ChemPubSoc Europe

DOI: 10.1002/ejoc.201501228

EurJOC European Journal of Organic Chemistry

Full Paper

Fused Aromatic Ring Systems

# High-Yielding Synthesis and Full Spectroscopic Characterization of 5,6:11,12-Di-*o*-phenylenetetracene and Its Synthesis Intermediates

Tobias Wombacher,[a] Sabine Foro,[b] and Jörg J. Schneider*[a]

**Abstract:** Herein we present a synthetic gram-scale route to 5,6:11,12-di-*o*-phenylenetetracene (DOPT, **8**), which is a member of the class of cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs). Full analytical characterization of the title compound was carried out by IR, Raman, UV/Vis, and high-field $^1$H NMR spectroscopy, as well as by mass spectrometry. A unique double-elimination of phenylide moieties, as the key reaction step, gave DOPT for the first time in high purity and in an isolated yield of >70 %. Re-aromatization of the annulated π-ring system occurred following the reductive elimination of the two phenyl groups from the DOPT precursor. Two alternative reaction pathways for this process are discussed. The synthetic method described herein may allow development of the chemistry of the title compound further, for example, to investigate the organometallic chemistry of DOPT as well as its semiconducting behavior in organic electronics.

## Introduction

According to their inter-ring connectivity, polycyclic aromatic hydrocarbons (PAHs)[1–3] can be categorized into PAHs with 1) exclusively alternating benzenoidic rings of preferentially high planarity and 2) geodesic polyarenes that exhibit five-membered rings with curved surfaces as a characteristic structural feature.[4] Both of them display different chemical reactivity and properties that have been intensively studied.[5,6] In this context, a rational gram-scale synthesis of 5,6:11,12-di-*o*-phenylenetetracene (DOPT, **8**; Figure 1) is of interest due to the expected planarity of its highly conjugated π-electron system. This structural property might offer new applications for the CP-PAH DOPT as a multifunctional π-perimeter ligand, for example, in arene–metal chemistry, as well as a unique material in organic electronic applications.

Our previous studies in the field of organometallic chemistry of polycondensed aromatics focused on the reactions of PAH anion ($PAH^{2-/3-/4-}$) solutions and their reactions with {($Cp^R$)M} half-sandwich complexes of iron, namely [($\eta^5$-$Me_4EtC_5$)-$Fe^{II}Cl$(*N*,*N*,*N*′,*N*′-tmeda)],[7] as well as cobalt and nickel, for example, [($\eta^5$-$Me_4RC_5$)M($\eta^2$-*O*-acac)] (M = Co, Ni; R = Me or Et).[8,9] Our attention was drawn to the coordination behavior and electron-transfer characteristics of the resulting multidecker metal complexes.[7–11] The extended conjugation of the title molecule

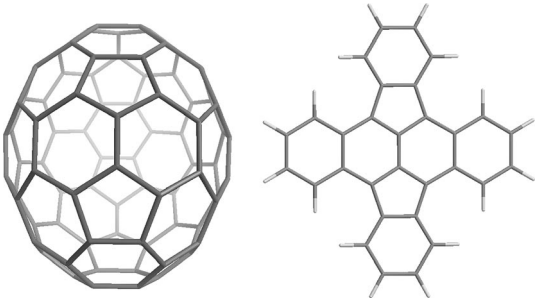

Figure 1. Left: $D_{2d}$ isomer of the geodesic $C_{84}$ fullerene showing the constituent half-bowl fragment of DOPT **8**. Right: Schematic representation of the all-planar cruciform skeleton of DOPT (**8**).

DOPT might enable comparable multiple electronic reduction behavior giving access to potentially stable anionic derivatives of **8**. As a consequence, **8** might serve as a bridging π-perimeter ligand in organometallic chemistry. The two-fold nonalternating fluoranthene moiety may enable the coordination of transition metals at the periphery or in the center ring of **8**. Such studies could help to elucidate general trends in the site preference of the metal coordination of polyarenes. For instance, we have already identified a systematic coordination scheme for the PAH decacyclene, depending on the coordinating metal–ligand fragments introduced.[7–9] We found that metal coordination occurs at those positions that result in the highest aromaticity for the remaining conjugated PAH fragment of the parent hydrocarbon. According to these results, a preferred coordination to the peripheral phenylene groups is expected for DOPT and will be a focus of future studies. In addition, the inner tetracenic, highly conjugated arene core of **8** might be of interest for organic electronic device applications. Most linearly condensed polyacenes, for example, anthracene,[12] rubicene,[13] tetracene,

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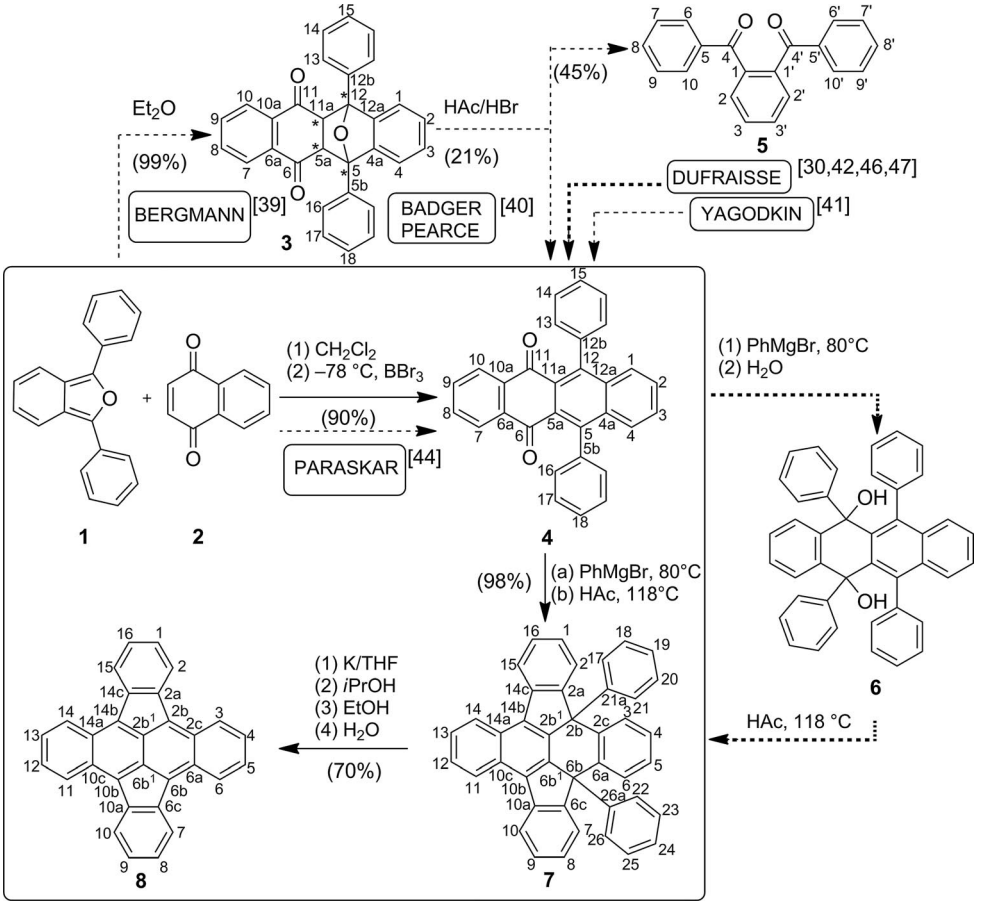
*Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejoc.201501228.*

rubrene,[14] and pentacene,[15] exhibit semiconducting properties and are used as organic p-type semiconductors in organic light-emitting diodes,[16] organic field-effect transistors (OFETs),[17] as well as for biosensor applications.[16] Interestingly the overall carbon connectivity in **8** is found as a basic structural feature in the three fullerenes $C_{78}$, $C_{82}$, and $C_{84}$. Moreover, most of the highly symmetrical fullerene isomers bearing isolated pentagonal rings show multiple fragments of the DOPT molecule (Figure 1).[18–21]

Because DOPT is embedded in the closed geodesic fullerene molecule (e.g., $C_{84}$), its structure deviates significantly from the overall planarity expected for the free DOPT molecule. The synthetic approaches to large polyacenes such as **8** (typically >6 fused rings) mostly involve harsh reaction conditions or high-temperature methods typically in the gas phase with a large number of synthesis steps and possibly with the formation of multiple isomers.[4,22,23] However, the synthesis of such large PAHs is possible in solution, for example, by utilizing enamine chemistry,[24] Diels–Alder,[3,25,26] aryne,[27] and aldol cyclization reactions,[28] allowing the construction of the main carbon skeleton followed by various re-aromatization steps to finally yield the desired PAH. Indeed, such routes have led to a broader scope of available polycyclic hydrocarbons with five- and six-membered rings and their derivatives.[1] The title PAH molecule DOPT was first claimed to be obtained in very low yields by Dufraisse and co-workers about 80 years ago.[29–31] Simultaneously, Badoche presented a route starting from 1,1-diphenyl-2-propyn-1-ol.[32,33] Several additional attempts to obtain DOPT were made by Lang and Theiling starting from 5,6,6,11,11,12-hexachloro-5,12-dihydrotetracene and by Wittig et al. employing a Diels–Alder [4+2] cycloaddition of 1,3-diphenylisobenzofuran (DPhIBF, **1**), and 1,4-dihydro-1,4-epoxynaphthalene about 30 years later.[34,35] However, all the above-mentioned routes give very low yields and various impurities that impede complete purification and subsequent characterization and scale-up, and as such suffer minor shortcomings with respect to exploring the chemistry of DOPT further. Very recently, Murata et al.[36] published a Pd-catalyzed route to DOPT and its derivatives starting from 5,11-dibromotetracene.[37] This route utilized an intramolecular Scholl coupling reaction with a high excess of $FeCl_3$ as oxidant.[36,38]

Herein, we present a straightforward synthetic approach to DOPT that combines and simplifies all of the various reported reaction sequences and give a complete spectroscopic and




Scheme 1. Complete schematic overview of the most important reaction sequences towards **8** from intermediate **4**. The initial routes of Dufraisse[30] and Bergmann[39] were confirmed by characterizing the intermediate reaction products completely and were further developed by the protocols of Badger and Pearce,[40] Yagodkin,[41] and Paraskar[44] and their co-workers. Our successful final route to DOPT is shown in the box. It yields 5,6:11,12-di-*o*-phenylenetetracene (DOPT, **8**) in an overall yield of >70 % with high purity.

structural characterization of the product as well as earlier proposed reaction intermediates that have now been analytically verified for the first time. Our route relies on the reported Diels–Alder-type chemistry, but introduces a new and, to the best of our knowledge, so far unprecedented elimination step based on an electron-transfer reduction sequence. The combination of both gives the title compound in high yield, without utilizing any transition-metal catalyst. Additionally, we have been able to confirm some long-standing assumptions[30,39–41] concerning the intermediates obtained en route to the title molecule, putting those earlier speculations on solid experimental ground.

