group electronegativity (or σ inductive) effect that alternates in sign along an aliphatic chain, as first suggested by semiempirical molecular orbital calculations on $X(CH_2)_nCH_3$ derivatives.[37] However, the data for CN and OH derivatives show a reasonable parallel with charge densities for HX and HCH_2X derivatives (Table II) by predicting a surprisingly large effect for $-CH_2CN$ (and also for $-CH_2COCH_3$). It is possible that there is a hyperconjugative contribution to J_{CC} for these derivatives, similar to that suggested for $H-CH_2-X$ charge densities. It should be noted in this regard that there may be minor errors in calculated σ_χ values for CH_nX_{3-n} groups due to this type of hyperconjugative interaction. In particular, σ_χ for CF_3 may be too small. It is interesting that if eq 1 is used to estimate σ_χ values for these groups, values for CH_2X groups (X = NH_2, OH, F, CN) are only slightly altered (although the relative order for X = NH_2, OH, and F seems more logical) but σ_χ for CF_3 is significantly increased. We suspect that $\sigma_\chi = 0.25$ is a more reasonable value for CF_3.

Earlier,[38] it was suggested that a series of "inductive" substituent constants could be obtained from olefinic geminal J_{HH} values. The experimental values were taken from several sources, and the derived σ^J_I values do not seem to follow either σ_F or σ_χ values.

(37) Pople, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 4253.
(38) Knorr, R. *Tetrahedron* 1981, *37*, 929.

Conclusions

In conclusion, hydrogen charge densities in compounds HX as determined by Mulliken population analysis of calculations at the ab initio molecular orbital 6-31G* level provide a straightforward method for estimating substituent group electronegativities. Comparison for simple substituents with previously determined atomic electronegativities indicates that our method is fundamentally sound. An empirical relationship is noted between group electronegativity and $J_{C(ipso)-C(ortho)}$ for many monosubstituted benzenes where the directly bonded atom is a first row element. This provides an alternative method for defining group electronegativities that may be more reliable for CH_nX_{3-n} groups, e.g., CF_3.

Registry No. H_2, 1333-74-0; LiH, 7580-67-8; BeH_2, 7787-52-2; BH_3, 13283-31-3; $HBMe_2$, 7216-97-9; HBF_2, 13709-83-6; CH_4, 74-82-8; C_2H_6, 74-84-0; CH_2Me_2, 74-98-6; $HCMe_3$, 75-28-5; $CH_2{=}CH_2$, 74-85-1; HC≡CH, 74-86-2; HC≡CMe, 74-99-7; H_2NMe, 74-89-5; HOMe, 67-56-1; CH_3F, 593-53-3; CH_3CHO, 75-07-0; CH_3CN, 75-05-8; HCN, 74-90-8; HOCN, 420-05-3; HCHO, 50-00-0; HCO_2H, 64-18-6; HCO_2Me, 107-31-3; $HOCONH_2$, 463-77-4; HCOF, 1493-02-3; HCF_3, 75-46-7; NH_3, 7664-41-7; $NHMe_2$, 124-40-3; NH_4^+, 14798-03-9; H_2NCHO, 75-12-7; H_2NNH_2, 302-01-2; HNC, 6914-07-4; HNCO, 75-13-8; HNO, 14332-28-6; HONO, 7782-77-6; H_2O, 7732-18-5; HOCOMe, 64-19-7; HO^-, 14280-30-9; HF, 7664-39-3; SiH_4, 7803-62-5; PH_3, 7803-51-2; H_2S, 7783-06-4; HSMe, 74-93-1; HCl, 7647-01-0; allene, 463-49-0.

An Anthrylidenequinodiquinocyclopropane and Related Compounds. Their Structure and Physical Properties

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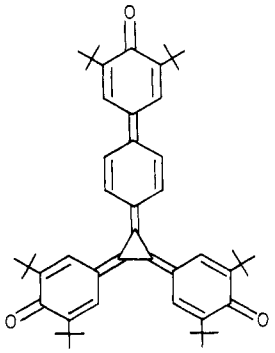
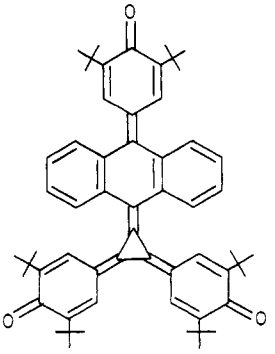
Received June 9, 1983

Dihydroquinones **6**, **10**, and **11** have been synthesized and characterized. Oxidation of **6** yields polyquinone **4**, which has its λ_{max} at 672 nm, with $E_1 = 0.09$ V and $E_2 = -0.20$ V. Evidence from cyclic voltammetry and from the ESR of the anion-radical of **4** indicates that steric interactions limit conjugation in this molecule.

The quinocycloalkanes are a family of compounds having intense, low-energy electronic transitions and are potentially useful as dyes, photoconductors, and photographic materials. As a part of our continuing study of these molecules,[1-3] a report from this laboratory several years ago discussed the synthesis and characterization of **1**, an



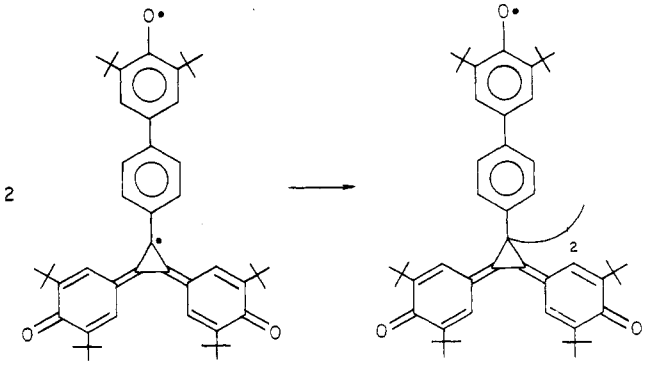
1



4

interesting triquinocyclopropane with a remarkable electronic excitation absorption at 1300 nm.[4] This absorption is well into the near-infrared region, an area approaching molecular bond vibrational energy and not often seen for electronic excitation of organic molecules.

Compound **1** is, however, unstable, decaying by first-order kinetics with a half-life of 92 min at 25 °C. The ESR spectrum of **1** suggests that it exists predominantly in the diradical form **2** which dimerizes to give the diradical dimer



2 **3**

(1) West, R.; Zecher, D. C. *J. Am. Chem.* Soc. **1970**, *92*, 155, 161.
(2) Benham, J. L.; West, R.; Norman, J. A. T. *J. Am. Chem. Soc.* **1980**, *102*, 5047 and references therein cited.
(3) Benham, J. L.; West, R. *J. Am. Chem. Soc.* **1980**, *102*, 5054.
(4) Wendling, L. A.; West, R. *J. Org. Chem.* **1978**, *43*, 1573.

