Syntheses and Properties of 1,2- and 1,3-Diquinocyclobutanediones
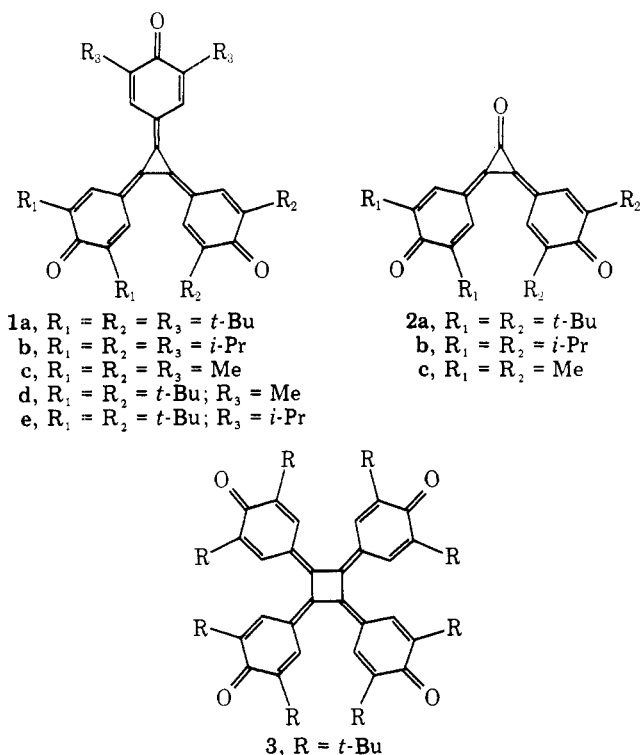
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The syntheses of two new isomeric polyquinocycloalkanes are described. 1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutanedione (4) was prepared by the Friedel–Crafts reaction of 2,6-di-*tert*-butylphenol with 1,2-dichlorocyclobutenedione and subsequent oxidation of the 1,2-diaryl compound. 1,3-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidine)cyclobutanedione (5) was synthesized by the reaction of perfluorocyclobutene with 2 equiv of 4-lithio-2,6-di-*tert*-butylphenyl trimethylsilyl ether, followed by methanolysis, hydrolysis, and oxidation. Compounds 4 and 5 display intense electronic absorptions in the visible spectrum. The immediate precursor (11) to 5, which appears to have a cyclobutenylium-type structure, shows strong dichroic properties. An ESR study of the anion radicals of 4 and 5 indicates that the unpaired electron is fully delocalized over the three-ring systems.

As an outgrowth of our interest in the cyclic oxocarbon anions, $C_nO_n{}^{2-}$,[1] we have undertaken the synthesis and characterization of the physical properties of a related family of compounds, the quinocarbons (polyquinocycloalkanes). The quinocarbons can be viewed as completely oxidized analogues of the oxocarbons in which one or more carbonyl functions have been replaced by a 4-oxo-3,5-dialkyl-2,5-cyclohexadiene ring. In this fully oxidized form (all keto or quino substituents) these quinocarbons are radialenes; the 3,5-dialkyl substituents are necessary for protection of the labile quinonoid carbonyl carbons. The known quinocarbons include the family of triquinocyclopropanes 1a–e,[2] the isolable but unstable diquinocyclopropanones 2a–c,[3] and the stable tetraquinocyclobutane 3.[4] These highly conjugated, brightly

1a, $R_1 = R_2 = R_3 = t$-Bu
b, $R_1 = R_2 = R_3 = i$-Pr
c, $R_1 = R_2 = R_3 = $ Me
d, $R_1 = R_2 = t$-Bu; $R_3 = $ Me
e, $R_1 = R_2 = t$-Bu; $R_3 = i$-Pr

2a, $R_1 = R_2 = t$-Bu
b, $R_1 = R_2 = i$-Pr
c, $R_1 = R_2 = $ Me

3, R = t-Bu

colored quinocarbons may have potential uses as dyes, organic semiconductors, and photographic materials.

In this paper we describe the syntheses of two new classes of quinocarbons, 4 and 5, each having two quinonoid rings and two oxygens on a central four-membered ring. The compound with adjacent carbonyl groups (4) is obtained as a purple solid. Like 2a–c, it undergoes decomposition rather rapidly in visible light. The other structure (5) with nonadjacent carbonyl groups is a light-stable, blue-green crystalline compound.


4   **5**
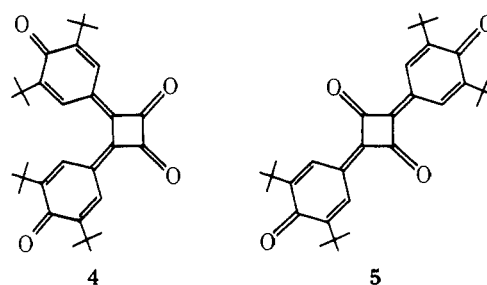
Synthesis. The route outlined in Scheme I was developed for the synthesis of 4. The Friedel–Crafts reaction of 2,6-di-