## Results and Discussion

Our synthetic route to DOPT relies on a three-step sequence that includes an optimized Diels–Alder reaction between **1** and **2** to give 5,12-diphenyltetracene-6,11-dione (**4**), a subsequent Grignard reaction to yield **7**, followed by a unique re-aromatization reaction to produce **8** (see reaction sequence in the box of Scheme 1). The analytical data for **8** are reported for the first time.

### Synthesis of 5,12-Diphenyltetracene-6,11-dione 4 (1 + 2 → 4)

A number of routes towards the intermediate **4** have been reported.[41,42] Dufraisse presented a three-step approach to **4** involving the cyclization of 3,3′-(1,2-ethanediylidene)bis-isobenzofuranone to yield 6,11-dihydroxytetracene-5,12-dione.[42] Even with an optimized synthesis of the dihydroxy intermediate, which was reported by Yagodkin et al. in 2009, **4** could only be obtained in low yield or low purity.[41] Our first attempts towards the synthesis of DOPT (**8**) thus concentrated on the protocols of Bergmann[39] and Badger and Pearce and co-workers[40] starting from 1,3-diphenylisobenzofuran (**1**) and 1,4-naphthoquinone (**2**), and included the full characterization of this reported reaction sequence for the first time.[39,40] Isolation of the accessible Diels–Alder compound 5,12-diphenyl-5,12-epoxy-5a,11a-dihydrotetracene-6,11-dione ("Bergmann's compound", **3**)[38] in a hitherto unreported quantitative yield was achieved by using diethyl ether as solvent. Crystallization from $CHCl_3$ yielded colorless prisms of **3**. Figure 2 shows the molecular structure of the crystallized *endo* isomer of **3**.

From the $^1H$ NMR spectroscopic data a ratio of *endo*-**3**/*exo*-**3** of 10:1 can be estimated. Due to an inevitable retro-Diels–Alder reaction, solutions of **3** are unstable and partially decompose back to **1** and **2**. We expect a preferential decomposition of the thermodynamically unstable *exo* isomer into its precursors accompanied by a slow oxidation of **1** in air. This fact together with the significantly lower amount of the *exo* isomer formed could explain the exclusive crystallization of the *endo* isomer of **3**. Its molecular structure is in full agreement with the principle of maximum accumulation of π electrons of unsaturated centers in the activated complex.[43]

Subsequent acidic de-epoxidation of **3** following the protocol of Badger and Pearce[40] afforded the product **4** only in low yield, most probably due to the competitive and thermodynamically favored retro-Diels–Alder reaction. A mixture of *o*-dibenzoylbenzene (**5**) as the major product and the desired product **4**, but only as a minor product, was obtained. The formation of **5** in the course of this synthesis could be proven for the first time and its crystal structure was successfully determined (Figure 3). A facile separation of both compounds was achieved by fractional crystallization from hot *n*-butyl acetate. In addition to the original routes of Dufraisse,[30] Yagodkin,[41] and Badger and Pearce,[40] Paraskar et al.[44] in 2008 presented a promising alternative approach to **4** to which our attention was drawn.

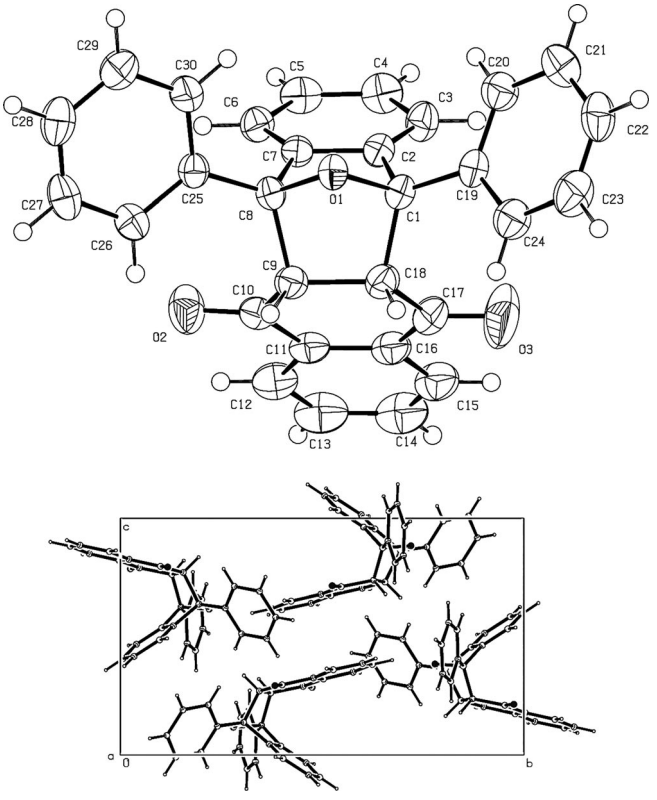



Figure 2. Top: ORTEP plot of the molecular structure of the *endo* isomer of 5,12-diphenyl-5,12-epoxy-5a,11a-dihydrotetracene-6,11-dione ("Bergmann"s compound", **3**). Bottom: View along the *a* axis of the unit cell of **3** showing two independent molecules. Deviation from the ideal tetrahedral geometry of the $sp^3$ carbon atoms C1 and C8 is observed. This is in line with the maximum variation in bond angle from 99.23(12) (O1–C1–C18) to 108.04(13)° (O1–C8–C25). The boat conformation of the cyclohexene ring with two equatorial protons results in a strong kinking at C9 and C18.

According to Paraskar et al.,[44] the Diels–Alder reaction of DPhIBF (**1**) and 1,4-naphthoquinone (**2**), followed by in situ de-epoxidation using $BBr_3$ as a Lewis acid catalyst gives **4**. This strong Lewis acid induces a double E1 elimination, which decreases the charge density at the oxygen in the naphthoquinone-like unit.[45] However, in contrast to the report by Paraskar et al., we were able to achieve a simple purification of **4** to give the product in high yield and purity, which also allowed a structural elucidation by single-crystal structure analysis (Figure 4).

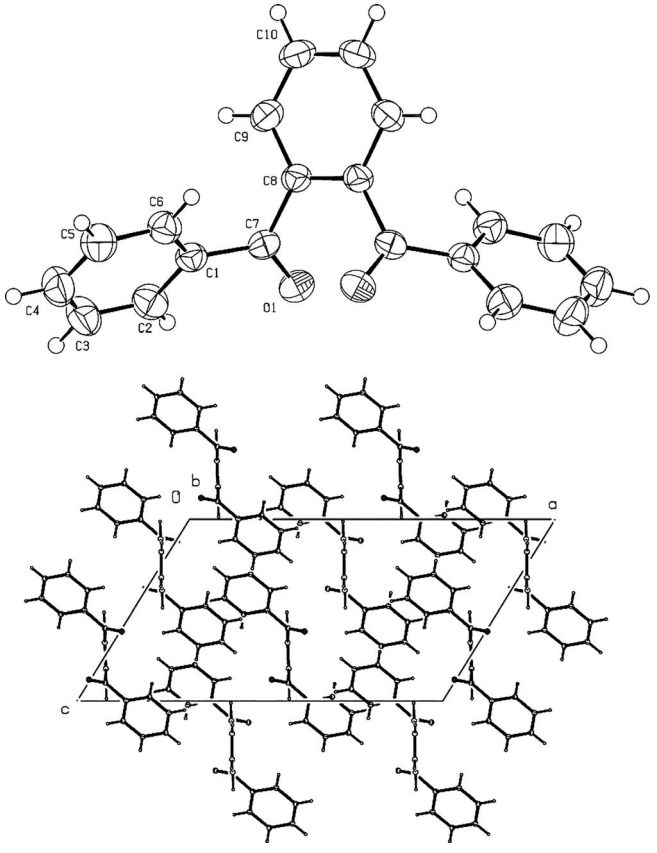



Figure 3. Top: ORTEP plot of the molecular structure of *o*-dibenzoylbenzene (**5**). Bottom: View along the *b* axis of the unit cell of **5**. C7 has no ideal trigonal environment, angles between the adjacent π systems are 117.50(12) (C1–C7–C8), 120.53(12) (O1–C7–C8), and 121.97(13)° (C1–C7–O1). The bond length of 121.70(16) pm (C7–O1) accounts for a typical C=O double bond. The phenyl plane $P_{Ph}$(C1–C2–C3–C4–C5–C6–C7) and phenylene plane $P_{Pn}$(C7–C8–C9–C10–C10′–C9′–C8′) are inclined by an angle of 73.31(5)° [<($P_{Ph}$–$P_{Pn}$)] with respect to C7.