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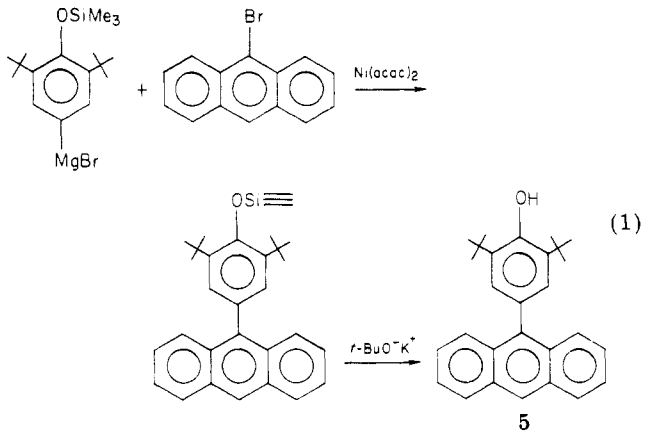


(1)

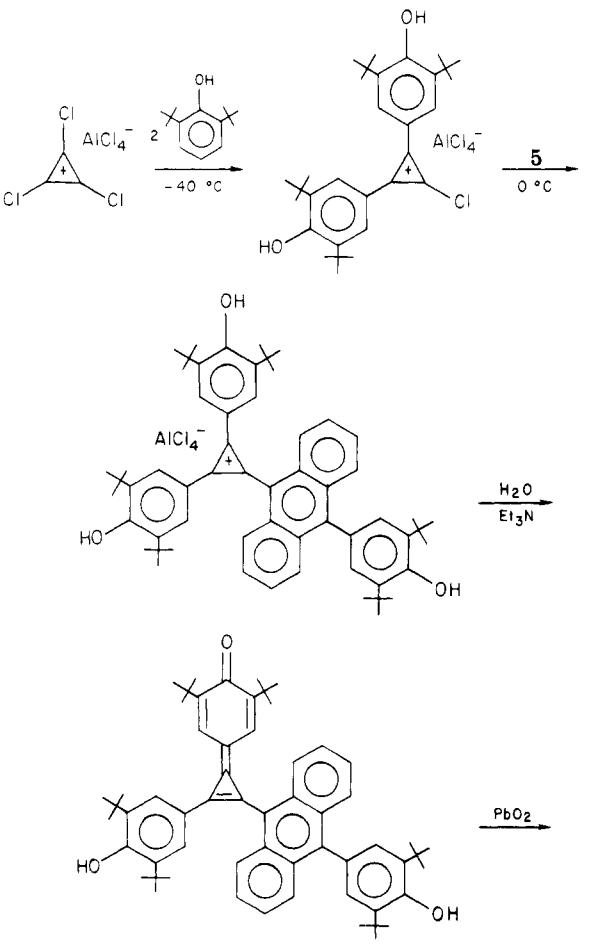
5

3. Magnetic susceptibility and spectral measurements on the end product confirmed the diradical dimer structure **3**.

Because it seemed possible that the dimerization of **1** via diradical species **2** might be blocked sterically, we sought to synthesize **4**, a compound having the same electronic structure as **1** but with the cyclopropane ring protected by the anthrylidene moiety.

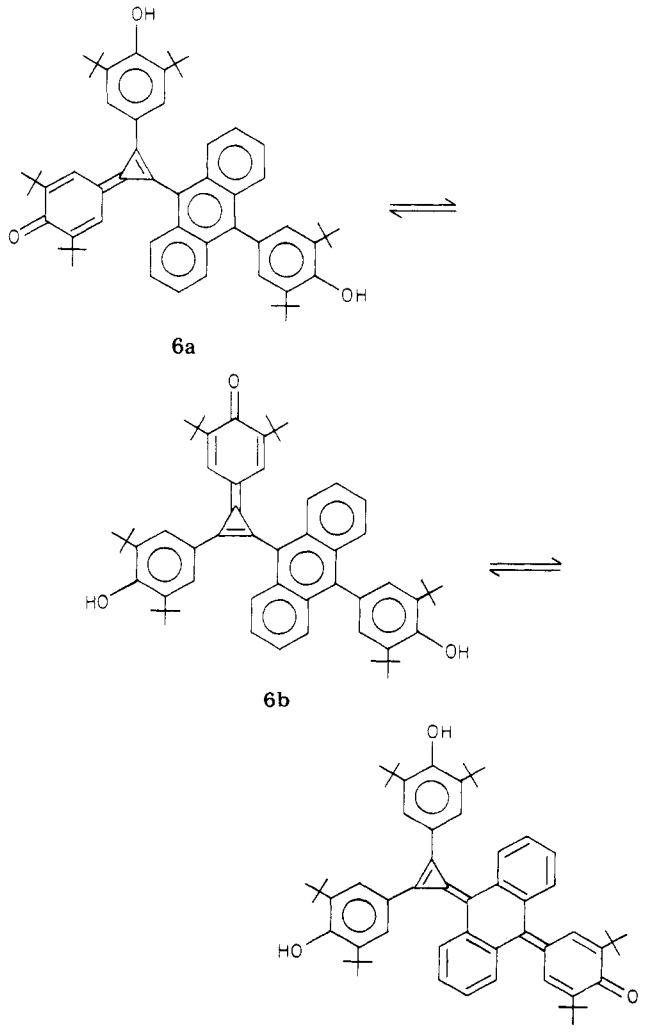
Synthesis. Anthrylphenol **5**, required as a starting material, was obtained by a nickel-catalyzed coupling reaction of the sort described by Roberts and co-workers (eq 1).[5] Compound **5** was then used to prepare **6**, the dihydro compound corresponding to **4**, as outlined in Scheme I. Trichlorocyclopropenium ion was disubstituted with 2,6-di-*tert*-butylphenol at low temperature. Following addition of **5** and a workup with aqueous base, **6** was isolated by column chromatography on alumina.

