From Metacyclophanes to Cyclacenes: Synthesis and Properties of [6.8]₃Cyclacene

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday







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Abstract: In this article we show synthetic pathways to $[6.8]_n$ cyclacenes demonstrated by the de novo synthesis of [6.8]₃cyclacene as the first purely hydrocarbon cyclacene and of precursors for [6.8]₄cyclacene. The design of the de novo synthesis by exploring alternative pathways is discussed and various precursors are shown. Crucial to the synthesis of [6.8]₃cyclacene were two cyclization steps. The first is a Wittig trimerization reaction which yielded the hexamethyl substituted all-cis- $[2_3]$ metacyclophanetriene. For the second cyclization step the methyl groups were converted to aldehyde functionalities by two subsequent oxidation steps of N-bromosuccinimide (NBS) bromination and oxidation with 2-iodoxybenzoic acid (IBX). The final cyclization of the second set of double bonds was achieved by a McMurrycoupling reaction. Towards the synthe-

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sis of [6.8]₄cyclacene different synthetic pathways to methyl substituted all-cis- $[2_4]$ metacyclophanetetraenes were explored. Insights into the structures of [2₃]metacyclophanetri- and [2₄]metacyclophanetetraenes were gained by Xray crystallographic investigations on various intermediates. A crystallographic analysis of [6.8]₃cyclacene revealed a D_{3h} symmetrical structure with planar benzene rings and a formation of tubular structures in the solid state.



Figure 1. [6]_nCyclacenes (1 with n=10) and cyclo[n]phenacenes (2 with n = 10) as subunits of carbon nanotubes.

however, and to transform the partially hydrogenated systems into fully conjugated ones have failed so far.

One of the reasons for this failure was unraveled by quantum chemical calculations.^[9,10] It was predicted that $[6]_n$ cyclacenes with an even number of n should exhibit small singlet-triplet gaps.^[9] These calculations also revealed that angularly annelated cyclacenes, such as 2, should have large singlet-triplet splittings.^[10]

The detour by way of bridged saturated systems to achieve the bending, and the intrinsic problem of small singlet-triplet splittings in evenly numbered [6], cyclacenes was circumvented in two ways: Either a cage molecule containing an angularly annelated cyclacene as substructure was used as starting point, or such ring structures were incorporated in the belt, which naturally adopt boat-like conformations. The first approach was successfully carried out by

Introduction

Belt-like macrocycles incorporating groups with donor functionalities (e.g. cyclodextrins, cavitands, curcurbiturils) are well known as hosts in supramolecular chemistry.^[1,2] Depending on the donor groups and the size of the belt they are capable of recognizing guests, which vary in size from small metal ions to complex organic molecules. A number of belt-like systems consisting of cylindrical π -conjugated entities are not only of interest because of their specific host/guest properties, but also because of their physical properties, such as absorption and emission spectra. These systems have in common a scaffold that forms a torus in which the p-orbitals of the π -system are oriented parallel to the molecular plane of the macrocycle and perpendicular to the torus axis.^[3] The prototype of such belt-like conjugated molecules are [6]_ncyclacenes. They are built from linear annelation of n six-membered, conjugated rings. In Figure 1 $[6]_{10}$ cyclacene (1) is shown. Such systems have been discussed since 1954^[4] and can as well as the related cyclo[10]phenacene (2) be regarded as subunits of single walled carbon nanotubes^[5] as shown in Figure 1.

Efforts to synthesize [6], cyclacenes started in the 80s of the last century.^[6,7,8] One clear problem was the bending of the planar π -system into a hoop. This task was approached by first preparing a partially saturated system utilizing a sequence of Diels-Alder reactions of 7-oxanorbornene derivatives. This allowed systems with 16 to 18 six-membered rings partially bridged by oxygen atoms to be achieved in good yields. Attempts to remove the ether functionalities,

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Scheme 1. Synthesis of $\mathrm{C}_{60}\text{-embedded}$ cyclo[10]phenacene 5 by Nakamura et al.

Nakamura et al. by utilizing methods to reduce the north and south pole of $\rm C_{60}$ (Scheme 1). $^{[11]}$

Our approach uses eight-membered rings as building blocks. The boat conformation of cyclooctatetraene provides excellent conditions to incorporate it in a conjugated medium sized π -system. In Scheme 2 we have shown the



Scheme 2. Construction of $[4.8]_n$ (6) and $[6.8]_n$ cyclacenes (7) by annelation of four- and eight-membered rings and six- and eight-membered rings, respectively.

cases for linear cyclacenes in which four- and eight-membered as well as six- and eight-membered rings alternate.^[3e] Recent quantum chemical calculations reveal that **6** (n=3,4) and **7** (n=3-8) should be thermodynamically stable species.^[12] The necessary bending of the smaller species is mainly achieved by a stronger bending of the flexible cyclo-octatetraene rings.

To achieve a $[4.8]_n$ cyclacene we irradiated tetradehydrodibenzo[a,e] cyclooctatetraene (8) with $[CpCo(CO)_2]$ (9) or $[CpRh(C_2H_4)_2]$ (10) in one-pot reactions. These yielded the benzo-derivatives of metal stabilized $[4.8]_3$ cyclacenes 11^[13a] and 12^[13b] (Scheme 3).



Scheme 3. Synthesis of [4.8]₃cyclacenes 11 and 12 by Gleiter et al.

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In this article we report the full details of our recent communication on the synthesis of $[6.8]_3$ cyclacene (13) as the first purely hydrocarbon cyclacene.^[14] We are discussing our synthetic approach via metacyclophane derivatives and experimental pathways to $[6.8]_4$ cyclacene.

Results and Discussion

Synthesis of [6.8]_3cyclacene: To find a reasonable synthetic path to $[6.8]_n$ cyclacenes (7) we had to choose between a stepwise procedure (Path A) and a multicomponent one-pot reaction (Path B), as shown in Scheme 4.



Scheme 4. Retrosynthetic approaches to $[6.8]_n$ cyclacenes (7).

We carried out model studies on dibenzo-[a,e]cyclooctatetraene (17) as the synthetic target, as it contains the representative structural unit of [6.8]_ncyclacenes. For a stepwise synthetic approach we found that the McMurry coupling of dialdehyde 18 yielded 17 (Scheme 5).



Scheme 5. Synthetic pathways to dibenzo[a,e]cyclooctatetraene (17) as model studies; a) TiCl₃·DME_{1.5}, Zn–Cu, DME, 90°C, 21%; b) LiOEt/EtOH, MeOH, 28%; c) LiOEt/EtOH, DMF, 18%.

An olefin metathesis reaction of the corresponding (Z)-1,2bis(2-vinylphenyl)ethene, on the other hand, turned out to be unsuitable. Corresponding to the one-pot approach for [6.8]_ncyclacenes (7) the best syntheses of our model compound **17** were those reported in the literature by Sargent^[15a] and Peters,^[15b] both of which applied a double Wittig reaction. In the first case (2-formylbenzyl)triphenylphosphonium chloride (**19**) is dimerized and in the second case phthalaldehyde (**20**) is reacted with (1,2-phenylenebis(methylene))bis(triphenylphosphonium) bromide (**21**).

We first explored synthetic routes to precursors of $[6.8]_n$ cyclacenes (7) suitable for multicomponent one-pot reactions (Path B in Scheme 4). In view of the results of our model studies we decided to focus on precursors for Wittig reactions and chose CHO and CH₂Br as substituents Y₁-Y₄ (24 and 26, Scheme 6). Our attempted synthesis of 24 start-



Scheme 6. Syntheses of 1,2,4,5-tetrasubstituted benzene derivatives **23** and **26**; a) NBS, dibenzoyl peroxide, CCl₄, 80 °C, 22 %; b) DIBAL-H, THF, RT, 61 %; c) PCC, CH₂Cl₂, RT; d) oxalyl dichloride, DMSO, Et₃N, CH₂Cl₂; e) DIBAL-H, toluene, $-90 \rightarrow -40$ °C, 44 %; f) PPh₃, toluene, reflux.

ed from dimethyl 4,5-dimethylphthalate (22),^[16] which was transformed to 23 by N-bromosuccinimide (NBS) bromination followed by reduction with DIBAL-H to the diol. Oxidation of the hydroxyl groups to 24 failed, as well as the direct reduction of 22 to 24 with DIBAL-H, because of the formation of a lactone. 4,6-Bis(bromomethyl)isophthalaldehyde (26) was synthesized from diethyl 4,6bis(bromomethyl)isophthalate (25),^[17] but transformation to the phosphonium salt 27 failed for reasons of product isolation. As our attempts to synthesize the desired precursors for multicomponent one-pot reactions were not successful, we focused on a stepwise approach for the synthesis of [6.8]_ncyclacenes.

