

isocyanate, tolyl 2,4-diisocyanate, or bis(*p*-isocyanato)-diphenylmethane in one portion. The resulting mixture was stirred at 25–30° for 20 hr. The precipitated solids were collected by filtration, washed with 50 ml. of cold *n*-heptane, and air-dried at 25–30°. The data are summarized in Table V.

Acknowledgment.—The writers wish to acknowledge their indebtedness to Mrs. M. Steele, Mr. E. E. Null, and Mr. C. Raynes for analyses performed and to Mr. R. W. Wise and Mr. Ira Hedrick for the differential thermal analyses.

Oxidation–Reduction Potentials and Absorption Spectra of Polycyclic Aromatic Quinones¹

EMIL J. MORICONI, BOHDAN RAKOCZY, AND WILLIAM F. O'CONNOR

Department of Chemistry, Fordham University, New York 58, N. Y.

Received March 23, 1962

Oxidation–reduction potentials, carbonyl, and ultraviolet and visible (240–600-m μ range) absorption frequencies of sixteen polycyclic aromatic quinones are reported. All available oxidation–reduction potential data of unsubstituted aromatic quinones are summarized and several new generalizations noted.

Oxidation–reduction potentials of polycyclic aromatic quinones normally provide a precise measure of both the oxidizing power of the quinone and the reducing intensity of the hydroquinone. These oxidation–reduction potentials, however, have also been used to account for the tendency of many aromatic compounds to give addition rather than substitution products.^{2,3} Thus Fieser and Price⁴ have correlated the velocity of the phenanthrene–bromine addition reaction for various phenanthrene derivatives with the magnitude of the redox potential of the corresponding *o*-quinone, while Badger⁵ has used redox potentials as a measure of the stability of dihydro compounds having the same nuclear bond structure as the corresponding quinones. Waters⁶ has found redox potentials also useful as guides to the position of substitution in polycyclic aromatics while Josien and co-workers⁷ have indicated the relationship between the carbonyl vibration frequency of a compound and its oxidation–reduction potential. The utility of oxidation–reduction potential data in interpreting the behavior of tautomers of hydroxy- and aminoquinones is well documented.⁸ Most recently, a linear relationship has been demonstrated between oxidation–reduction potentials and the rate of catalytic hydrogenation of *p*-quinones and their alkylated derivatives.⁹

Conversely Iball's¹⁰ measurement of the oxidation–reduction potentials of sixteen carcinogenic and noncarcinogenic benz[*a*]anthracene-7,12-dione derivatives plus dibenz[*a,h*]- and dibenz[*a,j*]anthracene-7,14-diones showed that substituent position on the benz[*a*]anthracene nucleus had a marked effect on the oxidation potential, but that there was no apparent correlation between potential and carcinogenic potency.

The Branch-Calvin relation¹¹ between the corrected normal potential of an aromatic quinone and the number of Kekulé structures in the hydroquinone and quinone has led Carter¹² to an empirical equation for the calculation of resonance energies of polycyclic aromatic hydrocarbons. Coulson¹³ has demonstrated the smooth curve relationship of these corrected redox potentials with experimental bond lengths, while other investigators have expanded this list to include bond localization energies^{14,15} and bond orders.^{5,11,14,16} Our most recent demonstrated qualitative correlation between corrected redox potentials of aromatic *o*- and *p*-quinones and both the position and ease of initial ozone attack in unsubstituted aromatic hydrocarbons¹⁷ necessitated a review of all known potentials in the field.¹⁸

In this paper we report specifically on the measurement of oxidation–reduction potentials, car-

(1) This research was supported by a grant C-3325(C4) from the U.S. Public Health Service, National Cancer Institute.

(2) L. F. Fieser, "Organic Chemistry," Vol. I, H. Gilman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 155.

(3) E. Clar, "Aromatische Kohlenwasserstoffe," 2nd ed., Springer-Verlag, Berlin, 1952, p. 20.

(4) L. F. Fieser and C. C. Price, *J. Am. Chem. Soc.*, **53**, 1838 (1936).

(5) G. M. Badger, "Structures and Reactions of the Aromatic Compounds," Cambridge University Press, 1954, p. 88.

(6) W. A. Waters, *J. Chem. Soc.*, 727 (1948).