Scheme I



6

4



6a

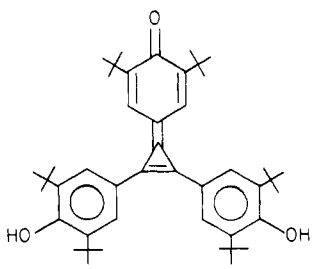
6b

6c

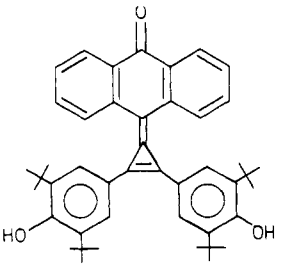
Compound **6** could exist in three tautomeric forms: the equivalent forms **6a,b** and the distinct "anthraquino" form **6c**. From observations on related quinocycloalkanes such as **7**, proton shifts between the tautomers are expected to be rapid in solution.[1,3] In accord with this, **6** shows only two *tert*-butyl resonances in the ^{1}H NMR, in a 1:2 ratio, as expected if proton exchange is rapid on the NMR time scale.

Some evidence concerning the equilibrium between **6a,b** and **6c** is provided by the electronic spectrum of **6**. Tautomers **6a,b** which contain only quinocyclopropene chromophores are predicted to have the longest wavelength absorptions at less than 500 nm (compare **7**, λ_{max} (THF) 462).[1] The more extended conjugation in **6c** should lead to lower energy absorption. No exact model is available,

(5) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252.



7



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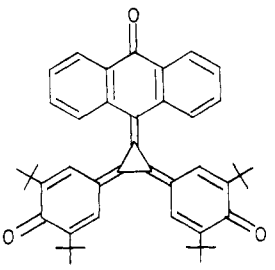


9

but effective comparison may be made with 8, λ_{max} (THF) 535 nm.[2] In fact, **6** shows both a strong absorption band at 445 nm and a much weaker one at 522 nm (log ϵ 4.50 and 3.72, respectively). Thus it seems likely that all three tautomers of **6** are present in solution, with **6a,b** probably present in a larger amount than **6c**.

Oxidation of a benzene solution of **6** with PbO_2 gave **4**, a rather unstable compound that decomposed during attempted chromatography. The compound was purified by filtration to remove the PbO_2, followed by slow evaporation of the solvent with argon to yield small rectangular crystals that were light purple with a metallic luster. Once in crystalline form, **4** could be exposed briefly to air without decomposition.

The proton NMR of **4** provides evidence for its structure. Because of the exocyclic double bonds on the cyclopropane ring of **4**, there should be a separate signal for each of the three pairs of equivalent *tert*-butyl groups, and these were observed at δ 1.20, 1.31, and 1.41. Signals at δ 1.20 and 1.41 are observed for the *tert*-butyl protons on 3,5-di-*tert*-butyl-4-oxocyclohexadien-1-ylidene groups for triquinocyclopropanes such as **9**. Therefore, the chemical shift at δ 1.31 most likely results from the *tert*-butyl groups of the cyclohexadiene moiety on the anthrylidene portion of **4**. The IR spectrum shows the loss of the hydroxyl and cyclopropene absorptions of **6** with an increase in the intensity of the carbonyl absorption at 1600 cm^{-1}.

A striking feature of compound **4** is its electronic spectrum, shown in Figure 1. There is a very strong absorption at 672 nm, but no other bands are observed out to 2000 nm. Thus **4** is quite different from **1**, which absorbs at 1300 nm. Apparently a steric interaction between the anthrylidene group and the cyclohexadiene moiety greatly decreases the overlap through the π framework in **4** as compared to **1**.

A sample of **4** as a solid or in solution showed only a very weak ESR signal, suggesting that any diradical contribution to the ground state is minimal.

Syntheses of compounds bearing two anthrylphenol moieties are outlined in Scheme II. Cyclopropenone **10** is an orange powder that decomposes at 195 °C. This compound exhibits a very strong IR band at 1835 cm^{-1}, typical for cyclopropenones, as well as a strong narrow band at 3630 cm^{-1} for the O–H stretch of the phenols. Additional spectral data are consistent with the assigned structure.

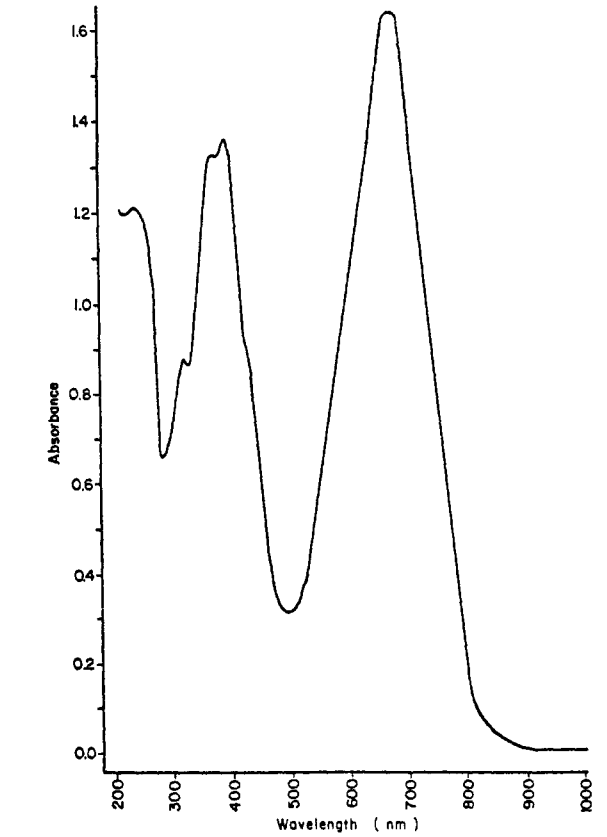
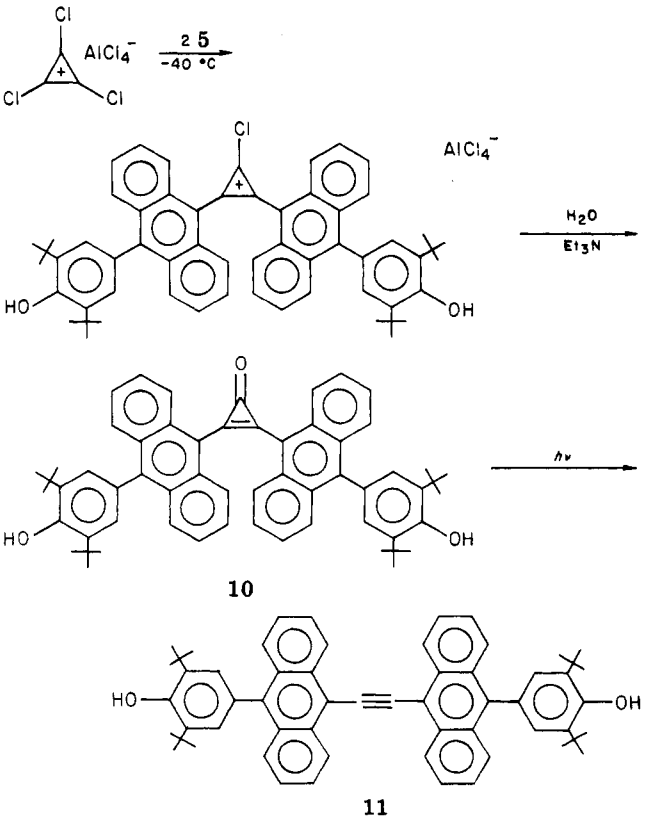


Figure 1. Electronic spectrum of **4** in THF (7.32×10^{-5} M, pathlength 1.0 cm).

