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# Singly and Doubly Twisted [36]Annulenes: Synthesis and Calculations

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**Abstract:** A cyclophane with a [36]annulene periphery, including four anthrylene and two phenylene units, was synthesized in a four-step sequence using a McMurry cyclization. Upon crystallization from different solvents, four different conformations were determined by X-ray structure analysis. Two conformations exhibit a double twist (Hückel topology) and two structures include a single twist (Möbius topology). By using DFT calculations a conformation with a triple twist (Möbius) was located. However, our calculations and the NMR spectroscopy data do not provide evidence for aromaticity (for Möbius structures) or antiaromaticity (for Hückel structures).

**Keywords:** annulenes · aromaticity · density functional calculations · NMR spectroscopy · twisted conformations

## Introduction

Most of the annulenes that are experimentally known are not twisted and follow the Hückel rule. The π systems, for example, in the cyclopentadienyl anion, benzene, and the tropylium cation, are planar and lie in the ring plane. Higher annulenes, such as the [14]- and [18]annulene, are somewhat distorted because of the steric hindrance of the inner hydrogen atoms, but still exhibit distinct aromaticity.[1] Theoretical calculations predict that the stability rules for annulenes are reversed if an odd number of half twists (180° twists) are included in the ring.[2] If in a gedankenexperiment a linear conjugated π system (or a strip of paper) is twisted by $n$ half twists and both ends are joined to form a ring, the system is said to exhibit a linking number $L_k$ of $n$. At first glance, such twisted annulenes might look very strained, however, as Rzepa et al. recently stated, part of the strain induced by the twist $T_w$ is projected into writhe, $W_r$.[3] The linking number $L_k$, twist $T_w$, and writhe $W_r$ are topological invariants that are connected by the Călugăreanu[4a] theorem given in Equation (1):

$$L_k = T_w + W_r \tag{1}$$

Whereas $W_r$ is difficult to depict, $T_w$ (in its topological sense) in annulenes is defined as the sum of all dihedral angles of all bonds included in the cyclic conjugation path (including their algebraic sign). According to this definition, $T_w$ is identical to $L_k$ if all carbon atoms lie in a plane. However, even if that seems counterintuitive, $L_k$ and $T_w$ are different if the object is distorted into 3D.

Figure 1 (left) presents a double-twisted band. The dashed line in the middle of the band forms a planar circle ($L_k = T_w = 2$). Topological transformation into a three-dimensional figure-of-eight-type structure (Figure 1, right) does not change the linking number, however, converts the twist into writhe ($T_w = 0$, $W_r = 2$). In an annulene such a transformation would reduce the molecular strain without affecting the electron-counting rules (Hückel or reverse Hückel).[3a,b]

A number of double-twisted extended porphyrins and annulenes have been synthesized that exhibit a figure-of-eight shaped geometry.[5] For cyclic conjugated systems with an even linking number ($L_k = 2$), these annulenes should follow the Hückel rule. In some cases, aromaticity with $4n+2$ π electrons has indeed been stated. Recently, the groups of Latos-Grażyński and Osuka synthesized extended porphyrins with a linking number $L_k = 1$.[6] Several of these Möbius

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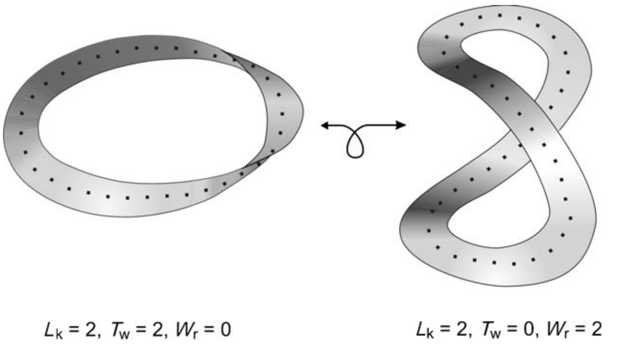


Figure 1. Both bands exhibit a linking number $L_k = 2$ and therefore are topologically homeomorphous. The twist of the object on the left ($T_w = 2$) is projected into writhe by distortion into a 3D figure-of-eight object (right, $T_w = 0$, $W_r = 2$).

porphyrins exhibit strong aromaticity with 4*n* π electrons in agreement with the theoretical predictions. The first annulene with Möbius topology ($L_k = 1$) and weak aromaticity was synthesized by our group.[7]

