

ture was basic. Solvents were removed under reduced pressure at 60 °C; the residue was dissolved in 10 mL of methanol and dry ether was added until turbidity was evident. Chilling in the refrigerator (18 h) afforded 1 g (4.1 mmol, 79%) of **4a** as white needles, mp 154 °C. NMR (δ , D₂O, DSS): 3.10 (s, 9 H Me₃N⁺), 4.40 (s, 2 H, N⁺CH₂), 7.53-6.90 (A₂B₂ q, 4 H, aryl). The free amine is unstable to storage and was used immediately upon preparation.

N-n-Cetyl-N,N-dimethyl-N-p-aminobenzylammonium Bromide (3a). In precisely the same way, acetamido surfactant **3** (X = NHAc) was converted to free base **3a**, mp 185 °C, in 60% yield. NMR (δ , Me₂SO-*d*₆): 0.85 (t, 3 H, CH₃(CH₂)₁₄), 1.27 (s, 28 H, (CH₂)₁₄), 3.27-2.90 (m + s, 8 H, Me₂N⁺CH₂(CH₂)₁₄), 4.33 (s, 2 H, N⁺CH₂Ar), 7.23-6.57 (A₂B₂ q, 4 H, aryl). The free amine is unstable to storage and was used immediately upon preparation.

Diazotization and Coupling of 3a and 4a. In 30 mL of distilled water were dissolved 0.3 g (1.2 mmol) of **4a** or 0.5 g (1.1 mmol) of **3a**. The solutions were cooled in ice and diluted with solutions of 0.080 g (1.2 mmol) of NaNO₂ in 10 mL of water. The pH was reduced to 2 by addition of 48% aqueous HBr, and the solutions were stirred at *t* ≤ 5 °C for 15 min. The solutions were then neutralized (ice bath) with 1 N NaOH to pH 7, thus affording solutions of diazonium ions **3b** or **4b**. These solutions are only moderately stable, so that coupling was carried out at once.

To the solution of **3b** or **4b** was slowly added a solution of 0.15 g (1.0 mmol) of β -naphthol in 12 mL of water at pH 10.5. The reaction mixture was stirred magnetically and kept at pH 7 by the addition of small quantities of aqueous HBr as needed. A red precipitate (**5** or **6**) was formed from solutions of either **3b** or **4b**, respectively. These precipitates were filtered and recrystallized.

From **3b**, we obtained, after recrystallization from ethereal ethanol, 0.4 g (0.66 mmol, 60%) of surfactant azo compound **5** as a red powder: mp 183-184 °C; λ_{\max} 485 nm, log ϵ ~ 3.8 (10⁻² M aqueous CTABr, PO₄ buffer, pH 7, μ = 0.1); NMR (δ , CDCl₃) 0.96 (t, 3 H, CH₃), 1.26 (s, 28 H, (CH₂)₁₄), 3.83-3.36 (m + s, 8 H, CH₂N⁺ and N⁺(CH₃)₂), 5.37 (s, 2 H, benzyl), 8.46-7.40 (m's, 10 H, aromatic).

Anal. Calcd for C₃₅H₅₂N₃OBr: C, 68.88; H, 8.59; N, 6.88. Found: C, 67.6; H, 8.40; N, 6.60.¹⁴

From **4b**, we obtained, after recrystallization from absolute ethanol, 0.3 g (0.75 mmol, 62%) of azo compound **6** as red needles: mp 221-222 °C; λ_{\max} 485 nm, log ϵ ~ 3.8 (aqueous PO₄ buffer, pH 7, μ = 0.1); NMR

(δ , Me₂SO-*d*₆) 3.20 (s, 9 H, Me₃N⁺), 4.77 (s, 2 H, benzyl), 8.80-7.50 (m's, 10 H, aromatic).

Anal. Calcd for C₂₀H₂₂N₃OBr: C, 60.0; H, 5.54; N, 10.5. Found: C, 59.1; H, 5.80; N, 10.1.¹⁴

Kinetic Studies. Solutions of diazonium ions **3b** (0.178 mmol) or **4b** (0.747 mmol) were prepared in 10 mL of water by diazotization of **3a** or **4a**, as described above. Calculated amounts of NaH₂PO₄ or KCl were added for proper ionic strength, and the desired pH was achieved by addition of aqueous HBr or NaOH. The diazonium ion solutions were then diluted to 25 mL with water.⁸ Concurrently, 8.5 mg of β -naphthol was dissolved in a total of 500 mL of aqueous solution by addition of 1 M NaOH-NaH₂PO₄ solution. The ionic strength was adjusted to 0.1 with NaH₂PO₄ or KCl; the pH was adjusted as necessary.

Appropriately diluted and pH-adjusted stock solutions of diazonium ion **3b** or **4b** and β -naphthol were charged into the drive syringes of a Durrum Model D-130 stopped-flow spectrophotometer equipped with a Beckman DU-2 monochromator and a Tektronix Model 5103N/D-15 storage oscilloscope. After stopped-flow reactions, the oscilloscope traces were photographed with a Polaroid camera. Constant-temperature circulating baths maintained reaction temperatures at 4 ± 1 °C. All solutions were prepared from nitrogen-purged, steam-distilled water.

Rate constants were obtained from computer-generated linear correlations of log (*A*[∞] - *A*^{*t*}) with time in the standard manner. Reaction traces were generally read to >70% of completion, using at least seven points from the oscilloscope trace. Infinity values were systematically varied to obtain the best least-squares fit. Correlation coefficients were routinely >0.999, and the optimized *A*[∞] varied by <8% from the experimental value.

Data appear in Tables I-III. Concentrations of all reagents and buffers, ionic strengths, and pHs are detailed in the footnotes of the individual tables. Also included are the appropriate λ values for the kinetics experiments. Tables I and II pertain to coupling experiments with β -naphthol (**2b**); analogous experiments with 2-naphthol-6-sulfonate (**2a**) are summarized in Table III, and were carried out in a completely parallel way.

Acknowledgments. We thank the National Cancer Institute (Research Grant CA-14912) and the National Science Foundation for financial support. The stopped-flow spectrophotometer was purchased under Public Health Service Grant RR-7058-09 to Rutgers University. R.A.M. thanks the Department of Organic Chemistry of the Weizmann Institute of Science for its hospitality during the composition of this manuscript.

(14) The observed % C was low, due most likely to traces of water absorbed by the hygroscopic salt during the analytical procedures.

Polyanthraquinocyclopropanes, Dianthraquinocyclopropanone, and Dianthraquinoethylene. Synthesis and Properties

Judith L. Benham,^{1a} Robert West,^{*1b} and John A. T. Norman^{1b}

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Research Laboratories, 3M Company, St. Paul, Minnesota 55101. Received October 25, 1979

Abstract: Tris(9-anthron-10-ylidene)cyclopropane (**7c**) was prepared by the Friedel-Crafts reaction of 9-methoxyanthracene with trichloropropenium tetrachloroaluminate, followed by demethylation and oxidation of the resulting bis(9-hydroxy-10-anthryl)cyclopropenylideneanthrone. The corresponding triquinocyclopropanes with one or two anthraquino groups replaced by 4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene groups (**7a,b**) were prepared by stepwise addition of 9-methoxyanthracene and 2,6-di-*tert*-butylphenol. Reaction of 2 equiv of 9-methoxyanthracene in an analogous fashion resulted in 2,3-bis(9-anthron-10-ylidene)cyclopropanone (**8**), which loses carbon monoxide photolytically to form dianthraquinoethylene (**9**). These materials are intensely colored, highly conjugated solids with electronic absorptions in the near infrared. Spectroscopic properties and results of Huckel MO calculations are reported.