For a stepwise procedure (Path A in Scheme 4) we decided on the McMurry coupling reaction for the closure of the second set of double bonds ($14 \rightarrow 7$ in Scheme 4), given the results of our model studies. For the first set of double bonds ($15 \rightarrow 14$) we found that intermediate 14 corresponds to an *o*,*o*'-substituted metacyclophene. We were inspired by the work of Wennerström et al.,^[18a] Oda et al.,^[18b] and Iyoda et al.^[18c] from their studies on *meta-* and *ortho-*cyclophane-trienes and higher oligomers. We chose [6.8]₃cyclacene (13) as our target. Our retrosynthetic concept is shown in Scheme 7. A first disconnection of three double bonds leads to the [2₃]metacyclophanetriene derivative 28 carrying six formyl substituents. As we planned to synthesize the meta-



Scheme 7. Retrosynthetic approach to [6.8]₃cyclacene (13).

cyclophanetriene scaffold by means of a Wittig reaction, the formyl substituents needed to be introduced in a later stage. For X we chose bromo or methyl substituents (**29** and **30**, respectively), which can be transformed to aldehyde functionalities. Disconnection of the second set of double bonds results in the bromo- and methyl substituted isophthalaldehydes **31** and **32**, respectively.

In the synthesis of the $[2_3]$ metacyclophanetriene derivatives **29** and **30** we chose the route via a Wittig trimerization according to Wennerström's synthesis of the unsubstituted analogue.^[18a] Both synthetic routes started from the substituted isophthalaldehydes **31**^[19] and **32** (Scheme 8).^[20] By se-

Scheme 8. Synthesis of phosphonium bromides **35** and **36**; a) NaBH₄, EtOH, RT; b) HBr, HOAc, reflux, 26% (X=Br), 65% (X=CH₃); c) PPh₃, toluene, reflux, 91% (X=Br), 99% (X=CH₃).

lective reduction of one aldehydic group with less than the equivalent amount of $NaBH_4$ the corresponding monoalcohols were generated. Subsequent substitution of the hydroxyl groups by bromide yielded the benzyl bromides **33** and **34**. Treatment with triphenylphosphine afforded the desired phosphonium bromides **35** and **36**.

Now the stage was set for the intermolecular Wittig reactions to assemble three benzene rings in a cyclic fashion. We first concentrated on the bromo substituted system. Treatment of bromo derivative **35** in DMF with LiOEt in ethanol at low temperature yielded the trimeric **37** with *all-cis* configured double bonds, as the main product in addition to other higher cyclic oligomers (Scheme 9). The structure of **37** was elucidated by X-ray crystallographic investigations and will be discussed in a later section. The bromine atoms in **37** had to be replaced by aldehyde groups for which we intended a halogen-metal exchange reaction. The Br/Li exchange with **37** was investigated under a variety of reaction conditions. Quenching with DMF followed by acidic hydrolysis did not lead to the desired hexaaldehyde **28**. Instead, a mixture of **38–40** was isolated in which three to four



Scheme 9. Synthesis of bromo substituted metacyclophanetriene **37** and Br/Li exchange; a) LiOEt/EtOH, DMF, -40 °C, 15%; b) i) *t*BuLi, THF, -78 °C; ii) DMF, -78 °C \rightarrow RT; iii) H₄O⁺.

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bromine atoms had been replaced by CHO. The structure of **39/40** (in a mixed crystal) was confirmed by X-ray crystallographic analysis. We assume that steric constraints are the reason that no sixfold Br/Li exchange was observed in **37**. As the bromine route had reached a dead end we set our attention on the methyl substituted system.

The Wittig cyclization reaction of the methyl substituted phosphonium bromide **36** was also successful. Reaction with LiOEt/ethanol in DMF yielded the trimeric systems **41a**,**b**, the cyclic tetramers **42a**–**c** as well as larger cyclic oligomers (Scheme 10). Interestingly, the



Scheme 11. Synthesis of formyl substituted metacyclophanetriene **28**; a) NBS, dibenzoyl peroxide, CCl₄, reflux, 40%; b) IBX, DMSO, 65°C, 37%; c) KOAc, DMF, 70°C, 69%; d) CaCO₃, dioxane/H₂O, reflux, 32%; e) KOH, H₂O, 100°C; f) IBX, DMSO, RT, 45%.



Scheme 10. Synthesis of methyl substituted metacyclophanetrienes **41** a,b and metacyclophanetetraenes **42** a–c; a) LiOEt/EtOH, DMF, -10 °C, 8%; b) $h\nu$, benzene, 5 °C, 85%.

predominantly formed trimeric isomer **41a** had *cis,cis,trans*configured double bonds. Its molecular structure was investigated by an X-ray crystallographic analysis (Figure 5).^[14,21] By irradiation in degassed benzene double-bond isomerization to the desired *all-cis* isomer **41b** was possible.^[14,21]

The next challenge was the crucial introduction of the aldehyde functionalities. In the conversion of the methyl groups in **41b** to aldehyde groups we were successful in two oxidation steps. The first was a sixfold benzylic bromination with NBS, yielding the hexa(bromomethyl) substituted metacyclophanetriene **43** (Scheme 11). This was then hydrolyzed to the alcohol **44** on which the second oxidation step to the aldehyde **28** was performed by using 2-iodoxybenzoic acid (IBX) as oxidizing agent.^[22] Compound **44** is poorly soluble in common solvents, but readily dissolves in DMSO. Thus, standard oxidation methods failed, such as those that use pyridinium chlorochromate (PCC) or the Swern oxidation, as they are usually performed in CH_2Cl_2 . An attempt to improve the yield of alcohol **44** by conversion to the acetate **45** failed in the subsequent hydrolysis step. However, we were able to abridge the route by direct oxidation of the benzylic bromide **43** into hexaaldehyde **28** by oxidation with IBX at elevated temperatures.^[23]

Now, as the last step of the synthesis, the second set of double bonds needed to be linked. For this step we had chosen a McMurry coupling reaction. We applied the improved procedure with the TiCl₃/DME complex and Zn–Cu as reductive agent on aldehyde **28** (Scheme 12).^[24] This



Scheme 12. Synthesis of $[6.8]_3$ cyclacene (13); a) TiCl₃·DME_{1.5}, Zn–Cu, DME, reflux, 8%.

coupling reaction was successful and yielded [6.8]₃cyclacene (13) as the only isolable product. The low yield of the reaction might partly be explained by the preferred conformation of hexaaldehyde 28. X-ray crystallographic analysis and theoretical calculations revealed that 28 adopts a twisted conformation, as indicated in Scheme 12.^[14,21] The ring closure to 13, on the other hand, requires a conformational change to a disfavored bowl-shaped conformation.

The anticipated D_{3h} symmetry of **13** was confirmed by Xray structural investigations (Figure 2).^[14,25] The benzene



Figure 2. Structure and packing of $[6.8]_3$ cyclacene (13) in the solid state. Hydrogen atoms are omitted for clarity.

units retain their planarity. The bending of the cyclooctatetraene moieties with an angle of 51.2° (as the deviation from planarity) is larger than in cyclooctatetraene itself $(41.9^{\circ})^{[26]}$ and in dibenzo[*a,e*]cyclooctatetraene (43.4°).^[27] This bending of the flexible cyclooctatetraene units leaves a strain energy of only 6.8 kcalmol⁻¹ per subunit^[12] for [6.8]₃cyclacene (**13**). The mean torsion between the planes of the double bonds and that of the adjacent aromatic rings amounts to 72°. This indicates about 31% conjugation for the cyclacene torus.

The crystal packing of $[6.8]_3$ cyclacene (13) in the solid state is shown in Figure 2. The molecules are stacked in piles on top of each other building molecular tubes. We found that CH- π interactions contribute to the molecular arrangement in the solid state. As shown in Figure 3 each



Figure 3. CH $-\pi$ interactions in the solid state of [6.8]₃cyclacene (13).

molecule has CH– π interactions with neighboring molecules. The distances all amount to 2.88 Å and are slightly smaller than the sum of the van der Waals radii of C and H (2.9 Å).^[28] The angles CH···C are close to linear (159.8°), which is typical for this type of interaction.^[29]

We also measured the UV absorption and emission. In the absorption spectrum **13** shows a strong band at $\lambda = 220$ nm with two shoulders at $\lambda = 278$ and 290 nm (log $\varepsilon = 4.73$, 3.85, and 3.27, respectively). Emission takes place at $\lambda = 370$ nm, corresponding to a Stoke's shift of 80 nm.

Structures of [2₃]metacyclophanetrienes: As mentioned above, X-ray crystallographic investigations were carried out on a number of the synthesized [2₃]metacyclophanetriene derivatives.^[14,21] As representative examples the molecular structures of **28**,^[14,21] **37**,^[30] and **41 a**^[14,21] are shown in Figure 4 and Figure 5. The *all-cis*-metacyclophanetrienes



Figure 4. Molecular structures of **28** (left) and **37** (right) in the crystal (aromatic hydrogen atoms are omitted for clarity).