Scheme I
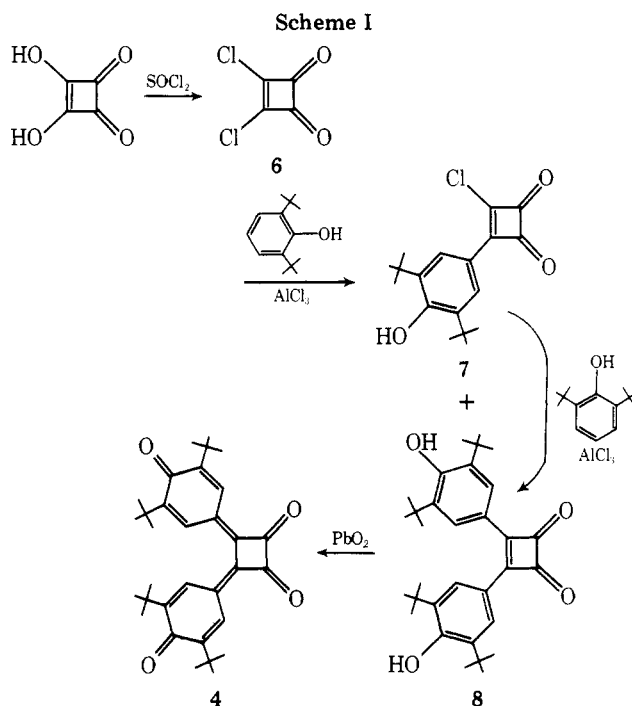
tert-butylphenol with 1,2-dichlorocyclobutenedione[5] (6) in refluxing dichloromethane produced 7 and 8 in 34.4 and 3.2% yields, respectively. Under more strenuous reaction conditions cleavage of a *tert*-butyl group from 8 became competitive with product formation. Compound 7 could be recycled to produce additional 8 in 13% yield. Compound 8 is readily oxidized to 4 with PbO₂, and 4 can be reduced back to 8 with hydroquinone.

Compound 5 was synthesized as shown in Scheme II. The reaction of perfluorocyclobutene with 4-lithio-2,6-di-*tert*-butylphenyl trimethylsilyl ether was based on analogy to the work of Broser and Seekamp,[6] who reported the synthesis of

Scheme II

9
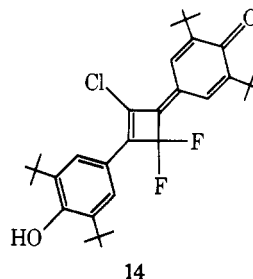
KOH/MeOH

10

HCl/MeOH

5   **11**
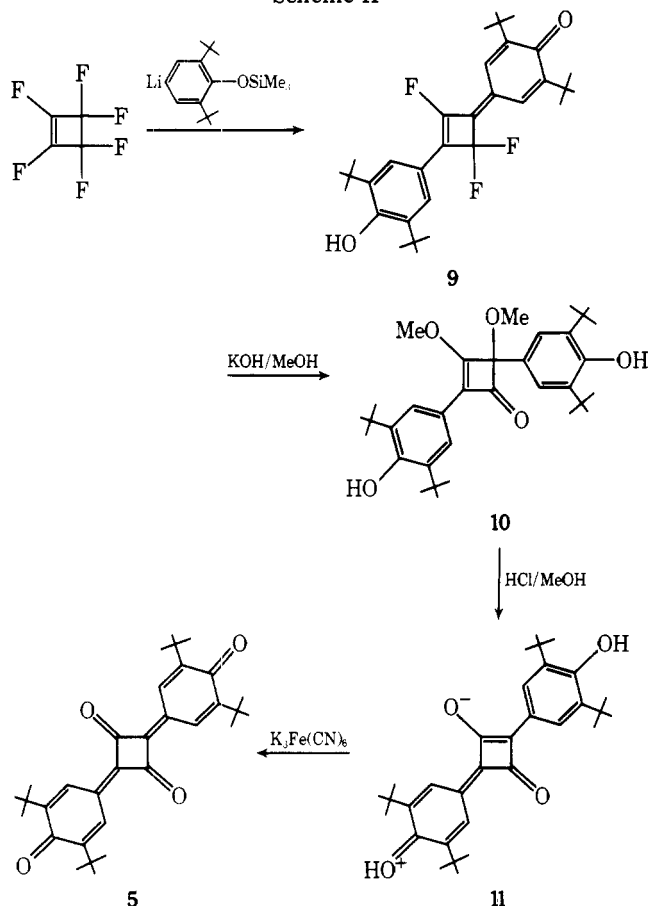
1,2-diphenolcyclobutenedione from the reaction of perfluorocyclobutene and lithium *p*-lithiophenolate, and was originally intended as an alternate synthetic route to **4**. However, we found that reaction of perfluorocyclobutene and 4-lithio-2,6-di-*tert*-butylphenyl trimethylsilyl ether led to the 1,3 compound (**9**). Both the elemental analysis and high-resolution mass spectral data are consistent with a molecular formula of $C_{32}H_{41}O_2F_3$. This implies loss of 3 equiv of F^- as well as both the trimethylsilyl groups. These data, combined with a ^{1}H NMR spectrum displaying three nonequivalent *tert*-butyl absorbances in a ratio of 2:1:1 suggest structure **9**, or possibly **12** or **13**. Structures **12** and **13** can be ruled out by the