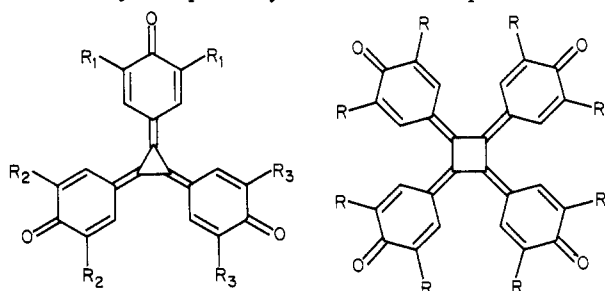
Recent work in these laboratories has been directed toward the synthesis and characterization of polyquinocycloalkanes. These compounds may be viewed as the fully oxidized analogues of cyclic oxocarbon anions, C_nO_{n-2}⁻², in which one or more of the oxygens

have been replaced by a 4-oxo-3,5-dialkyl-2,5-cyclohexadiene moiety (the 3,5-dialkyl substituents are necessary for protection

(1) (a) Chemical Resources, 3M Co., St. Paul, Minn. 55101; (b) University of Wisconsin.

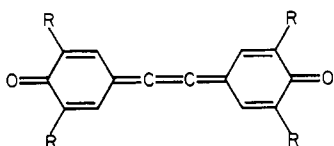
(2) (a) R. West and J. Niu, "Non-Benzenoid Aromatics", Vol. 1, J. P. Snyder, Ed., Academic Press, New York, 1969, Chapter 6; (b) "The Chemistry of the Carbonyl Group", Vol. 2, J. Zabicky, Ed., Interscience, New York, 1970, Chapter 4; (c) R. West, D. Eggerding, J. Perkins, D. Handy, and E. C. Tuazon, *J. Am. Chem. Soc.*, **101**, 1710 (1979), and references cited therein.

of the labile quinonoid carbonyl). The fully quinonoid members of the polyquinocycloalkanes include the series of triquinocyclopropanes **1a-e**,³ the stable tetraquinocyclobutane **2**,⁴ and the related family of diquinoethylenes **3a-c**.⁵ The quino-oxocarbon



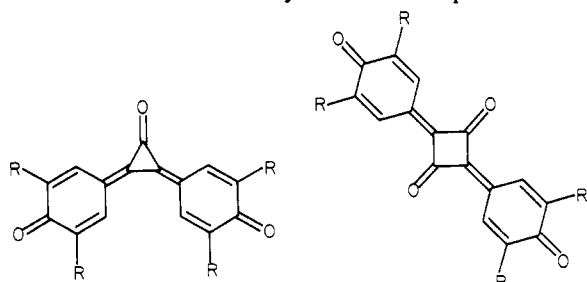
1a, $R_1 = R_2 = R_3 = t\text{-Bu}$
b, $R_1 = R_2 = R_3 = i\text{-Pr}$
c, $R_1 = R_2 = R_3 = \text{Me}$
d, $R_1 = R_2 = t\text{-Bu}$; $R_3 = \text{Me}$
e, $R_1 = R_2 = t\text{-Bu}$; $R_3 = i\text{-Pr}$

2, $R = t\text{-Bu}$



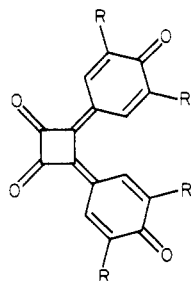
3a, $R = t\text{-Bu}$
b, $R = i\text{-Pr}$
c, $R = \text{Me}$

members of the family include the isolable but unstable diquinocyclopropanones **4a-c**,⁵ the stable 1,3-diquinocyclobutanedione **5**,⁶ and the rather labile 1,2-diquinocyclobutanedione **6**.⁶ The oxidation-reduction cycle of these compounds and their



4a, $R = t\text{-Bu}$
b, $R = i\text{-Pr}$
c, $R = \text{Me}$

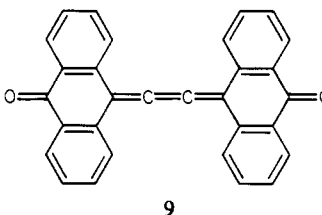
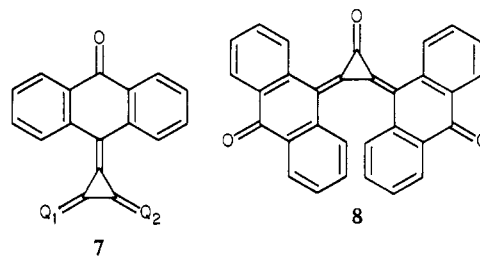
5, $R = t\text{-Bu}$



6, $R = t\text{-Bu}$

anions has been investigated in some detail.³⁻⁷ These highly conjugated, intensely colored, crystalline materials have potential uses as dyes and in photographic materials.⁸

In this paper we report the synthesis and spectroscopic properties of a series of compounds in which 9-anthron-10-ylidene groups take the place of one or more of the simple quinonoid groups in **1-6**. The substances obtained are the quinocyclopropanes **7a-c**, the dianthraquinocyclopropanone **8**, and the dianthraquinoethylene **9**.^{7a} Although inspection of models indicates that these compounds



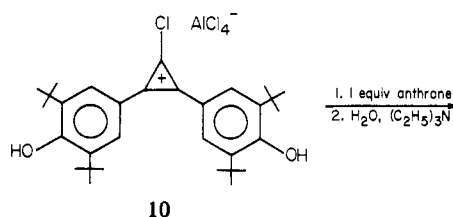
7a, $Q_1 = Q_2 = 4\text{-oxo-3,5-di-}t\text{-butyl-2,5-cyclohexadiene-1-ylidene}$
b, $Q_1 = 9\text{-anthron-10-ylidene}$; $Q_2 = 4\text{-oxo-3,5-di-}t\text{-butyl-2,5-cyclohexadiene-1-ylidene}$
c, $Q_1 = Q_2 = 9\text{-anthron-10-ylidene}$

(perhaps excepting **9**) cannot adopt planar conformations, they are generally more stable and less reactive than the analogous benzoquinonoid compounds.

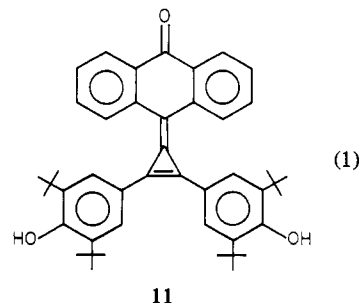
Like the other quinocycloalkanes, the anthraquino compounds are brightly colored dyes with semiconductive properties; they show electronic transitions at even lower energies than for the analogous compounds **1a-e**, **3a-c**, and **4a-c**. An accompanying paper will treat the oxidation-reduction cycles of these materials.⁹

Diarylcyclopropenylidenanthrones and Dianthrylcyclopropenones

The route outlined in eq 1 was used for the preparation of the



10



11

precursor to **7a**. The preformed diarylcyclopropenium ion, **10**,³ was reacted with 1 equiv of anthrone to give, after hydrolysis and treatment with triethylamine, 1,2-bis(4-hydroxy-3,5-di-*tert*-butylphenyl)cyclopropene-3-ylidenanthrone (**11**) as a rust-colored solid. The NMR and IR are consistent with structure **11**, showing only one type of *tert*-butyl protons and a medium-intensity band at 1800 cm^{-1} characteristic of the cyclopropene ring. This reaction

(9) J. L. Benham and R. West, *J. Am. Chem. Soc.*, following paper in this issue.

(3) D. C. Zecher and R. West, *J. Am. Chem. Soc.*, **89**, 153 (1967).

(4) (a) S. K. Koster and R. West, *Chem. Commun.*, 1380 (1971); (b) *J. Org. Chem.*, **40**, 2300 (1975); (c) S. K. Koster, Ph.D. Thesis, University of Wisconsin—Madison, 1974.

(5) R. West, D. C. Zecher, S. K. Koster, and D. Eggerding, *J. Org. Chem.*, **40**, 2295 (1975).

(6) L. A. Wendling, S. K. Koster, J. E. Murray, and R. West, *J. Org. Chem.*, **42**, 1126 (1977).

