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o-Quinones Derived from Tribenzotriquinacenes: Functionalization of Inner Bay Positions and Use for Single-Wing Extensions

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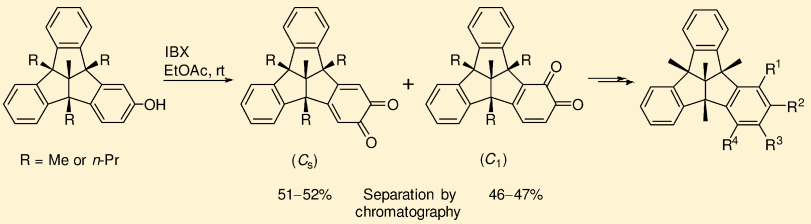
Supporting Information



ABSTRACT: Through a surprisingly nonregioselective oxidation process, the reaction of two analogous 2-hydroxy-substituted tribenzotriquinacenes (TBTQs) **8a**/**8b** by *o*-iodoxybenzoic acid was found to afford the corresponding C_s- and C_1-symmetrical TBTQ-*o*-quinones **6a**/**6b** and **7a**/**7b**, respectively, in 1:1 ratio and excellent combined yields. This finding represents the first example of direct introduction of a functional group into a sterically hindered, inner bay-positions of a parent TBTQ skeleton. In contrast, the analogous reaction with 1-hydroxy-TBTQ **15** failed to produce the desired *o*-quinone **7a**. After reduction of the quinones **6a** and **7a** to the corresponding catechols **17** and **23**, electrophilic aromatic substitution could also be realized at the activated inner bay-position(s) to afford several tri- and tetrafunctionalized TBTQ compounds **18**, **21**, and **25**. The C_s-symmetrical *o*-quinone **6a** was converted into further single-wing extended derivatives such as TBTQ-based phenazines **27a**–**f**, through condensation reactions, and to benzodioxine derivative **32** by Diels–Alder reaction with tetracyclone. The novel TBTQ-quinones and the corresponding TBTQ-catechols offer a variety of new accesses to single-wing-extended and -functionalized TBTQ derivatives.

INTRODUCTION

Tribenzotriquinacene hydrocarbons, including the bridgehead tetraalkyl derivatives **1** (Figure 1), are chemically versatile building blocks with a bowl-shaped, conformationally rigid, polycyclic aromatic framework bearing three mutually orthogonal indane wings. After the introduction of this structural motif in 1984,[1] the chemistry of TBTQ has evolved over two decades but regained interest since 2006.[2] A number of functionalized TBTQ-based key intermediates with achiral (C_{3v}, C_s) and chiral (C_3, C_1) substitution patterns have been developed and used for the construction of extended bowl-shaped molecular hosts. For example, the 2,3,6,7,10,11-hexaamino-TBTQ derivative **2a** and the hexabromo congener **2c** were used to synthesize fullerene receptors.[3−6] The hexahydroxy analogue **2b** was employed to prepare microporous polymers,[7] and more recently, a related TBTQ-tris-catechol served as a building block for molecular cubes in a dynamic covalent approach.[8,9] Other C_{3v}-symmetrical congeners, such as **2d** and **2e**, have also been used to extend the TBTQ skeleton by 6-fold C−C or C−heteroatom coupling reactions.[2,10] In particular, the C_{3v}-symmetrical hexachloromethyl derivative **2e** proved to be an important key intermediate for the synthesis of various expanded C_{3v}-symmetrical compounds bearing the concave TBTQ core, thus generating nanoscale cagelike molecules.[10] With regard to chiral TBTQ derivatives, the C_3-symmetrical trialdehyde **3a** was used in a dynamic covalent assembly to furnish three diastereomeric multiple Schiff-base TBTQ-cryptophanes.[11] The C_3-symmetrical trinitro **3b** and triamino **3c** derivatives offer further applications in this vein. A remarkably regioselective bis-formylation of the TBTQ hydrocarbon **1a** afforded a mixture of difunctionalized derivatives **4a**, **4b**, and **4c**. Optical resolution of C_1-symmetrical (chiral) dialdehyde **4a** was achieved via the diastereomeric (*R*)-BINOL diethers of the corresponding benzylic alcohols. The C_s-symmetrical (achiral) dialdehyde **4c** was used as the starting point for the synthesis of cyclophanes bearing the bowls of two TBTQ units attached to each other.[12] Very recently, the optically pure C_1-symmetrical dimethoxy derivative **4d**[13] was employed to construct a chiral molecular square.[14] Still another variant of this theme is functionalization of only one single aromatic nucleus of the

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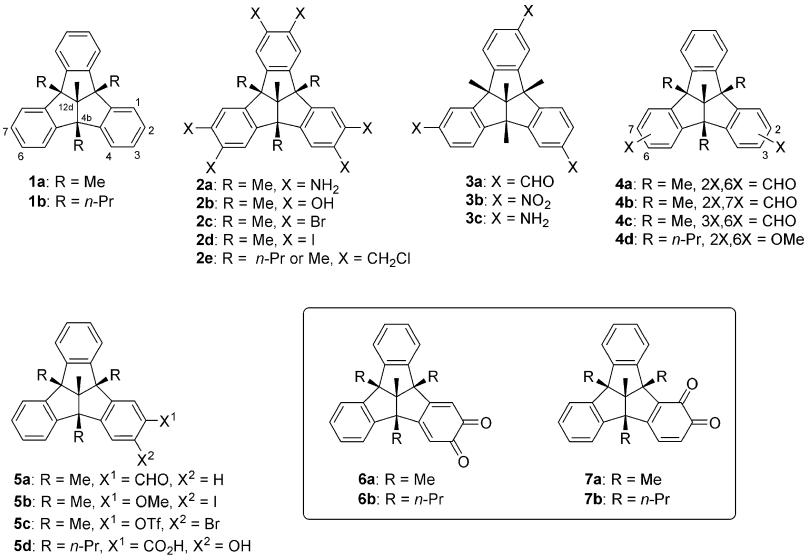


Figure 1. Parent tribenzotriquinacenes (**1**) and a selection of versatile derivatives (**2**–**5**) bearing various functionalization patterns and the novel TBTQ-*o*-quinones **6** and **7** described in the present work.

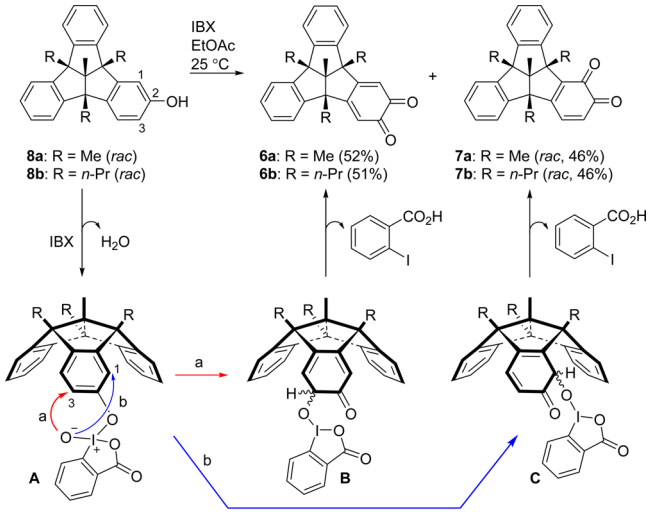
skeleton, such as in **5**[15] which has allowed us to extend only one of the three indane wings. Thus, TBTQ compounds have proved to be truly versatile building blocks for quite complex molecular architecture. A recently developed synthesis of the TBTQ framework by Hopf et al. has even extended the scope of this chemistry in that it offers a directed entry to C_3-symmetrical derivatives bearing *ortho*-substituents.[16,17] This approach may become of particular importance with regard to the regiocontrolled incorporation of one or more substituents at the "inner" (*ortho*-) positions of the aromatic periphery of the TBTQ skeleton, which may be relevant for the further development of TBTQ-based supramolecular chemistry. Functionalization of the *ortho*-positions is considered favorable, albeit not crucial, for the construction of polycyclic (graphene-like) curved hydrocarbon networks containing a TBTQ core.[2,18]

For these reasons, we envisioned that *o*-quinone units incorporated into the TBTQ scaffold are versatile synthetic intermediates since their inherent reactivity enables a number of useful conversions, such as condensation, (cyclo)addition, and redox reactions.[19−21] *o*-Benzoquinones can be easily reduced to the corresponding catechols and readily react with various 1,2-diamines to form a pyrazine ring through condensation reactions.[22,23] The highly reactive 8π-electron system of *o*-quinones exhibits various potential modes for cycloaddition reactions.[24] *o*-Quinones can also be used as catalysts in combination with O_2 as the terminal oxidant for the dehydrogenation reaction of amines.[25] Therefore, we embarked on the synthesis of novel TBTQ derivatives that bear an *o*-benzoquinone unit in place of one of the benzene rings and to study their use for the construction of new extended TBTQ derivatives. As will be shown, we found a useful and efficient access to the achiral, C_s-symmetrical TBTQ-quinones **6** and, at the same time, an unexpected, yet direct access to the regioisomeric chiral, C_1-symmetrical TBTQ-quinones **7** that was the result of direct functionalization at the sterically more hindered inner bay position. A number of conversions of the lower analogues **6a** and **7a** to several tri- and tetrasubstituted TBTQ derivatives functionalized at only one of the aromatic rings are also presented here. It should be noted that these heavily functionalized compounds are otherwise difficult to obtain by the conventional cyclization reactions reported by Kuck[1,2] and Hopf[16,17] or by direct functionalization of parent TBTQ compounds.