12   **13**
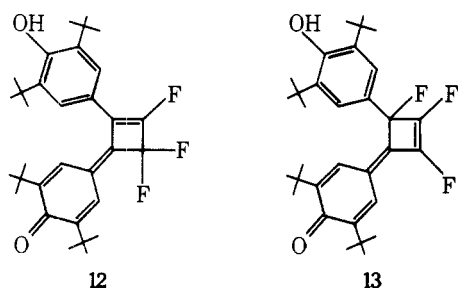
^{19}F NMR spectrum, which consists of a triplet (99.1 ppm upfield from CFCl$_3$, 1 F) and a doublet (110.8, 2 F). The coupling constant of 25.0 Hz is in good agreement with typical allylic fluorine couplings and strongly implies **9** to be the correct structure. In general, allylic fluorine couplings (16–19 Hz) for fluorocyclobutenes are significantly greater than the vicinal coupling constants (4–8 Hz).[7] Additional confirmation is provided by the analogy to the recently reported allylic fluorine coupling constant of 21.5 Hz for 3-phenyl-2,4,4,-trifluorocyclobut-2-en-1-one.[8] In addition with base **9** gives a deep blue anion (λ_{max} 630 nm) consistent with delocalization

of the negative charge over both six-membered rings, which is possible for **9** but not for **12** or **13**.

Condensation of 4-lithio-2,6-di-*tert*-butylphenyl trimethylsilyl ether with 1,2-dichlorotetrafluorocyclobutene gave

14

14; subsequent treatment of **14** in an analogous manner to **9** (Scheme II) yielded **10**, **11**, and **5**.

Various attempts at acid methanolysis of **9** were unsuccessful, but basic methanolysis with KOH/MeOH yielded compound **10**. Treatment of **10** with HCl/MeOH gave **11** which can be recrystallized from chloroform to yield metallic-looking green platelets.

We have *formally* chosen to represent compound **11** as in Scheme II; however, the relative contributions of resonance structures **11**, **15**, and **16** cannot be assessed from ^{1}H NMR,

Scheme III

11

15

16
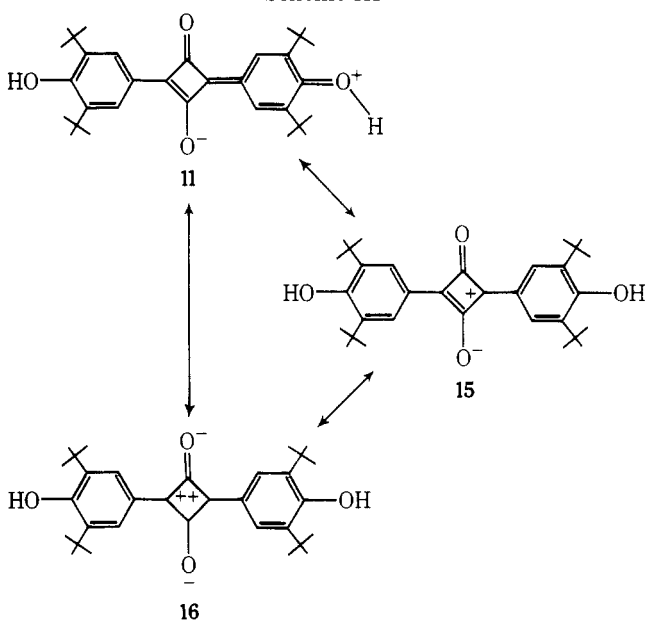
vibrational, and electronic spectral data. The ^{1}H NMR spectrum of **11** indicates the equivalency of all four *tert*-butyl groups, and also all four "aromatic" protons. The vibrational spectrum (chloroform) shows only one sharp O–H absorption at 3575 cm^{-1}. Compound **11** is directly analogous to the di-*p*-methoxyphenylcyclobutadiene compound prepared by Farnum and co-workers[9a] and represented as **17**; the same resonance possibilities exist as for **11**. Compounds **11** and **17**

17
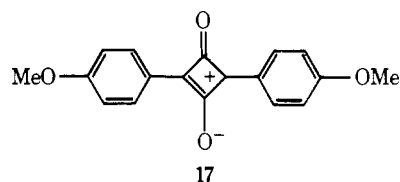
have very similar spectral properties.[10] A cyclobutenediylium structure analogous to **16** has been suggested by Sprenger and Ziegenbein for the 1,3-condensation products of *N,N*-dialkylanilines and squaric acid.[9b]
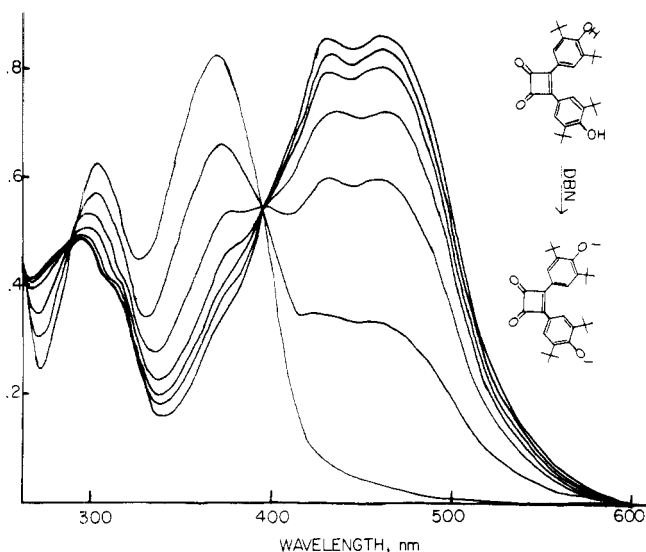
Figure 1. Electronic spectra of **8** (3.2×10^{-5} M, THF) showing the conversion to its dianion upon titration with 0.04 M DBN in THF.