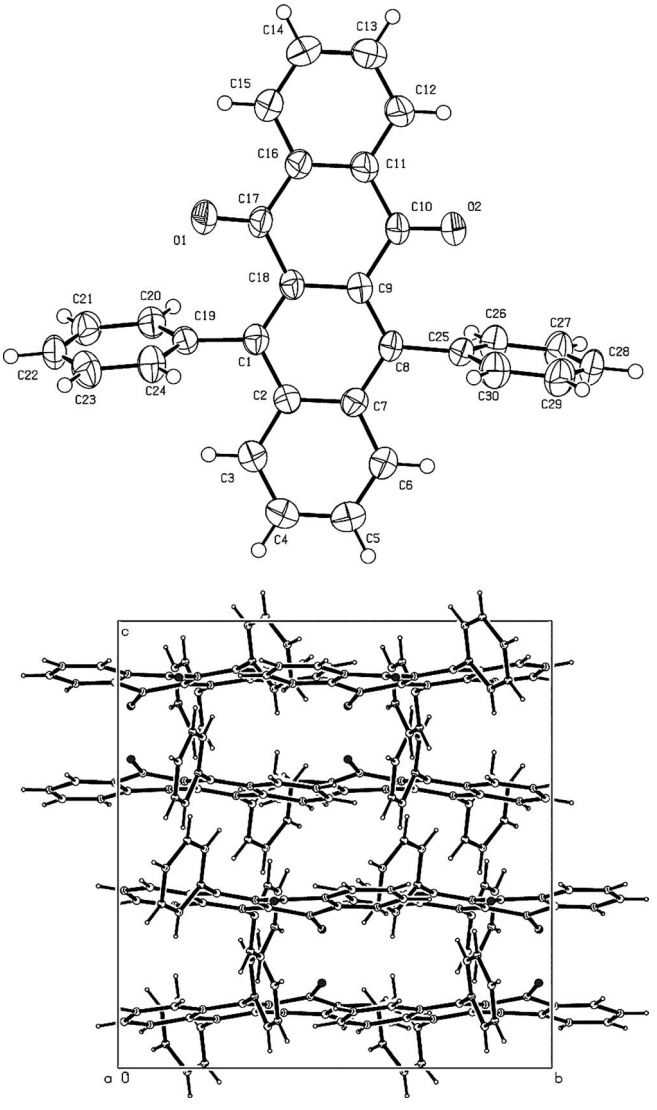



Figure 4. Top: ORTEP plot of the molecular structure of 5,12-diphenyltetracene-6,11-dione (**4**). Bottom: View along the *a* axis of the unit cell of **4**. Due to the sterically demanding phenyl groups, the tetracene backbone $P_{Pn}$(C10–C17–C16–C11) and $P_{Np}$(C10–C17–C18–C9) is slightly twisted out of plane at C10 and C17 [14.51(9)°]. The re-aromatization of the former epoxy-bearing ring (transformation of **3** into **4**) results in significantly shorter and characteristic bond lengths of **4** compared with **3**: 152.5(2) to 143.2(4) pm (C1–C2), 158.2(2) to 139.2(4) pm (C8–C9), and 155.5(2) to 143.8(4) pm (C9–C18).

### Synthesis of 5,12-Diphenyl-5,6:11,12-di-*o*-phenylene-5,12-dihydrotetracene (Pseudorubrene, 7; 4 → 7)

The subsequent conversion of diketone **4** with an excess of 20 equiv. of phenylmagnesium chloride, followed by acidic hydrolysis and in situ elimination of water in boiling glacial acetic acid resulted in the precipitation and isolation of pure 5,12-diphenyl-5,6:11,12-di-*o*-phenylene-5,12-dihydrotetracene (pseudorubrene, **7**; Figure 5). Thus, **7** was obtained in a modification of the Dufraisse route (see Scheme 1); however, no analytical characterization has previously been reported.[46,47] To elucidate its structure, full characterization by NMR, IR, and Raman spectroscopy, MS, and X-ray structure analysis was carried out.

In contrast to the literature,[43,44] we found that there is no need to isolate the purified dihydroxy Grignard product **6**. All the side-products, for example, phenol remained in acetic solution and could be separated directly. Furthermore, the course of the dehydration in glacial acetic acid, which can be easily monitored by EI-MS, is strongly influenced by the concentration of acid. Insufficient acidity and reaction time resulted in an incomplete conversion of **4** accompanied by the presence of hydroxy intermediates with an open-ring structure detected at *m*/*z* = 548 (three phenyl groups, single OH group) and 566 (four phenyl groups, two OH groups **6**). The sequential use of fresh glacial acetic acid in excess, however, ensured a full conversion of **4** (see the Supporting Information). Thus, it is possible to control the reaction with respect to the intermediates (single OH- and doubly OH-substituted compound **6**) simply by varying the strength of the acid employed.

### Synthesis of 5,6:11,12-Di-*o*-phenylenetetracene (DOPT, 8) and Possible Reaction Mechanisms (7 → 8)

In the final step of the DOPT synthesis, the aromaticity of the naphthacenic backbone of **7** is restored. This re-aromatization

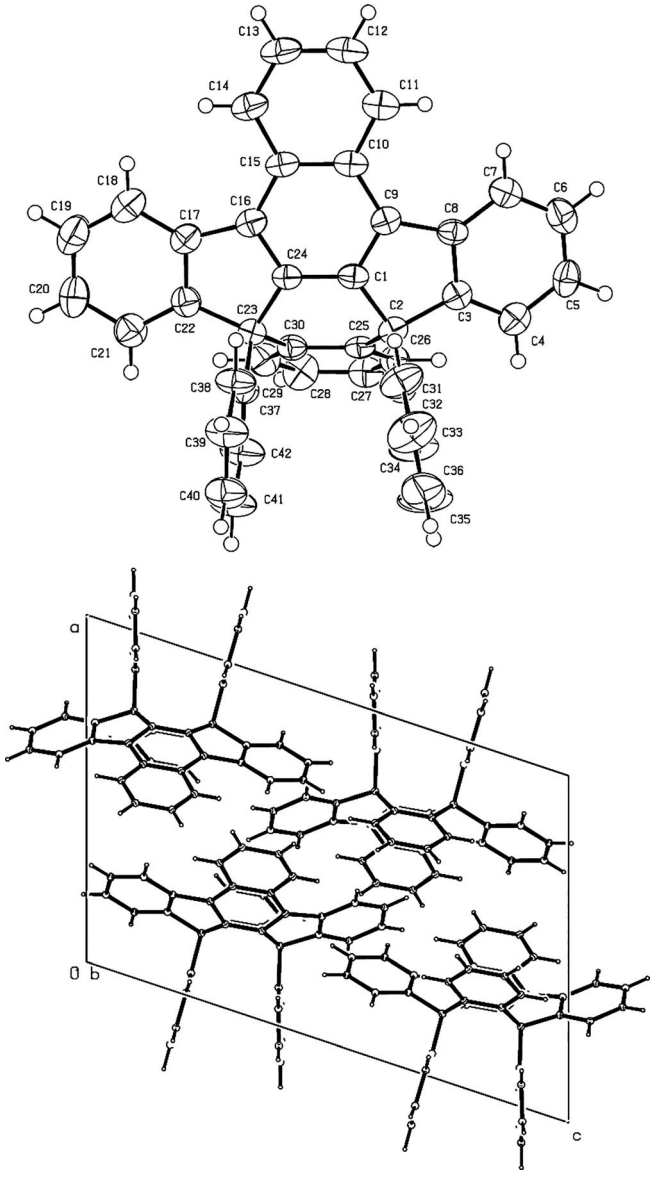
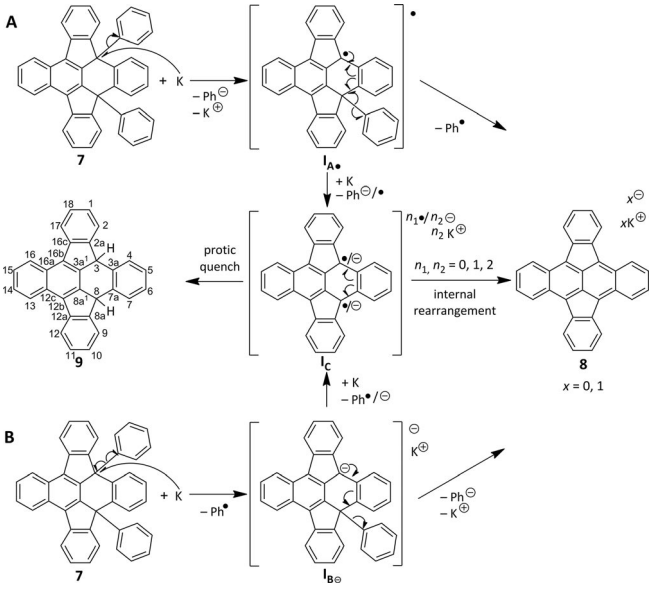



Figure 5. Top: ORTEP plot of the molecular structure of 5,12-diphenyl-5,6:11,12-di-*o*-phenylene-5,12-dihydrotetracene (pseudorubrene, **7**).[48,49] Bottom: View along the *b* axis of the unit cell of **7**. The re-aromatization at the former quinone position is reflected by the reduction of the bond length from **4** to **7**: 143.8(4) to 139.08(50) pm (C1–C24), 149.5(4) to 137.91(56) pm (C16–C24), 147.7(4) to 143.58(47) pm (C15–C16), and 138.9(4) to 143.99(54) pm (C10–C15). The out-of-plane tilt of the two phenylene groups is 25.45(23)°, resulting in an overall half-bowl-shaped curvature of **7**.

can be achieved by reductive elimination of the peripheral phenyl rings of **7** by using an excess of sodium or potassium. The stepwise reduction of **7** is accompanied by a characteristic color change from the purple intermediate to the deep-red solution presumably containing the dianionic complex [$\mathbf{8}^{2-}$][2M$^+$] (M = Na, K) at the end. Indeed, the parent neutral polyacene DOPT (**8**) is obtained from the dianion solution [$\mathbf{8}^{2-}$][2M$^+$] by slow hydrolysis in ethanol as an intensely colored, blue-black, analytically pure solid after sublimation at 270 °C/10$^{-3}$ mbar or multiple crystallization steps from hot toluene or pyridine. An independent reaction of the thus-obtained blue-black DOPT with one or two stoichiometric equivalents of potassium or sodium metal in dry THF resulted in either a stable clear green (1 equiv.) or stable deep-red solution (2 equiv.) after complete consumption of the appropriate amount of metal. Most probably, these solutions contain the stable [$\mathbf{8}^-$][K$^+$] and [$\mathbf{8}^{2-}$][2K$^+$] mono- or dianions of DOPT, respectively.