RESULTS AND DISCUSSION

The 2-hydroxy-TBTQ derivative **8a** bearing four methyl substituents was prepared according to previous studies.[15] In brief, monoformylation of hydrocarbon **1a** at position C2, followed by Baeyer−Villiger oxidation of the aldehyde with *m*-chloroperbenzoic acid and saponification of the resulting aryl formate with potassium hydroxide, afforded phenol **8a** in 57% overall yield. Compound **8a** was then treated with 1.2 equiv of *o*-iodoxybenzoic acid (IBX, Scheme 1)[26,27] at first in dimethylformamide (DMF). Much to our surprise, and in contrast to results of Pettus' work[28] in which a highly regioselective oxidation was observed, both the C_s-symmetrical quinone, **6a**, and the C_1-symmetrical isomer, **7a**, were formed

Scheme 1. Synthesis and Postulated Formation Mechanism of TBTQ-*o*-quinones 6 and 7



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and isolated in nearly the same yields (**6a**, 48% and **7a**, 43%) after column chromatography. The oxidation reaction was also conducted in other solvents, such as tetrahydrofuran (THF), ethyl acetate (EtOAc), and dichloromethane (DCM), and the reaction in ethyl acetate gave an excellent combined yield of 98% (**6a**, 52% and **7a**, 46%). It is also remarkable that virtually identical results were obtained when TBTQ-phenol **8b** bearing three sterically more demanding *n*-propyl groups at the bridgehead positions was subjected to oxidation with IBX. In that case, the isomeric TBTQ-*o*-quinones **6b** and **7b** were isolated in 51% and 46% yield, respectively. The four TBTQ-*o*-quinones (**6a**−**7b**) were stable under air and storable for several weeks without protection against light, which renders their further transformations very convenient.

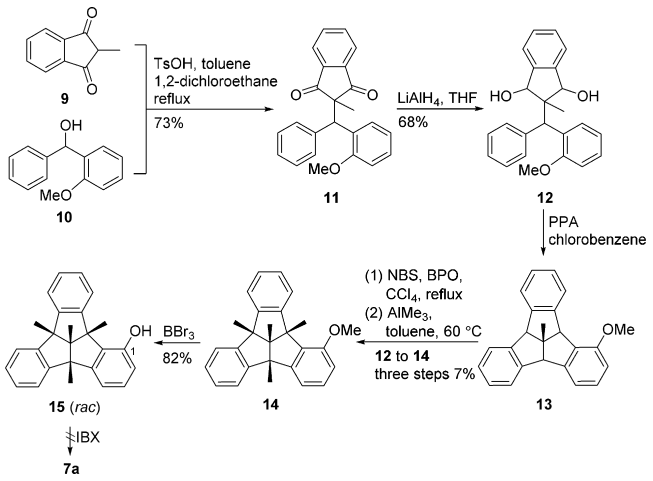
Compounds **6a** and **7a** were characterized by various spectroscopic methods, including ESI mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **6a** reflected the molecular C_s-symmetry and exhibited a characteristic singlet resonance at δ 6.50 for the two protons of the quinone unit and three signals at δ 1.65, 1.61, and 1.31 for the four methyl groups. The ^{13}C NMR spectrum of **6a** gave one signal at δ 179.1 that was attributed to the two equivalent carbonyl carbons. In addition, eight and six ^{13}C signals were identified in the aromatic/olefinic and aliphatic carbon regions, respectively.

This spectral feature is fully consistent with the C_s-symmetrical structure of compound **6a**. The (+)-ESI mass spectrum exhibited the molecular ion peak $[M + Na]^+$ at m/z 389.1522 as the sole signal. On the other hand, the ^{1}H NMR spectrum of isomer **7a** showed four signals at δ 1.72, 1.61, 1.57, and 1.31 due to the nonequivalent methyl groups. The ^{13}C NMR spectrum of **7a** was also consistent with its C_1-symmetrical structure. It gave 26 individual signals for each of the 26 nonequivalent carbon atoms. In analogy to the C_s-isomer **6a**, the (+)-ESI mass spectrum consisted exclusively of the molecular ion peak for the $[M + Na]^+$ ions at m/z 389.1515. Indirect confirmation of the two TBTQ-quinones **6a** and **7a** was obtained by X-ray crystallography of the corresponding catechols **17** and **23** obtained by reduction (Figures S2−S4 and S9).

The formation of both regioisomeric quinones **6a** and **7a** in similar amounts is unexpected. As shown in Scheme 1, the first step of the process should involve esterification of the TBTQ phenol **8a** with IBX to give an intermediate **A**.[28] However, the stereochemical course of the subsequent transformations is less obvious. Not only may the TBTQ-IBX ester **A** be formed as a mixture of diastereomers, but also the orientation of the iodine-coordinated oxygen atom being transferred to the adjacent ring position is ambiguous. The steric congestion of the aromatic moiety of the IBX residue at the concave side of the TBTQ framework may influence the attack, but it is not obvious whether the oxygen transfer takes place preferably from the convex side. Despite the apparently stronger steric hindrance around the C1 position as compared to that of the C3 position, formation of the ester intermediates **B** (pathway a, attack on C3) and **C** (pathway b, attack on C1) is not subject to significant steric hindrance. This unusual reaction also represents the first example of the direct functionalization of the inner bay position of a TBTQ parent compound. Previously, the introduction of functionalities at these positions could only be achieved via cyclization using Kuck's[1,2,13,18] and Hopf's[16] cyclization methods involving prefunctionalized precursor molecules.

In spite of the lack of regioselectivity, the unexpected access to both the "outer" and the "inner" TBTQ-*o*-quinones **6** and **7** and our interest in studying their chemistry prompted us to investigate the possibility of whether the "inner" quinones **7** could be synthesized specifically from a (previously unknown) 1-hydroxy-TBTQ derivative, such as **15**, by IBX oxidation (Scheme 2). We also hoped to gain more insight into the

Scheme 2. Synthesis of 1-Hydroxytribenzotriquinacene 15



reactivity of bowl-shaped hypervalent iodine intermediates of type **B** and **C** in this way. It should be emphasized that there has been no report on bridgehead-alkylated TBTQ derivatives bearing alkoxyl or hydroxyl functionalities at the C1-positions of the benzene units. The 1-methoxy-TBTQ derivative reported by Hopf was secured on the parent hydrocarbon without bridgehead substituents.[16]

To synthesize the 1-hydroxy-4b,8b,12b,12d-tetramethyl TBTQ derivative **15** required for comparison with the 2-hydroxy isomer **8a**, we employed our classical method (Scheme 2).[1,2,7,8,13] Reaction of 2-methyl-1,3-indanedione (**9**) and 2-methoxybenzhydrol (**10**) in the presence of *p*-toluenesulfonic acid in refluxing toluene gave benzhydryl-1,3-indanedione **11** in 73% yield. This diketone was then reduced with lithium aluminum hydride to give indane-1,3-diol **12** as the dominant product in 68% yield, the ^{1}H and ^{13}C NMR spectra of which appeared to indicate one single diasteromer. Unfortunately, the cyclodehydration step employing polyphosphoric acid (PPA) as a catalyst in refluxing chlorobenzene gave a low yield of the desired 1-methoxy-tribenzotriquinacene **13**, accompanied by some unidentifiable side products. This result is reminiscent of similarly inefficient cyclodehydration processes involving certain methoxy-substituted 1,3-diol precursors in either our[13] or Hopf's method.[16,17] It should be noted, however, that methoxy-substituted 2-benzhydryl-1,3-indanediols may undergo quite efficient 2-fold cyclodehydration in other cases.[2,7] Purification of **13** turned out to be excessively cumbersome due to the complex mixtures formed, and the crude product obtained after silica gel filtration was employed as the starting material for the next step. Thus, the crude product **13** was reacted with *N*-bromosuccinimide (NBS, 4.0 equiv) to give the corresponding bridgehead-substituted tribromide, which was not isolated either but converted to the tetramethyl derivative **14** by quenching with trimethylaluminum in toluene. In the end, 1-methoxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene (**14**) was isolated in 7% yield over the last three steps. Luckily,

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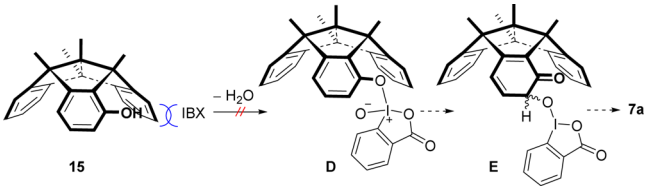
we were even able to grow crystals of **14** from ethyl acetate/petroleum ether that were suitable for X-ray crystal structure analysis (Figure S1). Finally, compound **14** was demethylated by using boron tribromide to give the 1-hydroxy-TBTQ derivative **15** in 82% yield. Surprisingly, and much to our dismay, treatment of **15** with IBX in ethyl acetate or DMF either at ambient temperature or at reflux temperature for 48 h failed to produce the desired TBTQ-*o*-quinone **7a**. We assume that severe steric hindrance impedes O−I bond formation in the esterification step of phenol **15** since the hydroxyl functionality is shielded by both the adjacent benzene ring and the bridgehead methyl group. It can also be speculated that the flexibility within the intermediate **D**, once formed, is too limited to adapt to a conformation that would allow oxygen atom transfer to give intermediate **E** (Scheme 3). A different oxidant system, $CuPF_6/Et_3N/O_2$,[29] was attempted at 25 °C but was found to be unsuccessful.