(7) M. L. Josien, N. Fuson, J. M. Lebas, and J. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

(8) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 850.

(9) H. Musso, K. Figge, and D. J. Becker, *Ber.*, **94**, 1107 (1961).

(10) J. Iball, *Am. J. Cancer*, **38**, 372 (1940).

(11) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 303.

(12) P. G. Carter, *Trans. Faraday Soc.*, **45**, 597 (1949).

(13) C. A. Coulson, *Proc. Roy. Soc., A*, **169**, 413 (1939).

(14) G. M. Badger, *Quart. Rev. (London)*, **5**, 147 (1951).

(15) M. G. Evans, J. Gergely, and J. deHeer, *Trans. Faraday Soc.*, **45**, 312 (1949); M. G. Evans and J. deHeer, *Quart. Rev. (London)*, **4**, 94 (1950).

(16) G. M. Badger, *J. Chem. Soc.*, 1809 (1950).

(17) (a) E. J. Moriconi, W. F. O'Connor, and L. B. Taranko, *Arch. Biochem. and Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6466 (1959); (c) E. J. Moriconi, W. F. O'Connor, W. J. Schmitt, G. W. Cogswell, and B. P. Furer, *ibid.*, **82**, 3441 (1960).

bonyl, and ultraviolet and visible (240–600-m μ range) absorption frequencies of sixteen quinones values had already been established by Fieser and co-workers.^{18a}

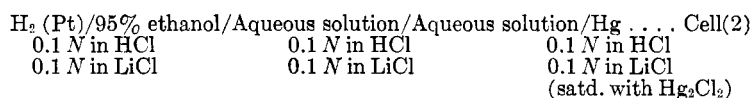
TABLE I

Quinone	Quinone solution		Indicator electrode ^a	Volts		
	Vol. (ml.)	Molarity ($\times 10^5$)		$E_{1/2}^b$	E_q^0 c, d	k
<i>p</i> -Benzoquinone	160	280	Au	0.350		
	710	14	Au	.342		
			Mean:	.346	0.709	-0.363
<i>p</i> -Toluquinone	200	96	Au	.306		
	750	12	Au	.284		
			Mean:	.295	.653	- .358
1,4-Naphthoquinone	200	44	Sh. Pt	.140		
	750	7.2	Sh. Pt	.147		
			Mean:	.143	.494	- .351
Phenanthrenequinone	750	7.1	Au	.123		
	200	220	Sh. Pt	.120		
	200	29	Sh. Pt	.122		
	750	6.4	Sh. Pt	.118		
	750	7.1	Sh. Pt	.119		
		Mean:	.120	.471	- .351	
					Mean: -0.356 \pm 0.007	

^a Either shiny platinum wire (Sh. Pt) or gold wire (Au). ^b At 30 \pm 2.0°. ^c Fieser's values^{18a} were used as standards. ^d At 25°.

derived from polycyclic aromatics whose ozonolysis

An independent check on the value of k was made by measuring the e.m.f. of the following cell:

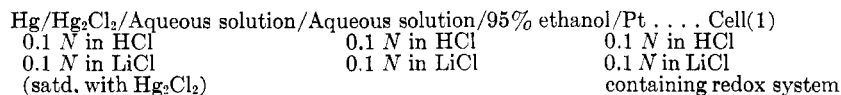


was anticipated or accomplished. Further, all available oxidation-reduction potential data of unsubstituted aromatic quinones are summarized and discussed.

Experimental

Preparation of Compounds.—The quinones were prepared by literature methods or acquired from generous benefactors (Table II). All afforded the calculated C, H values on elemental analysis.

Oxidation-Reduction Potentials.—The e.m.f. (E) was measured in the following cell:



E was measured while the redox system was titrated with the reductant titanium trichloride dissolved in 95% ethanol and 0.1 N hydrochloric acid and 0.1 N in lithium chloride. The value of $E_{1/2}$, the e.m.f. at the halfway point, was found from the usual e.m.f. vs. vol. titanium trichloride plot. The customary hydrogen half-cell used in these measurements,^{18a} was replaced by a less temperamental and reliable secondary standard, a modified calomel electrode. The calomel half-cell e.m.f., the small liquid junction potential introduced by its use, and the H⁺ term were incorporated into a single constant (k) and evaluated by calibration using the following equation:

$$E_{1/2} = k + E_q^0$$

where E_q^0 is the standard reduction potential of the redox system in 95% ethanol.

k was first experimentally evaluated to be -0.356 v. by measuring $E_{1/2}$ for four quinones (Table I) whose E_q^0

The mean value of E for this cell was found to be 0.347 \pm 0.005 v.