To the best of our knowledge there is no example of such a reductive phenyl elimination process leading to a fully aromatized pyracylene derivative reported in the literature. However, early speculations by Badoche on a related elimination process of phenylide fragments from the proposed isomeric structure of 6,12-diphenyl-5,6:11,12-di-*o*-phenylene-6,12-dihydrotetracene point towards that possibility.[32] We would expect the thermodynamically favored radical mechanism presented in Scheme 2.




Scheme 2. Proposed radical reaction mechanisms occurring in the final reductive elimination step of pseudorubrene (**7**) to DOPT (**8**). A) A primary single-electron transfer (SET) leads to the elimination of a phenylide radical anion (Ph$^-$) from **7**. The resulting PAH radical ($\mathbf{I_A}^{\bullet}$) releases the second phenyl (Ph$^{\bullet}$) as a radical species after internal π-electron redistribution with the subsequent formation of **8**. B) Elimination of a phenyl radical (Ph$^{\bullet}$) from **7** leads to an anionic intermediate ($\mathbf{I_B}^-$), which releases a phenylide (Ph$^-$) after internal π-electron redistribution to yield **8**. A two-fold reduction step ($\mathbf{I_C}$) towards the diradical species $\mathbf{I_C}^{\bullet\bullet}$, the anionic species $\mathbf{I_C}^{2-}$, or the mixed radical-anion intermediate $\mathbf{I_C}^{\bullet-}$ enables the formation of the observed side-product 5,12-dihydro-5,6:11,12-di-*o*-phenylenetetracene (**9**) after quenching, as well as of the delocalized anionic state of **8**. Due to the presence of excess potassium during the reaction, a subsequent reduction to [$\mathbf{8}^{2-}$][2K$^+$] should take place, resulting in a deep-red solution.

Two very similar sequences to yield DOPT seem favorable. First, the alkaline metal reduces the aromatic system of **7** by a single-electron-transfer (SET) enabling two conceivable reaction routes. In route A a heterolytic splitting of the weak C–C bond of one peripheral phenyl group would release a phenylide anion (Ph$^-$). A highly stabilized pseudo-triphenylmethane radical $\mathbf{I_A}^{\bullet}$ remains. In a second step, an internal electron redistribution initiates the elimination of an unstable phenyl radical (Ph$^{\bullet}$).

This highly reactive species tends to recombine with the formation of a biphenyl molecule. In route B the phenyl group is directly released after SET as a highly reactive phenyl radical (Ph$^{\bullet}$), generating a stable triphenylmethane carbanion $\mathbf{I_B}^-$. Internal redistribution of the electronic ring system finally releases a phenylide moiety (Ph$^-$). In both routes a phenyl anion (Ph$^-$) and a phenyl radical (Ph$^{\bullet}$) are formed during the reduction leading to biphenyl as a side-product. Indeed, biphenyl was detected by NMR spectroscopy and mass spectrometry ($m/z$ = 154). A second reduction of either the relatively stable anionic $\mathbf{I_B}^-$ or the radical intermediate $\mathbf{I_A}^{\bullet}$ in the presence of excess potassium is possible, yielding the dianionic $\mathbf{I_C}^{2-}$, diradical $\mathbf{I_C}^{\bullet\bullet}$, or the mixed $\mathbf{I_C}^{\bullet-}$ intermediate species $\mathbf{I_C}$. Through internal electron redistribution, negatively charged DOPT, [**8**$^-$][K$^+$], can be released. In the case of the formation of a two-fold negatively charged triphenyl moiety $\mathbf{I_C}^{2-}$, protic quenching also leads to the release of compound 5,12-dihydro-5,6:11,12-di-*o*-phenylenetetracene (Dihydro-DOPT, **9**), which we indeed isolated as a minor byproduct (1 % yield) in the ethanolic work-up procedure and which we were also able to characterize structurally by X-ray analysis (Figure 6). Moreover, recombination reactions of Ph$^{\bullet}$ or Ph$^-$ with the radical $\mathbf{I_A}^{\bullet}$ or anionic intermediate $\mathbf{I_B}^-$ or by an initial cleavage of one phenylene bond of **7** (C3–C26/C22–C23) may occur. This may result in the triphenyl-tetracene derivative 5,11,12-triphenyl-5,6-*o*-phenylene-5,12-dihydrotetracene upon protic work-up, which we indeed did isolate, however, so far we have obtained only crystals of poor quality (see the Supporting Information). Based on these findings, the formation of the triphenyl compound seems proven, and most probably rules out a fully concerted mechanism without the formation of the above-mentioned intermediates.

To further distinguish between the two routes we compared the different heats of formation ($\Delta H_{f,298}$) for the reaction pathways A and B. Nicolaides et al. calculated $\Delta H_{f,298}$ values for the phenyl radical (Ph$^{\bullet}$, $\Delta H_{f,298}$ = 340 kJ/mol) and the phenyl anion (Ph$^-$, $\Delta H_{f,298}$ = 224 kJ/mol) and could show that the formation of Ph$^-$ is favored.[50] Although lacking $\Delta H_{f,298}$ values for the intermediates $\mathbf{I_A}^{\bullet}$ and $\mathbf{I_B}^-$, we employed the enthalpy data of the triphenylmethane radical (TPM$^{\bullet}$, $\Delta H_{f,298}$ = 366–391 kJ/mol[51]) for $\mathbf{I_A}^{\bullet}$ and the triphenylmethane anion (TPM$^-$, $\Delta H_{f,298}$ = 180 kJ/mol[52]) for $\mathbf{I_B}^-$. The $\Delta H_{f,298}$ data for pseudorubrene (**7**) can be neglected for a first approximation of the reaction process. For $\Delta H_{f,298}$ for K$^+$ the ionization energy of potassium (4.34 eV[53]) was used. With these assumptions $\Delta H_{r,298}$ could be calculated as follows: $\Delta H_{r,298,A}$ = [($\Delta H_{f,298}$Ph$^-$) + ($\Delta H_{f,298}$K$^+$) + ($\Delta H_{f,298}$TPM$^{\bullet}$)] = 224 + 419 + 366(391) = 1009(1034) kJ/mol for route A. For route B, $\Delta H_{r,298,B}$ = [($\Delta H_{f,298}$Ph$^{\bullet}$) + ($\Delta H_{f,298}$K$^+$) + ($\Delta H_{f,298}$TPM$^-$)] = 340 + 419 + 180 = 939 kJ/mol.

Route B is therefore thermodynamically favored on the basis of the estimated distinctly lower activation barrier that has to be overcome. Additionally, only the formation of the two-fold triphenyl-like anionic moiety $\mathbf{I_C}^{2-}$ according to route B enables the release of compound **9**. Based on these considerations, the formation of **9** could give positive evidence for the predicted reaction mechanism (Scheme 2). Nevertheless, in both routes the driving force is certainly a minimization of the steric stress as well as a gain in the overall aromatization energy.

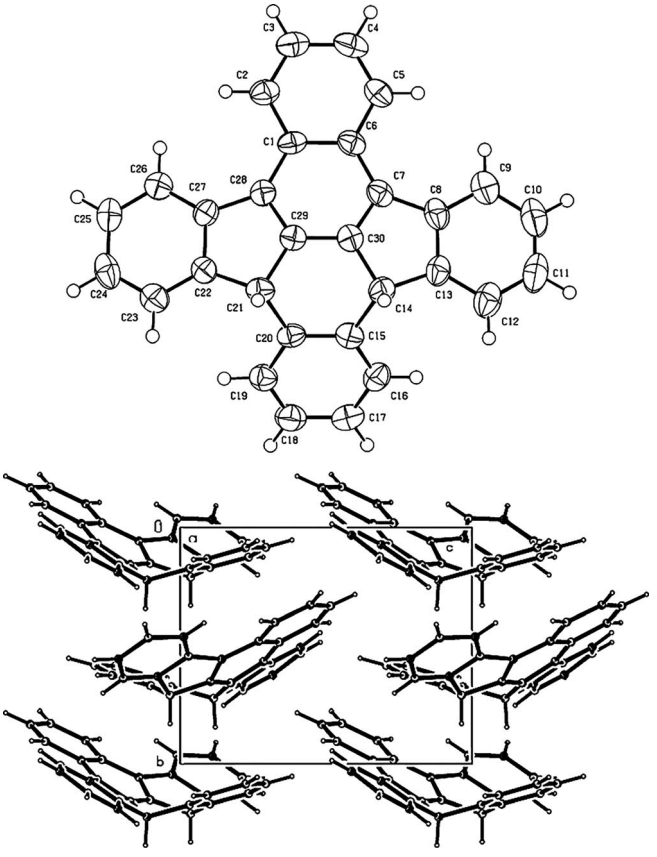



Figure 6. Top: ORTEP plot of the molecular structure of 5,12-dihydro-5,6:11,12-di-*o*-phenylenetetracene (Dihydro-DOPT, **9**). Bottom: View along the *a* axis of the unit cell of **9**. Like **7**, Dihydro-DOPT (**9**) adopts a similar bowl-shaped conformation, but shows minor curvature [**9**(C29–C30): 17.01(42)°; **7**: 19.66(27)°]. Both [⊥(C29–C30)] phenylene rings are similarly tilted [**9**: 24.84(35)°; **7**: 25.45(23)°].

