of the 1:1 mixture of diastereomeric spiroketals, the primary hydroxyl of **11** was oxidized to aldehyde, a Wittig reaction with methylenetriphenylphosphorane was carried out, and the product was subjected to hydrogenation over 10% Pd/C. Since the ^{1}H NMR of this new spiroketal **13** failed to match that reported for talaromycin A,[1] we can only assume that **11** and not **12** is the thermodynamically favored product of the spiroketalization event, a product favored perhaps by intramolecular hydrogen bonding as well as by the preference for the benzyloxymethyl group to assume the equatorial position because of its size.

In summation, the present synthesis further underscores the utility of NOC chemistry in the construction of the molecules of nature. The scheme is sufficiently flexible and efficient so as to be of practical use in the preparation of suitable quantities of talaromycin B for biological evaluation. A total synthesis approach to talaromycin B is especially timely, for *T. Stipitatus* has been reported to lose its ability to produce this spiroketal upon subculturing.[1]

Experimental Section

General Methods. Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 247 infrared spectrophotometer with the polystyrene absorption at 1601 cm^{-1} as a reference. The ^{1}H NMR spectra were recorded on a Brüker WH-300 spectrometer. Low-resolution mass spectra were obtained on a LKB 9000A gas chromatograph–mass spectrometer. High-resolution mass spectra were obtained on a Varian MAT CH-5DF mass spectrometer.

Dipolar Cycloaddition Reaction of 4 and 5. A two-phase system comprised of the aldoxime **4** (133 mg, 0.59 mmol), alkene **5** (1.03 g, 5.67 mmol) and 0.02 mL of triethylamine in 10 mL of methylene chloride and a 5.25% solution of sodium hypochlorite in water (1.30 g, 0.91 mmol) was stirred vigorously for 10 h. The layers were separated, and the aqueous layer was extracted with 10 mL of methylene chloride. The organic layers were combined, dried, filtered, and concentrated. The residue was chromatographed on silica gel with 60% ethyl acetate–hexanes to yield 160 mg (67%) of isoxazoline **6**: mp 108–108.5 °C; IR (CH$_2$Cl$_2$) 2920, 2850, 1440, 1360, 1250, 1150, 1130, 1100, 900 cm^{-1}; NMR (CDCl$_3$) δ 4.64 (m, 1), 4.03–3.57 (m, 8), 3.06–2.70 (d of ABq, 2, J = 9.7, 7.5 Hz), 2.34 (br t, 2, J = 7.8 Hz), 1.90–1.40 (m, 24).

Exact mass calcd for C$_{23}$H$_{37}$NO$_5$ 407.2673, found 407.2672. Anal. C, H, N.

Hydrogenolysis of the Isoxazoline 6. To a solution of the isoxazoline **6** (206 mg, 0.51 mmol) dissolved in 10 mL of methanol and 2 mL of water was added 2.35 mL of a 1 M solution of boron trichloride in methylene chloride and 50 mg of W-2 Raney nickel catalyst. The flask was flushed with hydrogen, and the reaction mixture was stirred under a balloon-filled atmosphere of hydrogen for 1 h. The reaction mixture was filtered through a cotton plug, the filtrate was concentrated, and the residue was taken up in ethyl acetate. The solution was again filtered and concentrated to yield 148 mg (71%) of the β-hydroxy ketone: mp 99–100 °C; IR (CH$_2$Cl$_2$) 3500, 2920, 2850, 1705, 1440, 1350, 1240, 1150, 1130, 1100, 900 cm^{-1}; NMR (CDCl$_3$) δ 4.16 (m, 1), 4.02–3.54 (m, 8), 3.23 (br s, 1), 2.67 (d of ABq, 2, J = 8.9, 3 Hz), 2.49 (t, 2, J = 7.3 Hz), 1.85–1.40 (m, 24).

Exact mass calcd for C$_{23}$H$_{38}$O$_6$ 410.2669, found 410.2671. Anal. C, H.

[3α,4β,6α(R*)]-4-Hydroxy-1,7-dioxaspiro[5.5]undecane-3,9-dimethanol (2). A mixture of the above β-hydroxy ketone (54 mg, 0.13 mmol) and 10 mg of Amberlyst 15 in 5 mL of methanol was stirred overnight at room temperature. After filtration the solvent was removed by rotary evaporation, and the residue was chromatographed on silica gel with 10% methanol–ethyl acetate to yield 28 mg (93%) of **2**: IR (neat) 3400, 2920, 2860, 1450, 1360, 1160, 1090, 1040 cm^{-1}; NMR (CDCl$_3$) δ 4.08 (ddd, 1, J = 10, 10, 4 Hz), 3.72 (d, 2, J = 6.1 Hz), 3.70–3.55 (m, 2), 3.33 (dd, 1, J = 11.5, 11.5 Hz), 3.31 (dd, 1, J = 11.1, 11.1 Hz), 2.02 (dd, 1, J = 12.7, 5.1 Hz), 1.85 (m, 1), 1.80–1.40 (m, 6).

Exact mass calcd for C$_{11}$H$_{20}$O$_5$–OH 215.1284, found 215.1284.

Acknowledgment. We are indebted to the National Institutes of Health (Grant No. HL20579-07) and the Camille and Henry Dreyfus Foundation for support of these investigations. We thank P. Stein for helpful discussions and Professor David Lynn of the University of Virginia for the sample comparisons.

