Conjugated Systems

A Hexapentaene-Extended Quinocumulene Cyclotrimerized to a Tricyclobutabenzene Derivative[**]

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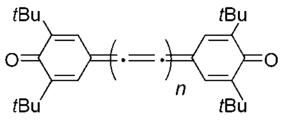
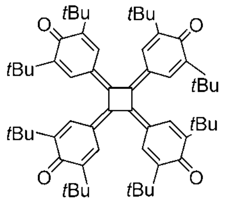
Quinocumulenes are extended biphenoquinones in which two quinoid rings are linked through a cumulenic π system. In 1967 West and Zecher reported the synthesis of the butatriene-extended quinocumulene **1**.[1] Later, this quinocumulene was shown to undergo thermal or metal-catalyzed dimerization to form [4]radialene derivative **2**.[2] However, a further extension of conjugation had not been explored to



1: $n = 1$
3: $n = 2$



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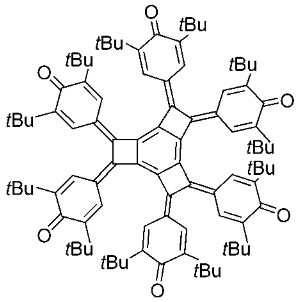

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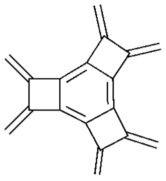

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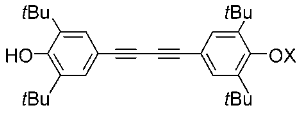
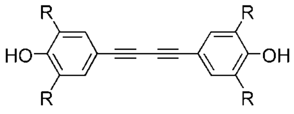


6: X = H, **12**: X = $COCH_3$



7: R = H, **8**: R = CH_3, **9**: R = Ph

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Supporting information for this article (selected physical data for **3**, **4**, **6**, **8**–**13**, selected NMR spectra, absorption spectra, and a cyclic voltammogram of **4**.) is available on the WWW under http://www.angewandte.org or from the author.

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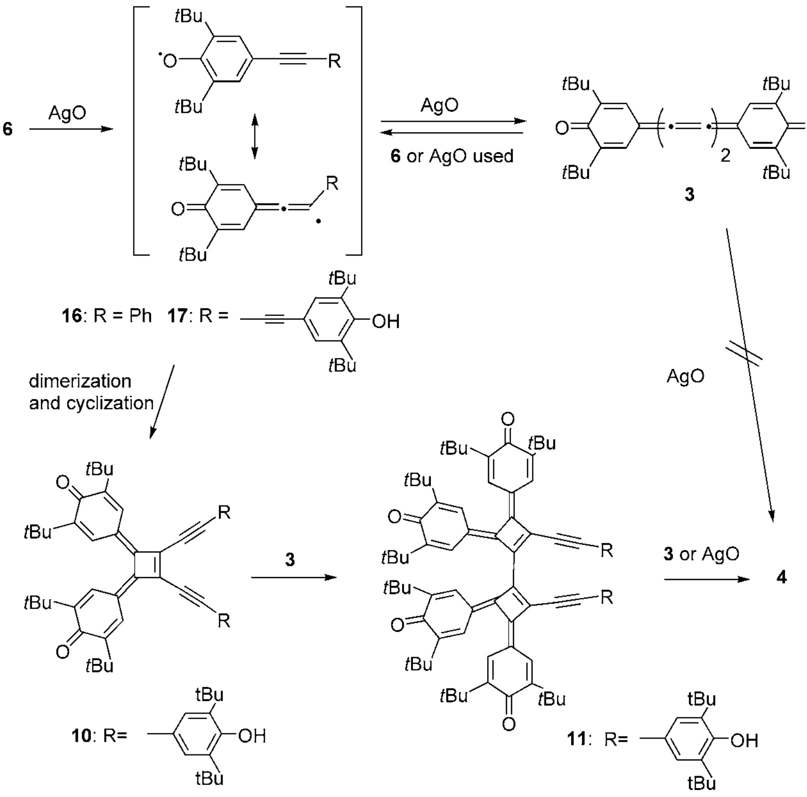
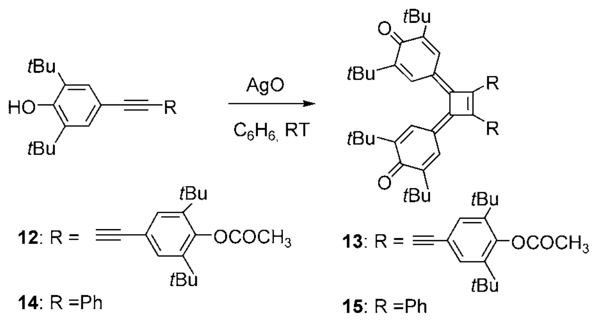
date. We have synthesized a new hexapentaene-extended quinocumulene **3** from the corresponding extended 4,4′-biphenol, and found that **3** underwent cyclotrimerization to form the novel tricyclobutabenzene derivative **4**. Tricyclobutabenzene derivatives have been extensively studied from synthetic[3] and theoretical[4] points of view. Although hexamethylenetricyclobutabenzene (**5**) has been regarded as a key model compound concerning the bond alternation of the central benzene ring,[4,5] no derivative has been prepared so far. We describe herein the mechanism of formation, the molecular structure, and physical properties of **4** as a first derivative of **5**.