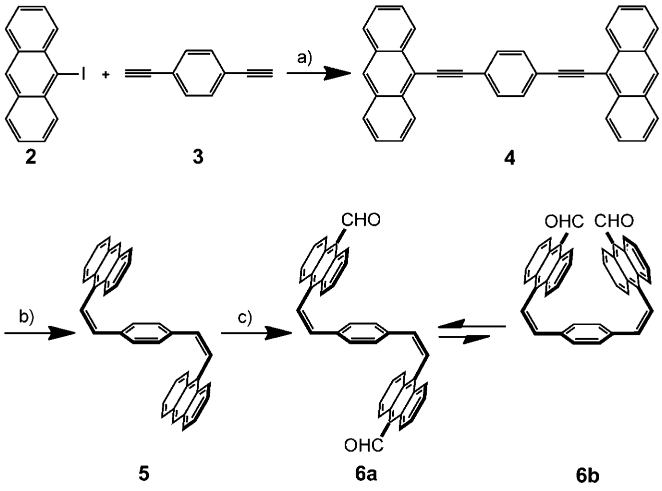
In search of a triple-twisted annulene ($L_k = 3$), we synthesized [36]annulene derivatives, including anthrylene and phenylene rings. The bulky anthracene units were introduced to force the system out of planarity and to ease the twist. Herein, we report the successful synthesis of a [36]annulene derivative **1**, which can adopt several conformations in the solid state with a single- or a double-twist, depending on the solvent used for recrystallization. An energetically low-lying triple-twisted conformation was located by DFT calculations.

## Computational Methods

All calculations were carried out by using the Gaussian 03 program.[8] Geometries were optimized at the B3LYP/6-31G* level of DFT. Recently, it became evident that this functional gives rise to large errors in the relative energy of conjugated systems.[9] We therefore also performed the calculations at the BH&HLYP/6-31G* level of DFT, which includes a larger contribution of HF exchange to attenuate this problem. $L_k$, $T_w$, and $W_r$ were recently introduced by Rzepa et al. in annulene chemistry[3] and are calculated by our program anewrithm using an implementation of the equations given by Klenin and Langowski.[10] The isomers of the [36]annulene **1** were generated by applying a Monte Carlo algorithm. After checking for redundancy, single-point calculations at the semiempirical PM3 level were performed and the 90 most stable isomers were optimized at B3LYP/6-31G* and BH&HLYP/6-31G*.

## Results and Discussion

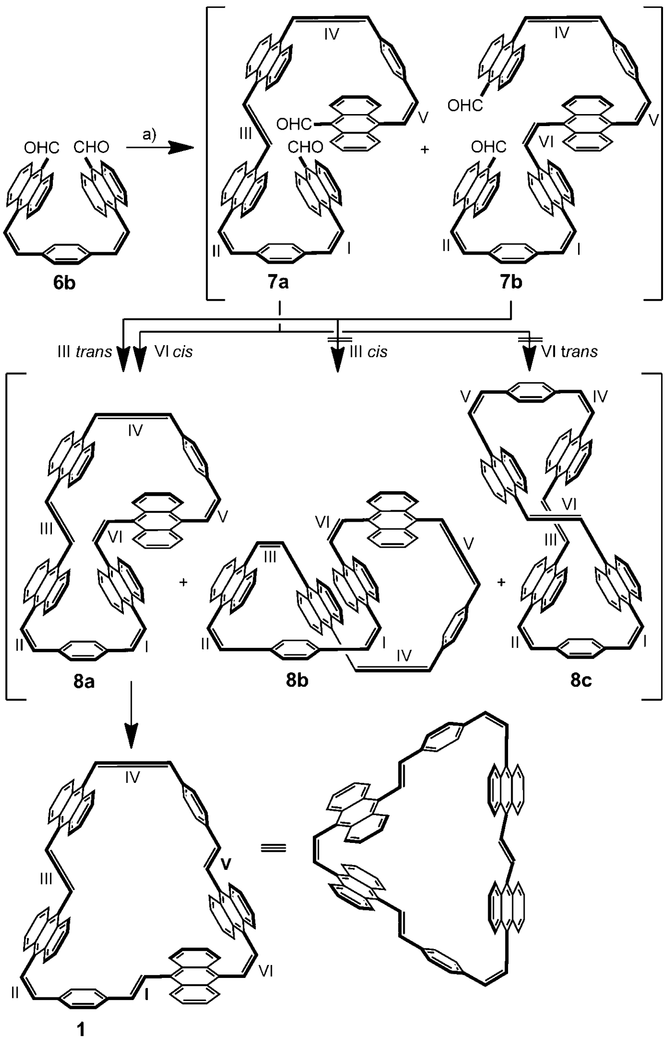
For an efficient cyclization reaction forming cyclic [*n*]-arylenepolyethylenes, a precursor with *Z,Z* configuration, such as *syn*-(*Z,Z*)-1,4-bis[(9-ethenyl-10-formyl)anthrylene]benzene (**6**), is required. Cyclization precursor **6** was prepared in a three-step synthesis (Scheme 1) starting from 9-iodoanthracene (**2**) and 1,4-diethynylbenzene (**3**).