### Analytical Data of 5,6:11,12-Di-*o*-phenylenetetracene (DOPT, 8)

As already mentioned, so far little spectroscopic characterization data for **8** has been published in the literature. The UV/Vis data we have obtained are in full accord with those reported previously. Deep-blue solutions of neutral **8** show maxima at $\lambda_{exp.,CHCl3}$ ($\lambda_{Dufraisse,CHCl3}$[30]|$\lambda_{Lang,benzene}$[34]) = 290, 304 (306), 431 (423), 523 (525|528), 561 (565|566), and 607 (610|610) nm, and are in accordance with the reported values of Dufraisse and Lang, also confirming their earlier reports. A bathochromic shift in absorption is observed by using $CS_2$ as solvent; the maxima appear redshifted at (427), 533, 573, and 622 nm.

Furthermore, we characterized **8** by $^1$H NMR and IR spectroscopy as well as by mass spectrometry. The mass spectrum of **8** shows neither detectable fragmentation in electron ionization mode (EI) nor any impurities after purification by sublimation. The doubly charged molecular ion of **8** ([M]$^{2+}$) is detected at $m/z$ (%) = 188 (20) and the single-charged molecular ion [M]$^+$, which constitutes the base peak, at $m/z$ (%) = 376 (100). Isomeric structures with the formula $C_{30}H_{16}$, for example, with phenyl substituents, can be ruled out due to the lack of a characteristic fragmentation pattern arising from phenyl groups, for example, at $m/z$ = 77 (see the Supporting Information for detailed spectra).

The IR spectrum of **8** is in accord with the presence of exclusively *ortho*-substituted benzene rings with $\tilde{\nu}$ = 761 $cm^{-1}$. The $^1H$ NMR spectrum reveals two characteristic AA′BB′ spin systems for **8**, with two sets of each *ortho*-substituted benzene rings A1A1′B1B1′ and A2A2′B2B2′ (Figure 7). Due to the cruciform centrosymmetric symmetry of DOPT (**8**), the number of magnetically distinguishable signals is reduced to four (A1 = A1′, A2 = A2′, etc.).

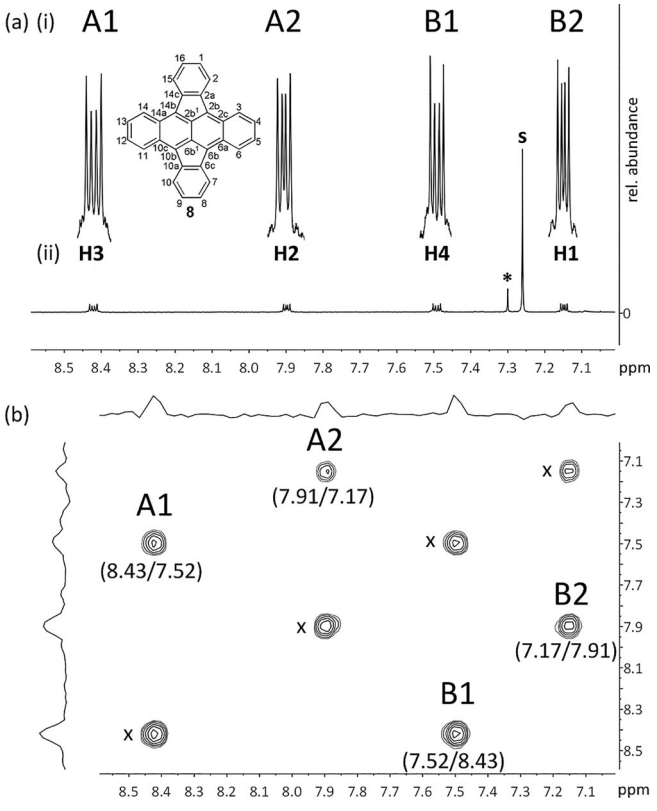



Figure 7. a) 500 MHz $^1H$ NMR and b) $^1H$ COSY NMR spectra of doubly purified **8** (recrystallized from toluene and sublimed) recorded in $CS_2$ ($CHCl_3$ as internal standard at $\delta$ = 7.26 ppm, upper trace shows magnification). $\delta$ (20 °C) = 8.43 (H3, A1), 7.91 (H2, A2), 7.52 (H4, B1), 7.17 (H1, B2) ppm. The signal denoted with * could not be assigned. The assignment of the spin systems I (A1A1′B1B1′) and II (A2A2′B2B2′) was carried out by means of a COSY analysis. × marks the cross-peaks in the COSY spectrum.

Nonetheless, both AA′BB′ spin systems can be clearly derived from the 2D COSY correlation spectra as well as from the different *J* couplings and the signal shape of the two spin systems I and II. From the observed cross-peaks we can assign the pairs of proton signals with $\delta$ = 8.43/7.52 (I) and 7.91/7.17 ppm (II). These spin systems can be approximately attributed to the naphthacenic (I, H3–H6/H11–H14) and phenylenic (II, H7–H10/H15–H2) rings of DOPT by comparison with the reported $^1H$ NMR data of unsubstituted naphthacene[54,55] and of the data of 3,4-*o*-phenylenefluoranthene[55] with fluoranthene.[56] Therefore the most downfield signal at $\delta$ = 8.43 ppm (A1A1′) was assigned to the supposed most deshielded protons H3/H6/H11/H14 of the substituted naphthacenic core. In consequence, the less downfield signal at $\delta$ = 7.91 ppm (A2A2′) of spin system II presumably corresponds to the protons H2/H15/H7/H10 of both pseudo-isolated phenylenes orthogonal to the fully conjugated naphthacene moiety. Likewise, the signals at $\delta$ = 7.52 (I) and 7.17 (II) emerge from the associated protons H4/H5/H12/H13 and H1/H16/H8/H9. The corresponding coupling constants determined from the $^1H$ NMR spectrum are $^3J_{ortho}$(H3,H4) = 3.6 Hz, $^4J_{meta}$(H3,H5) = 3.3 Hz and $^3J_{ortho}$(H1,H2) = 3.2 Hz, $^4J_{meta}$(H1,H15) = 2.4 Hz. No $^{13}C$ NMR spectrum could be obtained due to the extremely low concentration of **8** in all common NMR-solvents, even in $CS_2$.

## Conclusions

We have presented herein a drastically improved synthetic route to DOPT (**8**) in high yield and purity. We reinvestigated various earlier reported routes and were able to verify the occurrence of *o*-dibenzoylbenzene (**5**) by synthesis and full characterization of the hitherto uncharacterized intermediate **4**. Thus, **4** and **5** have been spectroscopically and structurally fully characterized for the first time. With all the experimental information that we have obtained, we have suggested a plausible reaction mechanism for the elimination of the phenyl groups during the reductive elimination step from **7** to **8** based on thermodynamic considerations. The investigation of the synthetic redox behavior of **8** revealed the accessibility of two reversible anionic states. This new controlled two-fold reduction route to the polycondensed aromatic DOPT in good yield opens the way to exploring the organometallic chemistry of DOPT as well as the properties of this molecule in organic electronic applications.

## Experimental Section

**General:** Compounds **7** and **8** were synthesized in high-purity argon. THF was dried with Na/benzophenone and stored over activated molecular sieves. 1,3-Diphenylisobenzofuran (DPhIBF, **1**, >95.0 %), 1,4-naphthoquinone (**2**, >98.0 %), and phenylmagnesium chloride solution (2.0 M in THF) were purchased from TCI Europe, and glacial acetic acid (≥99 %) and hydrobromic acid (48 wt.-% in $H_2O$) were purchased from Riedel-de Haën. Potassium (98 %) was received from Alfa Aesar and boron tribromide solution (1.0 M in $CH_2Cl_2$) was received from Sigma–Aldrich. The remaining solvents were all technical-grade. All chemicals were used as received. NMR spectra were recorded with a Bruker DRX 500 spectrometer with the residual proton signals of the deuterated solvents as references. The NMR data of **8** were collected in pre-distilled carbon disulfide ($CS_2$). IR spectra were recorded with a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with an ATR unit (diamond) and atmospheric correction. The Raman spectra were recorded with a Bruker IFS 55-FRA 106 spectrometer (Nd:YAG-laser at 1064 nm). The absorption spectra were obtained by using a Thermo Scientific Evolution 600 UV/Vis split-beam spectrometer. Mass spectroscopic analyses were performed with Finnigan MAT 95 (EI) and Esquire LC (ESI) spectrometers. Suitable crystals for structural analysis were obtained from solution (**3**, diethyl ether/$H_2O$; **4** toluene/hexane/$H_2O$; **7** toluene; **7** in THF yielded co-crystals of **7**·THF; **9**, $CHCl_3$/*n*-hexane). The X-ray diffraction data were collected with a STOE STADI IV 4-circle single-crystal diffractometer at ambient temperature. The graphical images of the molecules and unit cells were generated with the latest version of the PLATON software.[57] All rotational ellipsoids of the ORTEP plots were drawn at the 50 % probability level. The crystallographic data for compounds **3**–**5**, **7**, and **9** are presented in Table 1.