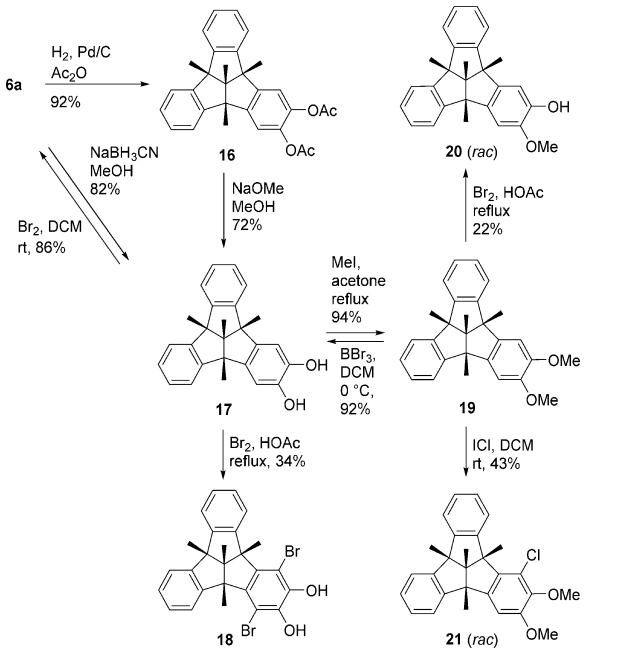
Scheme 3. Steric Hindrance Impedes the IBX Oxidation of 1-Hydroxy-TBTQ Derivative 15 to the "Inner" TBTQ-*o*-quinone 7a



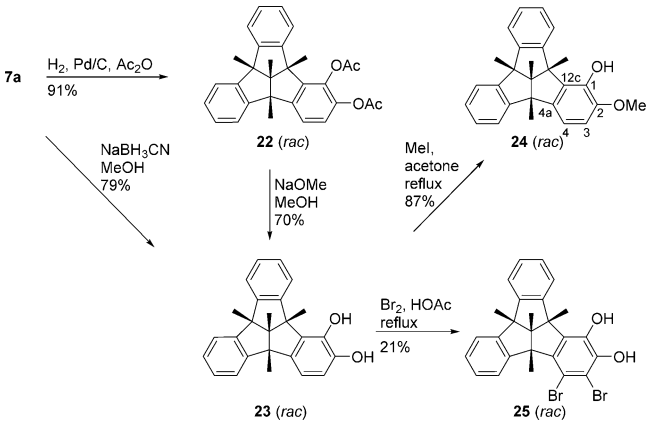
The availability of the two regioisomeric *o*-quinones **6a** and **7a** paved the way for the preparation of their corresponding electron-rich catechols. Thus, diester **16** was prepared in 92% yield from the corresponding *o*-quinone **6a** by hydrogenation over palladium-on-charcoal in the presence of potassium carbonate and acetic anhydride for 12 h (Scheme 4). Treatment of the diacetates with freshly prepared sodium methoxide in anhydrous methanol furnished the C_s-symmetrical TBTQ-catechol **17** (72%). Alternatively, the same catechol **17** was also obtained directly from quinone **6a** in 82% yield by using 6 equiv of sodium cyanoborohydride in methanol at 0 °C. Moreover, electrophilic aromatic halogenation of catechol **17** led to TBTQ derivatives that bear, site-selectively, three or even four functional groups at the very same benzene ring, substitution patterns that are difficult to obtain by conventional direct electrophilic aromatic substitution of the parent TBTQ compounds. Hence, bromination of **17** in boiling acetic acid provided 1,4-dibromo-2,3-dihydroxy-TBTQ **18** in 34% yield, and the crystal structure of **18** was obtained in ethyl acetate (Figure S5), whereas treatment of **17** with bromine in dichloromethane at 25 °C regenerated the *o*-quinone **6a** (86%). Methylation of **17** using methyl iodide in acetone at 80 °C afforded the 2,3-dimethoxy-TBTQ derivative **19**, and the subsequent reaction with bromine in acetic acid at reflux temperature produced 2-hydroxy-3-methoxy-TBTQ **20** in 22% yield,[30] whereas the reaction with iodine monochloride[31] gave the chlorination product 1-chloro-2,3-dimethoxy-TBTQ derivative **21** in 43% isolated yield. Demethylation of **19** with boron tribromide regenerated the TBTQ-catechol **17** in 92% yield.

In a similar manner, reduction of the inner *o*-quinone **7a** by hydrogenation over palladium-on-charcoal in the presence of potassium carbonate and acetic anhydride for 12 h gave the diacetate **22** in 91% yield (Scheme 5). The acetyl groups were

Scheme 4. Reduction of *o*-Quinone 6a to TBTQ-catechol 17 and Its Further Elaboration to Other Site-Selective Di-, Tri-, and Tetrafunctionalized Groups at the Same Benzene Ring in TBTQ Derivatives 16−21



Scheme 5. Reduction of *o*-Quinone 7a to TBTQ-catechol 23 and Subsequent Transformations to TBTQ Derivatives 22, 24, and 25



then removed by use of freshly prepared sodium methoxide in anhydrous methanol to give the C_1-symmetrical catechol **23** in 70% yield. Again, the same catechol was also obtained directly from **7a** by reduction with sodium cyanoborohydride in methanol at 0 °C. Methylation of **23** using 10 equiv of methyl iodide in acetone at 80 °C afforded exclusively the 1-hydroxy-2-methoxy-TBTQ **24** in 87% yield. The structure of compound **24** was confirmed by its HMBC spectrum, in which correlations from OCH_3 (δ_H 3.78, s) to C-2 (δ_C 145.8), from OH (δ_H 5.87, s) to C-2, C-4a (δ_C 141.4), and C-12c (δ_C 133.2), from H-3 (δ_H 6.71, d, J = 8.0 Hz, 1H) to C-1 (δ_C 143.8), C-2, and C-4a and from H-4 (δ_H 6.88, J = 8.0 Hz, 1H) to C-2, C-4a and C-12c could be established. This result is in accordance with the finding that the 1-hydroxy-TBTQ derivative **15** does not undergo oxidation by IBX, and once again, it demonstrates the efficient steric hindrance at the inner peripheral positions of the

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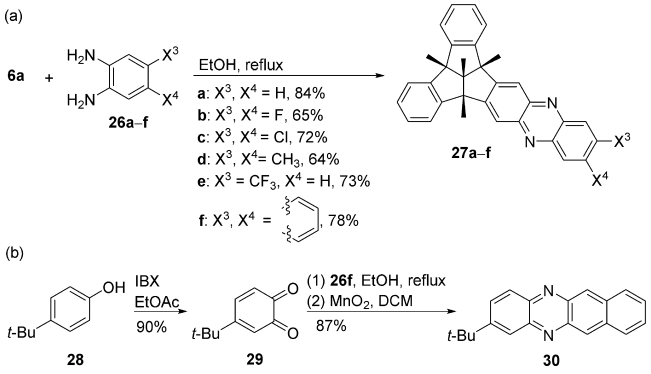
TBTQ skeleton. Bromination of **23** with bromine in boiling acetic acid furnished 1,2-dibromo-3,4-dihydroxy-TBTQ **25** in moderate yield (21%). Good-quality crystals of the two catechols **17** and **23** were obtained from a number of solvents, such as ethyl acetate/petroleum ether, acetone, and THF. The X-ray structure analyses performed with these various single crystals were revealing (Figures S2–S4 and S9). All of these di-, tri-, and tetrafunctionalized TBTQ compounds are potential key building blocks that can be further elaborated to produce single-wing-expanded TBTQ derivatives.

As mentioned in the Introduction, *o*-benzoquinones offer many possibilities for extensions of the molecular framework. With the "outer" isomer **6a** in hand, condensation reactions[22,23] with various commercially available *o*-phenylenediamines **26** in anhydrous ethanol were carried out under reflux and argon atmosphere (Scheme 6a). The product phenazines **27a–f** were

Scheme 6. (a) Condensation Reactions of TBTQ-*o*-quinone 6a with Various *o*-Phenylenediamines 26a–f Affording Phenazines 27a–f and (b) Synthesis of a Model Benzo[*b*]phenazine 30 for Comparison of the Photophysical Properties



obtained in good yields (64–84%). Diamines with electron-withdrawing groups gave lower yields (**27b**, **27c**, **27e**), presumably owing to their inferior nucleophilicity. These "single-wing" extended TBTQ derivatives were found to be quite soluble in common organic solvents, such as dichloromethane, ethyl acetate, benzene, and toluene. Their structures were determined by NMR spectroscopy, mass spectrometry, and in part, by X-ray single-crystal structure analysis (**27b** and **27c**, Figures S6, S7, and S10). In contrast, the "inner" *o*-quinone **7a** failed to react under the same conditions despite numerous attempts. This result was not too surprising because the steric hindrance should strongly disfavor the 2-fold addition–condensation steps. Compounds **27a–f** represent a number of single-wing extended TBTQ derivatives with rigid ladle-like molecular structures, and their particular geometry may have potential application in supramolecular chemistry and synthetic molecular machines. In order to shed some light on the electronic interaction of the three aromatic flaps fixed in the TBTQ cores of the diazatetracene **27f** in mutually orthogonal orientation, a simple "monomeric" model compound, the *tert*-butylated 5,12-diazatetracene (**30**), was synthesized in a three-step sequence and isolated in 78% yield (Scheme 6b).

The absorption and emission spectra of the TBTQ-phenazines **27a–f** and **30** were also studied. The absorption and emission maxima are summarized in Table 1. It was found that the maximum absorption wavelengths range from 376 to 412 nm (**27a–f**), and a much lower value (280 nm) was

Table 1. Photophysical Properties of 30 and the TBTQ-phenazines 27a–f

compd	30	27a	27b	27c	27d	27e	27f
λ_{abs} [a] (nm)	280	376	385	380	392	376	412
λ_{em} [b] (nm)	337	431	450, 470	524	482	477	537, 569
Φ_f [c] (%)	5.4	7.3	*d*	5.6	5.9	5.7	3.0

[a]Only the maximum absorptions are given (TBTQ-phenazines listed from 320 to 450 nm). [b]Wavelength of maximum emission when excited at the maximum absorption. [c]Absolute quantum yield, measured in THF (10 μM). [d]Quantum yield not measured because of weak fluorescence.

observed for the model compound **30**. Halogenation and trifluoromethylation of the phenazine unit does not induce any marked shift of the absorption bands. Compound **27f** exhibited significant red-shifted emission band to 569 nm as compared to model compound **30** (337 nm), which suggested that the three aromatic chromophores assembled at the TBTQ core of **27f** perturb the benzo[*b*]phenazine electronic system. The emission of **27a–f** covered the visible region with a center wavelength ranging from 431 to 569 nm by simply introducing different types of donor or acceptor functional groups (Figure 2). It is believed that electronic effects of the substitutent

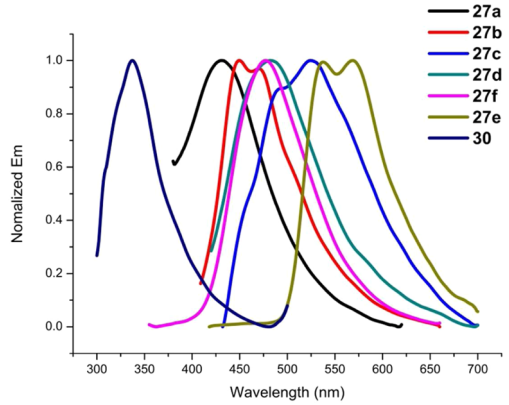


Figure 2. Normalized fluorescence spectra of **30** and TBTQ-phenazines **27a–f** in solution.

groups may be responsible for such color variations. The fluorescence quantum yields (Φ_f) were measured at 25 °C in air-saturated THF. Very weak or almost no fluorescence was observed in diluted solution. This may be ascribed to the lack of conjugation between the three aromatic wings of the TBTQ-based phenazines **27**.