Scheme II



Photolysis of a solution of **10** yielded the diarylacetylene **11** as a yellow powder. The strong cyclopropenone band present in the IR spectrum of **10** is absent in the IR of **11**. The structure of **11** was verified from proton NMR and mass spectrometry and elemental analysis.

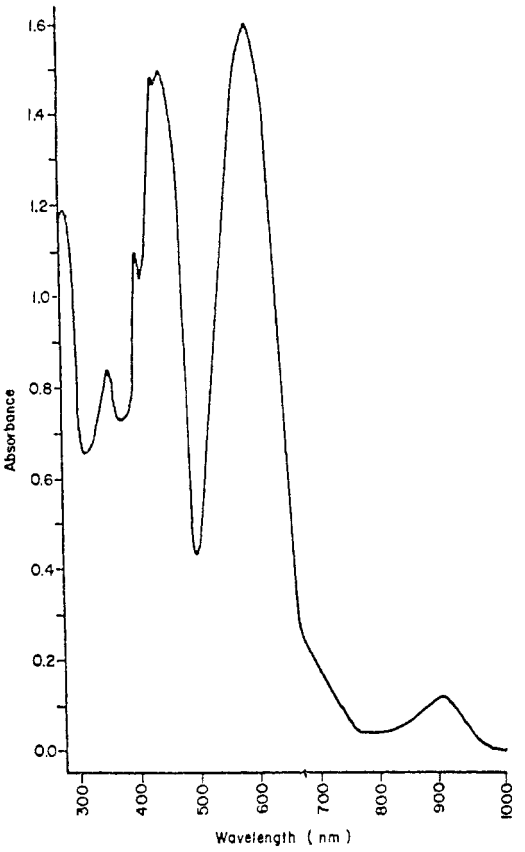
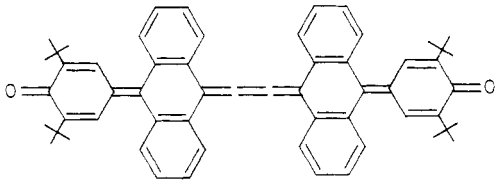


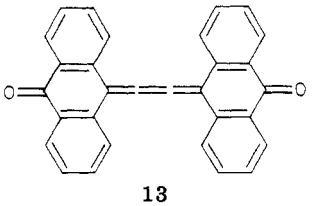
Figure 2. Electronic spectrum of the oxidized solution of 11 recorded 1 h after addition of PbO_2.

Attempted oxidation of a bright orange solution of **10** in benzene with PbO_2 yielded only a brown solution. After filtration of the PbO_2 and solvent removal, only a brown tar remained. Thus any quinone that may have formed decomposed rapidly.

When the acetylene compound **11** was oxidized with PbO_2 in benzene, a bright blue-green color slowly developed and then gradually turned to brown over a period of several hours. The electronic spectrum of the blue-green solution, shown in Figure 2, includes a strong band at 580 nm and a weaker one at 905 nm. It seems probable that this spectrum is due to the quinone **12**; the band at 580



12



13

nm resembles that found at 540 nm for the related compound **13**.[2] After 3 h, these initial absorption bands were nearly gone, and a complex mixture of decomposition products was present.

Spectrophotometric Titration of 6, 10, and 11. Figure 3 shows the result of a spectrophotometric titration of **6** in THF with DBU as the base. All the curves pass through a single set of isosbestic points, indicating that

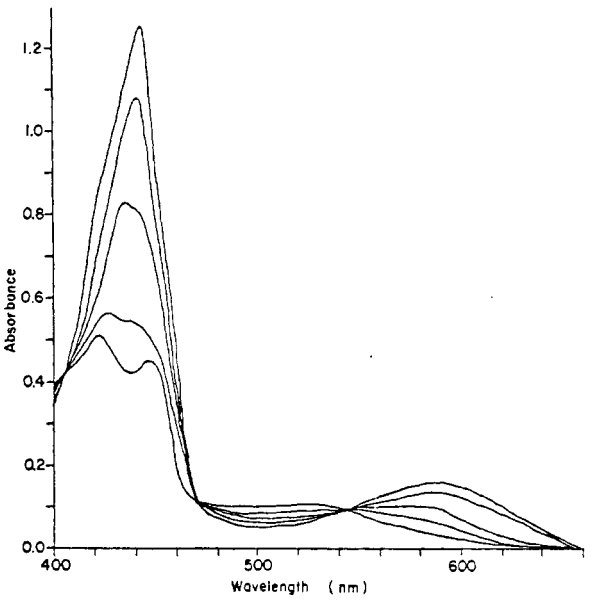


Figure 3. Spectrophotometric titration of **6** (1.41×10^{-5} M in THF) with DBU.

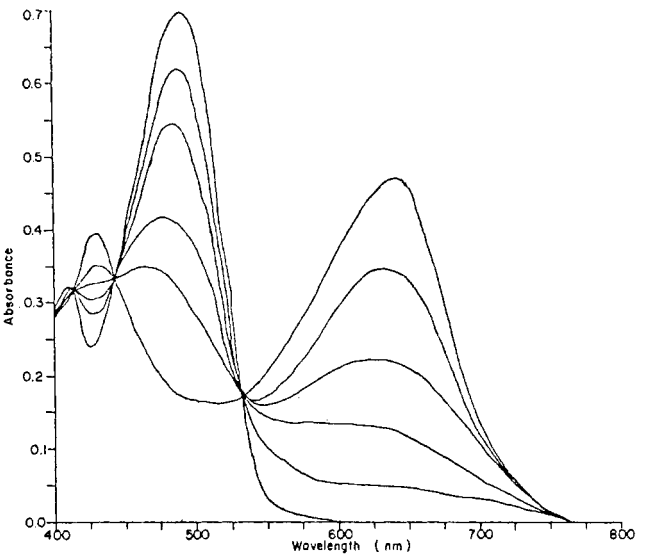


Figure 4. Spectrophotometric titration of **12** (2.72×10^{-5} M in THF) with DBU.

deprotonation takes place directly to the dianion. The spectrum of the resultant dianion was not altered by addition of excess DBU. Addition of excess acid regenerated the spectrum of **6**, showing that the deprotonation is completely reversible. The dianion exhibits an intense absorption at 443 nm (log ϵ 4.96) and an additional broad band at 587 nm (log ϵ 4.18).