The standard reduction potentials (E_q^0) of the polycyclic aromatic quinones were then measured using cell (1). Most of the studies were made with both shiny platinum wire and gold wire. The indicator electrode material could be changed at will by means of a switch. The low solubility of the quinones in 95% ethanol especially those with more than four rings, required the use of very dilute solutions and small samples (ca. 10 mg.). The reducing agent was a very dilute titanium trichloride solution (0.3%) stored under nitrogen, while the volume of quinone solution titrated was usually about 750 ml. Before and during titration, nitrogen, passed over hot copper and saturated with solvent, was bubbled

through the magnetically stirred redox solution (insulated however from the stirrer motor). In some cases equilibrium was established quickly (2 min.), in most very slowly (up to 65 min.). The graphs of e.m.f. vs. titanium trichloride volume were, in general, smooth and showed well defined changes of e.m.f. at the end point.

The results are summarized in Table II. E_q^0 was thus calculated from the halfway e.m.f. by the relation

$$E_q^0 = E_{1/2} + 0.356$$

In most instances the agreement between the values of gold and platinum was satisfactory. High dilution in titration, uncertainty in the value of k , and the variation in temperature (the temp. coefficient of most e.m.f.'s however, is only

(18) (a) Leading references to Professor L. F. Fieser and co-workers' classical work in the field of reduction potential measurements can be found in ref. 2, p. 159; other measurements are found in (b) ref. 7, and (c) G. M. Badger and H. A. McKenzie, *Nature*, **172**, 458 (1953).

TABLE II

Quinone	Quinone solution		Indicator electrode	E^1/E^2	$E_q^{0.11, p}$	Corrected E_q^0	Positions of predominant ozone attack
	Vol. (ml.)	Molarity ($\times 10^6$)					
5,6-Benzo[c]phenanthredione ^a (I)	750	4.4	Sh. Pt	0.133	0.492	0.442	5,6 ^v
	750	3.6	Sh. Pt	.133			
	750	3.6	Au	.141			
	Mean:			.136			
1,6-Pyrenedione ^b (II)	750	4.0	Sh. Pt	.254	.612		
	750	5.7	Sh. Pt	.257			
	Mean:			.256			
1,8-Pyrenedione ^c (III)	750	4.6	Sh. Pt	.262	.514		
	750	7.1	Sh. Pt	.255			
	750	7.1	Au	.256			
	Mean:			.258			
5,6-Dibenz[a,h]anthracenedione ^d (IV)	800	8.1	Sh. Pt	.081	.446	.396	5,6 ^{17c}
	750	4.0	Sh. Pt	.096			
	750	4.0	Au	.094			
	Mean:			.090			
7-14-Dibenz[a,h]anthracenedione ^e (V)	640	6.0	Sh. Pt	— .065	.292 ^g	.442	
	640	6.0	Au	— .062			
	Mean:			— .064			
2-(<i>o</i> -Carbomethoxyphenyl)-3-carbomethoxy-9,10-phenanthredione ^{17c} (VI)	750	3.0	Sh. Pt	.166	.527	.477	
	750	3.0	Sh. Pt	.170			
	750	3.0	Au	.176			
	Mean:			.171			
5,6-Dibenz[a,j]anthracenedione ^f (VII)	750	2.6	Sh. Pt	.098	.455	.405	
	750	2.6	Sh. Pt	.102			
	750	2.6	Sh. Pt	.097			
	750	2.6	Au	.101			
	750	2.6	Au	.099			
	750	2.6	Au	.098			
Mean:			.099				
7,14-Dibenz[a,j]anthracenedione ^g (VIII)	750	2.6	Sh. Pt	— .059	.302 ^v	.452	
	750	2.6	Sh. Pt	— .051			
	750	2.6	Au	— .057			
	750	2.6	Au	— .047			
	Mean:			— .054			
5,6,8,9-Dibenz[a,j]anthracenetetraone ^h (IX)	750	2.6	Sh. Pt	.048	.406	.306	
	750	2.6	Sh. Pt	.051			
	750	2.6	Au	.050			
	750	2.6	Au	.052			
	Mean:			.050			
5,6-Picenedione ⁱ (X)	850	8.4	Sh. Pt.	.098	.451	.426	5,6 ^z
	750	3.5	Sh. Pt	.092			
	Mean:			.095			
13,14-Picenedione ^j (XI)	750	1.5 ^p	Sh. Pt	.147	.503	.503	
	750	1.5 ^p	Au	.147			
	Mean:			.147			
5,6,7,8-Picenetetraone ^k (XII)	750	8.4	Sh. Pt	No end point ^q	.416	.366	
		Au	.060 ^u				
4,5-Benzo[a]pyrenedione ^l (XIII)	850	5.4	Sh. Pt	.083	.442 ^t	.392	
	750	2.8	Sh. Pt	.089			
	750	2.8	Au	.086			
	Mean:			.086			
1,6-Benzo[a]pyrenedione ^m (XIV)	750	3.8	Sh. Pt	.082	.438		
	750	3.8	Sh. Pt.	.081			
	750	3.8	Au	.082			
	750	3.8	Au	.083			
	Mean:			.082			