Synthesis and Characterization of a New Polyquinone Exhibiting a Two-Electron, Single-Wave Reduction

Daniel E. Wellman and Robert West*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received June 8, 1983*

Abstract: Two dicyanomethylidene-substtuted quinocyclopropenes, **1a** and **2a**, have been synthesized and studied. Oxidation of **1a** produced only decomposition products but oxidation of **2a** yielded the new polyquinone **2**. Compound **2** was studied by cyclic voltammetry in aprotic media; it is unique among polyquinones in undergoing two-electron reduction within a single voltammetric wave, with E_1 = 0.00 V and E_2 = –0.04 V vs. SCE.

Earlier papers from these laboratories have reported the synthesis of a number of polyquinocycloalkanes and related compounds, including the cyclopropane derivatives **3–8** and the four-membered rings **9** and **10**[1] (Chart I). All of these compounds show intense long-wavelength electronic absorption bands and are powerful organic oxidants;[2] many also show photoconductive properties.[3]

In this paper we report attempts to replace the quinonoid oxygen of **11** and **4** with the dicyanomethylidene group to prepare compounds **1** and **2**. Compound **1a**, the dihydro precusor to **1**, was isolated but oxidation of **1a** produced only an intractable tar containing no **1**. This finding is not particularly surprising, since earlier work has shown that triquinocyclopropanes analogous to **11** are unstable unless bulky groups are present in the positions ortho to the oxygen atoms.[4] The anthraquino compound **4** is however stable and similarly it is possible to isolate the di-

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[1] (a) West, R.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 150, 161. (b) Benham, J. L.; West, R.; Norman, J. A. T. *Ibid.* **1980**, *102*, 5047. (c) Wendling, L. A.; West, R. *J. Org. Chem.* **1978**, *43*, 1577. (d) Koster, S. K.; West, R. *Ibid.* **1975**, *40*, 2300. (e) Wendling, L. A.; Koster, S. K.; Murray, J. E. West, R. *Ibid.* **1977**, *42*, 1126. (f) Komatsu, K.; West, R.; Beyer, D. *J. Am. Chem. Soc.* **1977**, *99*, 6290 and references therein.

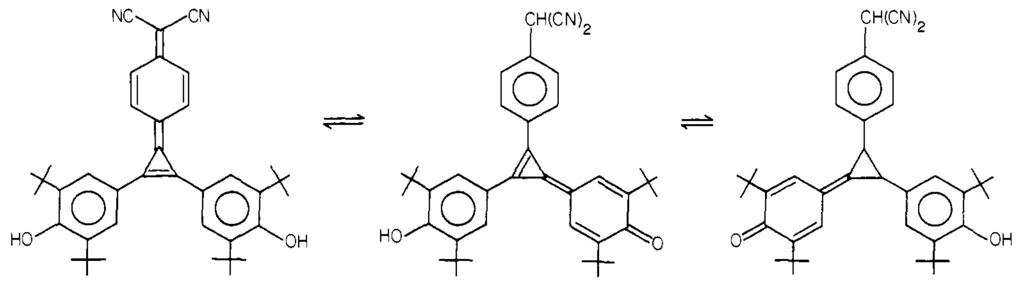
[2] Komatsu, K.; West, R. *J. Chem. Soc., Chem. Commun.* **1976**, 570.

[3] Huffman, W. A.; Birkeland, S. P.; O'Leary, K. P. U. S. Patent 4052209, Oct. 4, 1977.

[4] Zecher, D. C. Ph.D. Thesis, University of Wisconsin—Madison, Madison, WI, 1967.

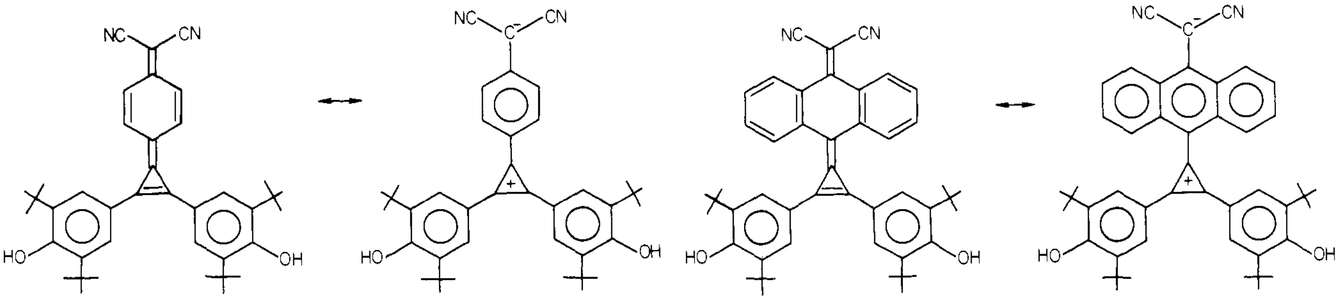
0002-7863/84/1506-0355$01.50/0

Scheme I



1a **1b** **1c**

Scheme II

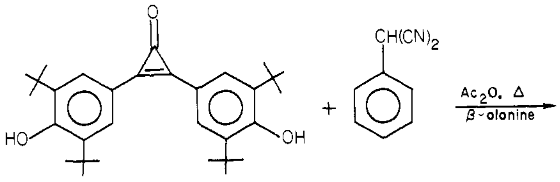


1a **1a′** **2a** **2a′**

cyanomethylidene analogue **2** from the oxidation of **2a**.