Figure 2. Transmittance (- - -; 1.4×10^{-4} M **11** in THF) and reflectance (—) electronic spectra of **11**.

Oxidation of **11** with either PbO_2 or $K_3Fe(CN)_6$ quantitatively yields **5**, which can be recrystallized from chloroform to give metallic-looking azure platelets. Compound **5** can be reduced back to **11** with hydroquinone.

The characteristic spectral data (^{1}H NMR, IR, UV) for **4** and **5**, combined with ESR experiments (described later), convincingly establish the structures of these two quinocarbons. The ^{1}H NMR spectrum of **4** shows two *tert*-butyl absorbances in a 1:1 ratio (δ 1.31 and 1.37), and two absorbances in a 1:1 ratio at δ 6.92 and 8.18 characteristic of the vinyl proton absorbances of the 2,5-cyclohexadien-1-ylidene moiety. The simple ^{1}H NMR spectrum for **5** (δ 1.32, s, 9, and 7.84, s, 1) is anticipated for this symmetrical structure.

Both compounds show an intense, broad IR band near 1600 cm^{-1} which is attributed to the quinonoid group.[2] The cyclobutanone carbonyl stretching for **4** shows the characteristic doublet of cyclic α,β-carbonyl-containing compounds (1765, 1753 cm^{-1}).[11] The relatively less strained and extensively conjugated **5** shows one ring carbonyl absorption at 1675 cm^{-1}.

Electronic Spectra. A very interesting physical property of the quinocarbon family is their extremely intense, long wavelength electronic spectrum.[2,3,4] Compounds **4** and **5** display λ_{max}'s at 557 nm (log ϵ 5.31) and 510 (4.94), respectively. This presumably $\pi \rightarrow \pi^*$ transition closely parallels that of the other quinocarbons: **2a** (542 nm);[3] **3** (595);[4] **1a** (770).[2] The hypsochromic shifts for **4** and especially **5** compared to **3** are in agreement with simple molecular orbital calculations.[3]

A spectrophotometric titration of **8** (Figure 1) using the hindered base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was performed in THF. All intermediate curves pass through one set of isosbestic points implying that the monoanion is unstable with respect to the dianion under the titration conditions; the dianion has λ_{max} 480 nm sh (log ϵ 2.92) and 462 (4.37). A similar titration was attempted for **11**; however, after the addition of 0.4 equiv of base, the isosbestic point was lost, indicating that a chemical reaction rather than simple deprotonation was occurring.

Compound **11** displays an electronic absorption spectrum with λ_{max} 534 nm (log ϵ 5.17), 498 (4.44), 335 (3.71). This compound also exhibits dichroic properties and has a specular reflection spectrum with λ_{max} 595, 530, 445 nm; end reflectance occurs until 670 nm (Figure 2). Consequently, a thin film of **11** deposited on a glass plate transmits red light and reflects green light.
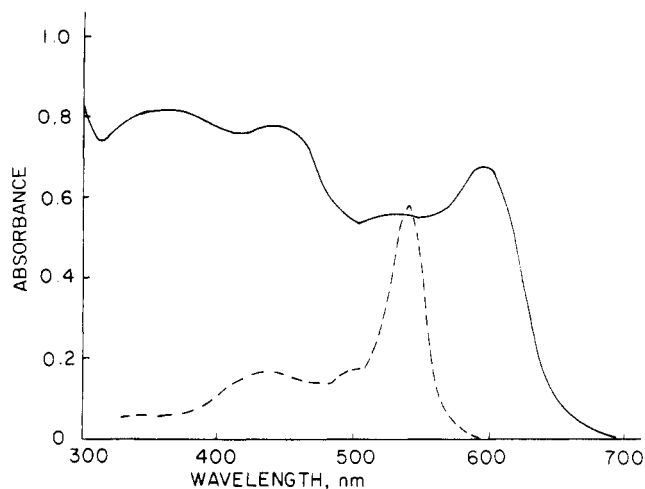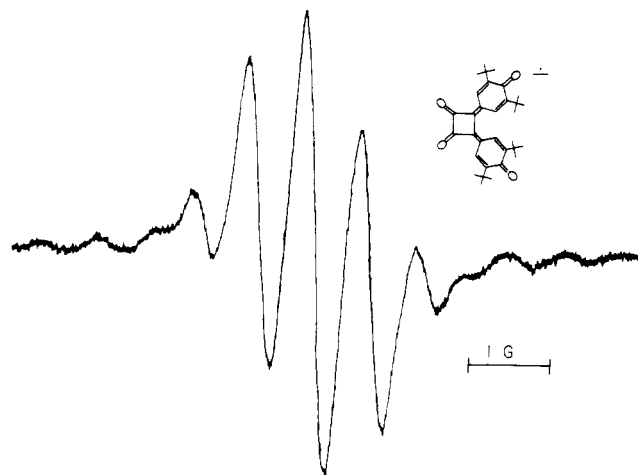

Figure 3. Electron spin resonance spectrum of the anion radical of **4**. The spectrum was obtained by electrolytic reduction of **4** in THF at -25 °C.