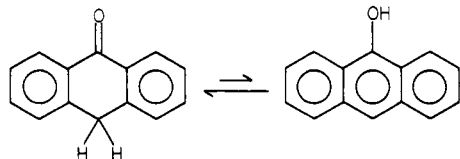
(7) R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **92**, 161 (1970).

(8) W. A. Huffman, S. P. Birkeland, and K. P. O'Leary, U.S. Patent 4052209 (Oct 4, 1977).

is similar to one reported by Fohlisch and Bürgle¹⁰ to give diphenylcyclopropenylidenanthrone. The presence of *p*-hydroxyl substituents on the phenyl rings makes **11** an oxidative precursor to the diquinoanthraquinocyclopropane **7a**.

The synthesis of other members of the anthraquinocyclopropane family was less straightforward, however. The reaction of 2 equiv of anthrone with trichlorocyclopropenium tetrachloroaluminate ($C_3Cl_3^+AlCl_4^-$) at low temperature (conditions analogous to the formation of **10**) resulted only in recovery of anthrone. Higher reaction temperatures and longer reaction times afforded mixtures of bis(9-hydroxy-10-anthryl)cyclopropenone (**12**) and 1,2-bis(9-hydroxy-10-anthryl)cyclopropen-3-ylidenanthrone (**13**), but only in low to moderate yields. Therefore a preparative route was sought to provide the controlled conditions necessary for synthesis of the precursors to **7b**, **8**, and **9**.

The difficulties in the synthesis of the di- and trianthraquinocyclopropanes probably result partly from steric hindrance to the attachment of several anthryl rings to a cyclopropenium ion. In addition, the reaction may be slow because of the natures of the reactive nucleophile and cyclopropenium intermediates in the reaction. The nucleophile is 9-anthrol, the unstable enol tautomer of anthrone.¹¹ In the synthesis of **11**, the reaction

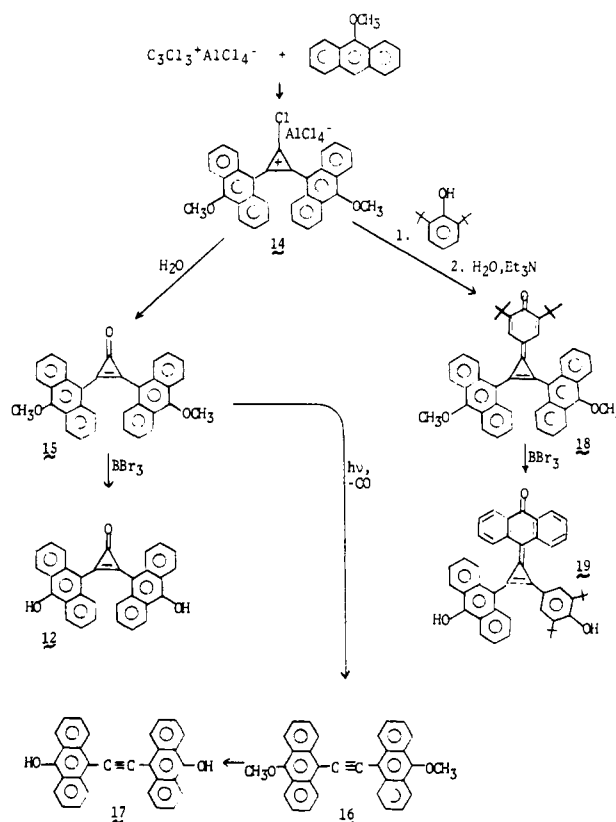


proceeds smoothly because the efficient consumption of 9-anthrol by the reactive and soluble diarylcyclopropenium ion **10** has driven the tautomer equilibrium toward the enol side. With $C_3Cl_3^+AlCl_4^-$ as the reactant, at the low temperatures which would be necessary to limit the reaction to disubstitution, the enol tautomer is not formed rapidly and the substitution reaction does not occur. At the higher temperatures, which should favor enolization, trisubstitution is slow not only for steric reasons but also because the intermediate bis(9-hydroxy-10-anthryl)cyclopropenium ion is both less reactive and less soluble than **10**.

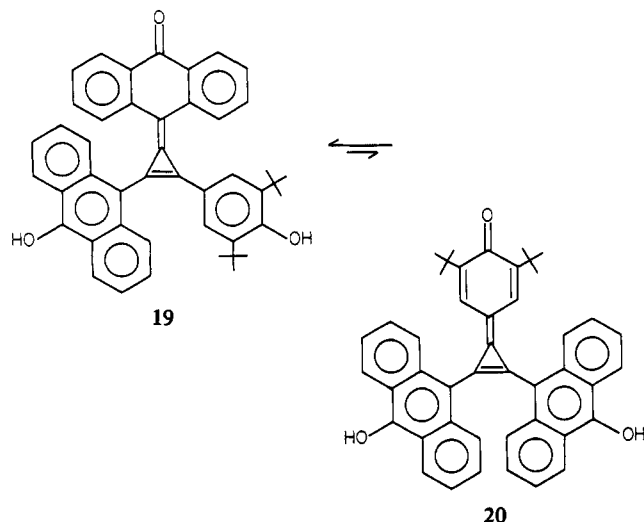
Control of the reaction was conveniently gained by the conversion of anthrone to the active enol form, 9-methoxyanthracene.¹² At low temperatures, 9-methoxyanthracene reacts with $C_3Cl_3^+AlCl_4^-$ to form bis(9-methoxy-10-anthryl)cyclopropenium ion (**14**), which can be hydrolyzed to bis(9-methoxy-10-anthryl)cyclopropenone (**15**) (see Scheme I). Demethylation of **15** may be effected with aluminum chloride, hydriodic acid, or boron tribromide to give bis(9-hydroxy-10-anthryl)cyclopropenone (**12**). Photolytic decarbonylation of cyclopropenones to the corresponding acetylenes is a well-known reaction¹⁴ and was applied in the earlier work on polyquinones to give acetylenes.⁴ Because of its insolubility, **12** could not be photolyzed to give the related acetylene. However, photolysis of **15** produced bis(9-methoxy-10-anthryl)acetylene (**16**) in nearly quantitative yield. Attempts to isolate bis(9-hydroxy-10-anthryl)acetylene (**17**) via demethylation of **16** were unsuccessful owing to the lability of the acetylene moiety under demethylation conditions. Small amounts of the oxidation product **9** were isolated, indicating the intermediacy of **17**.

If the bis(methoxyanthryl)cyclopropenium ion (**14**) is generated in situ and subsequently reacted with 1 equiv of 2,6-di-*tert*-butylphenol under very strenuous conditions, substitution occurs and 4-[1,2-bis(9-methoxy-10-anthryl)cyclopropen-3-ylidene]-2,6-di-*tert*-butyl-2,5-cyclohexadienone (**18**) is isolated in low yield, in addition to small amounts of the demethylated material, **19** (see

Scheme I



Scheme I). The major product is **15** via hydrolysis of unreacted **14**. The low yield of the trisubstituted cyclopropene is readily understood because the low solubility of the intermediate ion **14** and its relatively high stability make it unreactive to the phenolic nucleophile. Compound **18** may be demethylated to form **19**, the precursor to **7b**. The NMR shows only one type of *tert*-butyl proton at δ 1.33, indicating that of the two tautomers, **19** and **20**,



possible for this material only **19** is present in detectable amount. Since **19** is at least as crowded sterically as **20**, we believe that the equilibrium is controlled by electronic effects. Dearomatization of the central ring of anthracene, as in **19**, involves little loss of thermodynamic stability, whereas dearomatization of the phenolic ring which would occur in **20** is energetically disfavored.

When 3 equiv of 9-methoxyanthracene was reacted with the preformed $C_3Cl_3^+AlCl_4^-$ salt, the bis(9-methoxyanthryl)cyclopropenylidenanthrone (**21**) is formed in 50% yield. (Partial demethylation of the tris(methoxyanthryl)cyclopropenium ion apparently occurs under the reaction conditions.) Complete demethylation of **21** gives 1,2-bis(9-hydroxy-10-anthryl)cyclo-

(10) B. Fohlisch and P. Bürgle, *Tetrahedron Lett.*, 2661 (1965).