The spectrophotometric titration of **10** is shown in Figure 4. This compound also undergoes deprotonation directly to the dianion, as seen from the fact that all of the curves pass through one set of isosbestic points. The dianion of **10** readily protonates when exposed to air. The dianion displayed λ_{max} = 638 nm (log ϵ 4.21).

The spectrophotometric titration of **11** was attempted, but it appears that the compound reacts very slowly with either DBU or NaOH in THF. Similar behavior has been reported for other diarylacetylenes of this type.[6,7] Direct addition of 2 equiv of base yields an absorption at 565 nm, presumably from the dianion.

(6) See ref 2 for an anthraquino example.
(7) Zecher, D. C. Ph.D. Thesis, University of Wisconsin–Madison, 1967.

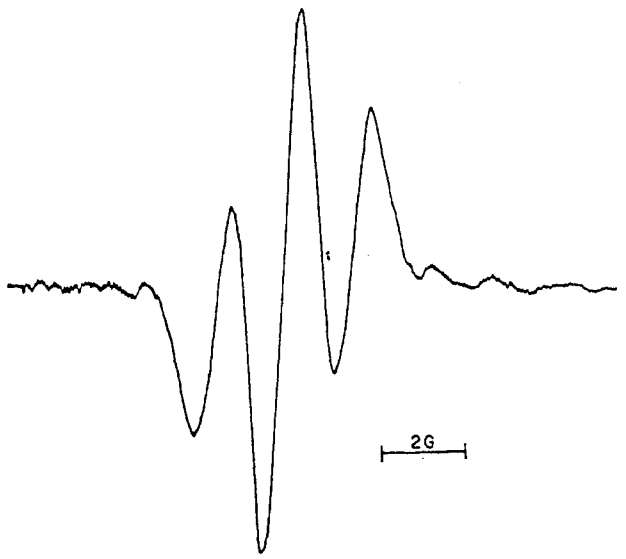
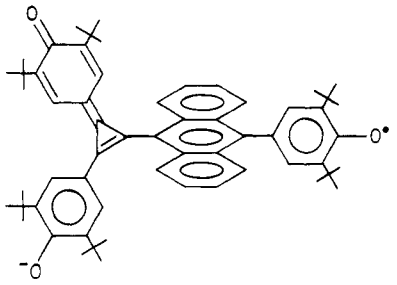


Figure 5. ESR spectrum for the anion radical of 4, generated with potassium in THF, at -40 °C.

ESR Spectrum of the Anion-Radical of 4. The ESR spectrum of the anion-radical of 4, generated with potassium metal in THF, is shown in Figure 5. The observed pattern is a simple triplet with a_H = 1.78 G and g = 2.0041. These results indicate that the unpaired electron spin is coupled to that of only two protons. The coupling constant is of the right magnitude for protons meta to the oxygen in a phenoxy radical.[8]

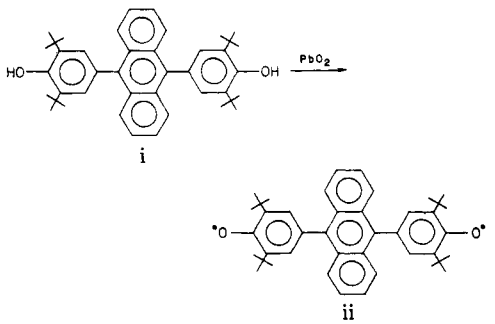
The most reasonable explanation is that the unpaired electron is mainly localized on the unique six-membered ring attached directly to the anthracene moiety. This is most surprising, because the unpaired electron on most triquinocyclopropane anion-radicals is fully delocalized.[1,3,4]

The localization of spin in $4^{-}\cdot$ may reflect interruption of conjugation due to a steric effect. Rotation of the anthracene ring out of the molecular plane in $4^{-}\cdot$ might relieve



$4^{-}\cdot$

(8) Further evidence comes from unpublished work of Jorgensen[9] and West where the reaction shown below yielded the diradical ii whose ESR spectrum was a triplet with a_H = 1.75 G.



(9) Jorgensen, J. Ph.D. Thesis, University of Wisconsin-Madison, 1981.

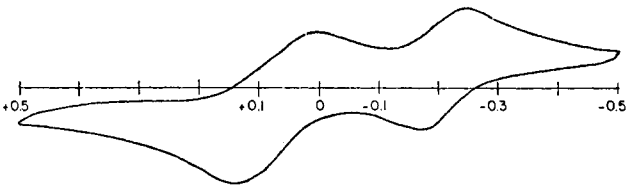


Figure 6. Cyclic voltammogram of 4 (ca. 5×10^{-5} M in CH_2Cl_2) scanned at 100 mV/s from +0.5 to -0.5 V.

strain while preventing rapid electron exchange between one oxygen and the other two. If so, structure $4^{-}\cdot$ would be favored over the alternate structure with the unpaired electron on the two equivalent six-membered rings, because in $4^{-}\cdot$ the negative charge can still be delocalized over two equivalent oxygens. Additional evidence for a steric change associated with the conversion of 4 to $4^{-}\cdot$ is found from the cyclic voltammetry experiments discussed below.

Cyclic Voltammetry of 4. The cyclic voltammogram of 4 is shown in Figure 6. The first wave exhibits a cathodic potential at 0.02 V and an anodic potential at 0.16 V, averaging to an E_1 value of 0.09 V vs. SCE. The ΔE_p for the first wave is 140 mV, which is much larger than the ideal value of 57 mV predicted for a reversible one-electron wave.[10] The large ΔE_p is indicative of a barrier to the electrode reaction. The quasi-reversible nature of this wave may be due to a slow conformational change necessary to convert the unhindered anion-radical $4^{-}\cdot$ back to neutral, sterically blocked 4.

The second wave displays a cathodic potential at -0.23 V and an anodic potential at -0.17 V, averaging to an E_2 value of -0.20 V. The ΔE_p for this wave is 60 mV, which is completely reversible according to theory. The E_1 and E_2 values for 4 are in the same range as those observed for related polyquinocycloalkanes but are slightly more positive. For example, 9 has E_1 = 0.02 and E_2 = -0.027 V, and TQCP, the oxidized form of 7, has E_1 = 0.05 and E_2 = -0.33.