Our next goal was to perform single-wing extension of TBTQ-quinone **6a** via the Diels–Alder reaction. The chemistry of *o*-quinones and their cycloaddition reactions, in particular, has invoked considerable interest.[32] We have examined the reactivity of TBTQ-*o*-quinone **6a** toward the highly electron-deficient tetracyclone **31** by reacting these compounds in a Schlenk tube in benzene at 100 °C for 8 h (Scheme 7).

The reaction could be easily followed by slow decolorization of the initially deeply red solution. Column chromatography through silica gel afforded the benzodioxine derivative **32** as a yellow solid in 80% yield, the ^{1}H NMR spectrum of which suggested the presence of one major component accompanied by some minor stereoisomeric products. Unfortunately, separation of the various stereoisomers by flash column chromatography failed. However, single crystals suitable for

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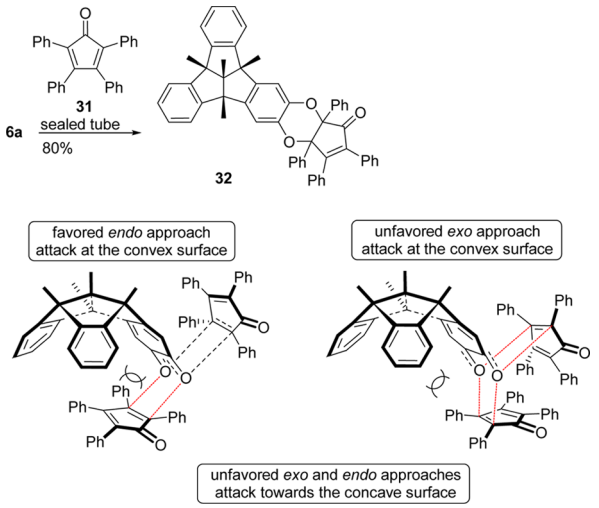
Scheme 7. (Top) Diels–Alder Reaction between TBTQ-*o*-quinone 6a and Tetracyclone (31) To Give 32; (Bottom) Four Possible Orientations of the Reactants during the Cycloaddition Process[a]



[a]The *endo* approach at the convex side of the TBTQ-quinone was favored.

X-ray structure analysis could be obtained by slow evaporation of a solution of **32** in hexane/dichloromethane (Figure S8). The resulting structure turned out to be the *endo-anti*-stereoisomer, bearing the added cyclopentenone ring and the TBTQ bowl on opposite sides of the extended indane wing (Scheme 7). It may be speculated that, besides the preferred *endo*-orientation of the cyclopentadienone π-electron system, steric hindrance between the incoming dienophile and the concave surface of TBTQ-quinone **6a** is a key factor in dictating the stereochemical outcome of the cycloaddition process.

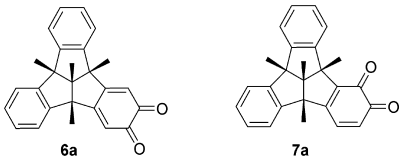
CONCLUSION

In summary, we have reported an unexpected, nonregioselective IBX oxidation method to synthesize novel bowl-shaped *o*-quinones from the 2-hydroxytribenzotriquinacenes **8a** and **8b**. Thus, the C_s-symmetrical ("outer") TBTQ-derived quinones **6a** and **6b** became accessible, together with the corresponding C_1-symmetrical ("inner") isomers **7a** and **7b**, which all can be obtained easily in pure form by chromatography from the 1:1 mixtures **6a**/**7a** and **7a**/**7b**. Rich follow-up chemistry of both compounds provided interesting new paths to construct single-wing extended TBTQ derivatives, such as TBTQ-based catechols **17** (C_s) and **23** (C_1), TBTQ-phenazines **27a–f**, and the benzodioxine derivative **32**.

The chemistry described here should be extendable in a number of directions, including the oxidation of other hydroxy-functionalized centropolyindanes[2] and the corresponding functionalization of more than one indane wing as well as further chemistry that could evolve from such investigations. In a more general view, owing to the ease of synthesis, the highly symmetrical structures involved, and the functional versatility, TBTQ-*o*-quinones may constitute powerful building blocks for future materials science. Our work on macrocycles of this type and on a large-scale synthesis of TBTQ-based catechols is ongoing.

EXPERIMENTAL SECTION

General Information. All reactions that required anhydrous conditions were carried out by standard procedures under argon atmosphere. Commercially available reagents **10**, **26a–f**, **28**, and **31** were used as received. The solvents were dried by distillation over appropriate drying reagents. Petroleum ether (PE) used had a boiling range of 60–90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was performed through silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 or 600 MHz NMR spectrometer, as were the DEPT 135 experiments. Chemical shift values (δ) are given in ppm and coupling constants (J) in hertz (Hz). Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference ($CDCl_3$: δ_H 7.26, δ_C 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet). Melting points were determined by use of a microscope apparatus and are uncorrected. High-resolution mass spectra were obtained on a 4G mass spectrometer using electrospray ionization (ESI). Single-crystal X-ray diffraction measurements were made on a diffractometer working with graphite-monochromated Mo Kα or Cu Kα radiation. Compounds **1a**,[2,15] **1b**,[33] **8a**,[15] **8b**,[33] and **9**[34] were synthesized as previously reported.



*4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydrobenzo-[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-d]-o-benzoquinone (**6a**) and 4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydrobenzo[5,6]-indeno[1′,2′,3′:3,4]pentaleno[1,2-c]-o-benzoquinone (**7a**).* (a) Prepared from phenol **8a**. A mixture of phenol **8a** (102 mg, 0.29 mmol) and IBX (98 mg, 0.35 mmol) in EtOAc (30 mL) was stirred at 25 °C for 24 h. A color change from yellow to dark red was observed. The reaction was quenched with water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1, R_f = 0.25 for **6a**, R_f = 0.20 for **7a**) afforded **6a** (55 mg, 52%) and **7a** (49 mg, 46%), respectively, as a green amorphous solid. Compound **6a**: mp 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.41 (dd, J = 8.0, 1.6 Hz, 2H), 7.27–7.22 (m, 6H), 6.50 (s, 2H), 1.66 (s, 3H), 1.62 (s, 6H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 179.1 (C), 168.8 (C), 148.9 (C), 144.0 (C), 128.9 (CH), 128.6 (CH), 123.3 (CH), 123.0 (CH), 121.9 (CH), 69.3 (C), 63.5 (C), 61.0 (C), 25.8 (CH_3), 25.0 (CH_3), 16.1 (CH_3); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{22}O_2Na$ 389.1512, found 389.1522. Compound **7a**: mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.69 (dd, J = 7.6, 0.8 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.41 (dd, J = 7.6, J = 0.8 Hz, 1H), 7.31–7.15 (m, 6H), 6.27 (d, J = 10.4 Hz, 1H), 1.73 (s, 3H), 1.62 (s, 3H), 1.57 (s. 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 181.0 (C), 177.5 (C), 155.5 (C), 150.0 (C), 148.5 (C), 145.9 (C), 144.4 (C), 142.0 (C), 136.9 (CH), 130.2 (CH), 129.0 (CH), 128.2 (CH), 127.78 (CH), 127.77 (CH), 125.9 (CH), 124.0 (CH), 122.7 (CH), 122.4 (CH), 69.0 (C), 63.9 (C), 63.4 (C), 62.7 (C), 26.6 (CH_3), 22.0 (CH_3), 21.4 (CH_3), 15.7 (CH_3); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{22}O_2Na$ 389.1512, found 389.1515. (b) Prepared from TBTQ-catechol **17**. A solution of bromine (26 μL, 0.50 mmol) was gradually added dropwise to a stirred solution of catechol **17** (85 mg, 0.23 mmol) in DCM (15 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred at 25 °C for 12 h. Then water was added (10 mL) to the mixture, and the mixture extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/

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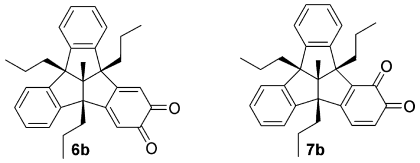
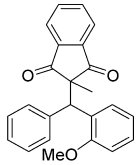
EtOAc 20:1, R_f = 0.25) afforded **6a** as a green amorphous solid (72 mg, 86%).