Scheme 1. Proposed mechanism for the formation of **4**.

A biphenol **6** as a promising precursor of **3** was synthesized from 1-acetoxy-2,6-di-*tert*-butyl-4-ethynylbenzene[6] by Eglinton coupling and deprotection of the acetyl groups under weak alkaline conditions in 77% total yield. The new quinocumulene **3** was readily prepared by treatment of **6** with silver oxide (AgO) in benzene at room temperature for 15 min in 72% yield. The presence of *tert*-butyl groups at C2 and C6 is critical to the formation of **3**, because oxidative treatment of the biphenols **7**–**9**[7] with AgO gave polymeric materials, probably owing to the high reactivity of the corresponding quinocumulenes. Actually, even **3** is thermally labile; when heated at 100 °C in the absence of solvent, **3** was converted into an insoluble material.

A reaction mixture of **6** and AgO was allowed to stand at room temperature for 3.5 h which led to the disappearance of the generated **3** and the appearance of new products in the mixture. The highly symmetrical cyclotrimer **4** was isolated as a sole product in 54% yield. On the other hand, treatment of **3** with freshly prepared AgO even for 3 days afforded unchanged **3**. Notably, even in the absence of AgO, **4** was obtained almost quantitatively by mixing a solution of **3** and **6** (3:1) in chloroform. The reaction process can be monitored by ^{1}H NMR spectroscopy (see Supporting Information). NMR spectroscopic experiments revealed the stepwise formation of dimer **10**, an acyclic trimer **11**, and **4** (Scheme 1). The reaction of **6** with **3** afforded **10**, and the reaction of **10** and **11** with **3** led to **11** and **4**, respectively. The quinone **3** acts as an oxidizing agent toward these biphenols. In fact, the reaction stopped when **3** is no longer present in the solution. The high lability of **10** and **11** to silica gel chromatography has so far prevented their isolation and further characterization; however, the structures can be deduced from the ^{1}H NMR spectra. Treatment of monoacetate **12** (prepared by partial deprotection of the diacetate of **6**) with AgO afforded the corresponding dimer **13** in 60% yield (Scheme 2). Moreover, when exposed to air or heated at 60 °C, **11** was readily converted into **4**. These results support the assignments. It was already known that oxidation of 2,6-di-*tert*-butyl-4-phenylethynylphenol (**14**) with appropriate oxidizing agents led to the formation of the bismethylenecyclobutene **15** in good yield (Scheme 2).[8] A radical species **16** (Scheme 1) is postulated as a reactive intermediate of the reaction. The intermediate **16** could dimerize through the allenic resonance structure to yield a conjugated bisallene. This, in turn, could cyclize to **15**.[9] In analogy with the mechanism, the cyclotrimerization of **3** would start with the oligomerization of the corresponding monoradical **17** generated by redox reaction of **3** with **6** or AgO used as shown in Scheme 1.