(11) Y. Bansho and K. Nukada, *Bull. Chem. Soc. Jpn.*, 33, 579 (1960).

(12) J. Meek, P. Monroe, and C. Boubovulis, *J. Org. Chem.*, 28, 2572 (1963). The methyl protecting group was selected because more conventional groups (i.e., trimethylsilyl, benzyl) are labile in the presence of the aluminum chloride needed to form the intermediate cyclopropenium ion.¹³

(13) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, p 30.

(14) G. Quinkert, K. Opitz, W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).

Scheme II

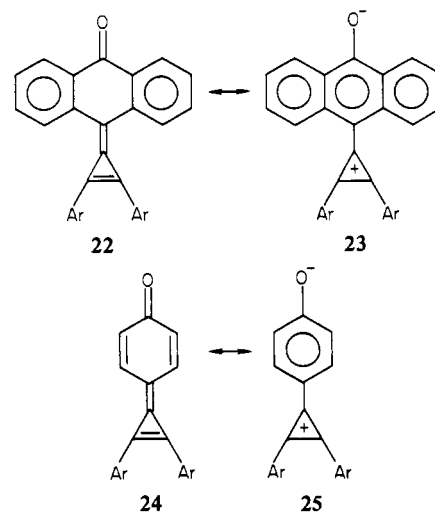
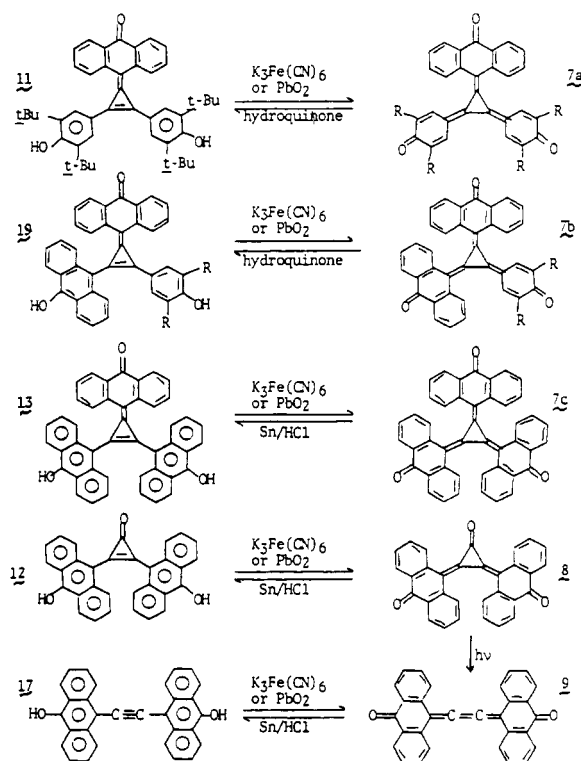


Table I. Electronic Spectra for Anthraquinocyclopropanes

compd	solvent	λ_{\max} (log ϵ)
13	MeOH	250 (4.96), 265 (4.92), 285 (sh, 4.69), 335 (3.91), 348 (3.89), 367 (3.84), 387 (3.88), 415 (3.69), 440 (sh, 4.02), 452 (4.16), 506 (4.41), 545 (sh)
	THF	450, 505, 535
19	MeOH	240 (4.75), 265 (4.81), 285 (sh, 4.60), 360 (3.98), 385 (3.86), 410 (3.99), 500 (4.34), 535 (sh)
	THF	365, 410, 475, 525 sh
11	MeOH	247 (4.58), 270 (4.42), 285 (4.35), 319 (3.54), 357 (3.80), 487 (4.24)
	THF	315, 357, 462
12	benzene	358, 459
	MeOH	260 (4.75), 320 (3.29), 350 (3.19), 368 (3.30), 390 (3.41), 412 (3.54), 440 (3.50), 485 (3.86), 510 (3.83)

propen-3-ylideneanthrone (13) (see Scheme II). Vigorous conditions are required for the trisubstitution reaction in order to overcome the steric hindrance to the introduction of the third ring.

The cyclopropenyliDENANThrones are orange- to rust-colored solids, having an intense electronic absorption band between 460 and 530 nm. Table I presents the electronic absorption maxima and extinction coefficients for these materials. It is noteworthy that these compounds show a distinctive *hypsochromic* shift on changing from polar to nonpolar solvents, in contrast to other quinodiarlylcyclopropanes, which show a *bathochromic* shift with similar solvent changes.⁷ The hypsochromic shift indicates that there is very little resonance contribution from charge-separated structures such as 23 in the ground state, and that charge separation increases in the excited state. Just the opposite seems to be true for benzoquinone compounds. The difference may be explained by the small gain in stabilization going from 22 to 23, compared to the large increase in aromatic resonance energy going from 24 to 25. Hence the charged form 25 makes a relatively larger contribution to the ground state than does 23.

Anthraquinocyclopropanes

The reduced precursors (11, 12, 13, 19) can be reversibly oxidized to the corresponding anthraquinocyclopropanes either

with lead dioxide or with alkaline potassium ferricyanide (see Scheme II). The oxidation is very facile for those compounds possessing two hydroxyanthryl rings (12, 13, and 17), occurring upon exposure of the solid material to air. Oxidation takes place readily even though considerable additional steric hindrance must be introduced in going to 7a-c. It is surprising that the dianthraquinocyclopropanone 8 is much less labile than the corresponding diquinocyclopropanone 4a, which loses carbon monoxide spontaneously in solution to form the diquinethylene 3a.⁵ In contrast 8 is stable indefinitely in benzene solution. Compound 8 is, however, photolytically labile and can be smoothly decarbonylated by irradiation at 2537 Å, yielding the dianthraquinethylene 9.¹⁵

Reduction of the anthraquinocyclopropanes is a further indication of the effects of the anthraquinone rings on their chemistry. Whereas the previously known triquinocyclopropanes are readily reduced to the corresponding diarylquinocyclopropanes with hydroquinone,² in this series only 7a and 7b are similarly reduced. In those materials where reduction must occur across two anthraquinone rings (7c, 8, 9) the more strenuous reduction conditions of tin/hydrochloric acid or zinc/hydrochloric acid are required, in spite of the fact that considerable steric strain is relieved upon reduction. Only those compounds, 7a and 7b, in which there is a large gain in aromatic stability going from benzoquinone to phenol are easily reduced with the mild conditions of hydroquinone.

Structures were confirmed by NMR, IR, mass spectra and elemental analysis. The 1800–1810-cm⁻¹ band which is characteristic of the cyclopropane system is absent in the IR of the oxidized compounds. 7a shows two types of *tert*-butyl protons at δ 1.20 and 1.42, indicating loss of rotation about the exocyclic bond, consistent with double-bond formation. 7b shows only one type of *tert*-butyl protons at δ 1.21 consistent with the symmetrical environments for the two *tert*-butyl groups. The aromatic region of the ¹H NMR spectrum for trianthraquinocyclopropane 7c is simplified, consisting of a doublet at δ 8.58 (6 H), a multiplet at δ 7.3–7.6 (6 H), and a multiplet at δ 7.0–7.2 (12 H), indicating high symmetry. Models show that 7c cannot be planar, and we suggest a propeller-like structure with *D*₃ symmetry.