Synthesis

Compounds **1a** and **2a** were synthesized by methods used previously to obtain compounds **7** and **8**.[1f] To prepare **1a**, phenylmalononitrile was treated with the diarylcyclopropenone **12a** in refluxing acetic anhydride in the presence of a catalytic amount of the amphoteric acid–base species β-alanine (eq 1). Compound

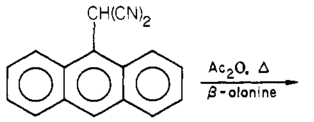


1a (1)

12a

1a is a bright orange solid that begins to decompose above 250 °C.[5] Compound **2a** was synthesized in the same way, substituting 9-(dicyanomethyl)anthracene[6] for phenylmalononitrile (eq 2), as

12a +



2a (2)

bright magenta crystals which begin to decompose above 270 °C. Both **1a** and **2a** show infrared absorptions between 1800 and 1840 cm^{-1}, characteristic for cyclopropene rings.[7]

Compounds **1a** and **2a** can exist in three tautomeric forms, illustrated below (for **1a**), as **1a**, **1b**, and **1c** (Scheme I). In the ^{1}H NMR spectrum for **1a**, the OH [or -CH(CN)$_2$] proton is not observed (probably because of exchange broadening) and the *tert*-butyl protons appear as one sharp singlet (36 H). These findings are similar to those for related diarylquinocyclopropanes such as **3a** and are compatible with the presence of any or all of the three tautomers. However the infrared spectrum suggests that only the dicyanomethylidene tautomer **1a** is present in significant amount. The CN stretching frequencies for **1a** at 2179 and 2160 cm^{-1} [8] are quite low, in the region for conjugated cyano groups. Likewise for **2a**, the ^{1}H NMR spectrum does not permit a distinction to be made, but the CN infrared stretching bands at 2220,

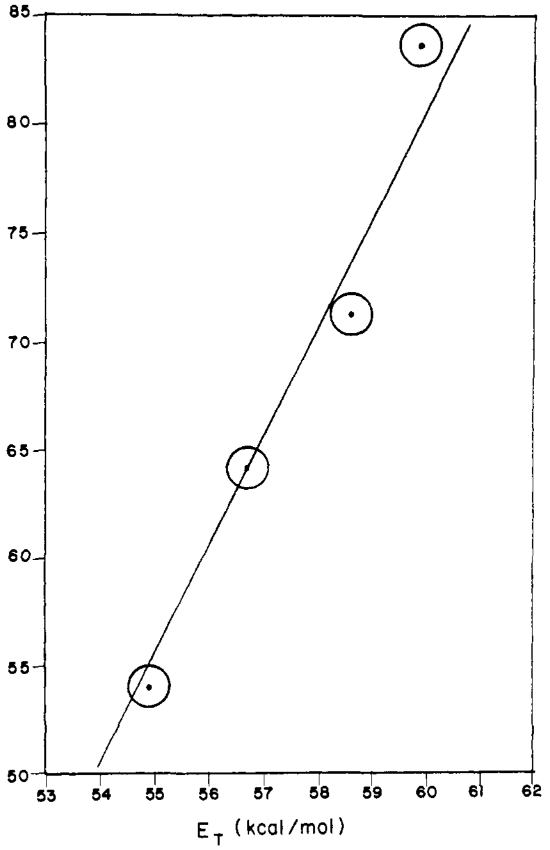


Figure 1. Plot of Z values for different solvents vs. E_T values for **1a** using the data from Table I.

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(5) Beyer, D. M. S. Thesis, University of Wisconsin—Madison, Madison, WI, 1975.

(6) We are indebted to Prof. Rudolf Gompper and Dr. Hans-Ulrich Wagner, Universität München, Müchen, West Germany, for kindly supplying their unpublished procedure for the synthesis of this compound.

(7) (a) Bergmann, E. D.; Agranat, I. *J. Am. Chem. Soc.* **1964**, *86*, 3587. (b) Kende, A. S.; Izzo, P. T. *Ibid.* **1964**, *86*, 3587. (c) Andreades, S. *Ibid.* **1965**, *87*, 3941.

(8) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Wiley: New York, 1953; p 264.

Table I. Solvatochromic Data for the Longest Wavelength Absorption of 1a and 2a in Various Solvents

		1a		2a	
solvent	Z	λ_{max}, nm	E_T	λ_{max}, nm	$E_T{}^b$
benzene	54.0	521	54.9	562	50.1
TMP[a]	60.1			546	52.5
CH_2Cl_2	64.2	504	56.7	581	49.0
CH_3CN	71.3	488	58.6	577	49.5
CH_3OH	83.6	477	59.9	569	50.2

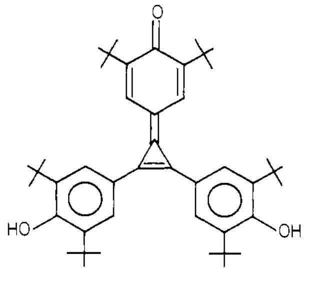
[a] 2,2,4-Trimethylpentane. [b] Kcal/mol.

2190 cm^{-1} again indicate that **2a** is the principal tautomer present.[8]

Compound **1a** forms solutions which appear red in aromatic hydrocarbons but orange in alcohols. The marked solvent dependence of the electronic spectrum of **1a** is illustrated by the data in Table I, showing the absorption maximum for the lowest-energy ($\pi \rightarrow \pi^*$) electronic transition as a function of solvent polarity. A plot of the transition energy vs. solvent Z value[9] (Figure 1) shows an approximately linear relationship between these parameters. This solvatochromism indicates that the ground state of **1a** is stabilized, or the excited state is destabilized, by interaction with polar solvents; that is, the ground state is more polar than the excited state. This result can be rationalized in terms of a large contribution of a polar canonical form, **1a′**, to the resonance hybrid for the ground state of **1a** and to reduced charge separation in the excited state[10] (Scheme II).