Anion and Monoradicals. Reduction of **4** or oxidation of **8** under basic conditions is expected to proceed via the anion radical. In an effort to obtain spectral evidence for this species, electrolytic reduction of **4** was performed in THF. A strong five-line pattern (a_H = 0.71 G; 1:4:6:4:1) was observed for the anion radical (Figure 3). This quintet demonstrates that the four "aromatic" protons are either accidentally equivalent or that rotation about the bonds between the four- and six-membered rings is rapid compared to the ESR time scale. A similar five-line pattern for the anion radical of diquinocyclopropanone has been reported (a_H = 0.63 G).[3]

The monoradical of **8** was generated by the comproportionation of equivalent amounts of **4** and **8** mixed in naphthalene in an ESR cavity. An extremely weak spectrum showing a triplet of triplets was observed at 110 °C (Figure 4). The major splitting (1.93 G) is interpreted as being due to the protons on the phenoxyl ring and the minor splitting (0.69 G) to the protons on the ring bearing the hydroxy group. Similar splitting patterns and coupling constants have been reported for the monoradicals of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (a_H = 1.86 and 0.72 G)[3] and bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (a_H = 1.86 and 0.93 G).[3] A similar comproportionation between **11** and **5** was attempted with no success.

Electrolytic reduction of **5** generates its respective anion radical which also exhibits a five-line pattern (a_H = 0.74 G;
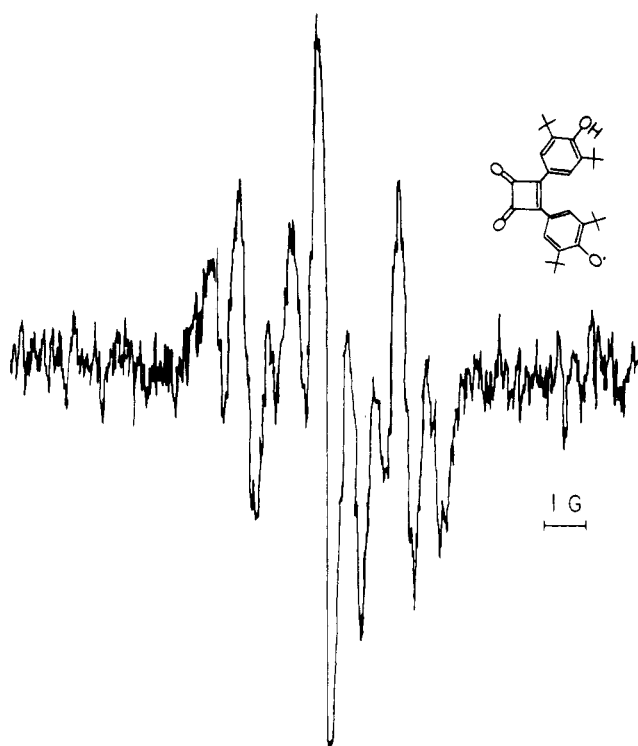
Figure 4. Electron spin resonance spectrum of the neutral monoradical of **4**. The spectrum was obtained by the comproportionation of equivalent amounts of **4** and **8** in naphthalene at 90 °C.
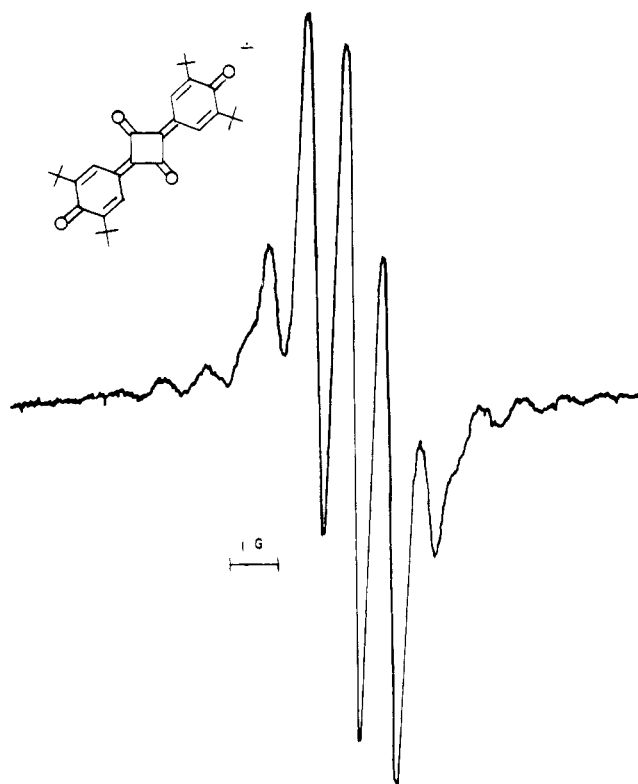

Figure 5. Electron spin resonance spectrum of the anion radical of **5**. The spectrum was obtained by electrolytic reduction of **5** in THF at 23 °C.

1:4:6:4:1) (Figure 5). The spectrum confirms the equivalency of the 4 "aromatic" protons.