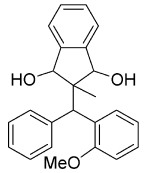


*4d-Methyl-4b,8b,12b-tripropyl-8b,12b-dihydrodibenzo[2,3:4,5]-pentaleno[1,2-d]-o-benzoquinone (**6b**) and 4d-Methyl-4b,8b,12b-tripropyl-8b,12b-dihydrodibenzo[2,3:4,5]pentaleno[1,2-c]-o-benzo-quinone (**7b**).* The preparation procedure was the same as that used for compounds **6a** and **7a** (procedure a). Starting from compound **8b** (100 mg, 0.23 mmol) and IBX (78 mg, 0.28 mmol), compounds **6b** (53 mg, 51%) and **7b** (48 mg, 46%) were obtained after flash column chromatography (petroleum ether/EtOAc 20:1, R_f = 0.30 for **6b**, 0.23 for **7b**) as a green amorphous solid. Compound **6b**: mp 151−153 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.32 (d, J = 6.8 Hz, 2H), 7.24−7.14 (m, 6H), 6.40 (s, 2H), 2.15−2.01 (m, 6H), 1.56 (s, 3H), 1.43−1.11 (m, 6H), 0.96−0.94 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 179.1 (C), 168.2 (C), 148.2 (C), 143.5 (C), 128.6 (CH), 128.3 (CH), 123.8 (CH), 123.4 (CH), 121.9 (CH), 71.4 (C), 68.2 (C), 65.7 (C), 41.0 (CH_2), 40.0 (CH_2), 20.3 (CH_2), 19.9 (CH_2), 15.06 (CH_3), 15.00 (CH_3), one CH_3 resonance was not resolved; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{32}H_{35}O_2$ 451.2632, found 451.2626. Compound **7b**: mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.63 (dd, J = 7.6, J = 1.2 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 1.2 Hz, 1H), 7.33−7.11 (m, 6H), 6.24 (d, J = 10.4 Hz, 1H), 2.43−2.35 (m, 1H), 2.11−2.03 (m, 5H), 1.56 (s, 3H), 1.43−1.26 (m, 6H), 1.00 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 181.0 (C), 177.4 (C), 155.4 (C), 149.1 (C), 147.6 (C), 145.6 (C), 143.8 (C), 141.7 (C), 137.4 (CH), 129.7 (CH), 128.6 (CH), 127.8 (CH), 127.4 (CH), 126.4 (CH), 124.4 (CH), 123.1 (CH), 122.8 (CH), 71.1 (C), 68.4 (C), 67.9 (C), 67.3 (C), 41.2 (CH_2), 36.9 (CH_2), 36.8 (CH_2), 21.0 (CH_2), 20.4 (CH_2), 20.2 (CH_2), 15.1 (CH_3), 14.9 (CH_3), 14.8 (CH_3), 14.6 (CH_3), one Ar-CH resonance was not resolved; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{32}H_{34}O_2Na$ 473.2451, found 473.2445.



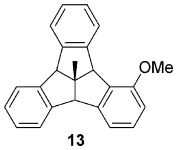
11

*2-[(2-Methoxyphenyl)phenylmethyl]-2-methyl-1H-indene-1,3(2H)-dione (**11**).* A mixture of 2-methyl-1,3-indanedione **9** (1.00 g, 6.25 mmol), 2-methoxybenzhydrole **10** (1.34 g, 6.26 mmol), and p-toluenesulfonic acid monohydrate (0.38 g, 2.00 mmol) in toluene (50 mL) was heated to reflux for 24 h with a Dean−Stark trap. Upon completion of the reaction, the mixture was cooled to 25 °C, washed with saturated aqueous K_2CO_3 solution (15 mL), and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 4:1, R_f = 0.6) afforded **11** (1.62 g, 73%) as a colorless solid: mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.86−7.80 (m, 3H), 7.69−7.67 (m, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.12−7.08 (m, 3H), 7.02 (t, J = 7.2 Hz, 1H), 6.89−6.85 (m, 1H), 6.69 (dd, J = 8.0, J = 0.8 Hz, 1H), 5.21 (s, 1H), 3.69 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 204.3 (C), 204.0 (C), 156.9 (C), 141.5 (C), 141.4 (C), 139.7 (C), 135.2 (CH), 130.8 (CH), 129.9 (CH), 128.2 (C), 127.9 (CH), 127.8 (CH), 126.5 (CH), 122.9 (CH), 120.2 (CH), 110.5 (CH), 57.8 (C), 55.2 (CH_3), 48.9 (CH), 19.7 (CH_3), four Ar-CH resonances were not resolved; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{24}H_{20}O_3Na$ 379.1305, found 379.1299.



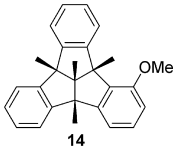
12

*2-[(2-Methoxyphenyl)phenylmethyl]-2-methyl-2,3-dihydro-1H-indene-1,3-diol (**12**).* A solution of the diketone **11** (1.00 g, 2.8 mmol) in anhydrous THF (40 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (168 mg, 4.43 mmol) in dry THF (20 mL) at 0 °C. After the addition was finished, the mixture was heated to reflux for 12 h. The mixture was allowed to cool, and the reaction was quenched by the addition of a small amount of cool water. The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 2:1, R_f = 0.5) afforded a diastereomeric mixture of product **12** as a colorless oil (686 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.86 (d, J = 1.6 Hz, 1H), 7.66 (d, J = 6.8 Hz, 2H), 7.38−7.28 (m, 2H), 7.24−7.21 (m, 6H), 7.00 (td, J = 7.6, J = 1.2 Hz, 1H), 6.92 (dd, J = 8.0, J = 1.2 Hz, 1H), 5.46 (s, 1H), 5.22 (s, 1H), 4.66 (s, 1H), 3.87 (s, 3H), 3.32 (s, OH, 1H), 1.40 (s, OH, 1H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.2 (C), 144.1 (C), 142.6 (C), 141.0 (C), 130.9 (CH), 130.2 (CH), 130.0 (CH), 128.9 (CH), 128.8 (CH), 127.9 (CH), 127.8 (C), 126.9 (CH), 125.2 (CH), 124.4 (CH), 121.0 (CH), 111.5 (CH), 81.4 (CH), 80.7 (CH), 56.2 (CH_3), 56.0 (C), 46.0 (CH), 16.3 (CH_3), two Ar-CH resonances were not resolved; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{24}H_{24}O_3Na$ 383.1618, found 383.1613.



13

*1-Methoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (**13**).* A solution of the diol **12** (0.28 g, 0.78 mmol) formed by gentle warming in chlorobenzene (20 mL) was added dropwise into a stirred solution of polyphosphoric acid (1.00 mL) in chlorobenzene (25 mL). After the addition was complete, the mixture was heated to reflux for 20 h. The reaction mixture was cooled to 25 °C and poured into water (40 mL). The organic layer was then washed with saturated aqueous $NaHCO_3$ solution and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 150:1, R_f = 0.7) afforded the product **13** as a light yellow oil (97 mg, impure): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{21}O$ 325.1587, found 325.1581. Further purification of **13** turned out to be a tedious process. The product isolated after flash column chromatography was used in the next step.



14

*1-Methoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**14**).* A mixture of compound **13** (97 mg, crude), NBS (213 mg, 1.20 mmol), and a small amount of benzoyl peroxide (15 mg) was heated to reflux in CCl_4 (30 mL) under the irradiation of an infrared lamp (245 W) for 5 h. The formed precipitate was removed by suction filtration. The solution was concentrated under reduced pressure, and the residue redissolved in anhydrous benzene (50 mL) while a solution of

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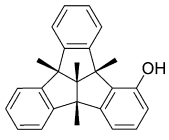
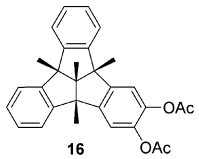
trimethylaluminum (1.08 mL, 2 M in toluene, 2.16 mmol) was added dropwise under argon. After the addition was complete, the mixture was heated to 50 °C for 8 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution and then extracted with DCM (3 × 10 mL).The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 25:1, R_f = 0.3) afforded the product **14** as a colorless solid [20 mg, the total yield in three steps (from **12** to **14**) was 7%]: mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.85 (d, J = 4.8 Hz, 1H), 7.84−7.34 (m, 4H), 7.18−7.13 (m, 4H), 7.04 (d, J = 7.6, Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 1.83 (s, 3H), 1.67 (s, 3H), 1.65 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.0 (C), 151.2 (C), 149.05 (C), 149.01 (C), 148.6 (C), 134.8 (C), 128.7 (CH), 127.47 (CH), 127.40 (CH), 127.37 (CH), 127.0 (CH), 125.5 (CH), 122.9 (CH), 122.8 (CH), 122.5 (CH), 115.4 (CH), 109.5 (CH), 69.6 (C), 64.2 (C), 62.6 (C), 62.5 (C), 55.0 (CH_3), 26.2 (CH_3), 25.9 (CH_3), 23.1 (CH_3), 16.2 (CH_3), one Ar-C resonance was not resolved; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{27}O$ 367.2056, found 367.2061.



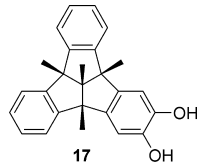
15

*1-Hydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**15**).* Boron tribromide (85 μL, 0.9 mmol) was added dropwise to a stirred solution of **14** (33 mg, 0.09 mmol) in anhydrous DCM (15 mL) at 0 °C. The mixture was stirred at 20 °C for 12 h until the starting material was no longer evident by TLC. The reaction was quenched by the addition of cold water (15 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1, R_f = 0.3) afforded product **15** as a colorless solid (26 mg, 82%): mp >350 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS) δ 7.94 (d, J = 0.8 Hz, 1H), 7.39−7.36 (m, 2H), 7.34−7.33 (m, 1H), 7.17−7.14 (m, 4H), 7.01−7.00 (m, 2H), 6.44 (dd, J = 3.6, J = 2.0 Hz, 1H), 4.77 (s, OH, 1H), 1.84 (s, 3H), 1.648 (s, 3H), 1.643 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS) δ 152.0 (C), 151.6 (C), 149.0 (C), 148.94 (C), 148.88 (C), 148.6 (C), 133.5 (C), 128.6 (CH), 127.5 (CH), 127.47 (CH), 127.41 (CH), 127.1 (CH), 125.4 (CH), 123.0 (CH), 122.8 (CH), 122.5 (CH), 115.6 (CH), 114.6 (CH), 69.7 (C), 63.8 (C), 62.8 (C), 62.6 (C), 26.1 (CH_3), 26.0 (CH_3), 22.9 (CH_3), 16.1 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}O$ 353.1900, found 353.1898.