Data in Table I show that for **2a** the lowest energy absorption does not change much with solvent polarity. This suggests that canonical form **2a′** does not contribute much to the ground state of **2a**. It is reasonable that **1a′** should be relatively more important than **2a′**, because the gain in resonance energy upon aromatization of the cyclohexadiene ring should be much greater going from **1a** to **1a′** than from **2a** to **2a′**.

The results of the spectrophotometric titration of **2a** in THF with 2 equiv of base are shown in Figure 2. Isosbestic points are maintained throughout, indicating that deprotonation takes place directly to give the dianion. Similar results are found for analogous quinocycloalkanes such as **3a**. The dianion of **2a** forms an emerald green solution with its lowest energy absorption at 610 nm. Addition of 2 equiv of acid regenerated the original spectrum of **2a**.



3a

Compound **1a** showed more complex behavior upon spectrophotometric titration. When 2 equiv of base were added to a solution of **1a** in THF a new absorbance at 445 nm was observed in the UV–vis spectrum as well as an absorption at 510 nm due to unreacted **1a**. The original spectrum of **1a** could however be regenerated if 2 equiv of acid were added soon after the addition of base.

Compound **2** was readily isolated by the oxidation of **2a** with either lead dioxide or alkaline potassium ferricyanide solution. Recrystallization afforded **2** as violet crystals with a strong metallic lustre which produce a deep royal blue solution in chloroform.

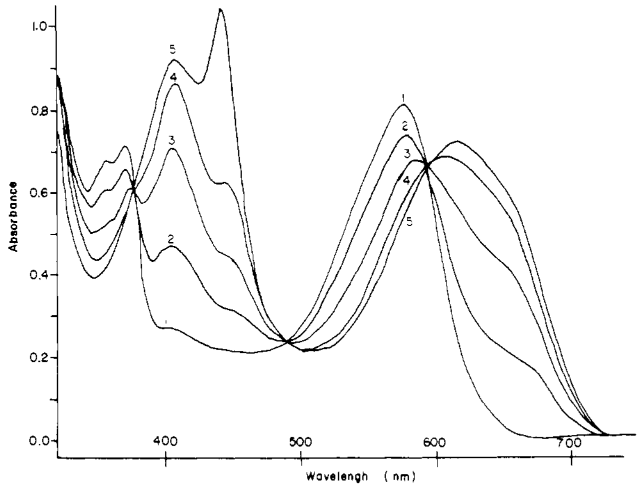


Figure 2. Spectrophotometric titration of a 9.55 × 10^{-4} M solution of **2a** in THF. Titrated with 1:0.0, 2:0.5, 3:1.0, 4:1.5, and 5:2.0 equiv of 0.09925 M NaOH (0.1-cm path length).

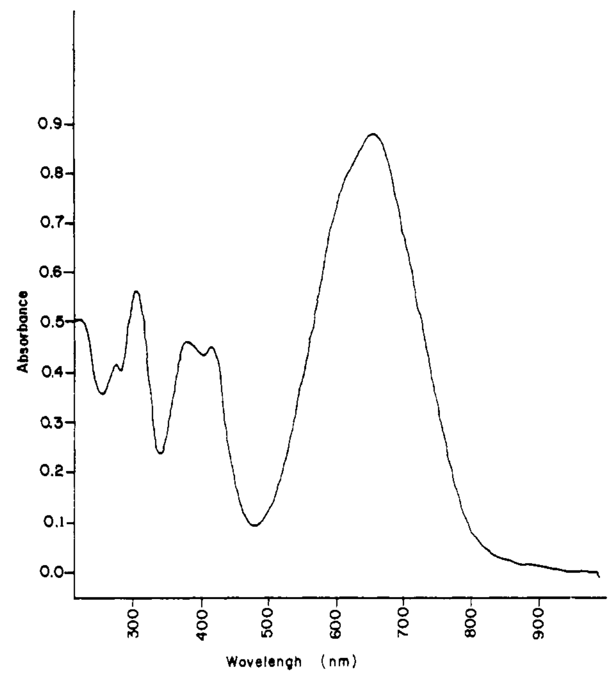


Figure 3. Electronic spectrum of **2**; 2.56 × 10^{-4} M in chloroform; 0.1-cm path length.

Table II. Reduction Potentials (V) of Polyquinones in Dichloromethane vs. SCE

	1st wave	2nd wave	ref
2	0.00	−0.04	this work
3	+0.05	−0.27	2
4	+0.02	−0.27	1b
5	+0.02	−0.28	1b
6	−0.08	−0.51	1c
7	+0.30	−0.24	1f
8	+0.25	−0.14	1f
9	−0.18	−0.51	1d
10	+0.20	−0.45	1e

The proton NMR of **2** exhibited two distinct *tert*-butyl signals in a 1:1 ratio confirming the presence of the exocyclic double bonds of the cyclopropane ring system. The hydroxyl and cyclopropene bands seen in the IR spectrum of **2a** were absent and a very strong absorption at 1590 cm^{-1} was observed, due to the quinonoid carbonyls present in **2**. The electronic spectrum of **2** in $CHCl_3$, shown in Figure 3, reveals an intense absorption at 660 nm (log ϵ 4.54).