The coupling constants for the anion radicals of **4** (0.71 G) and **5** (0.74 G) compare favorably with theoretical values of 0.60–0.70 and 0.70–0.81 G, respectively, as obtained from McLachlan-type Hückel molecular orbital calculations.[12] This agreement between empirical data and theoretical prediction further substantiates our previous utilization of certain parameters for polyquinonoid systems used in this type of calculation (these calculations are described in detail in a previous paper).[3]

Experimental Section

General Procedures. All syntheses were performed using purified grades of commercially available starting materials. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 237; ^{1}H NMR, JEOL MA-100; ultraviolet–visible, Cary 14; mass spectra, CEC Type 21-103C; ESR, Varian 4502-B.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclobutenedione (8). A solution of 1,2-dichlorocyclobutenedione[5] (4.5 g, 30 mmol) and 2,6-di-*tert*-butylphenol (12.4 g, 60 mmol) in 80 ml of dichloromethane was added dropwise to 4.8 g (40 mmol) of AlCl$_3$ in 35 ml of refluxing dichloromethane. After 1 h of reflux the solution was poured into 80 ml of ice water containing 2 drops of concentrated HCl. The organic layer was separated, washed with water, dried (MgSO$_4$), filtered, and evaporated. Crystallization from hexane/ether gave 3.3 g (34.4%) of 1-chloro-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclobutenedione (**7**) as light yellow crystals: mp 208–209.5 °C; IR (Nujol mull) 3600, 1775, 1760, 1590, 1550 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.25 (18 H), 7.30 (1 H), 8.18 (2 H); λ$_{max}$ (CHCl$_3$) 347 nm (log ε 4.58), 2.88 sh (3.73), 242 (4.14). Anal. Calcd for C$_{18}$H$_{21}$O$_3$Cl: C, 67.14; H, 6.90; O, 14.92; Cl, 11.04. Found: C, 67.28; H, 6.60; O, 15.19; Cl, 10.93 (diff).

Chromatography of the mother liquors on neutral alumina, eluting with hexane/ether, gave 0.5 g (3.2%) of **8**: mp 208–209 °C; ^{1}H NMR (CD$_3$CN) δ 1.43 (36 H), 6.23 (2 H), 7.97 (4 H); IR (Nujol mull) 3625, 3540, 1770, 1760, 1740, 1595, 1560 cm^{-1}; UV–visible λ$_{max}$ (CH$_3$CN) 370 nm (log ε 4.36), 305 (4.24), 260 sh (4.11), 253 (4.12); λ$_{max}$ (cyclohexane) 435 sh, 362, 296, 258, 249 nm; mass spectrum obsd 490.30724; mass spectrum calcd for C$_{32}$H$_{42}$O$_4$, 490.3083. Anal Calcd for C$_{32}$H$_{42}$O$_4$: C, 78.32; H, 8.64; O, 13.05. Found: C, 78.19; H, 8.78; O, 13.03 (diff).

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutanedione (4). Compound **8** (0.2 g, 0.41 mmol) was added to a slurry of 1 g of PbO$_2$ in 50 ml of dry benzene under nitrogen. After stirring at 25 °C for 30 min, the oxidizing agent was filtered off under nitrogen and the benzene evaporated to give a red-purple solid. The solid was recrystallized (yield 0.1 g, 50%) from dry hexane but the crystals obtained still contained 30% starting material as determined by ^{1}H NMR spectroscopy. A pure analytical sample was obtained by fractional recrystallizations from dry hexane: ^{1}H NMR (C$_6$D$_6$) δ 1.31 (18 H), 1.37 (18 H), 6.92 (2 H), 8.18 (2 H); IR (CCl$_4$) 2970 (s), 1765 (s), 1753 (s), 1610 (s, br), 1477 (w), 1400 (w), 1370 (m), 1335 (w), 1265 (m, br), 1100 (s), 1030 (m, br), 950 (w), 890 cm^{-1} (w); UV–visible λ$_{max}$ (benzene) 557 nm (log ε 4.31), 515 sh (4.03), λ$_{max}$ (hexane) 549, 508 nm sh; mass spectrum *m/e* 488 (parent). Anal. Calcd for C$_{32}$H$_{40}$O$_4$: C, 78.64; H, 8.25; O, 13.11. Found: C, 78.44; H, 8.18; O, 13.46.

4-(3,5-Di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-1,3,3-trifluoro-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclobutene (9). 2,6-Di-*tert*-butyl-4-bromophenol was silylated in 99% yield with n-BuLi followed by Me$_3$SiCl in THF according to the method of Kurreck et al.[13]