Scheme 1. Synthesis of the dialdehyde **6**. Reagents and conditions: a) [Pd(PPh$_3$)$_2$Cl$_2$], CuI, diisopropylamine, 82 %; b) H$_2$, Pd/C ethyl acetate, 100 %; c) SnCl$_4$, Cl$_2$CHOCH$_3$, CH$_2$Cl$_2$, 64 %.

Subsequently, a Sonogashira coupling[11] was applied to produce 1,4-bis(9-ethynylanthryl)benzene (**4**), followed by a *syn*/*syn*-selective palladium-catalyzed hydrogenation[12] to obtain (*Z,Z*)-1,4-bis(9-ethenylanthryl)benzene (**5**). Finally, a formylation reaction[13] was employed to form **6** in an overall yield of 52 %. Paracyclophane **1** was synthesized by applying the McMurry coupling[7] to precursor **6** (Scheme 2).

McMurry coupling reactions usually are not *cis*/*trans* selective. Precursor **6b**, thus, could furnish **7a** (III *trans*-) and **7b** (VI *cis* coupling). The second McMurry reaction would then give rise to ring closure. Compound **7a** would form either **8a** (VI *cis*) or **8c** (VI *trans*); **7b** gives either **8a** (III *trans*) or **8b** (III *cis*) (for numbering of double bonds, see Scheme 2). To our surprise, none of the isomers **8a–c** were isolated, but instead isomer **1** with alternating *cis* and *trans* double bonds was formed. The formation of [36]annulene **1** (Figure 2) can only be explained by subsequent *cis*/*trans* isomerization of the McMurry products. To elucidate the mechanism of its formation, we performed DFT calculations at the B3LYP/6-31G* level of theory (Table 1). Compound **7a** is thermodynamically more stable than **7b** by 4.71 kcal mol$^{-1}$. Model calculations (see the Supporting Information) revealed that the ring closure of **7b** to **8b** is sterically hindered. Upon approaching both terminal aldehyde groups, compound **7a** is more likely to form a *cis*- and **7b** a *trans*-double bond, both of which then form isomer **8a**. Hence, even though **8c** is the most stable isomer, which can be formed by two subsequent McMurry reactions, it would probably not be formed for kinetic reasons. Compound **8b** is 12.23 kcal mol$^{-1}$ higher in energy as **8c**, and therefore kinetically, and thermodynamically, unfavorable; this leaves **8a** ($E_{rel} = 11.43$ kcal mol$^{-1}$) as the compound that is most likely to be formed as the primary product of the McMurry reaction. Isomerization of double bonds I and V would then lead to the final product **1**. According to our calculations,



Scheme 2. Synthesis of paracyclophane **1** and the proposed mechanism of its formation. Reagents and conditions: a) $TiCl_4$–Zn(Cu), 1,2-dimethoxyethane (DME), toluene, 14%.

Table 1. Relative energy of proposed intermediates towards **1** (see Scheme 2).

| | **7a** | **7b** | **8a** | **8b** | **8c** | **1** |
|---|---|---|---|---|---|---|
| $E_{rel}$[a] [kcal mol$^{-1}$] | 0 | 4.71 | | | | |
| $E_{rel}$[b] [kcal mol$^{-1}$] | | | 11.50 | 12.30 | 0.07 | 0 |

[a] $E_{rel}$ is the relative energy with respect to the energetically most stable structure of **7a**. [b] $E_{rel}$ is the relative energy with respect to the energetically most stable structure **1**.

compound **1** is the most stable isomer of the [36]annulene system (11.50 kcal mol$^{-1}$ more stable than **8a**).

Osuka et al.[6b–f] observed different topologies (Hückel or Möbius) in X-ray crystal structures of the same compound, depending on the solvent used for recrystallization. This is due to the different packing arrangements of solvents included in the crystal. Therefore, we recrystallized **1** (Figure 2) from different solvents (benzene, DMF, dichloromethane/ether).