Figure 5. Molecular structure of 41a in the crystal (hydrogen atoms are omitted for clarity except for the olefinic ones).

show a twisted conformation in the solid state. The NMR spectra, on the other hand, point towards $C_{3\nu}$ symmetrical structures in solution and show no coalescence down to -105 °C. To elucidate this behavior we performed quantum chemical calculations on the unsubstituted [2₃]metacyclophanetriene.^[31] These calculations revealed that the twisted conformer is the thermodynamically most stable one, the degenerated rearrangement between the different twisted isomers proceeds via a barrier of only 1.3 kcal mol⁻¹ height (B3 LYP/6-31G*).

In the molecular structure of **37** in the solid state we found intermolecular contacts between bromine centers. Each molecule shows eight intermolecular Br–Br contacts with distances between 3.52 and 3.67 Å. These are shorter than the sum of two van der Waals radii (3.7 Å).^[28] Intermolecular interactions between neutral halogen centers have been addressed in the literature.^[32] Interactions between closed-shell systems have at first been interpreted on the

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basis of donor-acceptor interactions,^[32a] but correlation effects were later shown to contribute considerably.^[33]

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Structures of [24] metacyclophanetetraenes and synthesis of [24] metacyclophanedienediyne: Our synthetic strategy of a stepwise procedure for the synthesis of [6.8], cyclacenes was successful for the trimeric system and should be applicable in the syntheses of larger cyclacenes. In the case of a [6.8]₄cyclacene, an octamethyl substituted all-cis-[24] metacyclophanetetraene would be the precursor. In our explorations on the synthesis of such a system we investigated the cis-trans isomerism of [24]metacyclophanetetraenes. Of those, the methyl substituted derivatives, which were isolated as minor products in the Wittig reaction of phosphonium bromide 36 (Scheme 10), none showed the desired allcis stereochemistry. We isolated the E,Z,Z,Z- (42a), E,Z,E,Z- (42b), and E,E,E,Z-isomers (42c) and elucidated their structures by NMR-spectroscopy and X-ray crystallography. The molecular structures are shown in Figures 6 and 7. Irradiation of each of these isomers at $\lambda = 254$ nm did not lead to the *all-cis* isomer, but to a mixture of 42 a-c. In each of these mixtures the ratio of 42 a to 42 b to 42 c was roughly the same. To illuminate the question why we could not find the Z,Z,Z,Z-isomer we carried out quantum chemical calculations on the six cis-trans isomers of the unsubstituted [24]metacyclophanetetraene.^[31] We found out that the



Figure 6. Molecular structures of **42 a** $(left)^{[34]}$ and **42 b** $(right)^{[35]}$ in the crystal (hydrogen atoms are omitted for clarity except for the olefinic ones).



Figure 7. Molecular structure of $42c^{[36]}$ in the crystal (hydrogen atoms are omitted for clarity except for the olefinic ones).

E,*Z*,*E*,*Z*-isomer is the most stable, whereas the desired *Z*,*Z*,*Z*,*Z*-isomer owns the highest relative energy, 11.5 kcal mol⁻¹ above the former. This explains why this stereochemistry is disfavored in the Wittig tetramerization of **36**.

To obtain the desired double bond configuration we decided to make use of the *cis*-selective reduction of triple bonds. As a precursor for an octaformyl substituted $[2_4]$ metacyclophanetetraene (46) we chose the dienediyne 47. Our retrosynthetic approach is shown in Scheme 13. For the cyclization reaction we focused in this case on the McMurry coupling of dialdehyde 48.



Scheme 13. Retrosynthetic approach to the octaformyl substituted $[2_4]$ metacyclophanetetraene **46**.

Our synthesis of dialdehyde **48** started from 1,5-diiodo-2,4-dimethylbenzene (**49**)^[37] (Scheme 14). One of the iodine atoms was exchanged by an aldehyde group applying a



Scheme 14. Synthesis of the methyl substituted [24]metacyclophanedienediyne **47**; a) i) *n*BuLi, *n*Bu₃MgLi, toluene, -10° C, ii) DMF, toluene, -10° C, iii) aq. citric acid, 86%; b) TMSA, [Pd(PPh_3)4], CuI, *i*Pr₂NH, THF, 0°C, 97%; c) K₂CO₃, MeOH, CH₂Cl₂, RT, 99%; d) **50**, [Pd(PPh_3)4], CuI, *i*Pr₂NH, THF, RT, 98%; e) TiCl₄, Zn, CuI, DME, reflux \rightarrow RT, 11%.

method by Iida and Mase^[38] which led to **50**. The alkyne moiety was introduced by a Sonogashira coupling reaction, exchanging the remaining iodine atom by TMSA. Subsequent deprotection yielded 5-ethynyl-2,4-dimethylbenzalde-hyde (**51**). Coupling **51** with **50** under Sonogashira conditions led to dialdehyde **48** as the starting material of the cyclic dimerization. In the last and crucial step of the synthesis, the intermolecular McMurry homocoupling of **48**, we

tested different reaction conditions. Most successful turned out to be a mixture of $TiCl_4$, Zn, and CuI in DME,^[39] which led to the [2₄]metacyclophanedienediyne **47**.

The molecular structure of **47** was examined by X-ray crystallography and is shown in Figure 8.^[40] It is very similar to that of the methyl substituted E,Z,E,Z-metacyclophanete-traene **42b**. In **47** the place of the *E*-double bonds is taken by the triple bonds. Both double bonds are *cis*-configured, as anticipated.



Figure 8. Molecular structure of **47** in the crystal (hydrogen atoms are omitted for clarity except for the olefinic ones).

For a further synthetic path towards cyclacene precursor **46** we think that the functionalization of the methyl groups of **47** would be the next task. As the *cis-trans* isomerization of the double bonds in $[2_4]$ metacyclophanetetraene derivatives takes place easily, the hydrogenation of the triple bonds should be carried out at the latest possible stage of the synthesis.

We carried out UV/vis spectroscopical investigations on the tetrameric systems **42a–c** and **47**. The absorptions were found at $\lambda = 288$ nm (**42a**), 294 nm (**42b**), and 300 nm (**42c**) (log $\varepsilon = 4.51$, 4.66, 4.74, respectively). Analysis of **47** shows absorptions at $\lambda = 218$, 294, 304, and 314 nm (log $\varepsilon = 3.26$, 3.49, 3.37, 3.33, respectively). All of them also show fluorescence emission. For **47** this emission was found at $\lambda =$ 384 nm with a Stoke's shift of 70 nm. **42a–c** all emit at $\lambda =$ 412 nm corresponding to large Stoke's shifts of 124, 118, and 112 nm, respectively. This behavior correlates well with the data found from the irradiation experiments, which indicated that after photon absorption **42a**, **42b**, and **42c** pass through the same excited state before returning to a ground state.

Conclusion

Our synthetic efforts demonstrate that $[6.8]_n$ cyclacenes can be prepared in de novo syntheses by a stepwise strategy. By applying a threefold Wittig reaction and an intramolecular threefold McMurry coupling we succeeded in synthesizing $[6.8]_3$ cyclacene, the most strained member of the $[6.8]_n$ cyclacene family. The structural details found for $[6.8]_3$ cyclacene reveal that its strain energy, which was predicted by quantum chemical calculations, stems from a bending of the cyclooctatetraene moieties that is stronger than in dibenzo[a,e]cyclooctatetraene. The benzene rings are found to be planar. This indicates that higher, less strained [6.8]_ncyclacenes should also be accessible. The strong bending reduces the conjugation within the torus to 31% compared to a fully conjugated system. Our studies on the syntheses and configurations of [2_4]metacyclophanetetraenes are important steps on the way to [6.8]₄cyclacene. [6.8]_nCyclacenes furthermore present smallest subunits of a novel type of carbon nanotube with a pattern that comprises four-, six-, and eight-membered rings. An elongation of [6.8]₅cyclacene along its molecular axis leads to a carbon nanotube as shown in Figure 9.



Figure 9. [6.8], Cyclacenes as subunits of carbon nanotubes with a new ring pattern.

Experimental Section

General: Air- and moisture-sensitive reactions were carried out under argon in flame-dried glassware. Solvents were either distilled or dried and distilled (DMF: CaH₂; CCl₄: molecular sieves; DME, THF, toluene: Na, benzophenone) before use or purchased predried (DMSO: Fluka). All reagents obtained from commercial sources were used without further purification. Thin layer chromatography (TLC) was performed on precoated silica-gel SIL G/UV254 plates (Macherey-Nagel), detection was carried out by means of UV light (254 nm). Silica gel 60 (230-400 mesh, Macherey-Nagel) was used for column chromatography. ¹H and ¹³C NMR spectra were recorded at RT by using a Bruker Avance ARX 300, 500 or 600 spectrometer using the solvent as internal standard. Melting points are uncorrected and were measured in an open capillary with an apparatus (Dr. Tottoli) or a B-540 (Büchi). IR spectra were recorded as KBr pellets by using a Bruker Vector 22 FT-IR instrument. UV/vis spectra were recorded by using a Hewlett-Packard HP 8452 A spectrometer. Mass spectra were measured by using a JEOL JMS-700 instrument. Elemental analyses were performed by using a VarioEL (Elementar).