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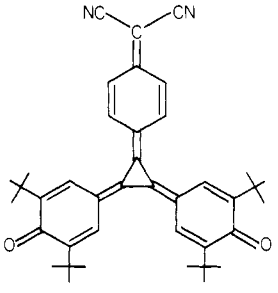
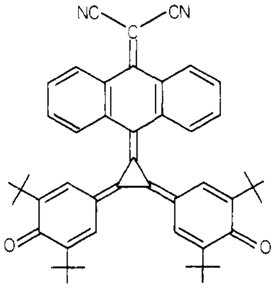
(9) Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; p 296.

(10) See ref 1b. For interesting similar situations with dicyanomethylidene groups see: Takahashi, K.; Takase, K.; Sakae, T. *Chem. Lett.* **1980**, 1485–1488.

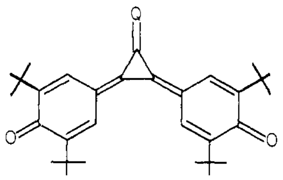
Chart I



1



2



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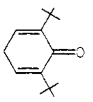
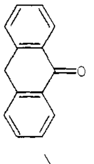
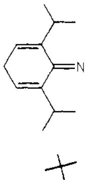
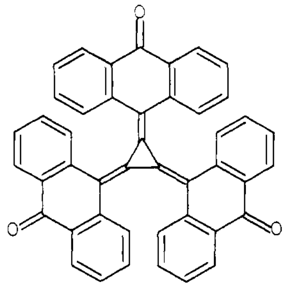


4, Q =



6, Q =





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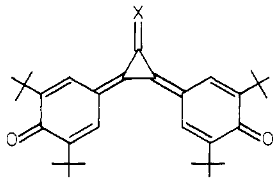

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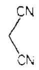

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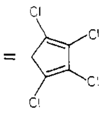

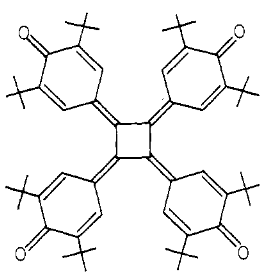

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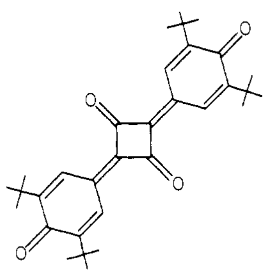

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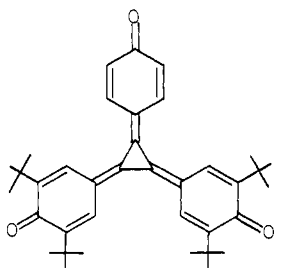


11

Electrochemical Studies of 2. Cyclic voltammetric studies of previously prepared polyquinones in aprotic media have shown them to have rather positive reversible first reduction potentials, followed by well-separated reversible second reduction potentials (Table II). The cyclic voltammogram for **2** is shown in Figure 4. The presence of only a single reversible wave is anomalous within the polyquinone series. This single wave corresponds to a two-electron reduction of **2**, as shown using thin-layer coulometry.[11]

Analysis of the cyclic voltammogram (Figure 4) using the method of Myers and Shain[12] yields values for $E_1°$ of + 2 mV and $E_2°$ of −44 mV. The small value for $\Delta E°$ (equivalent to $E_2° - E_1°$) is indicative of facile disproportionation of the anion–radical of **2** ($Q^{-}\cdot$):

$$2Q^{-}\cdot \overset{K_{\text{disp}}}{\rightleftharpoons} Q + Q^{2-} \qquad (3)$$

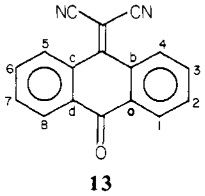
Inserting the values of $E_1°$ and $E_2°$ into eq 4

$$0.058 \log K_{\text{disp}} = E_2° - E_1° = \Delta E° \qquad (4)$$

yields a K_{disp} value of 0.16.

A computer simulation of the cyclic voltammogram of **2** using the experimentally obtained $E_1°$ and $E_2°$ is shown in Figure 5. The features of the simulated voltammogram are in close agreement with those of the experimental voltammogram in Figure 4.[13]

From its structure **2** is predicted to be a very strong oxidizing agent and the rather positive second reduction potential of −0.04 V is consistent with this prediction. The $E_2°$ value for **2** is 0.10 V more positive than that for the related dicyanomethylidene compound **8**; this is about as expected. The anomaly lies in the $E_1°$ value for **2**, which is far less positive than normal for such a compound. An explanation for the unexpectedly negative $E_1°$ value for **2** may be derived from a comparison of **2** to the known structure of 10-(dicyanomethylene)anthrone, **13**.[14] This structurally related compound exists in a butterfly conformation with the plane of the five atoms describing the dicyanomethylidene



13

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[11] We wish to thank Dr. Alanah Fitch for performinmg this experiment with us using a thin-layer cell which she constructed.

[12] Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980.

[13] The small reversible couple seen at +0.7 V in Figure 4 is probably due to an impurity.

[14] Silverman, J.; Yannoni, N. F. *J. Chem. Soc. B* **1967**, 194–201.