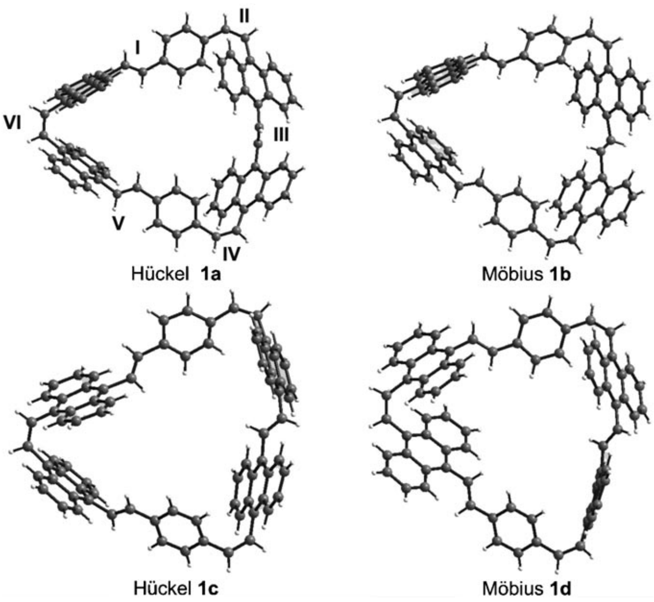


Figure 2. Crystal structures of compound **1**. Compounds **1a** and **1c** have Hückel topology, whereas compounds **1b** and **1d** have Möbius topology.

The unit cell of **1**, crystallized from benzene, includes two independent structures **1a** and **1b**. Structure **1a** has a Hückel-type conformation with a double twist ($L_k = 2$), whereas isomer **1b** is a single-twisted Möbius species ($L_k = 1$) (Figure 2, Table 2). Both structures differ only in the dihedral angle ($\theta$) of the single bond between double bond III and one of the neighboring anthracene units. Rotation around this bond gives rise to a change in topology from Hückel ($\theta = 137.2°$) to Möbius (53.9°).

Table 2. Linking number ($L_k$), twist ($T_w$), and writhe ($W_r$) of **1a–d** (see Figure 2).

| | $L_k$ | $T_w$ | $W_r$ | $\phi_{mean}$[a] [°] | $\phi_{max}$[b] [°] | Solvent[c] |
|---|---|---|---|---|---|---|
| **1a** | 2 | 2.10 | −0.10 | 18.0 | 78.6 | benzene |
| **1b** | 1 | 1.05 | −0.05 | 24.6 | 68.1 | benzene |
| **1c** | –[d] | – | – | 20.9 | 89.2 | DMF |
| **1d** | 1 | 1.11 | −0.11 | 18.6 | 74.4 | $Et_2O/CH_2Cl_2$ |

[a] Average deviation from planarity. [b] Maximum deviation of dihedral angles from planarity. [c] Solvent from which the crystals were grown. [d] The largest dihedral angle (89.2) is very close to 90°; therefore, the topology is ambiguous.

Crystals obtained by recrystallization of **1** from DMF exhibit a double-twisted Hückel structure **1c** ($L_k = 2$) in their unit cell. Compound **1c**, compared with **1b**, differs in the orientation of the ethenyl unit (I) (Figure 2). Yet another conformation (**1d**) was found in crystals grown from a mixture of diethyl ether and dichloromethane. Compound **1d** is a single-twisted Möbius isomer ($L_k = 1$). Compounds **1d** and **1b** differ in the orientation of ethenyl unit (V).

According to the $^1H$ and $^{13}C$ NMR spectra, the [36]annulene **1** is a very flexible structure that undergoes rapid conformational interconversions. With 16 signals in the $^{1}$H NMR and 26 signals in the $^{13}$C NMR spectrum, only a reduced number of signals are observed compared with the number of corresponding nuclei ($C_{80}H_{50}$) in structure **1**. Hence, the structure exhibits time-averaged $C_2$ or $C_s$ symmetry, including a rotation or rocking motion of the phenylene and anthrylene rings and a "crank handle type" motion of the *trans*-double bonds I, III, and V. Thus, inner and outer protons rapidly exchange.

The structure **1** was confirmed by NMR spectroscopy and all signals in the $^{1}$H and $^{13}$C NMR spectra were assigned by HMBC and HSQC spectra. $^{1}$H and $^{13}$C NMR spectroscopy data of **1** at room temperature are presented in Table 3.

Table 3. $^{1}$H and $^{13}$C NMR shifts of **1** in solution.

| Atom[a] number | $\delta$H [ppm] | $\delta$C [ppm] | Atom[a] number | $\delta$H [ppm] | $\delta$C [ppm] |
|---|---|---|---|---|---|
| 1 | 7.98 | 132.21 | 14 | 6.56 | 128.68 |
| 2 | – | 131.29 | 15 | – | 136.34 |
| 3 | – | 128.74 | 16 | 7.17 | 134.40 |
| 4 | 7.97 | 126.09 | 17 | 7.43 | 127.50 |
| 5 | 6.80 | 124.17 | 18 | – | 132.77 |
| 6 | 6.93 | 124.33 | 19 | – | 129.23 |
| 7 | 7.70 | 125.72 | 20 | 8.27 | 126.62 |
| 8 | – | 128.83 | 21 | 7.41 | 125.37 |
| 9 | – | 131.97 | 22 | 7.53 | 125.63 |
| 10 | 7.15 | 125.42 | 23 | 8.71 | 126.47 |
| 11 | 6.21 | 136.00 | 24 | – | 129.77 |
| 12 | – | 135.97 | 25 | – | 133.13 |
| 13 | 6.90 | 125.94 | 26 | 7.77 | 134.56 |

[a] For numbering of the nuclei see Figure 3.