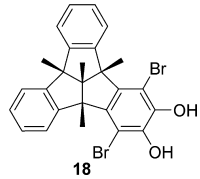
16

*2,3-Diacetoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**16**).* A mixture of TBTQ-*o*-quinone **6a** (59 mg, 0.16 mmol), 10% Pd/C (5 mol %), K_2CO_3 (47 mg, 0.34 mmol), and Ac_2O (39 μL, 0.41 mmol) in MeOH (20 mL) was stirred at 25 °C under H_2 (1.0 atm). The reaction was monitored by TLC, and upon completion of the reaction, the solvent was concentrated under reduced pressure. The mixture was taken up with water (15 mL) and the mixture extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 30:1, R_f = 0.3) afforded **16** as a colorless amorphous solid (67 mg, 93%): mp >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.38−7.36 (m, 2H), 7.28−7.27 (m, 2H), 7.24−7.15 (m, 4H), 7.13 (s, 2H), 2.25 (s, 6H), 1.65 (s, 3H), 1.64 (s, 6H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 168.3 (C), 148.8 (C), 148.1 (C), 147.0 (C), 141.5 (C), 127.78 (CH), 127.73 (CH), 122.9 (CH), 122.7 (CH), 117.3 (CH), 70.1 (C), 62.7 (C), 62.4 (C), 25.8 (CH_3), 20.7 (CH_3), 16.1 (CH_3); one CH_3 resonance was not resolved; HRMS (ESI-TOF) m/z [M + NH_4]$^+$ calcd for $C_{30}H_{32}NO_4$ 470.2326, found 470.2328.



17

*2,3-Dihydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**17**).* (a) Prepared from bis-acetylated TBTQ-catechols **16**. A solution of the diacetate **16** (104 mg, 0.23 mmol) in anhydrous CH_3OH (5 mL) was added dropwise to freshly prepared sodium methoxide in anhydrous CH_3OH (10 mL) at 25 °C and then the solution stirred for 6 h until no starting material was evident by TLC. A color change from green to light red was observed. The solvent was concentrated under reduced pressure. The mixture was quenched with water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 5:1, R_f = 0.2) afforded **17** as a colorless amorphous solid (61 mg, 72%): mp 279−281 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.37−7.35 (m, 2H), 7.28−7.24 (m, 2H), 7.15−7.13 (m, 4H), 6.78 (s, 2H), 4.97 (s, OH, 2H), 1.63 (s, 3H), 1.58 (s, 6H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 148.9 (C), 148.8 (C), 143.4 (C), 141.3 (C), 127.51 (CH), 127.48 (CH), 122.9 (CH), 122.7 (CH), 109.3 (CH), 69.9 (C), 62.6 (C), 62.3 (C), 26.0 (CH_3), 25.8 (CH_3), 16.1 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}O_2$ 369.1849, found 369.1860. (b) Prepared from TBTQ-*o*-quinone **6a**. A mixture of **6a** (100 mg, 0.27 mmol) and $NaBH_3CN$ (102 mg, 1.62 mmol) in anhydrous CH_3OH (15 mL) was stirred at 0 °C under argon atmosphere for 3 h until no starting material was visible by TLC. The solvent was concentrated under reduced pressure, and water was added (15 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 5:1, R_f = 0.2) afforded **17** as a colorless amorphous solid (80 mg, 82%). (c) Prepared from dimethoxy-TBTQ derivative **19**. BBr_3 (230 μL, 2.50 mmol) was added dropwise to a stirred solution of **19** (198 mg, 0.50 mmol) in DCM (20 mL) at 0 °C under argon atmosphere. The reaction was stirred for 10 h until no starting material was visible by TLC. The mixture was quenched with water (5 mL) and then extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 5:1, R_f = 0.2) afforded **17** as a colorless amorphous solid (169 mg, 92%).



18

*1,4-Dibromo-2,3-dihydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**18**).* A solution of bromine (26 μL, 0.50 mmol) in AcOH (5 mL) was added dropwise to a stirred solution of catechol **17** (85 mg, 0.23 mmol) in AcOH (15 mL). The reaction mixture was heated to reflux for 12 h under argon. After the solution was cooled to 25 °C, the solvent was concentrated under reduced pressure. Then water was added (10 mL) and the mixture extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine, dried over

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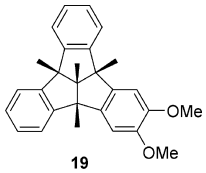
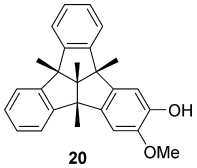
Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 100:1, R_f = 0.3) afforded **18** as a colorless solid (41 mg, 34%): mp 202−204 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.18 (dd, J = 8.0, J = 0.8 Hz, 2H), 7.39 (dd, J = 8.0, J = 1.2 Hz, 2H), 7.22 (dt, J = 7.6, 1.2 Hz, 2H), 7.16 (dd, J = 7.6, J = 4.2 Hz, 2H), 5.87 (s, OH, 2H), 1.93 (s, 6H), 1.55 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.3 (C), 147.4 (C), 140.6 (C), 139.8 (C), 128.1 (CH), 126.8 (CH), 126.1 (CH), 122.8 (CH), 106.4 (C), 71.0 (C), 65.4 (C), 62.4 (C), 27.1 (CH_3), 24.8 (CH_3), 16.9 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{23}{}^{79}Br^{81}BrO_2$ 527.0039, found 527.0036.



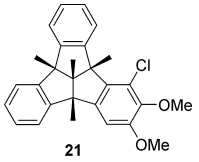
19

*2,3-Dimethoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**19**).* Iodomethane (70 μL, 1.13 mmol) was added dropwise into a stirred mixture of catechol **17** (200 mg, 0.54 mmol) and K_2CO_3 (186 mg, 1.35 mmol) in acetone (20 mL) under argon atmosphere at 25 °C. The reaction was stirred for 1.5 h and then heated at 60 °C for 10 h. The reaction mixture was cooled to 25 °C and concentrated under reduced pressure. The reaction mixture was diluted with water (10 mL) and extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 10:1, R_f = 0.3) afforded **19** (201 mg, 94%) as a colorless solid: mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.40−7.36 (m, 2H), 7.34−7.30 (m, 2H), 7.18−7.14 (m, 4H), 6.82 (s, 2H), 3.86 (s, 6H), 1.66 (s, 3H), 1.64 (s, 6H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.4 (C), 148.9 (C), 148.8 (C), 140.3 (C), 127.5 (CH), 123.0 (CH), 122.6 (CH), 105.7 (CH), 70.0 (C), 62.5 (C), 56.2 (CH_3), 26.0 (CH_3), 25.7 (CH_3), 16.2 (CH_3), one Ar-CH and one sp^3-C resonance were not resolved; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd for $C_{28}H_{32}NO_2$ 414.2428, found 414.2424.



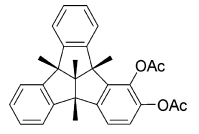
20

*2-Hydroxy-3-methoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**20**).* A solution of bromine (8 μL, 0.16 mmol) in AcOH (5 mL) was gradually added to a stirred solution of dimethoxy-TBTQ derivative **19** (28 mg, 0.07 mmol) in AcOH (15 mL). The reaction mixture was heated to reflux for 10 h under argon. The reaction mixture was cooled to room temperature, and solvent was concentrated under reduced pressure. Water was then added (10 mL) and the mixture extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 50:1, R_f = 0.1) afforded **20** as a colorless solid (6 mg, 22%): mp 161−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.39−7.30 (m, 4H), 7.17−7.13 (m, 4H), 6.90 (s, 1H), 6.79 (s, 1H), 5.46 (s, OH, 1H), 3.86 (s, 3H), 1.65 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.0 (C), 148.9 (C), 148.6 (C), 146.6 (C), 145.6 (C), 141.3 (C), 139.7 (C), 127.52 (CH), 127.48 (CH), 127.44 (CH), 123.0 (CH), 122.85 (CH), 122.84 (CH), 122.5 (CH), 108.2 (CH), 104.7 (CH), 69.8 (C), 62.5 (C), 62.4 (C), 56.1 (CH_3), 26.0 (CH_3), 25.96 (CH_3), 25.7 (CH_3), 16.2 (CH_3), one Ar-C, one Ar-CH, and one sp^3-C resonances were not resolved; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd for $C_{27}H_{30}NO_2$ 400.2271, found 400.2268.



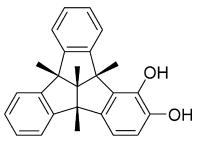
21

*1-Chloro-2,3-dimethoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**21**).* A solution of iodine monochloride (60 mg, 0.37 mmol) in DCM (5 mL) was added dropwise over 10 min into a stirred solution of dimethoxy-TBTQ derivative **19** (60 mg, 0.15 mmol) in DCM (40 mL) at 0 °C. The reaction was monitored by TLC. Upon completion of the reaction (12 h), the mixture was poured into an ice-cold saturated $Na_2S_2O_3$ solution and extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 10:1, R_f = 0.2) afforded **21** (34 mg, 43%) as a colorless solid: mp 191−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.07 (dd, J = 7.6, J = 1.2 Hz, 1H), 7.86 (dd, J = 7.6, J = 1.2 Hz, 1H), 7.39−7.35 (m, 2H), 7.21−7.13 (m, 4H), 6.73 (s, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.90 (s, 3H), 1.79 (s, 3H), 1.59 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 152.2 (C), 149.3 (C), 148.9 (C), 148.21 (C), 148.18 (C), 144.5 (C), 143.9 (C), 137.7 (C), 127.8 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 125.7 (CH), 125.5 (CH), 123.9 (C), 122.7 (CH), 122.4 (CH), 115.0 (CH), 70.5 (C), 64.5 (C), 63.9 (C), 62.5 (C), 60.9 (CH_3), 56.0 (CH_3), 26.5 (CH_3), 24.5 (CH_3), 23.9 (CH_3), 16.6 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{28}{}^{35}ClO_2$ 431.1772, found 431.1774.