3,6-Benzo[a]pyrenedione ^a (XV)	750	3.8	Sh. Pt	.084		
	750	3.8	Sh. Pt	.085		
	750	3.8	Au	.086		
	750	3.8	Au	.085		
			Mean:	.085	.441	
6,12-Benzo[a]pyrenedione ^b (XVI)	750	1.5	Sh. Pt	.089		
	750	1.5	Au	.085		
				Mean:	.087	.443

^a M.p. 181–183°, lit., m.p. 187–188° [J. W. Cook, *J. Chem. Soc.*, 2524 (1931)]. ^b M.p. 310–312° dec.,¹⁹ lit., m.p. 309° [H. Vollman, H. Becker, M. Correll, and H. Streeck, *Ann.*, **531**, 77 (1937)]. ^c M.p. 270–272° dec.,¹⁹ lit., m.p. 270° [ref. b, p. 80]. ^d M.p. 343–345° dec., lit., m.p. 348–350° [P. M. Bhargava, H. I. Hadler, and C. Heidelberger, *J. Am. Chem. Soc.*, **77**, 2877 (1955)]. ^e M.p. 243–244°, lit., m.p. 244–245° [E. Clar, *Ber.*, **62**, 350 (1929)]. ^f M.p. 308–309°, lit., m.p. 310° dec. [J. W. Cook and E. F. M. Stephenson, *J. Chem. Soc.*, 843 (1949)]. ^g M.p. 223–224°, lit. m.p. 225–226° [J. W. Cook, *J. Chem. Soc.*, 1472 (1932)]. ^h M.p. 410–411° dec., lit. m.p., >340° dec. [ref. f]. ⁱ Lit., m.p. 310°²⁰ [W. Davies and B. C. Ennis, *J. Chem. Soc.*, 915 (1959)]. ^j Lit., m.p. 285°²⁰ [ref. i]. ^k Lit., m.p. 386°²⁰ [ref. i]. ^l M.p. 253–254°, lit., m.p. 240° [J. W. Cook and R. Shoental, *J. Chem. Soc.*, 47 (1950)]. ^m M.p. 290–291°, lit., m.p. 292–293° [J. W. Cook, R. S. Ludwiczak, and R. Shoental, *ibid.*, 1112 (1950)]. ⁿ M.p. 288–289°, lit., m.p. 291° dec. [ref. m]. ^o Lit., m.p. 316°²¹ [H. E. Schroeder, F. B. Stilmer, and F. S. Palmer, *J. Am. Chem. Soc.*, **78**, 446 (1956)]. ^p Estimated concentration; a 4.5-mg. sample of XI was stirred in 750 ml. of 95% ethanol. After 3 hr., approximately 20% remained undissolved and was discarded. ^q We have no explanation for this behavior; similar anomalous results were observed by J. B. Conant and L. F. Fieser [*J. Am. Chem. Soc.*, **44**, 2480 (1922)], using two platinum electrodes (one bright and the other platinized). ^r At 30 ± 2.0°. ^s Iball¹⁰ reports a value of 0.255 v.; Fieser,² 0.268 v. ^t Badger¹⁸ observed 0.437 v. in 75% alcohol and estimated 0.441 v. in 95% alcohol. ^u This value is in doubt since calculated and observed end points are widely different. ^v Branch and Calvin corrections permit only of comparison of *o*- and *p*-quinones.¹¹ ^w Unpublished information, E. J. Moriconi, L. Taranko, and W. F. O'Connor. ^x P. G. Copeland, R. E. Dean, and D. McNeil, *Chem. Ind.*, 98 (1960); *J. Chem. Soc.*, 1232 (1961). ^y Iball¹⁰ reports a value of 0.238 v. Fieser and Dietz [*J. Am. Chem. Soc.*, **53**, 1128 (1931)] report a value of 0.264 v.