The $^{1}$H NMR signals of annulene **1** do not provide evidence for aromaticity or antiaromaticity. These results mean that 1) there is no diatropic or paratropic ring current, and hence no aromaticity; 2) there is a fast equilibrium of Hückel aromatic and Möbius antiaromatic conformations, the magnetic anisotropies of which cancel on the NMR spectroscopy timescale; or 3) inner and outer protons exchange by fast conformational motions (see above). Therefore, we recorded low-temperature NMR spectra (−10, −30, −50, −71, −92, −103, −113, −118, −124 °C). However, no decoalescence was observed and the conformational motions are not frozen at these temperatures. The rather large deviation from planarity in the X-ray structures (see $\phi_{max}$, Table 2) suggests that the ring currents, most probably, are rather small in the conformations of both topologies of **1**. Möbius structure **1b** is the conformation that exhibits the smallest deviation from planarity ($\phi_{max}$: 68.1°; Figure 3). The largest torsional angle ($\phi_{max}$ 89.2°) was determined in structure **1c**, hence the π conjugation should be completely interrupted and no ring current is expected in this conformation.

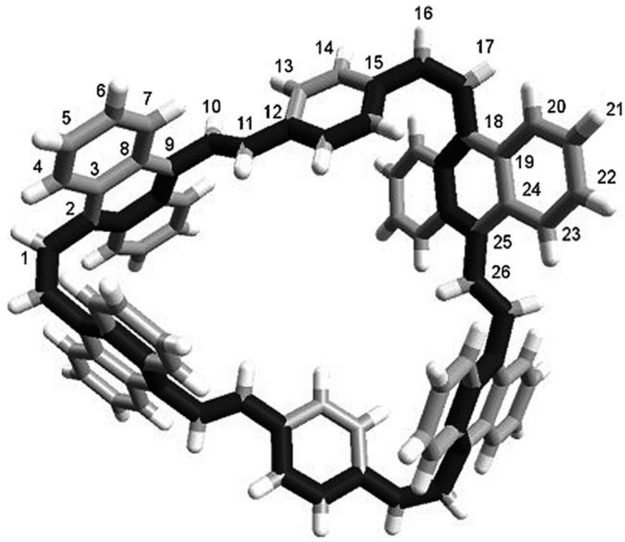


Figure 3. Möbius topology of the [36]annulene **1b**. The conjugated 36 π-electron circuit is indicated in darker color.

Table 4. "Energy ranking list" of the most stable isomers of the [36]annulene **1** calculated at B3LYP/6-31G* and BH&HLYP/6-31G*.

| Entry | $E_{rel}$[a] [kcal mol$^{-1}$] | $E_{rel}$[b] [kcal mol$^{-1}$] | $L_k$ | $T_w$ | $W_r$ | $\phi_{mean}$[c] [°] | $\phi_{max}$[d] [°] | c[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.000 | 0.771 | 2 | 2.21 | −0.21 | 17.8 | 63.9 | |
| 2 | 0.106 | 0.420 | 0 | 0.03 | −0.03 | 17.2 | 74.6 | |
| 3 | 0.144 | 0.000 | 1 | 1.12 | −0.12 | 18.6 | 64.3 | |
| 4 | 0.149 | 0.374 | 0 | 0.06 | −0.06 | 17.1 | 76.0 | **1d** |
| 5 | 0.150 | 0.001 | 1 | 1.15 | −0.15 | 18.6 | 64.1 | **1c** |
| 6 | 0.179 | 1.048 | 2 | 2.14 | −0.14 | 17.8 | 63.2 | **1a** |
| 7 | 0.289 | 0.691 | 3 | 3.21 | −0.21 | 18.7 | 64.8 | |
| 8 | 0.314 | 0.160 | 1 | −1.09 | 0.09 | 18.5 | 65.7 | **1b** |
| 9 | 0.335 | 0.374 | 0 | 0.09 | −0.09 | 17.7 | 65.0 | |
| 10 | 0.490 | 0.374 | 2 | 2.12 | −0.12 | 19.1 | 65.0 | |

[a] $E_{rel}$ is the relative energy at B3LYP/6-31G* with respect to the energetically most stable structure. [b] $E_{rel}$ is the relative energy at BH&HLYP/6-31G* with respect to the energetically most stable structure. [c] Average deviation from planarity (B3LYP/6-31G*). [d] Maximum deviation of dihedral angles from planarity (B3LYP/6-31G*). [e] c is the compound number.