Scheme 2. Oxidative dimerization of **12** and **14**.

Good single crystals of **4** (with solvent molecules in a 2:1 ratio) were collected from a solution in dioxane.[10] Figure 1 reveals that the molecule has a considerably distorted propeller structure largely deviated from the ideal C_3 symmetry; the torsion angles between the exo methylene double bonds on the same cyclobutane ring are 11.7°, 60.4°, and 62.2°. In particular, the two quinomethide rings involving C27 and C69 carbons are largely curved and slightly twisted from the central benzene plane, probably as a result of steric repulsion of the bulky *tert*-butyl groups. Table 1 shows the

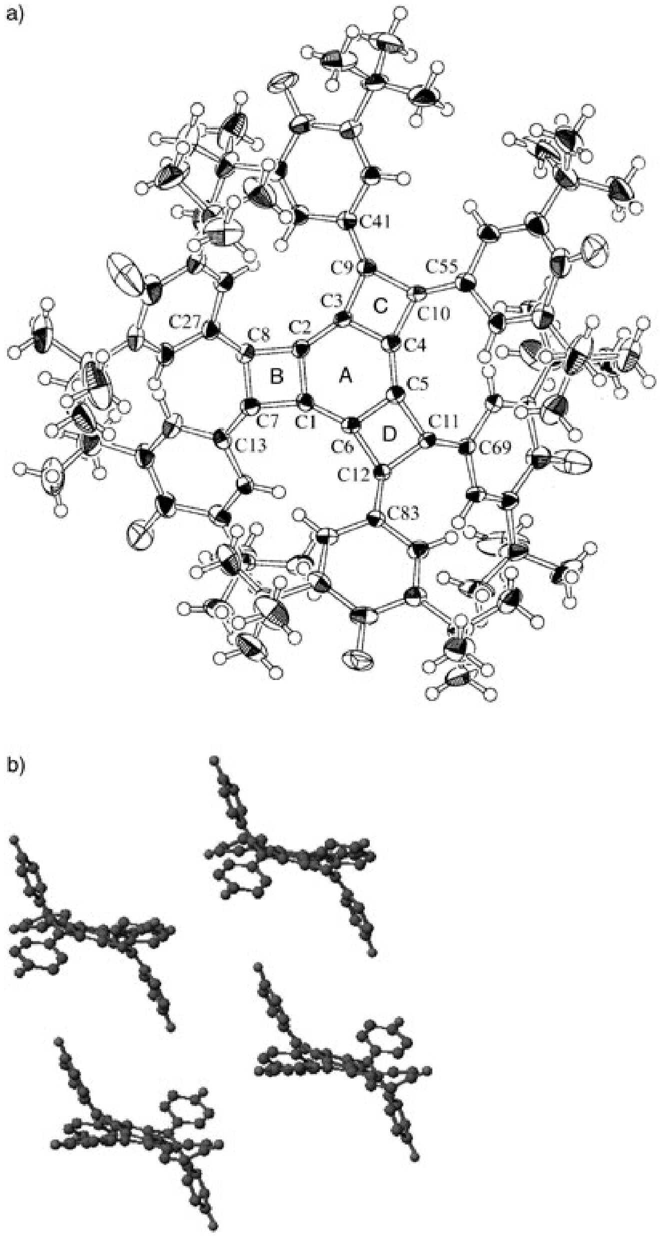
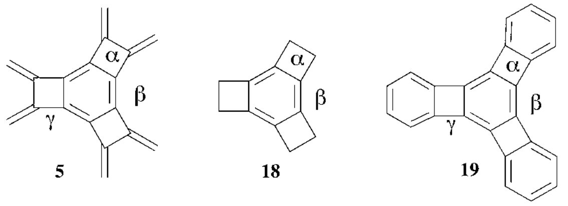