5-(Bromomethyl)-2,4-dimethylbenzaldehyde (34): NaBH₄ (1.55 g, 41.0 mmol) was added within 2 h in two equal portions to a solution of 4,6-dimethylisophthalaldehyde 32 (33.2 g, 205 mmol) in ethanol (700 mL). The solution was stirred at RT for 1.5 h. Another portion of NaBH₄ (0.54 g, 14.3 mmol) was added and the reaction mixture was stirred at RT overnight. The solvent was evaporated in vacuo and boiling water (300 mL) was added to the remaining yellow oil. The mixture was extracted with ethyl acetate (300 mL), the aqueous phase was made acidic with conc. HCl and extracted with ethyl acetate (200 mL). The aqueous phase was saturated with brine and extracted with another ethyl acetate (200 mL). The combined organic extracts were washed with brine, dried over MgSO₄ and evaporated to dryness. The raw material was dissolved in acetic acid (700 mL), hydrobromic acid (80 mL, 47% in water) was added and the solution was refluxed for 2 h. After cooling to RT dichloromethane (600 mL) were added and the reaction mixture was

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washed with sat. aq. NaHCO₃, water, and brine. The organic extracts were dried and the solvent evaporated. Column chromatography on SiO₂ (*n*-hexane/ethyl acetate, 20:1) afforded 5-(bromomethyl)-2,4-dimethylbenzaldehyde **34** (30.1 g, 65 %), as a colorless crystalline solid. $R_{\rm f}$ =0.58 (*n*-hexane/ethyl acetate, 7:3); m.p. =62 °C ; ¹H NMR (500 MHz, CDCl₃): δ =2.43 (s, 3H), 2.61 (s, 3H), 4.51 (s, 2H), 7.08 (s, 1H), 7.71 (s, 1H), 10.18 ppm (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ =19.0, 19.1, 31.0, 132.6, 133.4, 134.1, 134.4, 141.2, 143.7, 191.7 ppm; MS (EI+): *m/z*: 228/226 [*M*+]; HRMS: *m/z* calcd for C₁₀H₁₁⁸¹BrO: 227.9974, found: 227.9986; calcd for C₁₀H₁₁⁷⁹BrO: 225.9994, found: 225.9983; IR (KBr): $\tilde{\nu}_{\rm max}$ =3039 (w), 2955 (w), 2925 (w), 2862 (w), 2758 (w), 1688 (vs), 1608 (s), 1447 (m), 1260 (m), 1223 (s), 1188 (m), 1073 (m), 881 (w), 633 (w), 549 cm⁻¹ (m); UV/vis (CH₂Cl₂): $\lambda_{\rm max}(\log \varepsilon)$ =260 (4.15), 300 nm (3.21); elemental analysis calcd (%) for C₁₀H₁₁BrO: C 52.89, H 4.88; found: C 53.06, H 4.89.

(5-Formyl-2,4-dimethylbenzyl)triphenylphosphonium bromide (36): A solution of benzyl bromide 34 (30.1 g, 133 mmol) and triphenylphosphine (36.6 g, 140 mmol) in toluene (700 mL) was refluxed overnight. The precipitated phosphonium salt was isolated by suction filtration, washed with toluene and diethylether and dried in vacuo yielding 64.4 g (99%) of **36** as a white powder. ¹H NMR (300 MHz, $[D_6]DMSO$): $\delta = 1.74$ (s, 3 H), 2.58 (d, 3 H, ${}^{5}J_{HP} = 2.1$ Hz), 5.18 (d, 2 H, ${}^{2}J_{HP} = 15.0$ Hz), 7.15 (s, 1 H), 7.42 (d, 1H, ${}^{4}J_{HP} = 2.4$ Hz), 7.68–7.82 (m, 12H), 7.94–7.99 (m, 3H), 10.00 ppm (s, 1H); $^{13}{\rm C}$ NMR (75 MHz, [D₆]DMSO): $\delta\!=\!18.9,\,20.0,\,26.6,$ 118.3, 125.4, 131.1, 132.9, 133.6, 135.0, 135.1, 136.2, 141.6, 146.0, 192.4 ppm; ³¹P NMR (101 MHz, [D₆]DMSO): $\delta = 23.7$ ppm; MS (ESI, MeOH): m/z: 441 [(M-Br)⁺+MeOH], 409 [[(M-Br)⁺]; IR (KBr): $\tilde{\nu}_{max} = 3053$ (w), 3007 (w), 2859 (w), 1692 (vs), 1609 (m), 1587 (m), 1438 (s), 1111 (s), 748 (s), 721 (m), 691 (s), 539 (m), 507 (s), 493 cm⁻¹ (m); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \epsilon) = 250$ (4.34), 264 (4.07), 284 (2.82), 298 (2.94), 308 nm (2.85).

Bromo substituted [23]metacyclophanetriene 37: A solution of phosphonium salt 35 (2.79 g 4.51 mmol) in dry DMF (40 mL) was cooled to -40°C. A freshly prepared solution of LiOEt in ethanol [prepared by dissolving Li (38 mg, 5.5 mmol) in dry ethanol (10 mL)] was added in portions at $-40\,{}^{\rm o}{\rm C}$ during 4 h until the solution on addition of the base did not turn red anymore. After stirring overnight the reaction mixture was diluted with dichloromethane (300 mL) and washed several times with 5M HCl (total: 120 mL). The aqueous solutions were extracted with dichloromethane (100 mL). The combined organic extracts were washed with brine and dried over MgSO4. The solvent was evaporated and the residue purified by column chromatography on SiO₂ (n-hexane/CH₂Cl₂, 20:1-10:1) yielding bromo substituted [23]metacyclophanetriene 37 (170 mg, 15%), as colorless crystals. $R_f = 0.55$ (*n*-hexane/CH₂Cl₂, 5:1); m.p. = 221 °C; ¹H NMR (300 MHz, CD₂Cl₂): δ = 6.56 (s, 3 H), 6.65 (s, 6 H), 7.76 ppm (s, 3H); ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 122.6$, 130.5, 131.3, 136.2, 136.4 ppm; MS (EI+): *m*/*z*: =786/784/782/780/778/776/774 [*M*+]; HRMS: *m*/*z*: calcd for C₂₄H₁₂⁸¹Br₃⁷⁹Br₃: 779.5978, found: 779.5962; IR (KBr): $\tilde{v}_{max} = 3078$ (w), 2922 (w), 2850 (w), 1574 (m), 1450 (s), 1327 (w), 1049 (s), 954 (m), 945 (m), 764 (m), 744 cm⁻¹ (m); UV/vis (n-pentane): $\lambda_{\max}(\log \epsilon) = 224$ (4.32), 276 nm (4.05); elemental analysis calcd (%) for C24H12Br6: C 36.97, H 1.55, Br 61.48; found: C 36.85, H 1.77, Br 61.21.

Methvl substituted [2₃]metacyclophanetrienes 41 a/b and [24]metacyclophanetetraenes 42 a-c: A solution of phosphonium salt 36 (47.8 g, 97.3 mmol) in dry DMF (1 L) was cooled to -10°C. A freshly prepared solution of LiOEt in ethanol [prepared by dissolving Li (810 mg, 117 mmol) in dry ethanol(120 mL)] was added in portions at -10°C during 10 h until the solution on addition of the base did not turn red anymore. After being stirred overnight the reaction mixture was diluted with dichloromethane, washed several times with 5 M HCl and brine and dried over MgSO4. The solvent was evaporated and the residue purified by column chromatography on SiO₂ (n-hexane/CH₂Cl₂, 10:1) yielding the mixture 41a/41b (93:7, 961 mg, 8%), as colorless crystals and **42 a–c** (<1%).

Analytical data for **41** a: R_f =0.41 (*n*-hexane/CH₂Cl₂, 5:1); m.p. =193 °C; ¹H NMR (300 MHz, CD₂Cl₂): δ =1.62 (s, 6H), 2.28 (s, 6H), 2.31 (s, 6H), 6.39 (s, 2H), 6.54 (s, 1H), 6.73 (d, 1H, ³*J*=11.7 Hz), 6.74 (s, 1H), 6.79 (s, 1H), 6.81 (s, 2H), 6.81 (d, 1H, ³*J*=11.7 Hz), 6.89 (s, 2H), 7.19 ppm (s,