22

*1,2-Diacetoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**22**).* The preparation procedure was the same as that used for compound **16**. Starting from quinone **7a** (59 mg, 0.16 mmol), K_2CO_3 (47 mg, 0.34 mmol), and Ac_2O (39 μL, 0.41 mmol), the diacetate **22** was obtained as a colorless amorphous solid (66 mg, 91%). TLC: petroleum ether/EtOAc 20:1, R_f = 0.4; mp >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.64 (dd, J = 8.0, J = 1.2 Hz, 1H), 7.38−7.26 (m, 4H), 7.20−7.15 (m, 4H), 7.05 (d, J = 8.4 Hz, 1H), 2.48 (s, 3H), 2.22 (s, 3H), 1.67 (s, 3H), 1.64 (s, 6H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 168.1 (C), 168.0 (C), 149.1 (C), 148.9 (C), 148.6 (C), 148.1 (C), 147.7 (C), 141.6 (C), 140.3 (C), 137.7 (C), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 124.3 (CH), 123.0 (CH), 122.88 (CH), 122.82 (CH), 120.8 (CH), 70.5 (C), 63.7 (C), 62.7 (C), 62.4 (C), 26.6 (CH_3), 25.8 (CH_3), 23.8 (CH_3), 21.0 (CH_3), 20.8 (CH_3), 16.2 (CH_3), one Ar-CH resonance was not resolved; HRMS (ESI-TOF) m/z $[M + NH_4]^+$ calcd for $C_{30}H_{32}O_4N$ 470.2326, found 470.2339.



23

*1,2-Dihydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**23**).* The preparation procedure was the same as that used for compound **17**. Procedure a: Starting from compound **22** (104 mg, 0.23 mmol) and freshly prepared sodium methoxide in anhydrous CH_3OH (10 mL), the catechol **23** was obtained as a colorless amorphous solid (59 mg, 70%). Procedure b: Starting from **7a** (100 mg, 0.27 mmol) and $NaBH_3CN$ (102 mg, 1.62 mmol), compound **23** was obtained as a colorless amorphous solid (79 mg, 79%): TLC petroleum ether/EtOAc 9:1, R_f = 0.2; mp 271−273 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.97 (dd, J = 8.0, J = 2.0 Hz, 1H), 7.39−7.35 (m, 2H),

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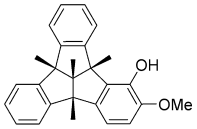
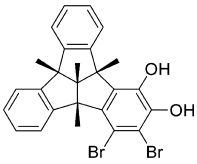
7.30−7.27 (m, 1H), 7.17−7.12 (m, 4H), 6.75 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 5.64 (s, OH, 1H), 4.74 (s, OH, 1H), 1.84 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.2 (C), 148.93 (C), 148.9 (C), 148.5 (C), 144.3 (C), 141.4 (C), 140.7 (C), 134.1 (C), 127.5 (CH), 127.42 (CH), 127.4 (CH), 127.2 (CH), 125.4 (CH), 122.86 (CH), 122.82 (CH), 122.6 (CH), 115.0 (CH), 113.7 (CH), 70.2 (C), 63.7 (C), 62.6 (C), 62.2 (C), 26.2 (CH_3), 26.1 (CH_3), 22.8 (CH_3), 16.2 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{26}H_{25}O_2$ 369.1849, found 369.1846.



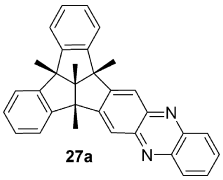
24

*1-Hydroxy-2-methoxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**24**).* The preparation procedure was the same as that used for compound **19**. Starting with catechol **23** (81 mg, 0.22 mmol), iodomethane (137 μL, 2.2 mmol), and K_2CO_3 (364 mg, 2.64 mmol), compound **24** was obtained as a colorless amorphous solid (73 mg, 87%): TLC petroleum ether/EtOAc 6:1, R_f = 0.6; mp 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.99 (dd, J = 7.6, J = 2.0 Hz, 1H), 7.38−7.34 (m, 2H), 7.32−7.29 (m, 1H), 7.16−7.12 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 5.87 (s, OH, 1H), 3.78 (s, 3H), 1.85 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.3 (C), 148.95 (C), 148.86 (C), 148.60 (C), 145.8 (C), 143.8 (C), 141.4 (C), 133.2 (C), 127.42 (CH), 127.37 (CH), 127.1 (CH), 125.5 (CH), 122.8 (CH), 122.4 (CH), 113.2 (CH), 110.5 (CH), 70.1 (C), 63.6 (C), 62.6 (C), 62.2 (C), 56.4 (CH_3), 26.3 (CH_3), 26.0 (CH_3), 22.8 (CH_3), 16.2 (CH_3), two Ar-CH resonances were not resolved; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{27}O_2$ 383.2006, found 383.2003.



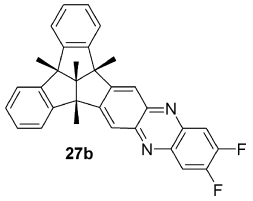
25

*1,2-Dibromo-3,4-dihydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (**25**).* The preparation procedure was the same as that used for compound **18**. Starting from catechol **23** (85 mg, 0.23 mmol) and Br_2 (26 μL, 0.50 mmol), the product **25** was obtained as a colorless amorphous solid (25 mg, 21%): TLC petroleum ether/EtOAc 20:1, R_f = 0.2; mp 207−209 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.23 (dd, J = 8.0, J = 0.8 Hz, 1H), 8.00 (dd, J = 7.6, J = 0.8 Hz, 1H), 7.41−7.35 (m, 2H), 7.20−7.11 (m, 4H), 5.69 (s, OH, 1H), 5.45 (s, OH, 1H), 1.96 (s, 3H), 1.81 (s, 3H), 1.58 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 149.3 (C), 149.0 (C), 148.1 (C), 147.3 (C), 141.0 (C), 140.1 (C), 139.8 (C), 136.6 (C), 128.0 (CH), 127.8 (CH), 127.2 (CH), 126.9 (CH), 125.9 (CH), 125.6 (CH), 122.9 (CH), 122.4 (CH), 114.0 (C), 109.4 (C), 70.6 (C), 66.4 (C), 63.3 (C), 62.6 (C), 26.6 (CH_3), 24.5 (CH_3), 23.1 (CH_3), 16.7 (CH_3); HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{22}{}^{79}Br_2O_2Na$ 546.9879, found 546.9883.



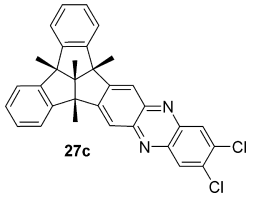
27a

*4b,8b,16b,16d-Tetramethyl-4b,8b,16b,16d-tetrahydrobenzo-[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-b]phenazine (**27a**).* A mixture of TBTQ-*o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26a** (17 mg, 0.16 mmol) in anhydrous EtOH (15 mL) was heated to reflux under argon for 12 h. The reaction mixture was then cooled and concentrated under reduced pressure. Water (15 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1, R_f = 0.4) afforded **27a** as a red solid (51 mg, 84%): mp >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.26 (s, 2H), 8.18−8.15 (m, 2H), 7.70−7.74 (m, 2H), 7.59−7.57 (m, 2H), 7.40−7.38 (m, 2H), 7.23−7.17 (m, 4H), 1.85 (s, 6H), 1.73 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.1 (C), 148.8 (C), 147.5 (C), 143.5 (C), 142.7 (C), 130.2 (CH), 129.3 (CH), 128.12 (CH), 128.07 (CH), 123.4 (CH), 122.9 (CH), 122.1 (CH), 70.1 (C), 63.3 (C), 62.5 (C), 26.9 (CH_3), 25.6 (CH_3), 16.3 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{32}H_{27}N_2$ 439.2169, found 439.2184.



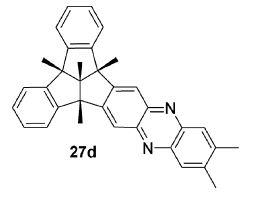
27b

*12,13-Difluoro-4b,8b,16b,16d-tetramethyl-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-b]phenazine (**27b**).* The preparation procedure was the same as that used for compound **27a**. Starting from *o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26b** (23 mg, 0.16 mmol), the product **27b** was obtained as a yellow solid (43 mg, 65%): TLC petroleum ether/EtOAc 20:1, R_f = 0.4; mp >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.20 (s, 2H), 7.86 (t, J = 9.2 Hz, 2H), 7.57−7.54 (m, 2H), 7.40−7.38 (m, 2H), 7.23−7.19 (m, 4H), 1.85 (s, 6H), 1.73 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.3 (C), 153.2 (dd, $J_{(C,F)}$ = 259.7, $J_{(C,F)}$ = 19.5 Hz, CF), 148.8 (C), 147.4 (C), 143.5 (C), 140.3 (t, $J_{(C,F)}$ = 5.8 Hz, CF), 128.2 (CH), 128.1 (CH), 123.3 (CH), 122.9 (CH), 122.0 (CH), 113.7 (dd, $J_{(C,F)}$ = 12.6, $J_{(C,F)}$ = 6.1 Hz, CF), 70.1 (C), 63.3 (C), 62.5 (C), 26.8 (CH_3), 25.6 (CH_3), 16.2 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{32}H_{25}N_2F_2$ 475.1980, found 475.1993.