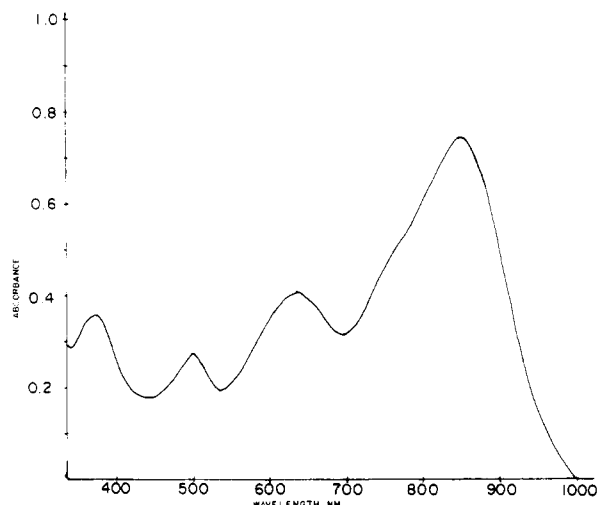
Electronic Spectra

The anthraquinocyclopropanes show intense absorptions in the visible and near-infrared region. Table II reports the absorption maxima and extinction coefficients for 7a-c, 8, and 9. Compounds 7a-c resemble other triquinocyclopropanes in that they have unusually low energy transitions. Moreover, the anthraquinone

(15) The structure 9 is mentioned in British Patent 726 429 to Cassella FarbwerkeMainkur Aktiengesellschaft [*Chem. Abstr.* 1955, 49, 15252e] as being the product of reaction of anthrone with glyoxal under alkaline conditions, described in an earlier British Patent, 299 972, to I. G. Farbenindustrie [*Chem. Abstr.* 1929, 23, 3582]. We have repeated the reactions described in these patents but were unable to obtain 9 under the conditions given.

Table II. Electronic Spectra of Anthraquinocyclopropanes

compd	λ_{\max} (log ϵ) ^a
7a	260 (4.24), 315 (3.74), 395 (4.13), 480 (3.19), 6.40 (sh, 4.01), 710 (4.18), 790 (4.11)
7b	310 (3.94), 368 (3.84), 495 (3.40), 550 (3.40), 700 (3.80), 795 (3.42), 830 (3.34)
7c	260 (4.76), 310 (3.88), 322 (3.86), 378 (3.87), 505 (3.74), 638 (3.93), 780 (sh, 4.04), 850 (4.18)
8	258 (4.40), 627 (4.20)
9	250 (4.81), 335 (4.20), 510 (sh), 540 (4.81)

^a In chloroform.Figure 1. Visible absorption spectra of 7c, 0.48×10^{-3} M in chloroform.

compounds show absorption at even longer wavelength than the corresponding benzoquino compounds. Figure 1 shows the visible electronic absorption spectrum for 7c. The longest wavelength transition is shifted approximately 75 nm from the corresponding absorption of triquinocyclopropane at 770 nm. Similarly, the lowest energy transitions for 8 and 9 occurring at 620 and 545 nm, respectively, take place at distinctly longer wavelength than for the corresponding diquinocyclopropanone (λ_{\max} 542 nm) and diquinoethylene (λ_{\max} 486 nm). These surprisingly low-energy, highly allowed transitions may be due in part to the twisting of the exocyclic double bonds relative to the central three-membered ring. Electronic effects which may also be important are illuminated by MO calculations.

Hückel Molecular Orbital Calculations

Figure 2 shows graphically the calculated Hückel orbital energies between -1.5 and $+1.0$ for the anthraquino compounds and for triquinocyclopropane.¹⁶ The HOMO of trianthraquinocyclopropane is doubly degenerate, as is the HOMO for triquinocyclopropane. Also, the two highest occupied MOs for 7a and 7b are nearly degenerate.

Symmetry analysis of the HMOs for 1a and 7c, assuming D_3 symmetry, shows that the HOMO is an E level and the LUMO is an A_2 level. The symmetry of the transition to the first excited state ($E \rightarrow A_2$) is also E , and is therefore electric dipole allowed and doubly degenerate. Two strongly allowed transitions with equal energy may be split by configuration interaction. This effect, which can also operate for nearly degenerate transitions in 7a and 7b, may lead to unusually low transition energies for triquinocyclopropanes generally.

The MO calculations, however, predict higher transition energies for the anthraquino compounds than for the benzoquino

analogues, just the opposite of what is observed. The unusually low transition energies for the anthraquino compounds may be associated with nonplanarity of these molecules, raising the energy of the ground state. As seen from the data in Table III, lowering the C-C resonance integral for the exocyclic double bond in the anthraquino compounds does lower the predicted transition energies. However, Hückel MO calculations cannot be expected to give good predictions for excited states. More elaborate calculations will be of value once the geometries of the molecules are more fully known.

Experimental Section

General Procedures. Melting points are uncorrected. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 237 or Beckman IR-33; ¹H NMR, Brüker WH 270, JEOL JNM-MH-100 spectrometer, Varian T-60 NMR spectrometer, Varian EM-390 spectrometer; ultraviolet-visible, Cary 14; mass spectra, AEI-MS-902; ESR, Varian 4502-13. The few combustion analyses reported were carried out by Galbraith Laboratories. Many of the compounds oxidized incompletely even when combusted with vanadium pentoxide. Because of this difficulty a combination of NMR and high-resolution mass spectrometry was mainly used for analytical purposes.

All starting materials were commercially available except for methoxyanthracene, which was prepared according to the procedure of Meek, Monroe, and Boubovils.¹²

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropen-3-ylidene-anthrone (11). Tetrachlorocyclopropene (1.78 g, 0.01 mol) and 1.33 g (0.01 mol) of aluminum chloride were gently warmed in a 100-mL three-neck flask equipped with condenser, addition funnel, magnetic stirrer, low-temperature thermometer, and nitrogen inlet to preform the $C_3Cl_3^+AlCl_4^-$ salt. A small amount of dry dichloromethane was added to aid stirring. The mixture was cooled to $-50^\circ C$ and a solution of 4.12 g of 2,6-di-*tert*-butylphenol (0.02 mol) in dry $CHCl_3$ was added dropwise over 30 min with the reaction temperature maintained below $-15^\circ C$. After 30 min of stirring at $0^\circ C$, the solution was warmed to room temperature. A solution of 1.94 g (0.01 mol) of anthrone in dry $CHCl_3$ was added over 30 min, and the reaction mixture refluxed for 2 h. The reaction mixture was poured into ice water and triethylamine added to prevent formation of the HCl salt of the product. The chloroform layer was separated, the water layer was extracted twice with chloroform, and the combined chloroform layers were washed twice with water. The chloroform solution was dried over magnesium sulfate and evaporated, yielding an orange solid which was recrystallized from MeOH to give 4.8 g (75%) of 11 as orange needles: mp $266-269^\circ C$ dec; IR (KBr) 3570 (m), 2950-2850 (m), 1790 (m), 1600 (m), 1550 (s), 1470 (s), 1330 (s), 1400 (s), 1350 (m), 1310 (s), 1250 (m), 1225 (s), 1190 (m), 1160 (s), 1100 (sh), 1110 (s), 1030 (m), 1000 (s), 960 (sh), 930 (m), 900 (w), 880 (m), 810 (w), 770 (s), 750 (m), 675 cm^{-1} (s); NMR ($CDCl_3$) δ 1.25 (s, 36 H), 5.98 (s, 2 H), 7.10-7.60 (m, 6 H), 7.82 (s, 4 H), 8.5-8. (m, 2 H); m/e calcd 638.37599, found 638.37383.