Figure 1. Single crystal structure of **4**: a) ORTEP drawing with 50% probability; b) molecular packing; *tert*-butyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.441(5), C2–C3 1.373(5), C3–C4 1.426(5), C4–C5 1.381(5), C5–C6 1.435(4), C6–C1 1.371(5), C1–C7 1.483(5), C2–C8 1.477(5), C3–C9 1.489(5), C4–C10 1.478(4), C5–C11 1.487(5), C6–C12 1.487(5), C7–C8 1.507(5), C9–C10 1.515(5), C11–C12 1.499(5), C7–C13 1.362(5), C8–C27 1.370(5), C9–C41 1.360(5), C10–C55 1.372(5), C11–C69 1.357(5), C12–C83 1.357(6); C41-C9-C10-C55 11.7(10), C69-C11-C12-C83 60.4(7), C13-C7-C8-C27 62.2(8); torsion angles between least squares planes: AB 9.4(2), AC 4.3(2), AD 11.1(2), BC 12.1(2), BD 15.4(2), CD 14.7(2).

Table 1: Average bond lengths of tricyclobutabenzene derivatives (Å).



5 18 19

	4	5	18	19
α	1.434	1.430	1.413	1.494
β	1.375	1.385	1.390	1.336
γ	1.484	1.484	–	1.500

observed bond lengths of the central benzene rings of **4**, tricyclobutabenzene **18**,[3d] and triangular [4]phenylene **19**[3b] together with the calculated values of **5**.[4b] Despite its nonplanarity, the values of **4** are similar to those of **5**. The degree of bond alternation of these compounds is in the order **19** ≫ **4** > **18**. In conclusion, the present results have experimentally proven that the aromatic character of the outer benzene rings of **19** plays an important role in the high degree of bond alternation of the central benzene ring.

Selected spectral data for **3** and **4** are shown in Table 2. The longest absorption maximum of **3** is considerably longer than those of **1** (486 nm in C_6H_6) and biphenoquinone **20** (426 nm in CH_2Cl_2). The trimer **4** shows intense absorptions in the visible region of about 400–600 nm which is responsible for its deep coloration. The absorption curve is similar to that of **2**; the longest absorption band of **4** is 20–30 nm shorter and the second-longest absorption band is ≈50 nm longer than

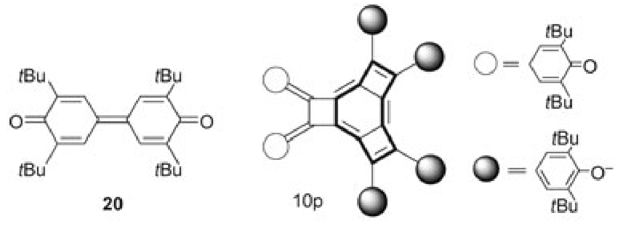
Table 2: Selected spectral data for new extended quinones **3**, **4**, **10**, **11**.

3: IR (KBr): $\tilde{\nu}$2954 s, 1586 s (C=O), 1456 m, 1357 m, 1250 m, 1220 w, 1082 m, 921 cm^{-1} (m); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.26$ (s, 36H), 7.06 ppm (s, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 29.71$, 35.96, 118.82, 123.83, 130.26, 140.34, 150.32, 185.84 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 301 (3.84), 351 (3.96), 477 (4.54), 491 (4.58), 531(5.24), 614 nm (sh) (4.18)

4: IR (KBr): $\tilde{\nu} = 2958$ s, 1617 s (C=O), 1458 m, 1363 s, 1091 m, 884 cm^{-1} (m); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.31$ (s, 54H), 1.35 (s, 54H), 7.38 (d, $J = 2.4$ Hz, 6H), 7.53 ppm (d, $J = 2.4$ Hz, 6H): ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 29.16$, 29.66, 36.06, 36.13, 124.21, 127.79, 128.92, 137.49, 146.70, 150.65, 151.50, 185.87 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 348 (4.83), 424 (5.14), 447 (5.38), 517 (4.76), 558 nm (4.76)

10: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.33$ (s, 18H), 1.41 (s, 18H), 1.47 (s, 36H), 5.66 (s, 2H), 7.38 (d, $J = 2.3$ Hz, 2H), 7.45 (s, 4H), 8.09 ppm (d, $J = 2.3$ Hz, 2H)