To a solution of 10.72 g (0.03 mol) of (2,6-di-*tert*-butyl-4-bromo)phenyl trimethylsilyl ether in 35 ml of dry diethyl ether under nitrogen was added dropwise 18.75 ml of 1.6 N n-butyllithium in hexane (0.03 mol) and the solution refluxed for 0.5 h. At −50 °C, 1.5 ml (0.015 mol of perfluorocyclobutene was collected in a gas trap and then allowed to condense into the reaction flask containing the substituted phenyllithium at −78 °C. The reaction mixture was stirred at −78 °C for 0.5 h, allowed to warm to room temperature over 2 h, and then refluxed for 0.5 h. The solution at this time was very deep blue. Adding 40 ml of 2% HCl discharged the blue color and resulted in the formation of a yellow-orange precipitate (1.9 g) which was collected and dried. The organic layer was separated, dried (MgSO$_4$), and filtered. The addition of hexane allowed the collection of an additional 0.8 g of **9** (total yield 35%). Recrystallization from hexane-ether gave sparkling, straw-colored platelets: mp 264–267 °C dec; ^{1}H NMR (C$_6$D$_6$) δ 1.29 (9 H), 1.32 (9 H), 1.48 (s, 18 H), 5.61 (s, 1 H), 7.10 (broad s, 2 H), 7.22 (2 H); ^{19}F NMR φ −99.1 (t, 1 F), −110.8 (d, 2 F); IR (CCl$_4$) 3620 (m), 3005 (w), 2961 (s), 2920 (m), 2940 (m), 1690 (w), 1640 (m), 1618 (m), 1611 (s), 1483 (m), 1455 (m), 1448 (m), 1430 (s), 1395 (m), 1377 (vs), 1350 (w), 1330 (m), 1290 (w), 1245 (s, br), 1220 (m), 1165 (m), 1149 (w), 1108 (s), 1090 (vs), 1030 (w, br), 952 (m), 917 (w), 890 (m), 875 cm^{-1} (m); UV–visible λ$_{max}$ (CCl$_4$) 265 nm (log ε 3.76),

416 (4.78), 428 sh (4.76), 462 sh (4.33); mass spectrum obsd 514.30760; mass spectrum calcd for $C_{32}H_{41}O_2F_3$, 514.30579. Anal. Calcd for $C_{32}H_{41}O_2F_3$: C, 74.66; H, 8.03; F, 11.08; O, 6.22. Found: C, 74.82; H, 8.03; F, 11.14: O, 6.01 (diff).

Anion of 9. Excess solid KOH was added to a solution of 9 in methanol (1.07×10^{-4} mol/l.) to generate the anion. After dilution (3:10) the UV–visible spectrum was run and gave the following bands: λ_{max} (CH_3OH) 590 nm sh (log ϵ 4.73), 629 (5.29).

1-Chloro-4-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3,3-difluoro-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-cyclobutene (14). This compound was prepared by the same method as 9 except that 1,2-dichlorotetrafluorocyclobutene was added with a syringe instead of hexafluorocyclobutene in a stream of N_2: mp 290 °C dec; ^1H NMR (C_6D_6) δ 1.30 (s, 18 H), 1.43 (s, 9 H), 1.46 (s, 9 H), 5.44 (s, 1 H), 48 (d, J = 0.06 Hz, 1 H), 7.70 (d, J = 0.06 Hz, 1 H), 7.84 (s, 2 H); IR (Nujol) 1300 (w), 1250, 1230 (m), 1100, 1080 (s), 3600 (sh, s), 1580 (m), 1530 (s), 1450 (s), 1415 (sh, m), 1370, 1360, 1340, cm^{-1} (m); UV λ_{max} (THF) 255 nm (log ϵ 3.74), 421 (4.78); mass spectrum obsd 531.27478; mass spectrum calcd for $C_{32}H_{41}O_2F_2Cl$, 531.27633. Anal. Calcd for $C_{32}H_{41}O_2F_2Cl$: C, 72.35; H, 7.78; Cl, 6.67; F, 7.15; O, 6.02. Found: C, 72.14; H, 7.99; Cl, 6.65; F, 7.35.

1,3-Bis(3,5-di-*tert*-butyl-4-hydroxyphenol)-1,4-dimethoxy-cyclobuten-3-one (10). The trifluoro compound (9, 12.5 g, 24 mmol) was added to 500 ml of methanol containing 14.0 g of KOH. This gave a dark blue solution which was stirred and heated at reflux for 36 h. After cooling, the solution was acidified with 10% aqueous HCl, causing the solution to turn bright red. The product was extracted into $CHCl_3$, dried with $MgSO_4$, and filtered. The solvent was evaporated, and recrystallization of the residue from methanol gave 7.5 g of a white solid (60%): mp 204–206 °C; ^1H NMR ($CDCl_3$) δ 1.40 (s, 18 H), 1.45 (s, 18 H), 3.56 (s, 3 H), 4.04 (s, 3 H), 5.16 (s, 1 H), 5.34 (s, 1 H), 7.23 (s, 2 H), 7.62 (s, 2 H); IR (CCl_4) 3618 (sh, m), 1750 (s), 1630, 1590 (m), 1430 (s), 1350 (s), 1000 (m), 600 cm^{-1} (s); UV ($CHCl_3$) λ_{max} 275 nm (log ϵ 4.41); mass spectrum obsd 536.35123; mass spectrum calcd for $C_{34}H_{48}O_5$, 536.35017. Anal. Calcd for $C_{34}H_{48}O_5$: C, 76.12; H, 8.96; O, 14.92. Found: C, 76.30; H, 8.96; 14.93.