1 H); ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 18.5$, 18.8, 19.0, 128.7, 129.7, 130.6, 131.1, 131.4, 132.2, 133.0, 133.6, 133.8, 133.9, 134.0, 135.9, 136.5 ppm; MS (EI+): *m/z*: 390 [*M*+]; HRMS: *m/z*: calcd for C₃₀H₃₀: 390.2347, found: 390.2359; IR (KBr): \tilde{v}_{max} =3003 (s), 2970 (m), 2942 (m), 2915 (s), 2858 (m), 1495 (s), 1448 (s), 1376 (m), 1032 (m), 991 (m), 922 (s), 869 (s), 760 (m), 724 cm⁻¹ (m); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \epsilon) = 282 \text{ nm} (4.06)$; elemental analysis calcd (%) for $C_{30}H_{30}{:}$ C 92.26, H 7.74; found: C 92.40, H 7.70. Analytical data for 42 a: $R_f = 0.34$ (n-hexane/CH₂Cl₂, 5:1); m.p. = 248 °C; ¹H NMR (500 MHz, CD_2Cl_2): $\delta = 1.96$ (s, 6 H), 2.09 (s, 6 H), 2.29 (s, 12 H), 6.31 (s, 2H), 6.50 (s, 2H), 6.61 (s, 2H), 6.63 (s, 2H), 6.82 (s, 2H), 6.85 (s, 2H), 6.93 (s, 2H), 6.96 ppm (s, 2H); 13 C NMR (125 MHz, CD₂Cl₂): $\delta =$ 19.1, 19.3, 19.9, 20.0, 128.3, 128.4, 128.6, 128.8, 129.6, 130.4, 131.6, 132.0, 133.7, 134.2, 134.3, 134.4, 134.5, 134.6, 134.9, 135.0 ppm; MS (EI+): m/z: 520 [*M*+]; HRMS: m/z: calcd for C₄₀H₄₀: 520.3130, found: 520.3121; IR (KBr): \tilde{v}_{max} = 3007 (m), 2966 (w), 2942 (w), 2918 (m), 2861 (w), 1496 (m), 1449 (m), 1376 (w), 1032 (w), 972 (m), 920 (m), 872 (w); UV/vis (CH₂Cl₂): λ_{max} (log ε) = 288 nm (4.51).

Analytical data for **42 b**: $R_{\rm f}$ =0.25 (*n*-hexane/CH₂Cl₂: 5/1); m.p.=289°C (decomp); ¹H NMR (300 MHz, CD₂Cl₂): δ =2.18 (s, 12 H), 2.26 (s, 12 H), 6.61 (s, 4H), 6.72 (s, 4H), 6.94 (s, 4H), 7.58 ppm (s, 4H); ¹³C NMR (75 MHz, CD₂Cl₂): δ =19.3, 19.4, 127.7, 128.0, 128.5, 131.8, 133.7, 134.3, 134.7, 135.5 ppm; MS (EI+): *m/z*: 520 [*M*+]; HRMS: *m/z* calcd for C₄₀H₄₀: 520.3130, found: 520.3137; IR (KBr): $\bar{\nu}_{\rm max}$ =3008 (m), 1968 (m), 2941 (m), 2918 (m), 2864 (w), 1491 (m), 1455 (m), 1376 (w), 1031 (w), 958 (s), 912 (w), 872 cm⁻¹ (w); UV/vis (CH₂Cl₂): $\lambda_{\rm max}(\log \varepsilon)$ =294 nm (4.66).

Analytical data for **42** c: $R_f = 0.16$ (*n*-hexane/CH₂Cl₂, 5:1); m.p. > 260 °C (decomp); ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 2.22$ (s, 6H), 2.34 (s, 6H), 2.45 (s, 6H), 2.48 (s, 6H), 6.68 (s, 2H), 6.98 (s, 4H), 7.04 (s, 2H), 7.08 (s, 2H), 7.09 (s, 2H), 7.30 (s, 2H), 7.64 ppm (s, 2H); ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 18.6$, 19.2, 19.5, 21.9, 128.3, 129.6, 130.4, 131.6, 132.3, 132.7, 132.9, 133.2, 133.3, 134.2, 134.3, 134.6, 134.6, 135.2, 135.9, 136.8 ppm; MS (EI+): *m*/*z*: 520 [*M*+]; HRMS: *m*/*z*: calcd for C₄₀H₄₀: 520.3130, found: 520.3122; IR (KBr): $\tilde{\nu}_{max} = 3006$ (w), 2947 (w), 2918 (w), 2863 (w), 1499 (w), 1453 (w), 1199 (w), 968 cm⁻¹ (w); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \varepsilon) = 300$ nm (4.74).

Methyl substituted *all-cis*-[2₃]metacyclophanetriene 41 b: In an irradiation flask of the mixture 41 a/41 b (961 mg, 2.46 mmol) were dissolved in degassed benzene (500 mL), magnetically stirred and cooled to 5 °C. After 18 h of irradiation at λ =254 nm the solvent was evaporated in vacuo and the residue was purified by column chromatography on SiO₂ (*n*-hexane/CH₂Cl₂, 10:1) yielding 41 b (820 mg, 85%), as colorless crystals. *R*_f=0.41 (*n*-hexane/CH₂Cl₂: 5/1); m.p.=189°C; ¹H NMR (500 MHz, CD₂Cl₂): δ =2.12 (s, 18H), 6.46 (s, 3H), 6.54 (s, 6H), 6.89 ppm (s, 3H); ¹³C NMR (125 MHz, CD₂Cl₂): δ =19.2, 129.1, 129.4, 131.3, 134.2, 134.5 ppm; MS (EI+): *m/z*: 390 [*M*+]; HRMS: *m/z*: calcd for C₃₀H₃₀: 390.2348, found: 390.2346; IR (KBr): $\tilde{\nu}_{max}$ =3004 (s), 2970 (m), 2945 (m), 2916 (s), 2860 (w), 1608 (w), 1491 (s), 1453 (s), 1376 (w), 1032 (w), 925 (s), 909 (m), 864 (m), 763 (m), 749 cm⁻¹ (m); UV/vis (*n*-pentane): λ_{max} -(log ε)=214 (4.38), 260 nm (4.39); elemental analysis calcd (%) for C₃₀H₃₀: C 92.26, H 7.74; found: C 92.27, H 7.64.

Bromomethyl substituted [23]metacyclophanetriene 43: A sample of Nbromosuccinimide (5.21 g, 29.3 mmol) and dibenzoylperoxide (45 mg, 0.186 mmol) were added to a solution of methyl substituted all-cis- $[2_3]\mbox{metacyclophantriene}$ 41 b (1.43 g, 3.66 mmol) in dry \mbox{CCl}_4 (225 mL). The mixture was stirred at reflux for 5 h, cooled to RT and filtrated to remove the succinimide. The filtrate was washed with aq. NaOH, water, and brine, dried (MgSO₄) and evaporated to dryness in vacuo. The residue was purified by column chromatography on SiO2 (n-hexane/CH2Cl2, 5:1-1:1) yielding benzylic hexabromide 43 (1.28 g, 40%), as colorless crystals. $R_{\rm f} = 0.39$ (*n*-hexane/CH₂Cl₂, 1:1); m.p. = 239 °C (decomp); ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 4.41$ (s, 18 H), 6.63 (s, 3 H), 6.83 (s, 6 H), 7.32 ppm (s, 3H); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 31.2, 129.0, 131.4, 132.2, 135.3, 136.8 ppm; MS (EI+): m/z: 870/868/866/864/862/860/858 [M+]; HRMS: m/z: calcd for $C_{30}H_{24}^{79}Br_3^{81}Br_3$: 862.6917, found: 862.6962; IR (KBr): $\tilde{\nu}_{max}$ = 3012 (w), 2972 (w), 1635 (b), 1489 (w), 1445 (w), 1210 (s), 933 (m), 587 cm⁻¹ (m); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \epsilon) = 236$ (4.75), 288 nm (4.50); elemental analysis calcd (%) for $\rm C_{30}H_{24}Br_6$: C 41.71, H 2.80, Br 55.49; found: C 41.52, H 2.85, Br 55.33.

Formyl substituted [23]metacyclophanetriene 28: To a solution of IBX (2.36 g, 8.43 mmol)^[23] in dry DMSO (13 mL) was added a solution of benzylic hexabromide 43 (607 mg, 0.703 mmol) in dry DMSO (5 mL). The resulting yellowish solution was stirred at 65 °C for 8 h and at RT overnight. Aqueous Na₂S₂O₃ (30 mL) and aq. sat. NaHCO₃ (30 mL) were added and the mixture was extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined organic extracts were washed with brine, dried, and the solvent was evaporated in vacuo. Column chromatography on SiO₂ (nhexane/ethyl acetate, 2:1-1:1) yielded hexaaldehyde 28 (125 mg, 37%), as colorless crystals. $R_{\rm f}$ =0.58 (*n*-hexane/ethyl acetate, 1:2); ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 6.53 \text{ (s, 3H)}, 7.30 \text{ (s, 6H)}, 8.25 \text{ (s, 3H)}, 10.10 \text{ ppm}$ (s, 6H); 13 C NMR (75 MHz, CDCl₃): $\delta = 130.8$, 133.1, 133.4, 135.3, 142.6, 190.4 ppm; MS (FAB+): m/z: 475 [(M+H)⁺]; HRMS: m/z: calcd for $C_{30}H_{19}O_6$: 475.1181, found: 475.1177; IR (KBr): $\tilde{\nu}_{max} = 2966$ (w), 2938 (w), 2853 (w), 1695 (vs), 1594 (s), 1540 (w), 1237 (m), 1224 (m), 1162 (m), 936 (w), 827 cm⁻¹ (w); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \epsilon) = 244$ (5.01), 310 nm (4.71); elemental analysis calcd (%) for C₃₀H₁₈O₆: C 75.94, H 3.82; found: C 75.54, H 3.79.