Table 1. Crystallographic data for 5,12-diphenyl-5,12-epoxy-5a,11a-dihydrotetracene-6,11-dione ("Bergmann's compound", **3**), 5,12-diphenyltetracene-6,11-dione (**4**), *o*-dibenzoylbenzene (**5**), 5,12-diphenyl-5,6:11,12-di-*o*-phenylene-5,12-dihydrotetracene (pseudorubrene, **7**), and 5,12-dihydro-5,6:11,12-di-*o*-phenylenetetracene (dihydro-DOPT, **9**).

| Molecule | **3** | **4** | **5** | **7** | **9** |
|---|---|---|---|---|---|
| Crystal size [mm$^3$] | 0.50 × 0.44 × 0.28 | 0.50 × 0.32 × 0.30 | 0.48 × 0.40 × 0.28 | 0.26 × 0.16 × 0.08 | 0.48 × 0.02 × 0.02 |
| Crystal system | | | monoclinic | | |
| Space group, *Z* | *P*21/*n*, 4 | *C*2/*c*, 4 | *C*2/*c*, 8 | *P*21/*n*, 4 | *P*21, 2 |
| *a* [Å] | 10.9508(9) | 19.631(3) | 17.313(1) | 12.905(2) | 10.735(2) |
| *b* [Å] | 18.118(1) | 7.7443(7) | 15.092(1) | 11.772(1) | 8.139(1) |
| *c* [Å] | 11.4477(9) | 11.450(2) | 15.663(1) | 18.918(3) | 11.144(2) |
| *β* [°] | 111.74(1) | 121.72(2) | 96.348(6) | 108.440(10) | 115.90(2) |
| *V* | 2109.8(3) Å$^3$ | 1480.7(4) Å$^3$ | 4067.5(4) Å$^3$ | 2726.4(6) Å$^3$ | 875.9(3) Å$^3$ |
| Empirical formula | $C_{30}H_{20}O_3$ | $C_{20}H_{14}O_2$ | $C_{30}H_{18}O_2$ | $C_{42}H_{26}$ | $C_{30}H_{18}$ |
| Formula mass [g/mol] | 428.46 | 286.31 | 410.44 | 530.63 | 378.44 |
| Density (calcd.) [g/cm$^3$] | 1.349 | 1.284 | 1.341 | 1.293 | 1.435 |
| Abs. coeff. [mm$^{-1}$] | 0.086 | 0.082 | 0.083 | 0.073 | 0.081 |
| *F*(000) | 896 | 600 | 1712 | 1112 | 396 |
| *θ* range [°] | 2.95 to 26.37 | 2.90 to 25.35 | 3.00 to 26.37 | 2.85 to 25.19 | 3.22 to 25.18 |
| Index ranges | –13/13, –16/22, –13/14 | –23/18, –8/9, –13/13 | –21/11, –8/18, –19/19 | –14/15, –13/14, –22/22 | –11/12, –7/9, –11/13 |
| Reflections collected | 8006 | 2573 | 8834 | 10049 | 2998 |
| Independent reflections | 4297 [*R*(int) = 0.0188] | 1354 [*R*(int) = 0.0092] | 4091 [*R*(int) = 0.0278] | 4859 [*R*(int) = 0.0526] | 1677 [*R*(int) = 0.0394] |
| Completeness | 99.4 | 99.3 | 98.0 | 99.3 | 99.2 |
| obsd. [%] | [$I > 2\sigma(I)$] | [$I > 2\sigma(I)$] | [$I > 2\sigma(I)$] | [$I > 2\sigma(I)$] | [$I > 2\sigma(I)$] |
| Reflections used for refinement | 4297 | 1354 | 4091 | 4859 | 1677 |
| Absorption correction | | | semi-empirical from equivalents | | |
| Largest difference peak and hole [e/Å$^3$] | 0.228 and –0.197 | 0.169 and –0.139 | 0.215 and –0.219 | 0.634 and –0.207 | 0.163 and –0.189 |
| Treatment of H atoms | | | H atoms positioned geometrically | | |
| Refined parameters | 299 | 100 | 289 | 379 | 271 |
| GOF on $F^2$ | 1.045 | 1.072 | 1.185 | 1.042 | 0.982 |
| $wR_2$ (all data) | 0.0905 | 0.0928 | 0.1360 | 0.1367 | 0.0918 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0447 | 0.0376 | 0.0694 | 0.0722 | 0.0508 |

CCDC 1423232 (*endo*-**3**), 1423233 (**4**), 1423234 (**5**), 1423235 (**6**), 1423236 (**7**·THF), and 1423237 (**9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

**Synthesis:** As a result of the proven potent carcinogenic activity of some polyarenes, an uncontrolled release of PAHs contributes to a serious environmental contamination that is potentially hazardous to health.[58] Thus, the handling and synthesis of PAHs has to be carried out with great care and any exposure should be precluded.

**5,12-Diphenyl-5,12-epoxy-5a,11a-dihydrotetracene-6,11-dione ("Bergmann's Compound", 3):** As a modification of the procedure of Bergmann,[39] a solution of powdered 1,3-diphenylisobenzofuran (DPhIBF, **1**; 5.0 g, 18.5 mmol; 1.05 equiv.) and 1,4-naphthoquinone (**2**; 3.0 g, 19.0 mmol; 1.03 equiv.) in diethyl ether (20 mL) was stirred for 12 h in a dark room. The precipitate was filtered off, washed with additional cold diethyl ether, and dried in vacuo. Tetracene derivative **3** was obtained as a pure white powder in high yield (7.8 g, 18.3 mmol; 99 %); IR (ATR): $\tilde{\nu}$ = 3055 [w, $\nu(C_{aryl}–H)$], 1676 [s, $\nu$(C=O)], 1589 (s), 1498 (m), 1458 (m), 1445 (s), 1349 (s), 1271 (s, epoxy), 1158 (w), 990 (s), 930 (m), 810 (w), 759 (s), 696 (s), 629 (m), 561 (w), 524 (w) cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): *endo*-**3**: $\delta$ = 7.99 [d, $^3J$(13H,14H) = 7.1 Hz, 4 H, 13-H], 7.61 [dd, $^3J$(1H,2H) = 3.3, $^4J$(1H,3H) = 2.6 Hz, 2 H, 1-H, 4-H], 7.52 [t, $^3J$(14H,13H|14H,15H) = 7.1 Hz, 4 H, 14-H], 7.48 [t, $^3J$(15H,14H) = 7.1 Hz, 2 H, 15-H], 7.44 [dd, $^3J$(2H,1H) = 3.3, $^4J$(2H,4H) = 2.6 Hz, 2 H, 1-H, 4-H], 6.89 [dd, $^3J$(7H,8H) = 3.0, $^4J$(7H,9H) = 2.5 Hz, 2 H, 7-H, 10-H], 6.84 [dd, $^3J$(8H,7H) = 3.0, $^4J$(8H,10H) = 2.5 Hz, 2 H, 8-H, 9-H], 4.41 (s, 2 H, 5a-H, 11a-H) ppm. $^{13}$C NMR (500 MHz, $CDCl_3$, 25 °C, TMS): *endo*-**3**: $\delta$ = 194.75 ($C_q$, 2 C, C-6, C-11), 144.79 ($C_q$, 2 C, C-6a, C-10a), 135.55 ($C_q$, 2 C, C-12b, C-5b), 135.09 ($C_q$, 2 C, C-4a, C-12a), 133.69 (CH, 2 C, C-2, C-3), 129.07 (CH, 2 C, C-15, C-18), 128.72 (CH, 4 C, C-13, C-16), 128.42 (CH, 4 C, C-14, C-17), 127.67 (CH, 2 C, C-8, C-9), 126.31 (CH, 2 C, C-1, C-4), 121.58 (CH, 2 C, C-7, C-10), 92.38 ($C_q$, 2 C, C-5, C-12), 55.04 (CH, 2 C, C-5a, C-11a) ppm. $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): *exo*-**3**: $\delta$ = 7.99 [d, $^3J$(13H,14H) = 7.1 Hz, 4 H, 13-H], 7.50 [dd, $^3J$(1H,2H) = 3.3, $^4J$(1H,3H) = 2.6 Hz, 2 H, 1-H, 4-H], 7.52–7.44 (m, 6 H, 14-H, 15-H), 7.28 [dd, $^3J$(2H,1H) = 3.3, $^4J$(2H,4H) = 2.6 Hz, 2 H, 1-H, 4-H], 7.42 [dd, $^3J$(7H,8H) = 3.0, $^4J$(7H,9H) = 2.5 Hz, 2 H, 7-H, 10-H], 7.27 [dd, $^3J$(8H,7H) = 3.0, $^4J$(8H,10H) = 2.5 Hz, 2 H, 8-H, 9-H], 3.71 (s, 2 H, 5a-H, 11a-H) ppm. $^{13}$C NMR (500 MHz, $CDCl_3$, 25 °C, TMS): *exo*-**3**: $\delta$ = 195.71 ($C_q$, 2 C, C-6, C-11), 146.57 ($C_q$, 2 C, C-6a, C-10a), 137.95 ($C_q$, 2 C, C-12b, C-5b), 134.10 ($C_q$, 2 C, C-4a, C-12a), 133.50 (CH, 2 C, C-2, C-3), 128.19 (CH, 2 C, C-15, C-18), 128.27 (CH, 4 C, C-13, C-16), 126.26 (CH, 4 C, C-14, C-17), 127.78 (CH, 2 C, C-8, C-9), 126.26 (CH, 2 C, C-1, C-4), 119.24 (CH, 2 C, C-7, C-10), 92.09 ($C_q$, 2 C, C-5, C-12), 59.25 (CH, 2 C, C-5a, C-11a) ppm. Ratio of *endo*-**3** to *exo*-**3** in solution at 25 °C = 11:1. MS (EI, 70 eV): *m*/*z* (%) = 270 (100) [**1**]$^+$, 158 (50) [**2**]$^+$ decomp. $C_{30}H_{20}O_3$ (428.49): calcd. C 84.09, H 4.70; found C 83.57, H 4.71.