11: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.11$ (s, 18H), 1.25 (s, 36H), 1.32 (s, 18H), 1.37 (s, 18H), 1.49 (s, 18H), 5.60 (s, 2H), 7.24 (d, $J = 2.3$ Hz, 2H), 7.34 (s, 4H), 7.44 (d, $J = 2.3$ Hz, 2H), 7.46 (d, $J = 2.3$ Hz, 2H), 8.16 ppm (d, $J = 2.3$ Hz, 2H)



20

21

those of **2**.[2] The carbonyl stretching of **3** (1586 cm^{-1}) is almost similar to that of **1** (1590 cm^{-1}), despite the extension of conjugation. On the other hand, the relatively high values of **2** (1630 cm^{-1}), **4** (1617 cm^{-1}), **13** (1608 cm^{-1}), and **15** (1609 cm^{-1})[11] are consistent with the order of distortion of the biphenoquinone structures. Because the average twist angle between the quinomethide rings of **2**[2] (36°) is the largest in these compounds.

The electrochemical properties of **3** and **4** as new electron acceptors were examined by cyclic voltammetry. The reduction potentials of **1**–**4** and **20** are summarized in Table 3.

Table 3: Reduction potentials of extended quinones **1**–**4**, **20**.

	$^{1}E_{1/2}$	$^{2}E_{1/2}$	$^{3}E_{1/2}$	$^{4}E_{1/2}$
1	−0.65	−0.85		
2	−0.52	−0.85		
3	−0.42	−0.76		
4	−0.61	−0.89	−1.03	−1.35
20	−0.96	−1.29		

V vs. Ag/Ag^{+} ($Fc/Fc^{+} = +0.26$ V) in 0.1 M nBu_4NClO_4/CH_2Cl_2, sweep rate 100 $mV s^{-1}$.

Quinocumulene **3** shows two sets of highly reversible one-electron reduction waves together with one irreversible oxidation wave (1.40 V). The longest conjugation of **3** in these compounds would account for the highest electron affinity. Moreover, **4** exhibits four sets of highly reversible one-electron reduction waves within the measurable range (1.5 to −2.4 V). The results suggest the facile formation of the tetraanion **21**, which has a 10π electronic periphery.

These results suggest that 2,6-di-*tert*-butyl-4-ethynylphenol derivatives would act as versatile building blocks for the construction of extended diphenoquinone derivatives with novel structure and redox properties.

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Keywords: aromaticity · cumulenes · quinones · redox chemistry · strained molecules

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[10] Crystal data for **4**·(dioxane)$_{1/2}$ ($C_{98}H_{124}O_7$): $M_w = 1413.93$, dark red prisms, crystal dimension: 0.2 × .0.2 × 0.1 mm^3, triclinic, space group $P\bar{1}$ (#2), $a = 13.765(6)$ Å, $b = 17.568(9)$ Å, $c = 19.722(9)$ Å, $\alpha = 77.18(4)°$, $\beta = 83.21(4)°$, $\gamma = 73.62(4)°$, $V = 4453(14)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.111$ $g cm^{-1}$, $Mo_{K\alpha}$ ($\lambda = 0.71075$ Å), $2\theta_{max} = 55.0°$; intensity data were collected on a Rigaku RAXIS-RAPID imaging-plate diffractometer at 200 K. The structure was solved with direct methods on F^2 with SHELXS-97. A total of 41147 reflections were collected, 19274 unique reflections were measured and used in the refinement, 946 parameters, $R1 = 0.056$, $Rw = 0.206$ for 4615 reflections with $I > 2\sigma(I)$, GOF = 0.58, max. peak in final diff. map 0.20 e $Å^{-3}$; all non-hydrogen atoms were refined anisotropically, hydrogen atoms (except the disordered dioxane protons) were placed geometrically and refined by using a rigid model. CCDC-241621 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] Our result; the reported value (1650 cm^{-1})[8] was not reproducible.