To gain more information into the dynamic structure of **1**, we performed DFT calculations at the B3LYP/6-31G* level of theory. The ten most stable isomers, which could be located at the potential energy surface (PES) of **1** are listed in Table 4. Since the structures were generated by a Monte Carlo algorithm (see computational methods), the results are non-deterministic, and there is no guarantee that the list of isomers is complete. However, we found all isomers that were detected by X-ray structure analysis among the 10 most stable theoretically predicted isomers. The isomers **1a**, **1b**, **1c**, and **1d** are identical with the entries 6, 8, 5, and 4 in Table 4. Calculated **1d** and the experimentally determined structure given in entry 4 of Table 4 differ in the rotation of the single bond between double bond III and the neighboring anthracene unit (Scheme 2) and therefore differ in topology.

$L_k$, $T_w$, and $W_r$ (Table 4) of each isomer were determined by using the program anewrithm.[14]

Among the ten most stable conformations, $L_k$ varies from 0 (no twist) to |3| (triple twist). Surprisingly, only a small fraction of the twist is converted into writhe, that is, the 36 carbon atoms defining the π circuit lie approximately in a plane. A figure-of-eight-type conformation is probably prohibited by the steric demand of the anthracene units. The most stable conformation (Table 4, entry 1), which was found theoretically, is a double-twisted structure ($L_k=2$) with a high value of twist (2.21) and a low value of writhe (−0.21). The most interesting conformation is that given in entry 7 (Table 4) with an $L_k$ value of 3, ($T_w=3.21$ and $W_r=-0.21$). The π system of this conformation includes three half twists (Figure 4). With one phase shift, the π system has Möbius topology.

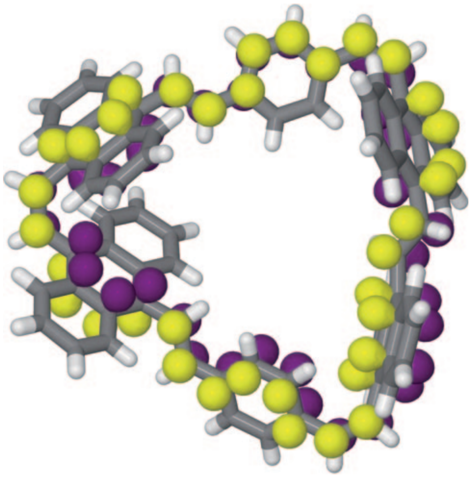


Figure 4. The linear combination of atomic orbitals (LCAO) *p* orbitals of the conjugated 36 π-electron pathway from data given in Table 4, entry 7, form a triple twist with one phase shift.

## Conclusion

A [36]annulene derivative (**1**) was synthesized in a four-step sequence with 7% overall yield. According to the NMR spectroscopy data, the structure is conformationally flexible even at temperatures as low as −124°C. Upon crystallization of **1** from different solvents, X-ray structures of four different conformations were determined. Two of the structures exhibit a double-twisted π system and two are Möbius structures with a single twist. Theoretical calculations and NMR spectroscopy data predict limited or no aromaticity. The cyclic conjugation in the 36 π-electron circuit is reduced by large dihedral angles. According to our calculations, there is an interesting triple-twisted ($L_k=3$) conformation among the 10 most stable structures.

## Experimental Section

**General**: All reactions were carried out under nitrogen (Schlenk conditions). Unless otherwise noted, all chemicals were obtained from commercial sources and used as received without further purification. Solvents were purified and dried by using common methods. Dichloromethane and DME were distilled from $CaH_2$ and toluene was distilled from sodium. Diisopropylamine was purchased predried from Fluka. Column chromatography (Ø cm × height cm) was carried out using Merck silica gel 60 (0.040–0.063 mm), and Merck neutral alumina 90, activity II-III (70–230 mesh). NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ using TMS as an internal standard. EI and CIMS mass spectra were recorded on a Finnigan MAT 8200 instrument, and MALDI-TOF mass spectra were recorded on a Brucker Biflex III instrument with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix in a saturated solution of dichloromethane.