***o*-Dibenzoylbenzene (5):** Bergmann's compound (**3**; 5.0 g, 11.7 mmol) was dissolved in a volume equivalent mixture of glacial acetic acid and hydrobromic acid (48 wt.-% in $H_2O$) and stirred at 37 °C for 2 d. The acidic phase was filtered through a porous glass drip (D4-type), washed with water and cold diethyl ether, and dried in vacuo. The yellow powder was recrystallized from *n*-butyl acetate. 5,12-Diphenyltetracene-6,11-dione (**4**) crystallized as intense sparkling yellow prisms in a first crop (1.0 g, 2.4 mmol; 21 % yield). Compound **5** was obtained as a second crop from the mother liquor as pure white crystals (1.5 g, 5.3 mmol; 45 % yield). IR (ATR): $\tilde{\nu}$ = 3084, 3062, 3039 [w, $\nu(C_{aryl}–H)$], 1661 [s, $\nu$(C=O)], 1595 (m), 1577

(m), 1448 (m), 1316 (m), 1275 (s), 1178 (m), 1155 (m), 938 (s), 920 (m), 776 (s), 705 (s), 691 (m), 645 (m), 432 (m) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.69 [dd, $^3J$(6H,7H) = 7.3 Hz, 4 H, 6-H, 6′-H, 10-H, 10′-H], 7.63 [d, $^3J$(3H,2H) = 2.5 Hz, 2 H, 3-H, 3′-H], 7.61 [d, $^3J$(2H,3H) = 2.5 Hz, 2 H, 2-H, 2′-H], 7.51 [t, $^3J$(8H,7H) = 7.4 Hz, 2 H, 8-H, 8′-H], 7.37 (t, 4 H, 7-H, 7′-H, 9-H, 9′-H) ppm. $^{13}C$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 196.65 ($C_q$, 2 C, C-4, C-4′), 140.17 ($C_q$, 2 C, C-1, C-1′), 137.37 ($C_q$, 2 C, C-5, C-5′), 133.09 (CH, 2 C, C-8, C-8′), 130.47 (CH, 2 C, C-3, C-3′), 129.95 (CH, 4 C, C-6, C-6′, C-10, C-10′), 129.78 (CH, 2 C, C-2, C-2′), 128.45 (CH, 4 C, C-7, C-7′, C-9, C-9′) ppm. MS (EI, 70 eV): *m/z* (%) = 286 (40) $[M - H]^+$, 209 (100) $[M - Ph]^+$, 152 (30), 105 (55) $[Bz]^+$, 77 (80) $[Ph]^+$. $C_{20}H_{14}O_2$ (286.33): calcd. C 83.90, H 4.93; found C 83.10, H 4.81.

**5,12-Diphenyltetracene-6,11-dione (4):** According to Paraskar et al.,[44] powdered 1,3-diphenylisobenzofuran (**1**; 5.0 g, 18.5 mmol, 1 equiv.) was slowly added to a solution of 1,4-naphthoquinone (**2**; 3.0 g, 19.0 mmol, 1.03 equiv.) in dichloromethane (50 mL) and stirred for 12 h at room temperature. Additional dichloromethane (100 mL) was added and the solution cooled to −78 °C. Dropwise addition of a $BBr_3$ solution (30 mL, 1.0 M in $CH_2Cl_2$, 30.0 mmol) and subsequent stirring for an additional 60 min completed the reaction. The darkish solution was heated under reflux for 4 h, cooled to room temperature and hydrolyzed by pouring on cold water. The aqueous phase was extracted with dichloromethane after stirring for 1 h, dried with disodium sulfate, and the solvent removed in vacuo. In contrast to the procedure of Paraskar et al., the orange powder was subsequently purified by recrystallization from hot *n*-butyl acetate resulting in yellow crystals of high purity (6.8 g, 16.6 mmol; 90 % yield). IR (ATR): $\tilde{\nu}$ = 3057 [w, $\nu(C_{aryl}–H)$], 1677 [s, $\nu_s$(C=O)], 1595 (m), 1505 (w), 1586 (w), 1439 (w), 1375 (m), 1367 (m), 1336 (m), 1259 (s), 1069 (w), 1045 (m), 1026 (w), 1001 (w), 991 (m), 964 (w), 795 (w), 773 (m), 737 (m), 722 (m), 697 (s), 671 (w), 641 (w), 596 (m), 506 (w), 450 (w) $cm^{-1}$. Raman (85 mW): $\tilde{\nu}$ = 3067 [w, $\nu(C_{aryl}–H)$], 1671 [m, $\nu_s$(C=O)], 1600 [m, $\delta(C–C)_{aryl}$], 1569 (w), 1502 (w), 1375 (s), 1316 (w), 1255 (m), 1156 (w), 1039 (m), 726 (w), 659 (w), 477 (w), 316 (w), 276 (w), 121 (w) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.09 [dd, $^3J$(7H,8H) = 3.3, $^4J$(7H,9H) = 2.5 Hz, 2 H, 7-H, 10-H], 7.67 [dd, $^3J$(8H,7H) = 3.3, $^4J$(8H,10H) = 2.5 Hz, 2 H, 8-H, 9-H], 7.63 [t, $^3J$(14H,13H) = 6.5 Hz, 4 H, 14-H], 7.57 (t, 2 H, 15-H), 7.59 [dd, $^3J$(1H,2H) = 3.3, $^4J$(1H,3H) = 3.2 Hz, 2 H, 1-H, 4-H], 7.50 [dd, $^3J$(2H,1H) = 3.3, $^4J$(2H,4H) = 3.2 Hz, 2 H, 2-H, 3-H], 7.34 [dd, $^3J$(13H,14H) = 6.5, $^4J$(13H,15H) = 1.5 Hz, 4 H, 13-H, 16-H] ppm. $^{13}C$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 184.36 ($C_q$, 2 C, C-6, C-11), 144.16 ($C_q$, 2 C, C-5, C-12), 140.40 ($C_q$, 2 C, C-12b, C-5b), 135.76 ($C_q$, 2 C, C-4a, C-12a), 133.70 (CH, 2 C, C-8, C-9), 133.13 ($C_q$, 2 C, C-6a, C-10a), 128.95 (CH, 2 C, C-15, C-18), 128.94 (CH, 2 C, C-2, C-3), 128.81 (CH, 2 C, C-13, C-16), 128.52 (CH, 4 C, C-14, C-17), 127.74 ($C_q$, 2 C, C-5a, C-11a), 127.24 (CH, 2 C, C-1, C-2), 127.05 (CH, 2 C, C-7, C-10) ppm. MS (EI, 70 eV): *m/z* (%) = 409 (30) $[M - H]^+$, 286 (70), 209 (100). MS (CI, 70 eV): *m/z* (%) = 410 (100) $[M]^+$. MS (ESI, 70 eV): *m/z* (%) = 411 (100) $[M + H]^+$, 433 (20) $[M + Na]^+$. $C_{30}H_{18}O_2$ (410.47): calcd. C 87.80, H 4.40; found C 87.74, H 4.36.