Experimental Section

General Procedures. All syntheses were performed by using high purity grades of commercially available materials. Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN. Spectra were recorded by means of the following instruments: infrared, Beckman IR 4230; ^{1}H NMR, JEOL MH-100 and Bruker-IBM WP-200; ultraviolet-visible, Cary 14; ESR, Varian E-15; mass spectra, CEC Type 21-103C.

3,5-Di-*tert*-butyl-4-(trimethylsiloxy)phenylmagnesium Bromide. After 28.6 g (0.080 mol) of 4-bromo-2,6-di-*tert*-butyl-1-(trimethylsiloxy)benzene was dissolved in 200 mL of dry THF and the solution stirred under N_2 with 2.09 g (0.090 mol) of Mg turnings, 2 drops of 1,2-dibromoethane were added to initiate reaction. The mixture turned yellow and was refluxed 12 h to ensure complete formation of the organomagnesium compound.

9-[3,5-Di-*tert*-butyl-4-(trimethylsiloxy)phenyl]anthracene. The Grignard reagent formed above was cooled to room temperature and diluted with 200 mL of dry THF. It was then transferred via cannula to an addition funnel and added over 4 h to a refluxing solution of 9-bromoanthracene (10.3 g, 0.040 mol) in 200 mL of dry benzene with 30 mg of $Ni(acac)_2$ as an aryl-aryl' coupling constant. After addition of the Grignard reagent was completed, the fluorescent green solution was refluxed an additional 3 h, poured into 500 mL of 10% HCl/ice slurry, and stirred for 0.5 h. The now fluorescent yellow organic layer was extracted with 10% $NaHCO_3$ and dried over Na_2SO_4. After solvent removal the yellow oil was purified by fractional crystallization from 95% ethanol. The first fraction consisted of the less soluble biphenyl product also formed in the reaction. Final fractional crystallization yielded 11.8 g (65%) of pure product:

(10) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

mp 164–165 °C; IR (Nujol mull and KBr) 1655 (w), 1560 (w), 1540 (w), 1510 (w), 1500 (w), 1425 (w), 1410 (s), 1360 (s), 1342 (w), 1270 (m), 1260 (s), 1235 (s), 1210 (m), 1152 (w), 1138 (m), 1018 (2), 932 (s), 895 (m), 880 (s), 845 (s), 800 (w), 760 (m), 745 (s), 735 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.48 (s, 9 H), 1.49 (s, 18 H), 7.34 (s, 2 H), 7.38–8.2 (m, 8 H), 8.52 (s, 1 H); mass spectrum, found m/e 454.2691 (calcd for $C_{31}H_{38}OSi$ 454.2672).

9-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)anthracene (5). The product from the above reaction (7.07 g, 0.016 mol) was dissolved in 70 mL of dry ether. To this solution were added 1.90 g (0.017 mol) of potassium *tert*-butoxide, another 70 mL of ether, and 3 mL of absolute ethanol. The red solution was stirred under N_2 for 0.5 h, acidified with 10% HCl, chilled on ice, and then filtered. The product was washed with cold ether and air-dried. The total yield of **5**, an off-white powder, was 4.34 g (71%): mp 234–236 °C; IR (KBr) 3652 (s, very sharp), 3090 (w), 3060 (m), 3010 (m), 2970 (s), 2930 (m), 2888 (m), 1628 (w), 1525 (w), 1486 (m), 1475 (m), 1445 (s), 1412 (s), 1365 (s), 1315 (s), 1260 (m), 1240 (s), 1225 (s), 1210 (s), 1165 (m), 1125 (m), 1015 (w), 885 (m), 845 (m) cm^{-1}; ^1H NMR (Me_2CO-d_6) δ 1.50 (s, 18 H), 6.31 (s, 1 H), 7.22 (s, 2 H), 7.34–7.52 (m, 4 H), 7.73 (d, 2 H, J = 8.9 Hz), 8.10 (d, 2 H, J = 8.3 Hz), 8.57 (s, 1 H); ^1H NMR ($CDCl_3$) δ 1.49 (s, 18 H), 5.34 (s, 1 H), 7.21 (s, 2 H), 7.32–7.49 (m, 4 H), 7.78 (d, 2 H, J = 8.69 Hz), 8.03 (d, 2 H, J = 8.24 Hz), 8.46 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.55, 34.53, 114.80, 124.96, 125.96, 127.28, 127.89, 128.28, 129.38, 130.65, 131.53, 135.79, 138.50, 153.14; UV–visible λ_{max} (CH_2Cl_2) 388 nm (log ϵ 4.04), 368 (4.08), 350 (3.08), 355 (sh, 3.58), 320 (sh, 3.26), 284 (sh, 3.64), 255 (4.93); mass spectrum, m/e found 382.2298 (calcd for $C_{28}H_{30}O$ 382.2289). Anal. Calcd for $C_{28}H_{30}O$: C, 87.91; H, 7.91. Found: C, 87.82; H, 7.76.