1,2-Bis(9-methoxy-10-anthryl)cyclopropenone (15). Trichlorocyclopropenium tetrachloroaluminate (0.01 mol) was preformed as explained above and the reaction mixture was cooled to $-78^\circ C$. A solution of 4.16 g (0.02 mol) of 9-methoxyanthracene in dichloromethane was added dropwise over 30 min with the temperature maintained below $-30^\circ C$. When addition was complete, the mixture was allowed to warm to $10^\circ C$ and stirred at $10^\circ C$ for 1.5 h. The reaction mixture was hydrolyzed by being poured into ice water containing a small amount of triethylamine. Orange 15 precipitated and was collected by filtration, washed with water and $CHCl_3$, and dried. Additional quantities of 15 were isolated from the organic layer which was separated from the water, washed with water, dried with calcium chloride, and concentrated. The crude product was recrystallized from chloroform to give 3.7 g (79%) of 15: mp $263-265^\circ C$ ($-CO$); IR 3050-3000 (w), 2960-2900 (w), 1815 (vs), 1600 (m), 1570 (s), 1545 (s), 1500 (m), 1470 (m), 1425 (m), 1370 (m), 1340 (m), 1290 (s), 1270 (m), 1200 (w), 1180 (w), 1160 (w), 1140 (w), 1085 (s), 1030 (w), 970 (m), 955 (m), 945 (m), 930 (w), 850 (w), 790 (w), 770 (s), 750 (w), 735 (m), 680 (s), 650 (w), 610 cm^{-1} (w); NMR ($CDCl_3$) δ 4.21 (s, 6 H), 7.53-7.78 (m, 8 H), 7.93-8.12 (m, 4 H), 8.21-8.35 (m, 4 H); UV-vis ($CHCl_3$) 250 nm (log ϵ 4.87), 263 (4.67), 362 (3.48), 382 (3.68), 404 (3.83), 478 (4.09), 500 (sh, 4.05); m/e calcd 466.15689, found 466.15882.

1,2-Bis(9-hydroxy-10-anthryl)cyclopropenone (12). 15 (500 mg, 1.07 mmol) was dissolved in dry dichloromethane and cooled to $-78^\circ C$ under an N_2 atmosphere. An excess of boron tribromide was added dropwise over 10 min. The maroon-colored BBr_3 -methoxyanthracene complex formed immediately. After addition was complete, the reaction mixture was allowed to warm to room temperature and hydrolyzed by dropwise addition to a large excess of water. The resulting red precipitate was

(16) The Coulomb and resonance integrals α_C and β_{CC} were assumed to be the same for all carbon atoms and carbon-carbon π bonds. The values of $h = 0.6$ and $k = 1.2$, which have been found to be the best choices for triquinocyclopropanes,⁵ were used in these calculations.

(17) F. A. Cotton in "Chemical Applications of Group Theory", Wiley-Interscience, New York, 1971, Appendix III.

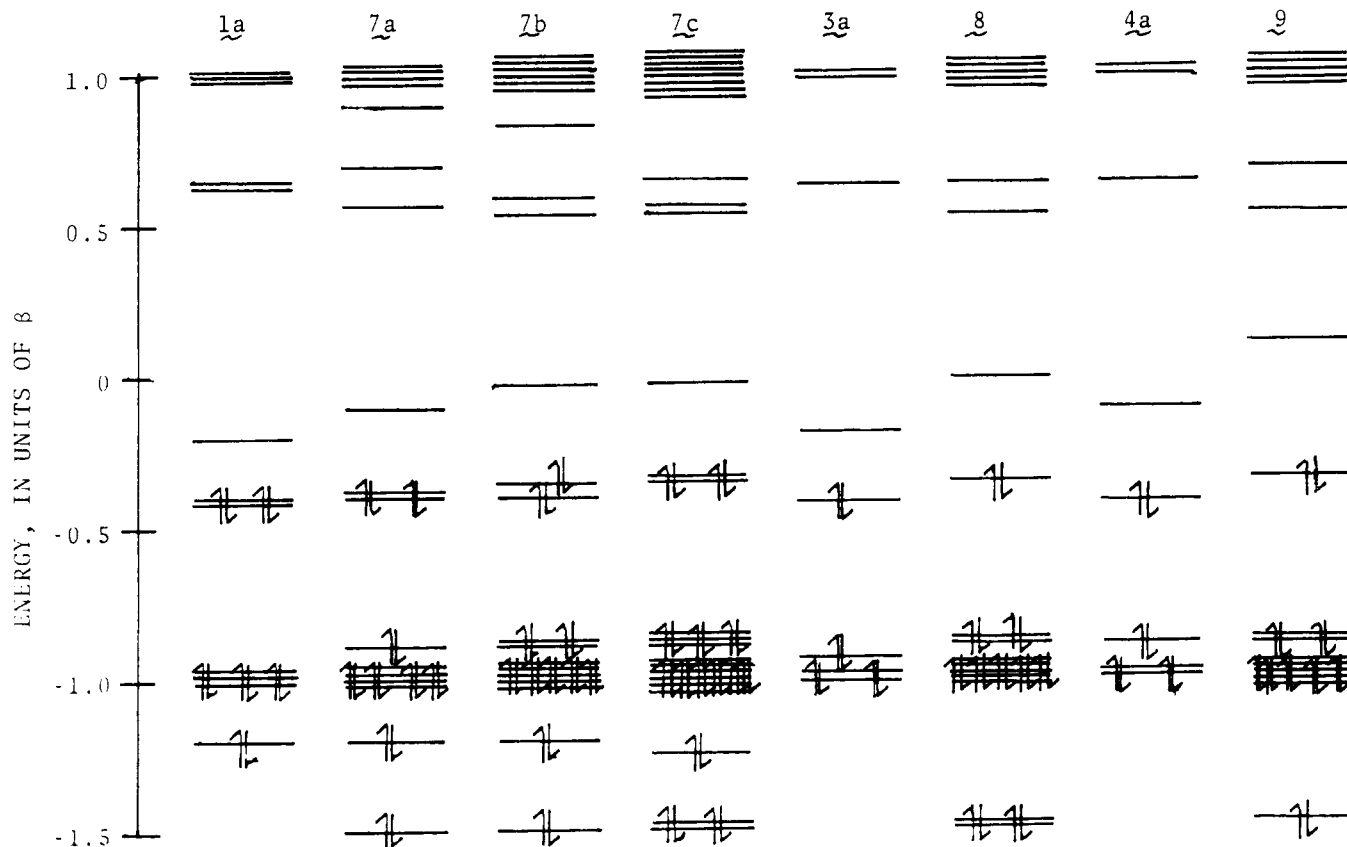


Figure 2. Graphic representation of calculated Hückel molecular orbital energy levels for various quinonoid compounds. Orbitals with energies $>+1.0\beta$ or less than $<-1.5\beta$ are not shown.

Table III. Calculated HOMO and LUMO Energies for Anthraquinocyclopropanes

	$\beta_{CC_{exo}} = 1.0$		$\beta_{CC_{exo}} = 0.8$	
	E_{LUMO}	ΔE	E_{LUMO}	ΔE
7a	$E_{LUMO} = -0.1017$ $E_{HOMO} = -0.3744$	$\Delta E = 0.2727$	$E_{LUMO} = -0.1061$ $E_{HOMO} = -0.3391$	$\Delta E = 0.2330$
7b	$E_{LUMO} = -0.0388$ $E_{HOMO} = -0.3454$	$\Delta E = 0.3066$	$E_{LUMO} = -0.0621$ $E_{HOMO} = -0.2756$	$\Delta E = 0.2135$
7c	$E_{LUMO} = +0.0212$ $E_{HOMO} = -0.3452$	$\Delta E = 0.3664$	$E_{LUMO} = -0.0258$ $E_{HOMO} = -0.2756$	$\Delta E = 0.2498$
8	$E_{LUMO} = -0.0201$ $E_{HOMO} = -0.3453$	$\Delta E = 0.3252$	$E_{LUMO} = +0.0410$ $E_{HOMO} = -0.2757$	$\Delta E = 0.3167$
9	$E_{LUMO} = +0.1178$ $E_{HOMO} = -0.3452$	$\Delta E = 0.4630$		

filtered and washed with water, dichloromethane, and diethyl ether. After drying, the yield of product was 0.39 g (83%): mp 290 °C dec; IR 3040–3000 (w), 1810 (s), 1770 (m), 1700 (m), 1630 (s), 1610 (s), 1589 (s), 1568 (s), 1555 (m, sh), 1532 (m), 1500 (s), 1435 (s), 1405 (m), 1340 (sh), 1319 (s), 1302 (s), 1268 (m), 1220 (m), 1191 (m), 1170 (m), 1120 (w), 1050 (w), 950 (m), 792 (s), 700 (m), 638 cm^{-1} (w); NMR (Me_2SO) δ 7.41–7.55 (m, 8 H), 8.26 (d, 4 H), 8.61 (d, 4 H); m/e calcd 438.12559, found 438.12762.