3-(3,5-Di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-1-hydroxy-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclobuten-3-one (11). (7.5 g, 14 mmol) was added to a solution of 300 ml of MeOH and 100 ml of concentrated HCl. (Note: too much HCl causes the reaction mixture to coagulate). The deep red solution was heated at reflux for 1.5 h, after which time a green precipitate formed. The flask was cooled and the green precipitate was filtered off with a Büchner funnel. Additional product was collected by extraction with $CHCl_3$. The combined solids were dissolved in $CHCl_3$ and dried over $MgSO_4$. After filtration and evaporation of solvent, the product was recrystallized from Skelly B to give a reddish-brown powder. After drying for 24 h in a drying pistol, 4.0 g (56%) of a brown powder was isolated. Recrystallization from $CHCl_3$ produces green, metallic-looking platelets: mp 185–190 °C dec; ^1H NMR ($CDCl_3$) δ 1.48 (s, 36 H), 6.32 (br s, 2 H), 8.44 (s, 4 H); IR (CCl_4) 3580 (sh, m), 1630 (s), 1586 (s), 1363 (s), 1333 (s), 1250 (m), 720 cm^{-1}; UV ($CHCl_3$) λ_{max} 534 nm (log ϵ 5.17), 498 (4.44), 335 (3.71); mass spectrum obsd 490.30867; mass spectrum calcd for $C_{32}H_{42}O_4$, 490.30830. Anal. Calcd for $C_{32}H_{42}O_4$: C, 78,33; H, 8.63; O, 13.04. Found: C, 78.19; H, 8.64; O, 12.86.

1,3-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-cyclobutanedione (5). KOH solution (1.4 N, 1 g, 150 ml) and 7 g of $K_3Fe(CN)_6$ in 70 ml of chlorobenzene and 20 ml of $CHCl_3$ were added to an Erlenmeyer flask and allowed to stir for 1 h. The suspension turned from red to brown after approximately 10 min. The two-phase system was extracted with $CHCl_3$; the $CHCl_3$ layers were combined and washed with H_2O; the organic layer was dried over $MgSO_4$ and filtered. Evaporation of the solvent yielded blue-green crystals which were collected on a Büchner funnel and washed with acetonitrile to remove any unoxidized material. Yields are almost quantitative; mp 270–280 °C dec; ^1H NMR ($CDCl_3$) δ 1.32 (s, 36 H), 7.84 (s, 4 H); IR ($CHCl_3$) 1675 (s), 1600 (s, broad), 1540 (s), 1381, 1354 (m), 1060 cm^{-1} (s, broad); UV–visible (benzene) λ_{max} 510 nm (log ϵ 4.94), 484 (4.88),

451 (4.58); mass spectrum obsd 488.29105; mass spectrum calcd for $C_{32}H_{40}O_4$, 488.29265. Anal. Calcd for $C_{32}H_{40}O_4$: C, 78.65; H, 8.25; O, 13.10. Found: C, 78.45; H, 8.12; O, 12.88.

Titration of 8 to Its Dianion. A solution of 47.3 mg (0.096 mmol) of 8 in 300 ml of dry THF was titrated with a solution of DBN in THF (4.04×10^{-2} mmol/ml). Aliquots of base (1 ml) were added to the solution of 8. Aliquots were withdrawn for UV–visible spectrum and returned after each addition. Isosbestic points were observed at 395 and 265 nm throughout the titration. The dianion has λ_{max} 480 nm sh (log ϵ 2.92), 462 (4.37), 432 (4.36), 310 sh (4.05), 293 (4.13); see Figure 1.

Electron Spin Resonance Experiments. Anion Radical of 4 and 5. About 1 mg of the DQCB with a small amount of (n-Bu)$_4$N$^+$ClO$_4^-$ was placed in an electrolytic cell. A small piece of glass wool was placed between the electrodes to slow diffusion. Aluminum foil was kept wrapped around the cell for 1,2-DQCB. The cell was evacuated and THF (distilled from LiAlH$_4$, stored over Na/K anthracene) was distilled into the cell. The solution was degassed twice, the foil removed, and the cell placed in the ESR cavity. A minimal current was passed through the cell and scanning begun. For 4 resolution of the spectrum improved as the temperature was raised, but at temperatures > -30 °C decay of the signal level became apparent. The spectrum in Figure 3 was observed at -25 °C. The spectrum for 5 was obtained at room temperature (Figure 5). 4: a_H = 0.71 G, 1:4:6:4:1, g = 2.0063. 5: a_H = 0.74 G, 1:4:6:4:1, g = 2.0043.

Monoradical of 8. A mixture of 8 mg each of 4 and 8 and 2 g of naphthalene were ground together in the dark in a mortar and pestle. A small amount of the mixture was placed in an ESR cell wrapped with aluminum foil. The cell was twice alternately evacuated and flushed with nitrogen leaving 1 atm of nitrogen in the cell. No signal was observed from the solid mixture until it melted at about 90 °C. Increasing the temperature increased the intensity of the spectrum somewhat but resolution was also somewhat lower. The best spectrum is that shown in Figure 4 at 110 °C with a_H (2 H) = 1.93 G, a_H (2 H) = 0.69 G, and g = 2.0054.

Registry No.—4, 61377-19-3; 4 anion radical, 55255-34-0; 5, 61377-20-6; 5 anion radical, 61377-21-7; 6, 2892-63-9; 7, 61377-22-8; 8 61377-23-9; 8 dianion, 61377-24-0; 8 monoradical, 61377-25-1; 9, 61377-26-2; 9 anion, 61377-27-3; 10, 61377-28-4; 11, 61377-29-5; 14, 61377-30-8; 2,6-di-*tert*-butylphenol, 128-39-2; (2,6-di-*tert*-butyl-4-bromo)phenyl (trimethyl)silyl ether, 27329-74-4; perfluorocyclobutene, 697-11-0; 1,2-dichlorotetrafluorocyclobutene, 377-93-5.

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