[6.8]₃Cyclacene (13): A suspension of 1.37 g TiCl₃·DME_{1.5}^[24] and Zn–Cu (1.24 g)^[24] in dry DME (35 mL) was stirred under reflux for 2 h. A solution of **28** (50 mg 0.105 mmol) in dry DME (8 mL) was slowly added to the black-grey suspension and the reaction mixture was stirred under reflux for 5 h. After stirring at RT overnight the mixture was filtrated over a pad of florisil, which was subsequently washed with dichloromethane. The solvent was evaporated in vacuo and the residue was purified by column chromatography on SiO₂ (*n*-hexane/CH₂Cl₂, 10:1) affording **13** (3 mg, 8%), as colorless needles. *R*_f=0.38 (*n*-hexane/CH₂Cl₂, 5:1); ¹H NMR (500 MHz, CD₂Cl₂): δ =6.36 (s, 6H), 6.73 ppm (s, 12H); ¹³C NMR (125 MHz, CD₂Cl₂): δ =125.2, 133.1, 136.1 ppm; MS (EI +): *m*/*z*: 378 [*M*+]; HRMS: *m*/*z*: calcd for C₃₀H₁₈: 378.1408, found: 378.1400; UV/vis (*n*-pentane): $\lambda_{max}(\log \varepsilon)$ =220 (4.69), 278 (3.40), 290 nm (3.32).

5-Ethynyl-2,4-dimethylbenzaldehyde (51): A solution of 5-iodo-2,4-dimethylbenzaldehyde 50 (32 g, 123 mmol) in THF (250 mL) and iPr_2NH (100 mL) was degassed by bubbling argon through the solution. After cooling to 0°C, [Pd(PPh₃)₄] (4.26 g, 3.69 mmol) and CuI (1.40 g, 7.35 mmol) were added and the mixture was stirred at RT for 10 min. An amount of TMSA (21.9 mL, 153 mmol) was slowly added in a dropwise manner, and the reaction mixture was stirred for 2 h at RT. After diluting with ethyl acetate (200 mL) the mixture was successively washed with ice cold 2M HCl (3×200 mL) and sat. aq. NH₄Cl (3×100 mL). The organic layer was dried over Na2SO4, evaporated to dryness, and the residue was purified by column chromatography on SiO2 (n-hexane/ethyl acetate, 20:1) giving 2,4-dimethyl-5-((trimethylsilyl)ethynyl)benzaldehyde (27.4 g, 97%), as white solid. $R_f = 0.72$ (*n*-hexane/ethyl acetate, 7:3); m.p. = 44°C; ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 0.25$ (s, 9H), 2.44 (s, 3H), 2.60 (s, 3H), 7.11 (s, 1H), 7.80 (s, 1H), 10.13 ppm (s, 1H); ¹³C NMR (125 MHz, CD_2Cl_2): $\delta = -0.3$, 19.3, 20.7, 99.1, 102.4 121.4, 132.2, 133.0, 135.7, 140.8, 146.6, 191.5 ppm; MS (EI+): m/z: 230 [M+]; HRMS: m/z: calcd for C14H18OSi: 230.1127, found: 230.1113; IR (KBr): vmax=2960 (m), 2155 (m), 1705 (s), 1690 (s), 1606 (m), 1251 (s), 1081 (m), 902 (m), 870 (s), 841 (s), 761 cm⁻¹ (s); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \varepsilon) = 244$ (3.66), 266 (3.27), 276 (3.04), 314 nm (2.16); elemental analysis calcd (%) for $C_{14}H_{18}OSi$: C 72.99, H 7.88; found: C 72.56, H 7.88.

To a solution of 2,4-dimethyl-5-((trimethylsilyl)ethynyl)benzaldehyde (22.6 g, 98.1 mmol) in degassed MeOH (1 L) and DCM (100 mL) was added K₂CO₃ (27.2 g, 196 mmol), and the resulting mixture was stirred for 1 h at RT under an argon atmosphere. After removal of the solvent in vacuo at RT the residue was poured into ice cold water (200 mL) and extracted with dichloromethane (3×100 mL). The combined organic extracts were washed with water (2×50 mL) and brine. After drying over Na₂SO₄, the solvent was evaporated in vacuo at RT. The residue was purified by column chromatography on SiO₂ (*n*-hexane/diethyl ether, 20:1–10:1) yielding 5-ethynyl-2,4-dimethylbenzaldehyde **51** (15.3 g, 98%), as colorless needles. R_i =0.56 (*n*-hexane/diethyl ether, 7:3); m.p.=88°C; ¹H NMR (500 MHz, CD₂Cl₂): δ =2.46 (s, 3H), 2.60 (s, 3H), 3.36 (s, 1H), 7.13 (s, 1H), 7.84 (s, 1H), 10.14 ppm (s, 1H); ¹³C NMR (125 MHz,

CD₂Cl₂): δ =19.3, 20.6, 81.1, 81.5, 120.3, 132.3 133.1, 136.1, 141.1, 146.7, 191.4 ppm; MS (EI+): *m*/*z*: 158 [*M*+]; HRMS: *m*/*z*: calcd for C₁₁H₁₀O: 158.0731, found: 158.0742; IR (KBr): $\tilde{\nu}_{max}$ =3206 (s), 2093 (w), 1682 (s), 1608 (m), 1378 (w), 1260 (w), 1175 (w), 1060 (w), 903 cm⁻¹ (w); UV/vis (CH₂Cl₂): λ_{max} (log ε)=238 (4.74), 262 (4.28), 308 nm (3.37); elemental analysis calcd (%) for C₁₁H₁₀O: C 83.51, H 6.37; found: C 83.50, H 6.39.

5,5'-(Ethyne-1,2-diyl)bis(2,4-dimethylbenzaldehyde) (48): A solution of 5-iodo-2,4-dimethylbenzaldehyde 50 (25.1 g, 96.5 mmol) in THF (200 mL) and $\mathit{i}Pr_2NH$ (80 mL) was degassed by bubbling argon through the solution. $[Pd(PPh_3)_4]$ (2.23 g, 1.93 mmol) and CuI (735 mg, 3.86 mmol) were added and the mixture was stirred at RT for 10 min. A solution of 5-ethynyl-2,4-dimethylbenzaldehyde 51 (15.3 g, 96.8 mmol) in THF (50 mL) was added dropwise, and the reaction mixture was allowed to stir for 2 h at RT. After diluting with dichloromethane (200 mL) the reaction mixture was successively washed with ice cold 2M HCl (3× 200 mL) and sat. aq. NH₄Cl (3×100 mL). The organic extracts were dried over Na₂SO₄, and the solvent was removed in vacuo. The residue was purified by column chromatography on SiO₂ (n-hexane/diethyl ether, 10:1-5:1) yielding 5,5'-(ethyne-1,2-diyl)bis(2,4-dimethylbenzaldehyde) 48 (27.4 g, 98%), as colorless needles. $R_{\rm f} = 0.40$ (n-hexane/diethyl ether, 7:3); m.p. = 164 °C; ¹H NMR (500 MHz, CD_2Cl_2): δ = 2.55 (s, 3H), 2.63 (s, 3 H), 7.17 (s, 1 H), 7.91 (s, 1 H), 10.18 ppm (s, 1 H); $^{13}\mathrm{C}\,\mathrm{NMR}$ (125 MHz, CD_2Cl_2): $\delta = 19.3$, 21.0, 91.4, 121.4, 132.4 133.2, 135.3, 140.8, 146.0, 191.5 ppm; MS (EI+): *m/z*: 290 [*M*+]; HRMS: *m/z*: calcd for C₂₀H₁₈O₂: 290.1307, found: 290.1322; IR (KBr): $\tilde{\nu}_{max}$ =2920 (w), 2864 (w), 1701 (s), 1687 (vs), 1609 (s), 1407 (m), 1178 (m), 1100 (w), 903 (w), 866 cm⁻¹ (w); UV/vis (CH₂Cl₂): $\lambda_{max}(\log \epsilon) = 258$ (4.70), 298 (4.44), 308 nm (4.37); elemental analysis calcd (%) for $C_{20}H_{18}O_2$: C 82.73, H 6.25; found: C 82.53, H 6.15.