Demethylation of 15 with Aluminum Chloride.¹³ **15** (300 mg, 0.64 mmol) was heated at reflux in benzene with 0.25 g (1.92 mmol) of AlCl_3 for 12 h. The reaction mixture was poured into ice water to which triethylamine had been added, and the resultant solid collected by filtration. After being washed with water and chloroform, the product was dried to give 226 g (80%) of **12**. Care was taken to minimize exposure to air, since surface oxidation of **12** to **8** occurred.

In an analogous manner **12** was demethylated in 6 h, using refluxing chlorobenzene as the solvent. Spectral properties were identical with those given above.

Demethylation of 15 with Hydriodic Acid. **12** (300 mg, 0.64 mmol) was stirred in acetic anhydride and excess hydriodic acid added dropwise over 15 min. The mixture was refluxed for 2 h and hydrolyzed to give 212 mg (76%) of **12**. Spectral properties were identical with those given above.

4-[1,2-Bis(9-methoxy-10-anthryl)cyclopropen-3-ylidene]-2,6-di-tert-butyl-2,5-cyclohexadienone (18). Tetrachlorocyclopropene (1.78 g, 0.01 mol) was reacted as previously described to form the $\text{C}_3\text{Cl}_3^+\text{AlCl}_4^-$ salt, and the reaction mixture was cooled to -78 °C. 9-Methoxyanthracene

(4.16 g, 0.02 mol) in dichloromethane was added over 30 min with the temperature maintained below -30 °C. The reaction mixture was then allowed to warm to 10 °C and stirred for 1 h at 10 °C. 2,6-Di-tert-butylphenol (2.06 g, 0.01 mol) in dry dichloroethane was added. The dichloromethane was distilled off and replaced with additional dichloroethane. The reaction mixture was refluxed overnight. Hydrolysis as above gave **15**, recovered di-tert-butylphenol, and 0.92 g (14%) of **18**. **18** was purified by preparative TLC (silica/benzene): mp 270 °C dec; IR 3080–2860 (m), 1835–1770 (m), 1700 (w), 1615 (m, sh), 1602 (s), 1570 (s), 1554 (s), 1521 (w), 1481 (s), 1447 (s), 1422 (w), 1390 (m), 1355 (s), 1330 (s), 1301 (s), 1280 (s), 1207 (w), 1171 (w), 1140 (w), 1100 (s), 1026 (m), 970 (m), 940 (w), 910 (m), 892 (m), 829 (w), 809 (w), 780 (s), 760 (m, sh), 735 (m), 685 cm^{-1} (m); NMR (CDCl_3) δ 1.28 (s, 18 H), 4.25 (s, 6 H), 7.20–7.54 (m, 8 H), 7.98–8.45 (m, 8 H); m/e calcd 654.31339; found 654.31482.

19 (0.21 g, 3%) was also isolated. Spectral properties were identical with those reported for **19** below.

1,2-Bis(9-methoxy-10-anthryl)cyclopropen-3-ylideneanthrone (21). Under nitrogen, in oven-dried glassware, 2.56 g (0.014 mol) of tetrachlorocyclopropene was added dropwise to 2.66 g (0.02 mol) of aluminum chloride stirred in a few milliliters of dry dichloromethane. The mixture was gently warmed to form the buff-colored $^+\text{C}_3\text{Cl}_4\text{AlCl}_4^-$ salt, then cooled to -35 °C. 9-Methoxyanthracene (8.32 g, 0.04 mol) in 40 mL of dry dichloromethane was then slowly added over 30 min while maintaining a -35 °C temperature. The stirred reaction mixture was allowed to warm to 0 °C, held at that temperature for 2 h, and then allowed to warm to 25 °C.

The mixture was then poured onto an ice-water-triethylamine solution, and the organic layer was extracted with dichloromethane, brine washed, dried over anhydrous $MgSO_4$, and stripped of solvent, yielding 4.6 g (50%) of crude **21**, a brown solid. Purification was achieved by repeated recrystallization in chloroform or by preparative TLC on silica (1:1 benzene-chloroform): mp 296–297 °C dec; IR 3050–2840 (w), 1790 (m), 1665 (w), 1625 (s), 1615 (s), 1600 (s), 1587 (s), 1550 (m), 1472 (vs), 1440 (s), 1411 (m), 1383 (m), 1350 (s), 1320 (s), 1297 (s), 1278 (s), 1265 (m), 1210 (m), 1169 (s), 1118 (s), 1095 (s), 1041 (w), 1018 (s), 964 (m), 940 (m), 779 (s), 760 (s, sh), 730 (m), 689 (m), 678 (m), 610 cm^{-1} (w); NMR ($CDCl_3$) δ 4.40 (s, 6 H), 7.05–7.65 (m, 12 H), 7.75–8.15 (m, 6 H), 8.37–8.75 (m, 6 H); UV-vis ($CHCl_3$) 260 (nm log ϵ 4.18), 444 (3.37), 490 sh (3.24); m/e calcd 642.219 49, found 642.221 02.

1,2-Bis(9-hydroxy-10-anthryl)cyclopropen-3-ylidenanthrone (13). In a procedure analogous to preparation of **12** with BBr_3 , 500 mg (0.77 mmol) of **21** was demethylated to give 370 mg (76%) of **13**. **13** was purified by trituration with benzene and chloroform. Surface oxidation occurs with minimal air contact with the solid, so operations were performed under N_2 : mp 262 °C dec; IR 3025–2920 (w), 1815 (w), 1610 (m), 1550 (s), 1482 (s), 1444 (w), 1410 (s), 1390 (s), 1320 (s), 1300 (s), 1275 (s), 1200 (s), 1275 (s), 1250 (s), 1034 (w), 1005 (w), 932 (w), 879 (w), 771 (m), 740 cm^{-1} (m); NMR (Me_2SO) δ 7.13 (t, 2 H), 7.36 (t, 2 H), 7.84 (d, 2 H), 8.57 (d, 2 H); m/e calcd 614.188 19, found: 614.191 13.

1-(9-Hydroxy-10-anthryl)-2-(4-hydroxy-3,5-di-*tert*-butylphenyl)-cyclopropen-3-ylidenanthrone (19). **18** (500 mg, 0.78 mmol) was dissolved in dry dichloromethane and treated with excess boron tribromide under the same conditions as given for **15**. After hydrolysis, filtration, washing, and drying, 387 mg (79%) of **19** was isolated: mp 212 °C dec; IR 3540 (m), 3150–3050 (w), 2950–2870 (w), 1800 (w), 1655 (m), 1630 (m), 1605 (s), 1580 (s), 1545 (s), 1512 (m), 1475 (s), 1438 (s), 1405 (s), 1375 (s), 1315 (sh), 1290 (sh), 1270 (s), 1220 (sh), 1180 (s), 1160 (s), 1140 (s), 1110 (m), 1022 (m), 1000 (m), 980 (w), 930 (m), 910 (sh), 900 (m), 875 (sh), 810 (w), 770 (s), 730 (m), 700 (w), 670 (m), 640 cm^{-1} (m); NMR (Me_2SO-d_6) δ 1.27 (s, 18 H), 5.5–6 (hr, H), 7.15–7.4 (m, 8 H), 7.66 (s, 2 H), 7.78–7.86 (m, 4 H), 8.32–8.55 (m, 4 H); m/e calcd 626.282 09, found 626.280 77.