1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-[10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-anthryl]-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropene (6). To 0.23 g (0.16 mL, 1.3×10^{-3} mol) of tetrachlorocyclopropene in 1 mL of dry methylene chloride was added 0.17 g (1.3×10^{-3} mol) of $AlCl_3$. This mixture was spot heated (hot air gun) while being stirred under N_2 to initiate trichlorocyclopropenium tetrachloroaluminate formation. After several minutes a buff-white paste had formed, which was diluted with 7 mL of dichloromethane. The resulting mixture was refluxed for 1 h to complete cyclopropenium ion formation. The mixture was cooled to −40 °C, and 0.53 g (2.6×10^{-3} mol) of 2,6-di-*tert*-butylphenol dissolved in 10 mL of dichloromethane was slowly added over 0.5 h. At this time the reaction mixture was allowed to warm to −20 °C for 1 h, to −10 °C for an additional 1 h, and finally to 0 °C for 1 h. When an aliquot was then removed and analyzed, there was evidence only for disubstitution of trichlorocyclopropenium ion with the 2,6-di-*tert*-butylphenol, with no evidence for unwanted trisubstitution. At 0 °C 0.50 g (1.31×10^{-3} mol) of 9-(3,5-di-*tert*-butyl-4-hydroxyphenyl)anthracene (**5**) in 10 mL of dichloromethane was slowly added over 0.5 h. The greenish brown solution of the disubstituted product became bright red as the reaction with **5** proceeded. This solution was refluxed for 4 h, cooled to room temperature, and quenched with tap water and 0.5 mL of triethylamine. The resulting brown-orange sludge (contaminated with insoluble aluminum salts) was filtered through glass wool and extracted several times with chloroform. The organic layers were combined and dried over Na_2SO_4. Filtration and solvent removal yielded a brown-orange amorphous solid. The desired compound was isolated from alumina via elution first with dichloromethane and then with 75:25 dichloromethane/chloroform. The yield of the orange **6** was 0.53 g (49%) following column chromatography. It decomposed at 240 °C: IR (KBr) 3660 (m), 3640 (m), 3010 (m), 2970 (s), 2925 (m), 2880 (m), 1830 (m), 1615 (s), 1608 (sh, m), 1580 (m), 1494 (vs), 1460 (s), 1434 (w), 1418 (m), 1397 (m), 1365 (vs), 1340 (vs), 1334 (vs), 1265 (m), 1258 (m), 1250 (m), 1204 (w), 1162 (m), 1126 (w), 1023 (w), 980 (w), 948 (w), 923 (w), 904 (m), 688 (m) cm^{-1}; ^1H NMR (Me_2CO-d_6) δ 1.42 (s, 36 H), 1.53 (s, 18 H), 5.61 (s, 1 H), 7.33 (s, 2 H), 7.61 (t, 2 H), 7.76 (t, 2 H), 7.87 (s, 4 H), 7.94 (d, 2 H), 8.22 (d, 2 H); UV–visible λ_{max} (THF) 522 nm (log ϵ 3.72), 445 (4.50), 422 (4.55), 405 (sh, 4.49), 367 (4.44), 350 (4.23), 272 (4.61), 268 (4.65); mass spectrum, m/e found 826.5355 (calcd for $C_{59}H_{70}O_3$ 826.5307). Anal. Calcd for $C_{59}H_{70}O_3$: C, 85.66; H, 8.54. Found: C, 85.49; H, 8.61.

Bis[10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-anthryl]cyclopropenone (10). Trichlorocyclopropenium tetrachloroaluminate was first prepared, as for **6**, by using 0.45 g (2.5×10^{-3} mol) of tetrachlorocyclopropene and 0.34 g (2.5×10^{-3} mol) of $AlCl_3$. This mixture was cooled to −30 °C, and 1.96 g (5.1×10^{-3} mol) of 9-(3,5-di-*tert*-butyl-4-hydroxyphenyl)anthracene (**5**) in 25 mL of dichloromethane was slowly added over 1 h. The initially magneta solution became deep purple-blue after the final addition of **5**. This solution was allowed to warm slowly to −20 °C for 0.5 h, −10 °C for 0.5 h, and 0 °C for 0.5 h. The solution was refluxed for 2 h and then cooled to room temperature. The reaction mixture was quenched with water and triethylamine, transforming the solution from deep purple-blue to bright orange. After the mixture was filtered through glass wool to remove the emulsion of aluminum salts and the usual workup, a bright orange-red solid was isolated which was purified by column chromatography (alumina, elution with chloroform). The resulting orange powder (1.36 g, 67%) decomposed at 195 °C: IR (KBr) 3630 (s, very sharp), 3050 (w), 2990 (w), 2950 (s), 2900 (m), 2860 (m), 1835 (s), 1808 (w), 1580 (m), 1570 (m), 1550 (m), 1530 (w), 1515 (w), 1475 (w), 1460 (w), 1435 (s), 1408 (m), 1387 (m), 1358 (m), 1300 (s), 1255 (s), 1230 (s), 1210 (m), 1150 (s), 1115 (m), 1085 (w), 1000 (w), 960 (w), 882 (w), 860 (w), 680 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51 (s, 36 H), 5.42 (s, 2 H), 7.26 (s, 4 H), 7.36–7.41 (m, 9 H), 7.83 (m, 4 H), 8.49 (m, 4 H); UV–visible λ_{max} ($CHCl_3$) 482 nm (log ϵ 4.41), 408 (4.21), 390 (sh, 4.08), 360 (sh, 3.96), 2.68 (4.79); mass spectrum, m/e found, 814.4417 (calcd for $C_{59}H_{58}O_3$, 814.4371). Anal. Calcd for $C_{59}H_{58}O_3$: C, 86.93; H, 7.18. Found: C, 86.61; H, 7.04.

Bis[10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-anthryl]acetylene (11). For preparation of **11**, 0.050 g (6.14×10^{-5} mol) of bis[10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-anthryl]cyclopropenone (**10**) was dissolved in 500 mL of benzene. This solution was photolyzed by using a broad band sun lamp. The rich orange solution of **10** became fluorescent yellow as **11** was formed. The photolysis was monitored by removing aliquots and observing the decrease of the 480-nm band of **10** via UV–visible spectroscopy. The time required for complete photolysis was about 3 h. After solvent removal, 0.48 g (100%) of a yellow powder was isolated, which decomposed at 265 °C. This compound proved to be of limited solubility in organic solvents. FT proton NMR required more than 200 scans: IR (KBr) 3630 (m, sharp), 3078 (w), 3056 (w), 3020 (m), 2992 (w), 2950 (s), 2918 (s), 2864 (m), 2948 (w), 1730 (w), 1620 (w), 1600 (w), 1515 (w), 1490 (m), 1480 (w), 1465 (w), 1450 (s), 1435 (s), 1422 (m), 1396 (s), 1388 (m), 1382 (m), 1342 (w), 1300 (m), 1286 (w), 1255 (m), 1242 (m), 1230 (s), 1200 (w), 1190 (m), 1146 (s), 1140 (s), 1115 (s), 1090 (m), 1060 (w), 1038 (w), 1020 (s), 932 (w), 900 (w), 880 (w), 802 (w), 786 (w), 762 (s), 752 (m), 690 (s), 673 (w), 662 (m), 626 (w), 607 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51 (s, 36 H), 5.64 (s, 2 H), 7.31 (s, 4 H), 7.43 (t, 4 H), 7.63 (t, 4 H), 7.82 (d, 4 H), 8.99 (d, 4 H); UV–visible λ_{max} ($CHCl_3$) 476 nm (sh, log ϵ 4.26), 453 (4.37), 410 (sh, 4.07), 372 (3.77), 352 (3.64), 265 (4.90), 252 (4.96); mass spectrum, found m/e 786.4462 (calcd $C_{58}H_{58}O_2$ 786.4422). Anal. Calcd for $C_{58}H_{58}O_2$: C, 88.50; H, 7.43. Found: C, 88.39; H, 7.32.

Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)[10-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-9-anthrylidene]cyclopropane (4). Compound **6** (0.050 g, 6.05×10^{-5} mol) was dissolved in 50 mL of dry deaerated benzene. This solution was stirred under Ar with 0.025 g (1.04×10^{-4} mol) of PbO_2 overnight. The blue-green benzene solution of **4** was filtered under Ar to remove the PbO_2. Very slow purging with Ar (about 12 h to remove 50 mL of benzene) yielded light purple metallic crystals. These were carefully removed by hand (tweezers) from decomposition products, yielding 0.022 g (44%) of **4**, which decomposed at 270 °C. It should be noted that all attempts to purify **4** by chromatography failed due to the instability of this compound to alumina, water, and/or air. However, once **4** has been crystallized by the slow evaporation method, it is relatively stable in air: IR (KBr) 3080 (w), 3060 (w), 3022 (m), 3000 (w), 2958 (s), 2920 (s), 2854 (m), 1740 (w), 1608 (s), 1602 (s), 1590 (m), 1500 (m), 1490 (w), 1458 (s), 1388 (s), 1366 (m), 1256 (w), 1155 (w), 1128 (m), 1112 (s), 1092 (s), 1046 (w), 1027 (m), 940 (w), 930 (w), 910 (w), 892 (w), 852 (w), 820 (w), 766 (m), 758 (m), 698 (s), 666 (w) cm^{-1}; ^1H NMR δ 1.20 (s, 18 H), 1.31 (s, 18 H), 1.41 (s, 18 H), 7.49 (s, 4 H), 7.51 (s, 2 H), 7.70 (m, 4 H), 8.42 (m, 4 H); UV–visible ($CHCl_3$) λ_{max} 672 nm (log ϵ 4.35), 432 (sh, 3.98), 396 (4.27), 365 (4.26), 320 (4.07), 245 (4.20); mass spectrum, found

m/e 824.5109 (calcd for $C_{59}H_{68}O_3$ 824.5151), 826.5304 (M + 2). Anal. Calcd for $C_{59}H_{68}O_3$: C, 85.87; H, 8.31. Found: C, 85.71; H, 8.49.

Oxidation of 11. A solution was prepared by dissolving 0.002 g (2.54×10^{-6} mol) of 11 in 100 mL of dry degassed benzene. PbO_2 (0.002 g, 8.37×10^{-6} mol) was added, and the reaction was monitored by UV-visible spectroscopy. After about 1 h, the spectrum in Figure 2 was recorded. The absorption at 580 nm, attributed to 12, did not appear to follow a first-order decomposition pathway. The solution that was blue-green after 1 h was brown at the end of 3 h. A portion of the brown residue was analyzed by ESR spectroscopy and exhibited a weak paramagnetic signal. A UV-visible spectrum of the brown residue yielded a weak absorption at 580 nm and several absorptions below 450 nm.

Spectrophotometric Titrations of 6 and 10. Both compounds were titrated under similar conditions with DBU as a base and THF as a solvent. The results of the titrations are shown in Figures 3 and 4. Base was added to each solution as follows: 0.5 equiv was added to 6 in increments until a total of 2.0 equiv was added; 0.4 equiv of base was added in increments to 10 until a total of 2.0 equiv was added.

Anion Radical of 4. Into an ESR tube was placed about 0.2 mg of 4. Degassed THF was vacuum transferred, and the resultant solution was freeze-thaw degassed several times. A potassium mirror was formed above the solution level, and after the solution was brought into contact with the potassium, and orange solution developed. A strong signal developed and exhibited a triplet splitting pattern with a_H equal to 1.78 G (g = 2.0041). No other hyperfine splitting could be detected on using various modulation adjustments.

Cyclic Voltammetry of 4. An ASS 169 Electrochemistry system was used, composed of the following modules: A Princeton Applied Research Potentiostat/Galvanostat with a PAR 179 coulometer, a PAR Universal Programmer, a Houston 2000 X-Y recorder with time base, and a Tektronix 5103 N storage oscilloscope with a Polaroid camera. Positive feedback resistance compensation was employed. The measurement was carried out at room temperature (ca. 21 °C) in purified dichloromethane.

A three-electrode voltammetric cell was employed with a Pt disk working microelectrode, a Pt wire counter electrode, and an SCE reference. The sample solution was about 5×10^{-5} M, with 10^{-1} M tetrabutylammonium perchlorate as the supporting electrolyte.

The scan range was generally +0.5 to -0.5 V, and scan rates from 0.02 to 0.50 V/s were employed. The cathodic portion of E_1 was difficult to distinguish at fast scan speeds (greater than 0.2 V/s) and shifted anodically at slower scan rates. The anodic portion of E_1 was observable and did not change potential at the various scan rates. The E_2 couple remained reversible at all scan rates.

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Registry No. 4, 87842-45-3; 4 radical anion, 87842-46-4; 5, 87842-41-9; 6, 87842-42-0; 6 dianion, 87842-50-0; 10, 87842-43-1; 10 dianion, 87842-51-1; 11, 87842-44-2; 12, 87842-49-7; i, 87842-47-5; ii, 87842-48-6; $AlCl_3$, 7446-70-0; $Ni(acac)_2$, 3264-82-2; DBU, 6674-22-2; 9-bromoanthracene, 1564-64-3; tetrachlorocyclopropene, 6262-42-6; trichlorocyclopropenium tetrachloroaluminate, 10438-65-0; 2,6-di-*tert*-butylphenol, 128-39-2; 3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenylmagnesium bromide, 54907-62-9; 4-bromo-2,6-di-*tert*-butyl-1-(trimethylsiloxy)benzene, 27329-74-4; 9-[3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]anthracene, 87842-40-8.

Carbonylation and Valence Isomerization of 1,3-Dihomocubane Derivatives by Chlorodicarbonylrhodium Dimer

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1,3-Dihomocubane and several analogous cage compounds react with $Rh_2(CO)_4Cl_2$ to give dinuclear acyl-rhodium complexes. These complexes are transformed into dicyclopentadiene and/or D_3-trihomocubanone derivatives either upon heating or by treatment with triphenylphosphine. 1,3-Ethanomethanocubane reacts analogously. The kinetics of these metal-induced transformations follow the second-order rate law. A linear relationship exists between the constants and the calculated strain energies of the starting cage compounds.

The interaction of transition-metal complexes with carbocyclic compounds containing strained structures has been the subject of both considerable research and controversy.[1] Rhodium complexes, e.g., were found to induce valence isomerization in cage compounds having three to six fused cyclobutane rings. The rearrangement of a system with *two* condensed cyclobutanes has been studied only in an open noncage system and was shown to proceed by an isomerization mechanism different from that of the more complicated polycyclobutane structures.[2] We thus found it warranted to investigate the effect of transition-metal complexes on the isomerization of a *cage* compound

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