27c

*12,13-Dichloro-4b,8b,16b,16d-tetramethyl-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-b]phenazine (**27c**).* The preparation procedure was the same as that used for compound **27a**. Starting from *o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26c** (28 mg, 0.16 mmol), compound **27c** was obtained as a yellow solid (51 mg, 72%): TLC petroleum ether/EtOAc 20:1, R_f = 0.3; mp 246−248 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.27 (s, 2H), 8.19 (s, 2H), 7.54 (dd, J = 8.0, 2.0 Hz, 2H), 7.37 (dd, J = 8.0, J = 2.0 Hz, 2H), 7.21−7.18 (m, 4H), 1.83 (s, 6H), 1.71 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 157.0 (C), 148.8 (C), 147.2 (C), 144.0 (C), 141.3 (C), 134.8 (C), 129.6 (CH), 128.2 (CH), 128.1 (CH), 123.3 (CH), 122.9 (CH), 122.2 (CH), 70.1 (C), 63.3 (C), 62.5 (C), 26.8 (CH_3), 25.6 (CH_3), 16.2 (CH_3); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{32}H_{25}{}^{35}Cl_2N_2$ 507.1389, found 507.1386.



27d

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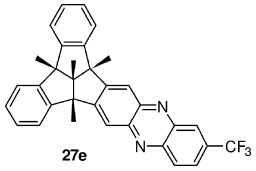
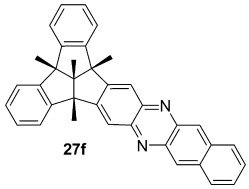
*4b,8b,12,13,16b,16d-Hexamethyl-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-b]phenazine (**27d**).* The preparation procedure was the same as that used for compound **27a**. Starting from *o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26d** (22 mg, 0.16 mmol), compound **27d** was obtained as a yellow solid (42 mg, 64%): TLC petroleum ether/EtOAc 20:1, R_f = 0.4; mp 256−258 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.24 (s, 2H), 7.92 (s, 2H), 7.58 (dd, J = 6.4, 2.4 Hz, 2H), 7.39−7.37 (m, 2H), 7.21−7.18 (m, 4H), 2.53 (s, 6H), 1.85 (s, 6H), 1.73 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 155.2 (C), 148.8 (C), 147.6 (C), 141.7 (C), 128.03 (CH), 128.01 (CH), 127.5 (CH), 123.4 (CH), 122.8 (CH), 121.8 (CH), 70.1 (C), 63.3 (C), 62.5 (C), 26.8 (CH_3), 25.6 (CH_3), 20.7 (CH_3), 16.3 (CH_3), two Ar-C resonances were not resolved; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{34}H_{31}N_2$ 467.2482, found 467.2492.



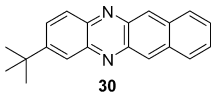
27e

*(±)-4b,8b,16b,16d-Tetramethyl-12-(trifluoromethyl)-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno-[1,2-b]phenazine (**27e**).* The preparation procedure was the same as that used for compound **27a**. Starting from *o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26e** (28 mg, 0.16 mmol), the product **27e** was obtained as a yellow solid (52 mg, 73%): TLC petroleum ether/EtOAc 20:1, R_f = 0.2; mp 273−275 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.51 (s, 1H), 8.32−8.28 (m, 3H), 7.91 (dd, J = 9.2, 2.0 Hz, 1H), 7.57 (dd, J = 6.0, J = 2.0 Hz, 2H), 7.39 (dd, J = 7.6, J = 2.0 Hz, 2H), 7.23−7.20 (m, 4H), 1.87 (s, 6H), 1.74 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl3, 25 °C, TMS) δ 158.7 (C), 157.8 (C), 148.8 (C), 147.0 (C), 146.9 (C), 144.2 (C), 143.4 (C), 141.8 (C), 141.0 (C), 131.8 (d, $J_{(C,F)}$ = 32.8 Hz, C), 130.0 (CH), 128.3 (CH), 128.2 (CH), 127.48 (q, $J_{(CH,F)}$ = 4.5 Hz, CH), 125.9 (CH), 123.5 [q, $J_{(C,F)}$ = 271.1 Hz, CF_3], 123.34 (CH), 123.27 (CH), 123.0 (CH), 122.1 (CH), 121.4 (CH), 70.1 (C), 63.4 (C), 62.7 (C), 62.6 (C), 26.84 (CH_3), 26.77 (CH_3), 25.6 (CH_3), 16.2 (CH_3); one Ar-C and three Ar-CH resonances were not resolved; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{33}H_{26}N_2F_3$ 507.2043, found 507.2038.



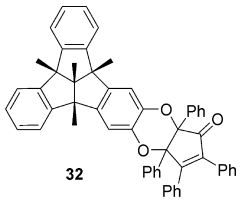
27f

*4b,8b,18b,18d-Tetramethyl-4b,8b,18b,18d-tetrahydrobenzo-[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-b]-5,12-diazatetracene (**27f**).* The preparation procedure was the same as that used for compound **27a**. Starting from *o*-quinone **6a** (51 mg, 0.14 mmol) and diamine **26f** (25 mg, 0.16 mmol), compound **27f** was prepared as a red solid (53 mg, 78%): TLC petroleum ether/EtOAc 20:1, R_f = 0.4; mp 261−263 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.76 (s, 2H), 8.21 (s, 2H), 8.01 (dd, J = 6.8, J = 3.2 Hz, 2H), 7.59 (dd, J = 7.6, J = 1.6 Hz, 2H), 7.41−7.35 (m, 4H), 7.23−7.18 (m, 4H), 1.86 (s, 6H), 1.73 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.7 (C), 148.8 (C), 147.4 (C), 144.7 (C), 139.5 (C), 134.3 (C), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 126.6 (CH), 123.5 (CH), 122.9 (CH), 122.1 (CH), 70.1 (C), 63.4 (C), 62.4 (C), 26.9 (CH_3), 25.6 (CH_3), 16.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{36}H_{29}N_2$ 489.2325, found 489.2335.



30

*2-tert-Butylbenzo[b]phenazine (**30**).* A mixture of phenol **28** (230 mg, 1.53 mmol) and *o*-iodoxybenzoic acid (515 mg, 1.84 mmol) in EtOAc (30 mL) was stirred at 25 °C for 24 h. A color change from yellow to dark red was observed. The reaction was monitored by TLC. Upon completion of the reaction, the mixture was quenched with water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford crude **29**. Then the crude **29** and diamine **26f** (242 mg, 1.53 mmol) in anhydrous EtOH (35 mL) were heated to reflux under argon atmosphere for 12 h. The reaction mixture was cooled, filtered through MnO_2, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1, R_f = 0.2) afforded **30** as a red solid (342 mg, 78%): mp 180−182 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.89 (d, J = 6.4 Hz, 2H), 8.18−8.12 (m, 4H), 7.94−7.91 (dd, J = 9.2, J = 2.0 Hz, 1H), 7.54−7.52 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 154.1 (C), 144.7 (C), 143.6 (C), 140.0 (C), 139.8 (C), 134.4 (C), 134.2 (C), 131.0 (CH), 129.1 (CH), 128.53 (CH), 128.49 (CH), 127.6 (CH), 127.2 (CH), 126.8 (CH), 126.6 (CH), 123.7 (CH), 35.6 (C), 30.5 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_2$ 287.1543, found 287.1540.



32

*(13a-cis)-12,13,10a,13a-Tetraphenyl-4b,8b,15b,15d-tetramethyl-4b,8b,15b,15d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno-[1,2-b]-1,4-cyclopenta[b][1,4]benzodioxin-11-one (**32**).* A mixture of TBTQ-*o*-quinone **6a** (40 mg, 0.11 mmol) and tetracyclone **31** (42 mg, 0.11 mmol) in benzene (2 mL) in a Schlenk glass tube was heated at 100 °C for 8 h. The solvent was concentrated under reduced pressure. The mixture was quenched with water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1, R_f = 0.3) afforded compound **32** (66 mg, 80%) as a yellow solid. The NMR spectrum is not pure enough and reflects a mixture of stereoisomers that cannot be separated by flash column chromatography: mp 173−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.45−7.43 (m, 2H), 7.36−7.34 (m, 4H), 7.23−7.21 (m, 2H), 7.18−7.14 (m, 4H), 7.13−7.09 (m, 9H), 7.02−6.81 (m, 8H), 6.27 (s, 1H), 1.61−1.59 (m, 6H), 1.29−1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 195.7 (C), 163.0 (C), 148.7 (C), 148.55 (C), 148.50 (C), 144.2 (C), 144.0 (C), 142.4 (C), 142.3 (C), 142.2 (C), 138.1 (C), 134.8 (C), 131.9 (C), 130.2 (C), 129.9 (CH), 129.6 (CH), 129.59 (CH), 129.51 (CH), 129.2 (CH), 128.9 (CH), 128.5 (CH), 128.23 (CH), 128.20 (CH), 127.92 (CH), 127.85 (CH), 127.6 (CH), 127.57 (CH), 127.54 (CH), 127.51 (CH), 127.4 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 122.93 (CH), 122.86 (CH), 122.83 (CH), 122.7 (CH), 122.5 (CH), 110.5 (CH), 89.91 (C), 89.85 (C), 69.7 (C), 62.6 (C), 62.3 (C), 62.1 (C), 25.93 (CH_3), 25.89 (CH_3), 16.1 (CH_3), one Ar-C, five Ar-CH, and one CH_3 resonances were not resolved; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{55}H_{43}O_3$ 751.3207, found 751.3198.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02806.

^{1}H, ^{13}C NMR and DEPT 135 spectra of all new compounds: **6a**, **7a**, **6b**, **7b**, **11**, **12**, **14**−**25**, **27a**−**f**, **30**, and **32**; HMBC spectrum of **24** (PDF)

X-ray crystallographic data for *rac*-**14** (CIF)

X-ray crystallographic data for **17**·EtOAc (CIF)

X-ray crystallographic data for **17**·THF (CIF)

X-ray crystallographic data for **18** (CIF)

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X-ray crystallographic data for **23**·acetone (CIF)
X-ray crystallographic data for **27b** (CIF)
X-ray crystallographic data for **27c** (CIF)
X-ray crystallographic data for **32** (*endo-anti*-stereoisomer) (CIF)

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Notes

The authors declare no competing financial interest.

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