Methyl substituted [24]metacyclophandienediyne 47: To a suspension of Zn dust (20.8 g, 320 mmol) and CuI (2.13 g, 11.2 mmol) in dry DME (700 mL) were added TiCl₄ (17.6 mL, 160 mmol). The bluish-green suspension was refluxed for 3 h resulting in a dark grey suspension. After cooling to RT, a solution of 5,5'-(ethyne-1,2-diyl)bis(2,4-dimethylbenzaldehyde) 48 (4.64 g, 16.0 mmol) in dry DME (150 mL) was added by means of a syringe pump within 7 h and the mixture was stirred another 15 h at RT. The reaction mixture was filtered through a pad of Al₂O₃, which was subsequently washed with dichloromethane (500 mL). The solvent was evaporated in vacuo, the residue absorbed on Al_2O_3 (4 g) and purified by column chromatography on Al2O3 (n-hexane/dichloromethane, 10:1-5:1) yielding methyl substituted[24]metacyclophandienediyne 47 (445 mg, 11%), as colorless needles. $R_{\rm f} = 0.22$ (*n*-hexane/CH₂Cl₂, 5:1); ¹H NMR (500 MHz, CDCl₃): $\delta = 2.19$ (s, 12H), 2.34 (s, 12H), 6.69 (s, 4H), 6.91 (s, 4H), 7.59 ppm (s, 4H); 13 C NMR (151 MHz, CDCl₃): $\delta =$ 19.9, 20.5, 91.5, 120.2, 130.0, 130.7, 133.3, 133.7, 136.0, 138.2 ppm; MS (EI+): *m*/*z*: 516 [*M*+]; HRMS: *m*/*z*: calcd for C₄₀H₃₆: 516.2817, found: 516.2792; IR (KBr): $\tilde{\nu}_{max}$ =3011 (w), 2944 (w), 2916 (w), 2862 (w), 1495 (m), 1448 (m), 1376 (w), 1032 (w), 969 (w), 908 (w), 873 $\rm cm^{-1}$ (w); UV/ vis (*n*-pentane): $\lambda_{max}(\log \epsilon) = 218$ (3.26), 228 (3.24), 294 (3.49), 304 (3.37), 314 nm (3.33).

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- a) J. W. Steed, J. L. Atwood, Supramolecular Chemistry, Wiley, New York, 2000; b) H. J. Schneider, Y. Yatsimirsky, Principles and Methods in Supramolecular Chemistry, Wiley, New York, 2000.
- [2] a) J. M. Lehn, "Supramolecular Chemistry: Concepts and Perspectives", VCH, Weinheim, 1995; b) F. Vögtle, "Supramolekulare Chemie", Teubner, Stuttgart 1992; c) D. Philp, J. F. Stoddart, Angew. Chem. 1996, 108, 1242–1286; Angew. Chem. Int. Ed. Engl. 1996, 35, 1154–1196.

A EUROPEAN JOURNAL

- [3] Reviews: a) F. H. Kohnke, J. P. Mathias, J. F. Stoddart, Top. Curr. Chem. 1993, 165, 1-69; b) A. Schröder, H.-B. Mekelburger, F. Vögtle, Top. Curr. Chem. 1994, 172, 179-201; c) L. T. Scott, Angew. Chem. 2003, 115, 4265-4267; Angew. Chem. Int. Ed. 2003, 42, 4133-4135; d) R. Herges in Modern Cyclophane Chemistry (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim 2004, pp. 337-358; e) R. Gleiter, B. Hellbach, S. Gath, R. J. Schaller, Pure Appl. Chem. 2006, 78, 699-706; f) K. Tahara, Y. Tobe, Chem. Rev. 2006, 106, 5274-5290.
- [4] E. Heilbronner, Helv. Chim. Acta 1954, 37, 921-935.
- [5] a) S. Iijima, T. Ichihashi, Nature 1993, 363, 603-605; b) D. S. Bethune, C. H. Klang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 1993, 363, 605-607.
- [6] a) F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, Angew. Chem. 1987, 99, 941-943; Angew. Chem. Int. Ed. Engl. 1987, 26, 892-894; b) P. R. Ashton, N. S. Isaacs, F. H. Kohnke, A. M. Z. Slawin, C. M. Spencer, J. F. Stoddart, D. J. Williams, Angew. Chem. 1988, 100, 981-983; Angew. Chem. Int. Ed. Engl. 1988, 27, 966-969; c) P. R. Ashton, G. R. Brown, N. S. Isaacs, D. Giuffrida, F. H. Kohnke, J. P. Mathias, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart, D. J. Williams, J. Am. Chem. Soc. 1992, 114, 6330-6353.
- [7] a) R. M. Cory, C. L. McPhail, A. J. Dikmans, J. J. Vittal, Tetrahedron Lett. 1996, 37, 1983-1986; b) R. M. Cory, C. L. McPhail, Tetrahedron Lett. 1996, 37, 1987-1990.
- [8] a) A. Godt, V. Enkelmann, A.-D. Schlüter, Angew. Chem. 1989, 101, 1704-1706; Angew. Chem. Int. Ed. Engl. 1989, 28, 1680-1682; b) O. Kintzel, P. Luger, M. Weber, A.-D. Schlüter, Eur. J. Org. Chem. 1998, 99-105; c) W. D. Neudorff, D. Lentz, M. Anibarro, A. D. Schlüter, Chem. Eur. J. 2003, 9, 2745-2757; d) M. Stuparu, D. Lentz, H. Rüegger, A. D. Schlüter, Eur. J. Org. Chem. 2007, 88-100; e) M. Stuparu, V. Gramlich, A. Stanger, A. D. Schlüter, J. Org. Chem. 2007, 72, 424-430.
- [9] a) H. S. Choi, K. S. Kim, Angew. Chem. 1999, 111, 2400-2402; Angew. Chem. Int. Ed. 1999, 38, 2256-2258; b) Z. Chen, D. Jiang, X. Lu, H. F. Bettinger, S. Dai, P. v. R. Schleyer, K. N. Houk, Org. Lett. 2007, 9, 5449-5452.
- [10] a) J. Aihara, J. Chem. Soc. Perkin Trans. 2 1994, 971-974; b) L. Türker, THEOCHEM 2001, 536, 235-241; c) Y. Matsuo, K. Tahara, E. Nakamura, Org. Lett. 2003, 5, 3181-3184.
- [11] a) E. Nakamura, K. Tahara, Y. Matsuo, M. Sawamura, J. Am. Chem. Soc. 2003, 125, 2834-2835; b) Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, J. Am. Chem. Soc. 2004, 126, 8725-8734.
- [12] B. Esser, J. A. Raskatov, R. Gleiter, Org. Lett. 2007, 9, 4037-4040.
- [13] a) B. Hellbach, F. Rominger, R. Gleiter, Angew. Chem. 2004, 116, 5970-5973; Angew. Chem. Int. Ed. 2004, 43, 5846-5849; b) S. C. Kornmayer, B. Hellbach, F. Rominger, R. Gleiter, Chem. Eur. J. 2009, 15, 3380-3389.
- [14] B. Esser, F. Rominger, R. Gleiter, J. Am. Chem. Soc. 2008, 130, 6716-6717.
- [15] a) C. Brown, M. V. Sargent, J. Chem. Soc. C 1969, 1818-1820; b) C. E. Griffin, J. A. Peters, J. Org. Chem. 1963, 28, 1715-1716.
- [16] O. Farooq, Synthesis 1994, 1035–1036. [17] A. Schröder, D. Karbach, R. Güther, F. Vögtle, Chem. Ber. 1992,
- 125.1881-1887. [18] a) D. Tanner, O. Wennerström, Acta Chem. Scand. Ser. B 1983, 37, 693-698; b) T. Kawase, N. Ueda, M. Oda, Tetrahedron Lett. 1997.
- 38, 6681-6684; c) Y. Kuwatani, J. Igarashi, M. Iyoda, Tetrahedron Lett. 2004, 45, 359-362. [19] A. Jakobs, L. Christiaens, M. Renson, Bull. Soc. Chim. Belg. 1991,
- 100.1-4.
- [20] Dialdehyde 23 was prepared from 1,5-bis(chloromethyl)-2,4-dimethyl-benzene (M. Gerisch, J. R. Krumper, R. G. Bergman, T. D. Tilley, Organometallics 2003, 22, 47-58) in a Sommelet reaction following the procedure by Wood (J. H. Wood, C. C. Tung, M. A. Perry, R. E. Gibson, J. Am. Chem. Soc. 1950, 72, 2992-2993) for 2,5-dimethylterephthalaldehyde.
- [21] CCDC 676676 (28), 676674 (41a), 676673 (41b), and 676675 (43) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_ request/cif