Bis(9-methoxy-10-anthryl)acetylene (16). **15** (500 mg) was dissolved in 500 mL of dry, N_2 -purged benzene and photolyzed by using a 450-W Hanovia mercury lamp for 1 h. The solution was evaporated to give 430 mg (92%) of **16**, which was recrystallized from methanol: mp 207–208 °C; IR 3050–3010 (w), 2970 (m), 2959 (m), 2920 (m), 1780 (w), 1770 (w), 1610 (m), 1680 (w), 1600 (m), 1550 (w), 1500 (w), 1470 (s), 1455 (sh), 1442 (m), 1432 (m), 1420 (m), 1380 (s), 1296 (s), 1280 (m), 1260 (m), 1188 (w), 1158 (w), 1128 (s), 1075 (s), 1020 (w), 968 (m), 942 (w), 832 (w), 790 (w), 760 (s), 700 (w), 675 (w), 660 cm^{-1} (w); NMR ($CDCl_3$) δ 4.15 (s, 6 H), 7.3–7.7 (m, 8 H), 8.2–8.35 (dd, 4 H), 8.7–8.9 (dd, 4 H); UV-vis ($CHCl_3$) 248 nm (log ϵ 4.87), 265 (4.81), 354 (3.32), 371 (3.50), 407 (sh, 3.83), 430 (sh, 4.08), 448 (4.13); m/e calcd 438.161 98, found 438.158 55.

2,3-Bis(9-oxo-10-anthrylidene)cyclopropanone (8). **12** (300 mg, 0.68 mmol) was stirred in a two-phase system of chloroform and 0.56 g (1.712 mmol) of potassium ferricyanide in 1 N potassium hydroxide. A deep blue-green color developed immediately. After 30 min of stirring, the layers were separated, the water layer was washed with chloroform, and the combined organic layers were washed with water until the water contained no yellow ferricyanide color. The chloroform solution was dried over magnesium sulfate for 10 min and evaporated to give 280 mg (93%) of **8** as a copper-colored solid.

Alternatively, **8** may be prepared from **15** by demethylation with BBr_3 in CH_2Cl_2 , followed by treatment with aqueous $K_3Fe(CN)_6$, without intermediate isolation of **12**: yield 62%; mp 270–272 °C (–CO); IR 2980 (m), 1784 (s), 1642 (s), 1581 (s), 1500 (w), 1465 (m), 1455 (m), 1430 (m), 1380 (m), 1329 (s), 1310 (s), 1190 (m), 1170 (m), 1150 (m), 941 (w), 926 (w), 775 (s), 682 cm^{-1} (m); NMR ($CDCl_3$) δ 6.72 (d, 2 H), 7.14

(t, 2 H), 7.63–7.72 (m, 4 H), 7.94 (t, 2 H), 8.49 (t, 4 H), 8.93 (d, 2 H); m/e calcd 436.109 93, found 436.111 28.

Dianthraquinoethylene (9). A suspension of **8** (100 mg) in dichloromethane was gently irradiated under nitrogen, using a UV sunlamp. The less soluble **9** precipitated as metallic green needles, pure after washing with dichloromethane: yield 64 mg (75%); mp 220 °C dec; IR 2990–2930 (m), 1645 (s), 1590 (s), 1492 (w), 1449 (m), 1312 (m), 1300 (s), 1210 (w), 1160 (w), 1150 (m), 935 (m), 880 (w), 810 (w), 780 (sh), 770 (s), 760 (sh), 705 (m), 670 cm^{-1} (s); NMR ($CDCl_3$) δ 7.6–7.65 (m, 4 h), 7.79–7.82 (m, 2 H), 8.29–8.33 (m, 2 H); m/e calcd 408.115 02, found 408.116 08.

Diquinoanthraquinocyclopropane (7a). Oxidation of **11** was performed analogously to the preparation of **8**, using alkaline potassium ferricyanide in a two-phase system, with a yield of 83%: mp 214 °C dec; IR 2970–2920 (m), 1750 (w), 1710 (w), 1665 (m), 1630 (s), 1570 (s), 1530 (sh), 1470 (sh), 1455 (s), 1445 (sh), 1430 (sh), 1371 (w), 1452 (m), 1322 (sh), 1312 (m), 1300 (m), 1280 (w), 1250 (w), 1200 (w), 1160 (m), 1120 (sh), 1107 (m), 1090 (s), 1062 (m), 1018 (m), 935 (m), 912 (w), 892 (s), 812 (m), 780 (m), 750 (w), 725 (w), 598 (sh), 590 cm^{-1} (m); NMR ($CDCl_3$) δ 1.20 (s, 18 H), 1.42 (s, 18 H), 7.30–7.66 (m, 8 H), 8.0–8.15 (m, 2 H), 8.25–8.42 (m, 2 H); m/e calcd 636.360 34, found 636.362 04. Anal. calcd for $C_{45}H_{48}O_3$: C, 84.86; H, 7.60; O, 7.54. Found: C, 84.66; H, 7.66, O (by difference), 7.68.

1,2-Bis(9-oxo-10-anthrylidene)-3-(4-oxo-3,5-di-*tert*-butyl-2,5-cyclohexadien-1-ylidene)cyclopropane (7b). In a procedure analogous to those reported above, **19** was oxidized to **7b** in 73% yield: mp 230–235 °C dec; IR ($CHCl_3$) 3050–3000 (m), 1600 (w), 1520 (w), 1500 (w), 1470 (w), 1420 (w), 1260 (w), 1200 (m), 1140 (m), 1090 (s), 1010 (w), 925 (w), 850 (w), 780 (s), 720 (s), 670 (m), 630 cm^{-1} (m); NMR ($CDCl_3$) δ 1.19 (s, 18 H), 7.25–7.75 (m, 8 H), 8.0–8.5 (m, 8 H); m/e calcd 624.264 44, found 624.264 45.

Tris(9-oxo-10-anthrylidene)cyclopropane (7c). Similarly, **13** was oxidized to **7c** in 74% yield: mp 256 °C dec; IR (KBr) 3000–2950 (w), 1630 (s), 1572 (s), 1545 (m), 1450 (m), 1400 (s), 1315 (s), 1295 (s), 1257 (7), 1200 (m), 1150 (m), 1100 (w), 935 (m), 810 (w), 775 (m), 730 (w), 680 cm^{-1} (m); NMR ($CDCl_3$) δ 7.0–7.2 (m, 12 H), 7.3–7.6 (m, 6 H), 8.6 (d, 6 H); m/e calcd 612.172 54, found 612.171 03. Anal. Calcd for $C_{45}H_{24}O_3$: C, 88.12; H, 3.95; O, 7.83. Found: C, 87.88; H, 3.97; O (by difference), 8.05.

Oxidation Using Lead Dioxide. Compound **11** (0.319 g, 0.5 mmol) was added to a slurry of 1.3 g of PbO_2 in dry benzene. After the mixture was stirred for 30 min, the oxidizing agent was filtered out under N_2 and the benzene evaporated to give a blue-green solid (0.29 g, 90%) whose spectral properties were identical with those of **7a**.

Reduction of Anthraquinocyclopropanes with Hydroquinone. Treatment of the blue-green benzene solutions of the anthraquinocyclopropanes **7a** and **7b** with aqueous hydroquinone resulted in red solutions. The electronic spectra of these solutions indicated that the products were the diarylcyclopropenylidenanthrone **11** and the 1-aryl-2-(9-hydroxy-anthryl)cyclopropenylidenanthrone **19**, respectively, by comparison with the spectra listed in Table I. The electronic spectra of **7a** and **7b** were regenerated upon treatment with lead dioxide or alkaline potassium ferricyanide.

7c, **8**, and **9** were unaffected by treatment with aqueous hydroquinone.

Reduction with Tin and HCl. Treatment of the deep blue solutions of **7c** and **8** with granular tin and HCl resulted in red and orange solutions. These were identified as **13** and **12**, respectively, by comparing their electronic spectra with the spectra in Table I.

Reduction of a solution of **9** with tin and HCl resulted in disappearance of the red color giving a colorless solution, which upon treatment with PbO_2 or alkaline $K_3Fe(CN)_6$ regenerated the electronic spectrum of **9**. The reduced material **17** could not be isolated as a stable material and was not characterized except by its intermediacy in sequences.

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