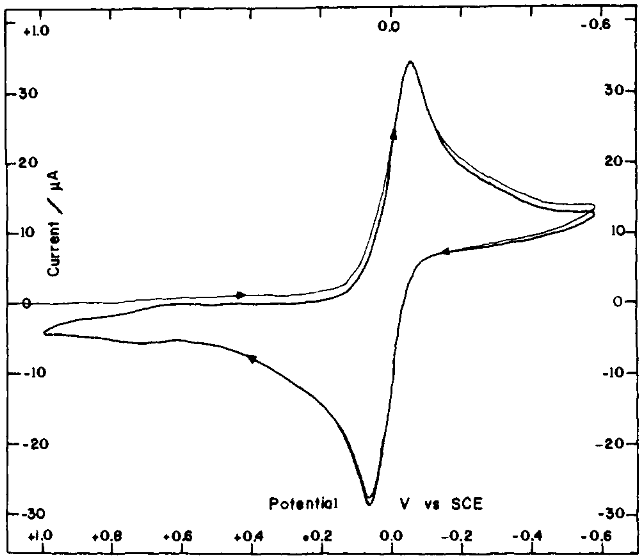


Figure 4. Cyclic voltammogram of 10^{-4} M **2** with 10^{-1} M TBAP as supporting electrolyte in CH_2Cl_2. Scanned from +1.0 V to −0.6 V at a scan rate of 200 mV/s.

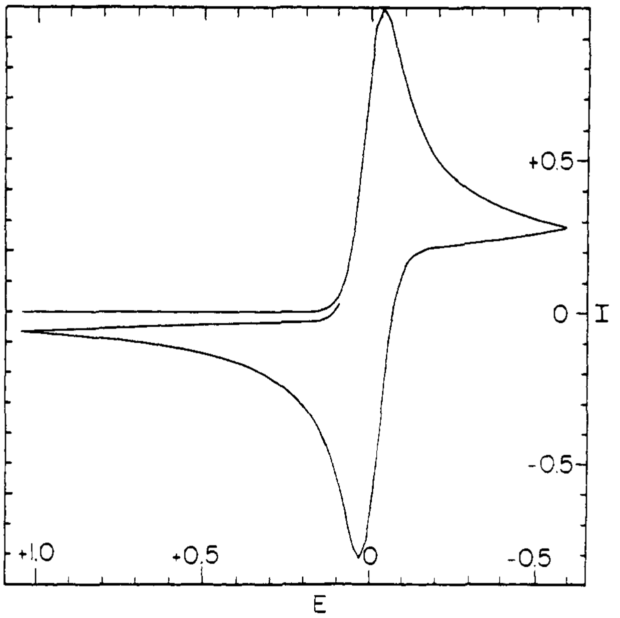
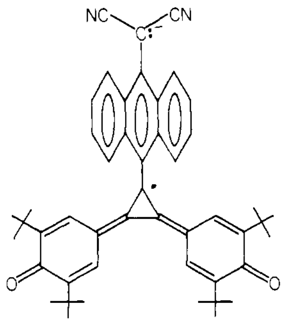


Figure 5. Computer simulation of the cyclic voltammogram for **2** using the data for **2** in Table II. The reaction was assumed to be completely reversible at +21 °C.

group bent out of the plane of the four carbon atoms a, b, c, and d by 36°. The oxygen atom on the opposite side is bent by 11° in the same direction as the dicyanomethylidene group. Similar structural features may be found in **2** and could result in a greatly decreased tendency for **2** to undergo one-electron reduction. After addition of the first electron, either the dicyanomethylene group or the anthracene moiety might undergo rotation out of the plane containing the quinone and the three-membered ring. The steric barrier to reduction would now have been overcome, so that $2^{-\cdot}$ (one of several canonical forms is shown below) undergoes further reduction to 2^{2-} and a "normal" $E_2°$ value.

E_1 and E_2 values lying very close together are also found for another sterically crowded quinone, bianthrone.[15] The two-electron reduction for bianthrone is similarly accounted for by conformational changes during reduction. However these two compounds differ in that for **2** the voltammogram does not change



$2^{-\cdot}$

with scan rates. Reversibility is observed even at 5 V/s for **2** while for bianthrone an effective scan rate of ~10^{-5} V/s is required. Therefore, whatever structural changes occur on reduction of **2** must take place several orders of magnitude faster than the bianthrone structural interconversions.

The electrochemical results also reveal that **2** has the most positive $E_2°$ of any polyquinone studied thus far. Compound **2** should be very effective as a two-electron oxidizing agent.

ESR Spectrum of the Anion Radical of 2 The ESR spectrum of the anion radical of **2**, generated electrolytically, is a broad single line. The same signal could be generated with potassium metal or Na/K alloy. No hyperfine splitting could be detected, perhaps because of electron exchange taking place in the disproportionation as discussed above. This would lead to line broadening which could mask any hyperfine coupling present. There may be other line-broadening effects from accidental equivalence of coupling constants of the interacting nuclei. No change in the ESR spectrum was observed over the temperature range from −70 to 60 °C.

Experimental Section

General Procedures. Melting points reported are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Spectra were recorded by means of the following instruments: infared, Perkin-Elmer 457 and Beckmann IR 4230; ^{1}H NMR, JEOL MH-100 and Bruker-IBM WP-200; Ultraviolet-visible, Cary 14; ESR, Varian E-15; Mass, CEC Type 21-103C.