**Synthesis of 1,4-bis(9-ethynylanthryl)benzene (4)**: A two-necked, round-bottomed flask containing **3** (0.252 g, 2 mmol), 9-iodoanthracene (1.216 g, 4 mmol), $[Pd(PPh_3)_2Cl_2]$ (30 mg), and CuI (30 mg) was charged with diisopropylamine (40 mL). After stirring for 4 h at ambient temperature, the reaction mixture was heated to reflux for an additional 30 min. The resulting precipitate was collected by filtration, redissolved in hot toluene, and filtered through a short column (6×10) of silica gel, eluting with toluene. Cooling the hot toluene solution yielded **4** as an orange solid (0.784 g, 82%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.68$ (d, $J=8.7$ Hz, 4H; anthracene-H), 8.48 (s, 2H; anthracene-H), 8.05 (d, $J=8.5$ Hz, 4H; anthracene-H), 7.85 (s, 4H; Ar-H), 7.55–7.65 ppm (m, 8H; anthracene-H); MS (EI+): $m/z$ (%): 478 (100) $[M^+]$, 239 (20).

**Synthesis of (*Z*,*Z*)-1,4-bis(9-ethenylanthryl)benzene (5)**: A two-necked, round-bottomed flask with a gas outlet tube was equipped with **4** (0.400 g, 0.836 mmol), ethyl acetate (400 mL), and 5% Pd/$BaSO_4$ (800 mg). Under a hydrogen atmosphere, the slurry was vigorously stirred at room temperature for 40 min. After filtering the mixture through a pad of Celite, the solvent was evaporated to afford **5** as a yellow solid (0.404 g, 100%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.36$ (s, 2H; anthracene-H), 8.03 (d, $J=8.8$ Hz, 4H; anthracene-H), 7.96 (d, $J=8.5$ Hz, 4H; anthracene-H), 7.27–7.40 (m, 8H; anthracene-H), 7.03 (d, $J=12.5$ Hz, 2H; CH=CH), 6.87 (d, $J=12.5$ Hz, 2H; CH=CH), 6.88 ppm (s, 4H; Ar-H); $^{13}$C NMR (125.8 MHz, $CDCl_3$, TMS): $\delta=133.6$, 132.4, 131.5, 128.7, 128.6, 128.5, 126.4, 126.3, 126.1, 125.5, 125.3 ppm; MS (EI+): $m/z$ (%): 482 (100) $[M^+]$, 293 (27), 279 (26), 241 (21), 203 (36), 191 (72).

**Synthesis of (*Z*,*Z*)-1,4-bis[(9-ethenyl-10-formyl)anthryl]benzene (6)**: A suspension of **5** (0.404 g, 0.837 mmol) in $CH_2Cl_2$ (in 40 mL) was cooled to 1°C. $SnCl_4$ (0.35 mL, 3.0 mmol) was slowly added to this mixture over a period of 30 min. The stirring was continued for an additional 30 min before the mixture was allowed to warm to room temperature and maintained there for 10 min. Afterwards, the mixture was cooled to 1°C and $Cl_2CHOCH_3$ (0.32 mL, 3.6 mmol) was added before the reaction was allowed to warm to room temperature again. After stirring for 3 h at ambient temperature the reaction mixture was quenched by adding cooled water. The crude product was filtered off, and washed with acetone to give **6** as an orange solid (0.290 g, 64%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta=11.58$ (s, 2H; CHO), 9.03 (d, $J=8.9$ Hz, 4H; anthracene-H), 8.49 (d, $J=8.8$ Hz, 4H; anthracene H's), 8.02 (d, $J=16.6$ Hz, 2H; CH=CH), 7.80 (s, 4H; Ar-H), 7.58–7.72 (m, 8H; anthracene-H), 7.02 ppm (d, $J=16.6$ Hz, 2H; CH=CH); MS (EI+): $m/z$ (%): 538 (91) $[M^+]$, 510 (37), 481 (10), 322(18), 279 (49), 203 (100); IR (KBr): $\tilde{\nu}=1663$ cm$^{-1}$ (C=O). Due to the low solubility of compound **6**, a $^{13}$C NMR spectrum could not be measured. The analytical data are in agreement with the literature.[12]