- [22] M. Frigerio, M. Santagostino, Tetrahedron Lett. 1994, 35, 8019-8022.
- [23] J. N. Moorthy, N. Singhal, K. Senapati, Tetrahedron Lett. 2006, 47, 1757 - 1761.
- [24] J. E. McMurry, T. Lectka, J. G. Rico, J. Org. Chem. 1989, 54, 3748-3749.
- [25] Crystallographic data for 13: Colorless crystals (plates), dimensions $0.44 \times 0.09 \times 0.05$ mm, crystal system monoclinic, space group $P2_1/c$, Z=4, a=15.3781(6) Å, b=6.8444(3) Å, c=18.2608(7) Å, $a=90^{\circ}$, $\beta = 90.6650(10)^{\circ}$, $\gamma = 90^{\circ}$, $V = 1921.89(13) \text{ Å}^3$, $\rho = 1.308 \text{ g cm}^{-3}$, T =200(2) K, $\Theta_{\text{max}} = 22.00^{\circ}$, radiation Mo_{Ka}, $\lambda = 0.71073$ Å, 0.3° ω -scans with CCD area detector Bruker Smart CCD, covering a whole sphere in reciprocal space: 11783 reflections measured, 2340 unique (R(int) = 0.0699), 1722 observed ($I > 2\sigma(I)$); intensities were corrected for Lorentz and polarization effects; an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 0.07 \text{ mm}^{-1}$, $T_{\min} = 0.97$, $T_{\max} = 1.00$; structure solved by direct methods and refined against F^2 with a Fullmatrix least-squares algorithm using the SHELXTL-PLUS (6.10) software package,^[41] 273 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.11 for observed reflections, final residual values R1(F) = 0.050, $wR(F^2) = 0.101$ for observed reflections, residual electron density -0.20 to 0.15 eÅ⁻³. CCDC 676676 contains the supplementary crystallographic data for this structure.
- [26] K. H. Claus, C. Krüger, Acta Cryst. Sect. C 1988, 44, 1632-1634.
- [27] H. Irngartinger, W. R. K. Reibel, Acta Cryst. Sect. B 1981, 37, 1724-1728.
- [28] A. Bondi, J. Phys. Chem. 1964, 68, 441-451.
- [29] a) G. R. Desiraju, T. Steiner, The Weak Hydrogen Bond, Oxford University Press, Oxford, 1999, pp. 122 ff.; b) M. Nishio, M. Hirota, Y. Umezawa, The CH- π Interaction, Evidence, Nature, and Conseauences Wiley-VCH Weinheim 1998.
- [30] Crystallographic data for 37: Colorless crystals (irregular), dimensions 0.30×0.06×0.03 mm, crystal system monoclinic, space group $P2_1/c$, Z=4, a=13.616(3) Å, b=12.804(3) Å, c=14.385(3) Å, a=12.804(3) Å 90°, $\beta = 112.778(4)$ °, $\gamma = 90$ °, V = 2312.2(9) Å³, $\rho = 2.240$ g cm⁻³, T =100(2) K, $\Theta_{max} = 25.03^{\circ}$, radiation Mo_{Ka} , $\lambda = 0.71073$ Å, 0.3° ω -scans with CCD area detector, covering a whole sphere in reciprocal space, 17926 reflections measured, 4069 unique (R(int) = 0.0572), 3197 observed $(I > 2\sigma(I))$, intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 10.43 \text{ mm}^{-1}$, $T_{\min} = 0.15$, $T_{\max} = 0.75$, structure solved by direct methods and refined against F^2 with a Full-matrix leastsquares algorithm using the SHELXTL (6.12) software package,^[41] 271 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F) = 0.032, $wR(F^2) = 0.065$ for observed reflections, residual electron density -0.81 to 0.67 $e \text{ Å}^{-3}$
- [31] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh

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PA, **2003**, method using the B3LYP functional in combination with Pople's 6-31G* basis set; R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.

- [32] a) H. A. Bent, Chem. Rev. 1968, 68, 587–648; b) N. Ramasubbu, R. Parthasarathy, P. Murray-Rust, J. Am. Chem. Soc. 1986, 108, 4308–4314; c) G. R. Desiraju, R. Parthasarathy, J. Am. Chem. Soc. 1989, 111, 8725–8726; d) M. Baier, R. Gleiter, F. Rominger, Eur. J. Org. Chem. 2006, 5264–5278; e) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, Angew. Chem. 2008, 120, 6206–6220; Angew. Chem. Int. Ed. 2008, 47, 6114–6127.
- [33] a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636; b) K. W. Klinkhammer,
 P. Pyykkö, *Inorg. Chem.* **1995**, *34*, 4134–4138; c) C. Bleiholder, D. B.
 Werz, H. Köppel, R. Gleiter, *J. Am. Chem. Soc.* **2006**, *128*, 2666–2674.
- [34] Crystallographic data for 42a: Colorless crystals (needle), dimensions $0.36 \times 0.22 \times 0.14$ mm, crystal system triclinic, space group $P\bar{1}$, Z=2, a=7.8036(10) Å, b=13.3424(18) Å, c=15.320(2) Å, a=73.608(3)°, β=81.289(3)°, γ=85.850(3)°, V=1511.9(3) Å³, ρ= 1.144 g cm⁻³, T=200(2) K, $Θ_{max}$ =28.35°, radiation Mo_{Kα}, λ= 0.71073 Å, 0.3° ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 16047 reflections measured, 7473 unique (R(int) = 0.0353), 4694 observed $(I > 2\sigma(I))$, intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 0.06 \text{ mm}^{-1}$, $T_{\min} = 0.98$, $T_{\max} = 0.99$, structure solved by direct methods and refined against F^2 with a Fullmatrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package,^[41] 536 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.08 for observed reflections, final residual values R1(F) = 0.073, $wR(F^2) = 0.149$ for observed reflections, residual electron density -0.17 to $0.19 \ e \text{ Å}^{-3}$.
- [35] Crystallographic data for 42b: Colorless crystals (polyhedron), dimensions 0.50×0.10×0.08 mm, crystal system monoclinic, space group P2₁/c, Z=8, a=9.2735(2) Å, b=21.0321(2) Å, c=30.5409(7) Å, $\alpha = 90^{\circ}$, $\beta = 91.6290(10)^{\circ}$, $\gamma = 90^{\circ}$, V = 5954.3(2) Å³, $\rho =$ 1.162 g cm⁻³, T = 200(2) K, $\Theta_{max} = 21.51^{\circ}$, radiation $Mo_{K\alpha}$, $\lambda =$ 0.71073 Å, 0.3° ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 36055 reflections measured, 6846 unique (R(int)=0.1644), 3319 observed $(I>2\sigma(I))$, intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 0.06 \text{ mm}^{-1}$, $T_{\min} = 0.97$, $T_{\max} = 0.99$, structure solved by direct methods and refined against F^2 with a Fullmatrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package,^[41] 737 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 0.98 for observed reflections, final residual values R1(F) = 0.058, $wR(F^2) = 0.107$

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for observed reflections, residual electron density -0.21 to $0.18 e \text{ Å}^{-3}$.

- [36] Crystallographic data for 42c: Colorless crystals (polyhedron), dimensions $0.26 \times 0.16 \times 0.15$ mm, crystal system monoclinic, space group $P2_1/c$, Z=4, a=21.7693(1) Å, b=16.6745(3) Å, c =8.2746(2) Å, $\alpha = 90^{\circ}$, $\beta = 94.9370(10)^{\circ}$, $\gamma = 90^{\circ}$, V = 2992.47(9) Å³, $\rho =$ 1.156 g cm⁻³, T = 200(2) K, $\Theta_{max} = 21.52^{\circ}$, radiation $Mo_{K\alpha}$, $\lambda =$ 0.71073 Å, 0.3° ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 17181 reflections measured, 3439 unique (R(int)=0.1351), 2200 observed $(I>2\sigma(I))$, intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 0.06 \text{ mm}^{-1}$, $T_{\min} = 0.98$, $T_{\max} = 0.99$, structure solved by direct methods and refined against F^2 with a Fullmatrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package,^[41] 370 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F) = 0.058, $wR(F^2) = 0.125$ for observed reflections, residual electron density -0.22 to $0.23 \ e \text{ Å}^{-3}$.
- [37] P. Lulinski, L. Skulski, Bull. Chem. Soc. Jpn. 1997, 70, 1665-1669.
- [38] T. Iida, T. Wada, K. Tomimoto, T. Mase, *Tetrahedron Lett.* 2001, 42, 4841–4844.
- [39] T. Kawase, Y. Nishiyama, T. Nakamura, T. Ebi, K. Matsumoto, H. Kurata, M. Oda, Angew. Chem. 2007, 119, 1104–1106; Angew. Chem. Int. Ed. 2007, 46, 1086–1088.
- [40] Crystallographic data for 47: Colorless crystals (needle), dimensions $0.37 \times 0.08 \times 0.05$ mm, crystal system monoclinic, space group C2/c, Z=4, a=16.282(2) Å, b=13.810(2) Å, c=13.013(2) Å, $a=90.0^{\circ}, \beta=$ 98.207(3)°, $\gamma = 90.0°$, $V = 2896.0(7) \text{ Å}^3$, $\rho = 1.185 \text{ g cm}^{-3}$, T = 200(2) K, Θ_{max} =26.37°, radiation Mo_{Ka}, λ =0.71073 Å, 0.3° ω -scans with CCD area detector, covering a whole sphere in reciprocal space, 12972 reflections measured, 2963 unique (R(int) = 0.0460), 2330 observed $(I > 2\sigma(I))$, intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS^[41] based on the Laue symmetry of the reciprocal space, $\mu = 0.07 \text{ mm}^{-1}$, $T_{\min} = 0.98$, $T_{\max} = 1.00$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (6.12) software package,^[41] 253 parameters refined, hydrogen atoms were refined isotropically, goodness of fit 1.20 for observed reflections, final residual values R1(F) = 0.071, $wR(F^2) = 0.133$ for observed reflections, residual electron density -0.17 to 0.21 e Å⁻³.
- [41] G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 2006.

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