Materials. All solvents and starting materials were carefully purified before use. Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**12a**) was prepared as previously reported.[1a]

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(4-(1,1-dicyanomethylidene)cyclohexadien-1-ylidene)cyclopropene (1a). A mixture of 1.34 g (2.90 mmol) of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**12a**), 0.75 g (5.3 mmol) phenylmalononitrile, and 0.01 g of β-alanine in 3.5 mL of freshly distilled acetic anhydride was heated to reflux with stirring for 15 min. The white mixture rapidly turned to an orange solution. The solution was cooled to room temperature and the orange precipitate was collected by filtration and recrystallized from chlorobenzene to give 1.27 g (74.7%) of **1a** as orange platelets: mp 250 °C dec; IR (KBr) 3620 (s), 3065 (w), 2970–2840 (m), 2179 (m), 2160 (w), 1812 (w), 1595 (m), 1490 (s), 1470 (m), 1410 (m), 1390 (s), 1370 (m), 1320 (m), 1280 (m), 1240 (m), 1195 (m), 1100 (w), 910 (w), 820 (w), 790 (m), 650 (w) cm^{-1}; ^{1}H NMR (Me_2CO-d_6) δ 1.60 (s, 36 H), 7.12 (d, 2 H, J = 10 Hz), 7.95 (d, 2 H, J = 10 Hz), 8.32 (s, 4 H); UV-visible λ_{max} (THF) 236 nm (log ε 4.28), 280 (3.86), 305 (4.04), 330 (4.31), 344 (4.38), 510 (4.80); Mass spec, *m/e* 586.3517; calcd, 586.3548.

Anal. Calcd for $C_{40}H_{46}N_2O_2$: C, 81.91; H, 7.85; N, 4.78. Found: C, 81.87; H, 7.88; N, 4.76.

9-(Dicyanomethyl)anthracene.[6] To prepare 9-(dicyanomethyl)anthracene, 30.1 g (0.25 mol) of freshly synthesized phenylcyanate, prepared by the recent and excellent method of Murray and Zweifel,[16] was slowly added to a mixture of 45.5 g (0.21 mol) of 9-anthrylacetonitrile[17] and 20.3 g (0.42 mol) of sodium hydride (50% in mineral oil) stirring in 250 mL of absolute diglyme. The temperature was maintained below 30 °C. The mixture was allowed to stir at room temperature for six additional h and then 750 mL of water was carefully added. The slurry was filtered and the alkaline filtrate was extracted two times with 250 mL of ether and the *organic* layers were discarded. The aqueous layer was then acidified with hydrochloric acid to a pH less than 3 which caused precipitation of the 9-(dicyanomethyl)anthracene. The precipitate was carefully recrystallized from glacial acetic acid to give 28.2 g (55.5%)

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(15) Evans, D. H.; Olsen, B. A. *J. Am. Chem. Soc.* **1981**, *103*, 839. Neta, P.; Evans, D. H. *Ibid.* **1981**, *103*, 7041. Evans, D. H.; Busch, R. W. *Ibid.* **1982**, *103*, 5057.

(16) Murray, R. E.; Zweifel, G. *Synthesis* **1980**, 150.

(17) Kluiber, R. W. *J. Org. Chem.* **1965**, *30*, 2037.

of 9-(dicyanomethyl)anthracene as pale yellow needles: mp 190–192 °C; IR (KBr) 3090 (w), 3060 (m), 3018 (w), 2912 (s), 2250 (m), 2230 (w), 1960 (w), 1626 (m), 1530 (m), 1454 (s), 1404 (w), 1382 (w), 1338 (m), 1292 (s), 1266 (m), 1188 (w), 1158 (m), 1045 (m), 1005 (s), 960 (m), 902 (vs), 870 (m), 840 (s), 785 (vs), 725 (vs), 712 (s), 686 (m) cm^{-1}; ^1H NMR (Me_2CO-d_6) δ 7.36 (s, 1 H), 7.76 (m, 4 H), 8.32 (d, 2 H), 8.56 (d, 2 H), 8.88 (s, 1 H); mass spec, *m/e* 242.0837; calcd, 242.0842.

Anal. Calcd for $C_{17}H_{10}N_2$: C, 84.27; H, 4.16; N, 11.57. Found: C, 84.31; H, 4.22; N, 11.49.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(10-(1,1-dicyanomethylidene)anthrylidene-9-ylidene)cyclopropane (2a). In a manner analogous to the preparation of **1a**, 1.30 g (2.81 mmol) of **12a** was mixed in 3.5 mL of freshly distilled acetic anhydride with 1.40 g (5.78 mmol) of 9-(dicyanomethyl)anthracene and 0.01 g of β-alanine. This was heated to reflux, with stirring, for 15 min traversing a color change from slightly yellow to violet to deep purple-red. The solution was cooled to room temperature and then rotary evaporated to remove solvent. The purple tar was dissolved in chloroform and extracted two times with sodium bicarbonate solution to remove excess 9-(dicyanomethyl)anthracene, then washed with water and dried over magnesium sulfate. Column chromatography with alumina and chloroform as eluant gave 0.97 g of **2a** (50.3%). The red-purple **2a** decomposed at 270 °C; IR (KBr) 3639 (m), 3020 (w), 2970 (m), 2940 (s), 2880 (w), 2870 (m), 2220 (m), 2190 (w), 1836 (w), 1640 (w), 1605 (w), 1572 (w), 1530 (w), 1488 (s), 1430 (m), 1422 (s), 1358 (m), 1322 (m), 1256 (m), 1194 (w), 1168 (m), 1110 (w), 1010 (m), 892 (w), 814 (w), cm^{-1}; ^1H NMR (Me_2CO-d_6) δ 1.51 (s, 36 H), 7.36 (t, 2 H), 7.62 (t, 2 H), 7.81 (s, 4 H), 7.95 (d, 2 H), 8.39 (d, 2 H); UV–visible λ_{max} (THF) 256 nm (log ϵ 4.04), 267 (4.04), 278 (4.06), 288 (4.09), 307 (4.14), 355 (3.85), 370 (3.87), 410 (sh, 3.44), 575 (3.92); λ_{max} ($CHCl_3$) 583 (3.87). Mass spec, *m/e* 686.3841; calcd, 686.3860.