**Synthesis of paracyclophane 1**: A flame-dried, round-bottomed flask equipped with a nitrogen inlet tube was charged with Zn–Cu (325 mg, 5 mmol) and anhydrous DME (50 mL). After cooling the mixture to 0°C, $TiCl_4$ (0.27 mL, 2.5 mmol) was added carefully before the black–gray suspension was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and **6** (134 mg, 0.25 mmol) dissolved in anhydrous DME (25 mL) and toluene (50 mL) was slowly added. The mixture was stirred for 2 d at room temperature and afterwards heated at reflux for 3 h. The mixture was filtrated through a short column (3×15) of neutral alumina eluting with dichloromethane. The solvent was evaporated and the residue was purified by column chromatography (3×30) on silica gel eluting with hexane/$CH_2Cl_2$ (3/1) to give **1** as an orange solid (17.6 mg, 14%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.71$ (d, $J=8.8$ Hz, 4H), 8.27 (d, $J=8.8$ Hz, 4H), 7.98 (s, 2H), 7.97 (d, $J=9.3$ Hz, 4H), 7.77 (s, 2H), 7.70 (d, $J=8.8$ Hz, 4H), 7.53 (ddd, $J=8.8$, 6.5, 1.3 Hz, 4H), 7.43 (d, $J=12.3$ Hz, 2H), 7.41 (ddd, $J=8.5$, 6.5, 1.1 Hz, 4H), 7.17 (d, $J=12.2$ Hz, 2H), 7.15 (d, $J=16.5$ Hz, 2H), 6.93 (ddd, $J=8.8$, 6.5, 1.2 Hz, 4H), 6.90 (d, $J=8.5$ Hz, 4H), 6.80 (ddd, $J=8.8$, 6.6, 1.2 Hz, 4H), 6.56 (d, $J=8.4$ Hz, 4H), 6.21 ppm (d, $J=16.5$ Hz, 2H); $^{13}$C NMR (125.8 MHz, $CDCl_3$, TMS): $\delta=136.3$, 136.00, 135.97, 134.6, 134.4, 133.1, 132.8, 132.2, 132.0, 131.3, 129.8, 129.2, 128.8, 128.7, 128.7, 127.5, 126.6, 126.5, 126.1, 126.0, 125.7, 125.6, 125.42, 125.37, 124.3, 124.2 ppm; MALDI-TOF MS: $m/z$: 1012.24, 1013.21, 1014.21; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\log\varepsilon$) = 235 sh (0.75), 255 (2.55), 320 (0.37), 406 nm (0.55). Due to the presence of multiple solvent molecules in crystals of **1**, a suitable elemental analysis could not be obtained. For assignment of signals in the $^1H$ and $^{13}C$ NMR spectrum see Table 3.

**X-ray crystallography**: All data collections were performed with an imaging plate diffraction system (IPDS-1) with Mo-$K_\alpha$ radiation from STOIE & CIE. The structure solutions were done with direct methods by using SHELXS-97. Structure refinements were performed against $|F|^2$ by using SHELXL-97. All non-hydrogen atoms except those that are disordered were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters by using a riding model. In all compounds some C atoms are disordered and were refined by using a split model. Details of the structure determination are given in Table 5.

CCDC-755277 (**1a**, **b**), 755275 (**1c**), and 755279 (**1d**) contain 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.

Table 5. Selected crystal data and results of the structure refinements for compound **1** in different solvents.

| | Benzene | DMF | Diethyl ether |
|---|---|---|---|
| formula | $C_{116}H_{88}$ | $C_{80}H_{52}$ | $C_{84}H_{62}O$ |
| $M_r$ [$g\,mol^{-1}$] | 1481.86 | 1013.22 | 1087.34 |
| crystal system | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $a$ [Å] | 15.3793(11) | 28.9655(16) | 9.1670(8) |
| $b$ [Å] | 29.488(2) | 9.8062(4) | 15.0221(11) |
| $c$ [Å] | 31.100(2) | 46.272(3) | 22.2194(18) |
| $\beta$ [°] | 91.063(9) | 105.960(6) | 79.086(10) |
| $V$ [Å$^3$] | 12640.5(15) | 12636.6(11) | 2895.8(15) |
| $T$ [K] | 170 | 170 | 170 |
| $Z$ | 6 | 8 | 2 |
| $\rho_{calcd}$ [$g\,cm^{-3}$] | 1.168 | 1.065 | 1.247 |
| $2\theta$ range [°] | 1.78–22.40 | 1.83–22.37 | 2.29–25.96 |
| $\mu(Mo_{K\alpha})$ [$mm$]$^{-1}$ | 0.066 | 0.060 | 0.072 |
| measured reflns | 72374 | 20404 | 27359 |
| $R_{int.}$ | 0.0328 | 0.0530 | 0.0341 |
| independent reflns | 32247 | 7873 | 10918 |
| parameters | 3274 | 822 | 779 |
| $R_1[I>2\sigma(I)]$ | 0.0564 | 0.0865 | 0.0513 |
| $wR_2$(all data) | 0.1650 | 0.2597 | 0.1448 |
| GooF | 1.022 | 0.958 | 1.033 |
| residual electron density [$e\,Å^{-3}$] | 0.359/ −0.224 | 0.498/ −0.291 | 0.868/−0.359 |

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[14] $T_w$ and $W_r$ depend on the pathway defined for the [36]annulene circuit. The conjugation path was chosen as depicted in Figure 3. $T_w$ and $W_r$ were calculated with the program anewrithm (unpublished). The absolute value of $W_r$ is small regardless of the definition of the conjugation path.

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