**5,12-Diphenyl-5,6:11,12-di-*o*-phenylene-5,12-dihydrotetracene (Pseudorubrene, 7):** Compound **4** (3.0 g, 7.3 mmol; 1 equiv.) was suspended in dry toluene (300 mL) and heated at 60 °C. An excess (73.1 mL, 20 equiv.) of phenylmagnesium chloride (27 wt.-% in THF, 2.0 M) was purged into the clear solution and the reaction mixture was kept at 80 °C for 48 h. After cooling to room temperature the green-brown solution was quenched with 1 M HCl (150 mL) and stirred intensely for 1 h. Ice (90 g) and after another 30 min additional 1 M HCl (150 mL) was added. The resulting orange organic layer was decanted, extracted with water, dried with magnesium sulfate, and solvent was removed under high vacuum at 70 °C. The pale-orange foamed solid was dehydrated in boiling glacial acetic acid for 12 h. White pseudorubrene precipitated and was separated by centrifugation. Washing with acetic acid, ethyl acetate, and hexane and drying in vacuo yielded **7** as a white powder (3.8 g, 7.2 mmol; 98 % yield), which was sublimed at 310 °C under high vacuum ($10^{-3}$ mbar). IR (ATR): $\tilde{\nu}$ = 3059 [w, $\nu(C_{aryl}–H)$], 3023 (w), 1596 (w), 1489 (m), 1461 (m), 1447 (m), 1377 (w), 1351 (w), 1182 (w), 1154 (w), 782 (m), 758 (m), 737 (s), 690 (m), 665 (s), 613 (m), 590 (w), 522 (w), 459 (w) $cm^{-1}$. Raman (85 mW): $\tilde{\nu}$ = 3059 [w, $\nu(C_{aryl}$-H)], 1596 [s, $\delta(C–C)_{aryl}$], 1525 (w), 1463 (w), 1382 (w), 1352 (w), 1267 (w), 1174 (w), 1159 (w), 1097 (w), 1059 (w), 994 (w), 925 (w), 300 (w), 226 (w), 194 (w), 171 (w), 105 (w) $cm^{-1}$. $^1H$ NMR [500 MHz, $CS_2$/$CHCl_3$ (v/v, 400:1), 25 °C]: $\delta$ = 8.78 [dd, $^3J$(11H,12H) = 3.3, $^4J$(11H,13H) = 3.1 Hz, 2 H, 11-H, 14-H], 8.23 [d, $^3J$(10H,9H) = 7.8 Hz, 2 H, 10-H, 15-H], 8.01 [dd, $^3J$(3H,4H) = 3.4, $^3J$(3H,5-H) = 2.4 Hz, 2 H, 3-H], 7.72 [dd, $^3J$(12H,11H) = 3.3, $^3J$(12H,14H) = 3.1 Hz, 2 H, 12-H, 13-H], 7.54 [d, $^3J$(2H,1H) = 7.4 Hz, 2 H, 2-H, 7-H], 7.40 [t, $^3J$(9H,10H) = 7.8, $^3J$(9H,8H) = 1.2 Hz, 2 H, 9-H, 16-H], 7.28 [dd, $^3J$(4H,3H) = 3.4 Hz, 2 H, 4-H, 5-H], 7.26 [t, $^3J$(1H,2H) = 7.6, $^3J$(1H,16H) = 1.2 Hz, 2 H, 1-H, 8-H], 6.68–6.61 (m, 10 H, 17-H–21-H, 22-H–26-H) ppm. $^{13}C$ NMR [500 MHz, $CS_2$/$CHCl_3$ (v/v, 400:1), 25 °C]: $\delta$ = 151.97 ($C_q$, 2 C, C-2a, C-6a), 146.99 ($C_q$, 2 C, C-2b[1], C-6b[1]), 141.85 ($C_q$,2 C, C-2c, C-6a), 141.53 ($C_q$, 2 C, C-10a, C-14c), 140.61 ($C_q$, 2 C, C-21a, C-26a), 135.19 ($C_q$, 2 C, C-10b, C-14b), 130.46 ($C_q$, 2 C, C-10c, C-14a), 127.90 (CH, 4 C, C-18, C-20, C-23, C-25), 127.56 (CH, 4 C, C-17, C-21, C-22, C-26), 127.37 (CH, 2 C, C-9, C-15), 126.58 (br., CH, 2 C + 2 C, C-2, C-7 + C-3, C-6), 126.16 (CH, 2 C, C-1, C-8), 126.02 (CH, 2 C, C-12, C-13), 125.93 (CH, 2 C, C-4, C-5), 125.59 (CH, 2 C, C-19, C-24), 125.25 (CH, 2 C, C-11, C-14), 122.92 (CH, 2 C, C-10, C-15), 60.88 ($C_q$, 2 C, C-2b, C-6b) ppm. MS (EI, 70 eV): *m/z* (%) = 530 (100) $[M]^+$, 453 (40) $[M - Ph]^+$, 376 (30) $[M - 2Ph]^+$. $C_{42}H_{26}$ (530.67): calcd. C 95.06, H 4.94; found C 95.02, H 4.99.

**5,6:11,12-Di-*o*-phenylenetetracene (DOPT, 8):** Freshly cut potassium (0.44 g, 11.3 mmol; 6 equiv.) was placed in a flame-dried flask under argon. The alkali metal was sublimed and deposited in high vacuo onto the bottom of the flask. Dried **7** (1.0 g, 1.89 mmol; 1 equiv.) in THF (100 mL) and a pre-dried magnetic stirring bar was added. The sealed suspension was vigorously stirred for 1 d at room temperature. The end of the reaction was monitored by a color change from purple to deep-red. Subsequently *i*PrOH, EtOH, and water were added in small portions under a flow of argon. Stirring for 1 h at room temperature led to a blue-black precipitation. The solid was filtered off, washed with hot *i*PrOH (*) and water, and dried with activated molecular sieves (3 Å). The solid was recrystallized from dry toluene to obtain pure **8** (497 mg, 1.32 mmol, 70 %; overall yield: 62 %). IR (ATR): $\tilde{\nu}$ = 3068 [w, $\nu(C_{aryl}–H)$], 1472 (w), 1428 (m), 1382 (w), 1307 (w), 1140 (w), 760 (s, 4H-tetracene), 681 (s, 4H-phenylene), 460 (w) $cm^{-1}$. Raman (85 mW): $\tilde{\nu}$ = 3075 [w, $\nu(C_{aryl}–H)$], 1682, 1612, 1588 [m, $\delta(C–C)_{aryl}$], 1448 [s; $\delta(C–C)_{aryl}$], 1400, 1340, 1337, 1284, 1170, 1068, 1005 [w, $\delta[(C–C)_{aryl}$], 872, 658, 387, 348, 178 $cm^{-1}$. UV/Vis ($CHCl_3$): $\lambda_{max}$ = 290, 304, 431, 523, 561, 607 nm. UV/Vis ($CS_2$): $\lambda_{max}$ = 427, 533, 574, 622 nm. UV/Vis (THF): $\lambda_{max}$ = 290, 304, 431, 523, 561, 607 nm. $^1H$ NMR [500 MHz, $CS_2$/$CDCl_3$ (v/v, 40:1), 25 °C, TMS]: $\delta$ = 8.43 [dd, $^3J$(3H,4H) = 3.6, $^4J$(3H,5H) = 3.3 Hz, 4 H, 3-H], 7.91 [dd, $^3J$(2H,1H) = 3.2, $^4J$(15H,1H) = 2.4 Hz, 4 H, 2-H], 7.52 [dd, $^3J$(4H,3H) = 3.6, $^3J$(4H,6H) = 3.3 Hz, 4 H, 4-H], 7.17 [dd, $^3J$(1H,2H) = 3.2, $^3J$(1H,15H) = 2.4 Hz, 4 H, 1-H] ppm. HRMS: calcd. for $C_{30}H_{16}$ 376.13; found 376.1252. MS (EI, 70 eV): *m/z* (%) = 376 (100) $[M]^+$, 188 (15) $[M]^{2+}$. $C_{30}H_{16}$ (376.46): calcd. C 95.72, H 4.28; found C 95.58, H 4.26.

**5,12-Dihydro-5,6:11,12-di-*o*-phenylenetetracene (Dihydro-DOPT, 9):** From the synthesis of DOPT, the purple *i*PrOH washing solution (*) from the final work-up was separated and dried with

$MgSO_4$. All the solvent was removed in vacuo and the residue separated by column chromatography on Kieselgel 60 with $CH_2Cl_2$ as the eluent. Pure white crystals were obtained in trace quantities (7 mg, 18.5 μmol, 1 %). IR (KBr): $\tilde{\nu}$ = 2921, 2857, 1623 (m), 1528 (w), 1461 + 1445 (m), 1383 (m), 1357 (w), 1262 (m), 1180 (w), 1098 (m), 1023 (m), 944 (w), 859 (w), 804 (w), 775 (s, 4H-dihydrotetracene), 745 (w), 714 (s, 4H-dihydrotetracene), 690 (m, 4H-phenylene), 662 (m), 622 (w), 431 (w) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 8.79 [dd, $^3J$(13H,14H) = 3.4, $^4J$(13H,15H) = 2.8 Hz, 2 H, 13-H, 16-H], 8.39 [d, $^3J$(12H,11H) = 7.7 Hz, 2 H, 12-H, 17-H], 8.15 [d, $^3J$(2H,1H) = 7.5 Hz, 2 H, 2-H, 9-H], 7.90 [dd, $^3J$(4H,5H) = 3.3, $^3J$(4H,6H) = 2.0 Hz, 2 H, 4-H, 7-H], 7.69 [dd, $^3J$(14H,13H) = 3.4, $^4J$(14H,15H) = 3.1 Hz, 2 H, 14-H, 15-H], 7.57 [t, $^3J$(11H,10H) = 7.7, $^3J$(11H,12H) = 7.7 Hz, 2 H, 11-H, 18-H], 7.50 [t, $^3J$(1H,2H) = 7.5, $^3J$(1H,18H) = 7.5 Hz, 2 H, 1-H, 10-H], 7.20 [dd, $^3J$(5H,4H) = 3.3, $^3J$(5H,6H) = 2.5 Hz, 2 H, 5-H, 6-H], 5.19 (s, 2 H, 3-H, 8-H) ppm. $^{13}C$ NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 145.93 ($C_q$, 2 C, C-2a, C-8a), 144.32 ($C_q$, 2 C, C-12a, C-16a), 143.20 ($C_q$, 2 C, C-3a$^1$, C-8a$^1$), 138.47 ($C_q$, 2 C, C-3a, C-7a), 134.27 ($C_q$, 2 C, C-12b, C-16b), 130.77 ($C_q$, 2 C, C-12a, C-16a), 128.60 (CH, 2 C, C-2, C-9), 128.69 (CH, 2 C, C-11, C-18), 126.28 (CH, 2 C, C-5, C-6), 126.42 (CH, 2 C, C-4, C-7), 126.37 (CH, 2 C, C-1, C-10), 126.18 (CH, 2 C, C-14, C-15), 125.61 (CH, 2 C, C-13, C-16), 124.17 (CH, 2 C, C-12, C-17), 47.94 (CH, 2 C, C-3a, C-8a) ppm. MS (EI, 70 eV): *m/z* (%) = 378 (100) $[M]^+$, 377 (45) $[M - H]^+$, 376 (40) $[M - 2H]^+$, 188 (10) $[M - 2H]^{2+}$.

**Supporting Information** (see footnote on the first page of this article): 2D NMR spectra (HSQC, HMBC) of **8**, MS of **4**, **5**, **7**, and **8**, IR and Raman spectra of **4**, **7**, and **8**, UV/Vis spectra of **8**.

**Keywords:** Aromaticity · Fused-ring systems · Hydrocarbons · Reaction mechanisms

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Received: September 23, 2015
Published Online: December 11, 2015