Anal. Calcd for $C_{48}H_{50}N_2O_2$: C, 83.92; H, 7.34; N, 4.08. Found: C, 83.89; H, 7.29; N, 4.11.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(10-(1,1-dicyanomethylidene)anthrylidene-9-ylidene)cyclopropane (2). For the preparation of **2** 0.69 g (1.0 mmol) of **2a** was stirred in 25 mL of benzene with 1.00 g (3.00 mmol) of potassium ferricyanide in 25 mL of 1 M KOH solution. The red-purple solution of **2a** immediately turned deep blue when the two solutions were mixed together, and this mixture was stirred for 0.5 h under a nitrogen atmosphere. The organic layer was separated, washed with water until all traces of yellow were removed in the water layer, and then dried over magnesium sulfate. After removal of solvent the blue-purple solid was recrystallized in acetonitrile–chloroform (95%-5%) to give 0.62 g (91%) of **2** as metallic violet crystals: mp 270 °C dec; IR (KBr) 3000 (w), 2962 (s), 2920 (m), 2864 (m), 2210 (m), 1638 (w), 1592 (vs), 1542 (m), 1510 (w), 1482 (m), 1462 (s), 1456 (s), 1390 (m), 1360 (s), 1320 (w), 1300 (w), 1250 (m), 1164 (w), 1110 (s), 1090 (s), 1042 (m), 938 (w), 910 (m), 888 (m), 818 (w), 730 (s), 680 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 18 H), 1.41 (s, 18 H), 7.62 (m, 8 H), 8.16 (d, 2 H), 8.42 (d, 2 H); UV–visible λ_{max} ($CHCl_3$) 276 nm (log ϵ 4.22), 307 (4.35), 380 (4.25), 420 (4.24), 610 (sh, 4.48), 660 (4.54); λ_{max} (THF 658 (4.43). Mass spec, *m/e* 686.3865;[18] calcd, 684.3704.

Anal. Calcd for $C_{48}H_{48}N_2O_2$: C, 84.16; H, 7.07; N, 4.09. Found: C, 84.05; H, 7.11; N, 4.11.

Electrochemical Measurements. An A.S.S. 169 Electrochemistry System was used for the cyclic voltammetry and chronocoulometry experiments. This system was composed of the following modules: a Princeton Applied Research Potentiostat/Galvanostat with PAR 179 Coulometer, a PAR 175 Universal Programmer, a Houston 2000 X–Y recorder with time base, and a Tektronix 5103N storage oscilloscope with Polaroid camera. Positive feedback resistance compensation was employed. All measurements were carried out at room temperature (ca. 21 °C) in dichloromethane which was twice extracted with concentrated H_2SO_4 and distilled from P_2O_5 under an Ar atmosphere. Tetrabutylammonium perchlorate was used as supporting electrolyte and this was dried a minimum of 12 h at 100 °C at a pressure of 1.5×10^{-6} torr before use.

The voltammetric cell was of the three electrode type with Pt disk working micro electrode and Pt wire counter electrode. A saturated Calomel electrode was employed as the reference electrode. The sample solution of **2** was 10^{-4} M with 10^{-1} M tetrabutylammonium perchlorate. The cyclic voltammogram did not change with scan rate from 5 V/s to 50 mV/s.

Coulometry was performed with a thin-layer spectroelectrochemical cell[11] with a working volume of 7.9 μL. It was equipped with a gold minigrid working electrode and SCE reference electrode. The first sample was electrolyzed at a constant potential of −0.02 V and after charge passage was complete at this potential the same sample was then electrolyzed at a constant potential of −0.1 V until charge passage was finished. Other samples were electrolyzed at a constant potential of −0.1 V only. All of these samples gave similar coulometric readings using a 6.87×10^{-4} M solution of **2** with 0.1 M TBAP. New samples were introduced into the cell by a purge/refill technique.

Spectrophotometric Titrations. A 9.55×10^{-4} M solution of **2a** was prepared in THF. The compound was titrated with 0.5, 1.0, 1.5 and 2.0 equiv of 0.09925 M NaOH and the electronic spectrum of each titration was recorded. The spectra were plotted together as shown in Figure 2. The spectrophotometric titration of **1a** was performed in a similar manner but a complex behavior was observed for this compound.

Electron Spin Resonance. About 1 mg of **2** and a small amount of tetrabutylammonium perchlorate were placed in an electrolytic ESR cell. An appropriate amount of dry/degassed THF was vacuum transferred and the cell was freeze–thaw degassed. A minimal current was passed through the cell to generate the signal, a single line with width 10.6 G and $g = 2.0039$. Alternatively, the same signal was obtained from **2** with potassium or Na/K alloy in a cell with degassed THF as solvent. In the latter two cases extensive exposure of the sample to the active metals led to a deep emerald green denoting conversion of **2** to its dianion.

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Registry No. 1a, 88000-81-1; **2**, 88000-82-2; **2** radical anion, 88015-27-4; **2a**, 88000-83-3; **12a**, 14106-41-3; phenylmalonitrile, 3041-40-5; β-alanine, 107-95-9; 9-(dicyanomethyl)anthracene, 88015-28-5; phenyl cyanate, 1122-85-6; 9-anthrylacetonitrile, 2961-76-4.

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(18) This is the mass value for **2a**. Presumably traces of water in the mass spectrometer entrance port and ionization chamber are reducing the strong oxidizing agent **2** back to **2a**. M + 2 peaks have been seen before for quinones with large reduction potentials. See: Patai, S., Ed. "The Chemistry of the Quinonoid Compounds"; Wiley: New York, 1974; Part 1, p 236.