-3}.

CCDC-708481 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] H. Hopf, Z. Pechlivanidis, J. Grunenberg, L. Ernst, *Eur. J. Org. Chem.* **2009**, 238–252. For the most recent comprehensive review on cylophanes see: R. Gleiter, H. Hopf (Eds.), *Modern Cyclophane Chemistry*, Wiley-VCH, Weinheim, **2004**; H. Hopf, *Tetrahedron* **2008**, *64*, 11504–11516.

[2] F. Sondheimer, R. Wolovsky, *J. Am. Chem. Soc.* **1959**, *81*, 1771–1771; full paper: F. Sondheimer, R. Wolovsky, *J. Am. Chem. Soc.* **1962**, *84*, 260–269.

[3] F. Sondheimer, R. Wolovsky, Y. Amiel, *J. Am. Chem. Soc.* **1962**, *84*, 274–284.

[4] Y. Gaoni, A. Melera, F. Sondheimer, R. Wolovsky, *Proc. Chem. Soc. London* **1964**, *84*, 397–398.

[5] Summary: F. Sondheimer, *Acc. Chem. Res.* **1972**, *5*, 81–91; for a recent review on annulene chemistry see: E. L. Spitler, C. A. Johnson II, M. M. Haley, *Chem. Rev.* **2006**, *106*, 5344–5386.

[6] X-ray structural analysis of **5**: S. Gorter, E. Rutten-Keulemans, M. Krever, C. Romers, D. W. J. Cruickshank, *Acta Crystallogr., Sect. B: Struct. Science* **1995**, *51*, 1036–1045; F. L. Hirshfeld, D. Rabinovich, *Acta Crystallogr.* **1965**, *19*, 235–241; J. Bregman, F. L. Hirshfeld, D. Rabinovich, G. M. J. Schmidt, *Acta Crystallogr.* **1965**, *19*, 227–234.

[7] F. Sondheimer, D. A. Ben-Efraim, Y. Gaoni, *J. Am. Chem. Soc.* **1961**, *83*, 1682–1685.

[8] H. Hopf, *Chem. Ber.* **1971**, *104*, 3087–3095.

[9] H. Hopf, *Tetrahedron Lett.* **1970**, *11*, 1107–1109.

[10] By separation of the isomerization mixture obtained from **1** on a $AgNO_3$-impregnated alumina column Wolovsky also obtained an isomer of **4** as well as a tetradehydro[18]annulene: R. Wolovsky, *J. Am. Chem. Soc.* **1965**, *87*, 3638–3644.

[11] C. Werner, I. Dix, H. Hopf, P. Bubenitschek, P. G. Jones, *Chem. Eur. J.* **2007**, *13*, 9462–9477.

[12] U. Nüchter, G. Zimmermann, V. Francke, H. Hopf, *Liebigs Ann./Recueil* **1997**, 1505–1515.
[13] A. Krebs, J. Wilke, *Top. Curr. Chem.* **1982**, *109*, 189–233.
[14] H. Meier, H. Petersen, H. Kolshorn, *Chem. Ber.* **1980**, *113*, 2398–2409.
[15] G. A. Kaminski, R. A. Friesner, J. Tirado-Rives, W. L. Jorgensen, *J. Phys. Chem. B* **2001**, *105*, 6474–6487.
[16] S. Grimme, *Chem. Eur. J.* **2004**, *10*, 3423–3429.
[17] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157–167.
[18] H. Hopf, H. Musso, *Angew. Chem.* **1969**, *81*, 704–704; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 680–680.
[19] Review: G. Zimmermann, *Eur. J. Org. Chem.* **2001**, 457–471.
[20] a) D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature* **2003**, *426*, 819–821; b) D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758–3772; c) H. S. Rzepa, *Chem. Rev.* **2005**, *105*, 3697–3715.
[21] R. Herges, *Chem. Rev.* **2006**, *106*, 4820–4842.
[22] S. M. Rappaport, H. S. Rzepa, *J. Am. Chem. Soc.* **2008**, *130*, 7613–7619.
[23] a) R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214–3220; b) see ref.[20b]
[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
Received: February 11, 2009
Published Online: April 16, 2009