TABLE III
INFRARED, ULTRAVIOLET, AND VISIBLE ABSORPTION MAXIMA OF POLYCYCLIC AROMATIC QUINONES

Quinone	Infrared (KBr Wafer)		Ultraviolet and visible (in ether), λ_{\max} m μ ^d
	Carbonyl bands ν_{\max} μ (cm. ⁻¹)		
I	5.64 (1773) <i>w</i> , 5.94 (1684) <i>s</i>		268, 284, 295, 310, 335, 355, 372, 414, 432
II	6.08 (1645) <i>s</i> , 6.11 (1637) <i>s</i> ^a		<i>256, 266, 277, 297, 318, 334, 351, 398, 424, 448</i>
III	6.08 (1645) <i>s</i> ^a		<i>256, 266, 272, 277, 318, 335, 351, 368, 379, 400, 424, 436</i>
IV	5.94 (1684) <i>s</i>		<i>310, 323, 342, 357, 370, 390</i>
V	5.99 (1669) <i>s</i> ^b		<i>270, 285, 295, 320, 332, 385, 426, 454</i>
VI	5.82 (1718) <i>s</i> , 5.95 (1709) <i>s</i>		337, 399, 424
VII	5.93 (1686) <i>s</i>		
VIII	6.01 (1664) <i>s</i>		<i>270, 279, 286, 297, 318, 358</i>
IX	5.94 (1684) <i>s</i>		
X	5.88 (1701) <i>w</i> , 5.98 (1672) <i>s</i>		<i>267, 279, 286, 296, 332, 350, 355, 367, 380, 406, 436</i>
XI	5.99 (1669) <i>s</i> ^c		<i>242, 252, 262, 270, 286, 297, 323, 371, 386</i>
XII	5.91 (1692) <i>s</i>		<i>290, 318, 335, 444</i>
XIII	5.96 (1678) <i>s</i>		<i>264, 272, 283, 305, 321, 335, 376, 338, 418, 450</i>
XIV	6.04 (1656) <i>s</i>		<i>248, 256, 263, 276, 288, 299, 312, 342, 395, 430, 456, 484</i>
XV	5.62 (1779) <i>m</i> , 5.74 (1742) <i>m</i> , 5.99 (1669) <i>s</i> , ^d 6.04 (1656) <i>s</i>		<i>286, 297, 347, 384, 400, 424, 454</i>
XVI	5.81 (1721) <i>m</i> , 5.99 (1669) <i>s</i> , 6.02 (1661) <i>s</i> , 6.08 (1645) <i>s</i>		277, 287, 298, 348, 364, 404, 418, 442

^a Previously reported: 6.10 μ (1639 cm.⁻¹) (paraffin oil paste) C=O stretching vibration for both quinones II and III.⁷ This carbonyl doublet for II and the single carbonyl band in III were also observed using a calcium fluoride prism. ^b 6.02 μ (1661 cm.⁻¹) in carbon tetrachloride solvent.⁷ ^c 5.95 μ (1681 cm.⁻¹) in carbon tetrachloride solvent.⁷ ^d Values in italics represent inflections; bold face represent major bands.

about 0.0001 v. per degree) combine to produce an estimated probable error in the actual E_a values listed in Table II of somewhat less than 10 millivolts. There is however far less uncertainty attached to the relative values of E_a .

Absorption Spectra.—Infrared spectra were determined on a Perkin-Elmer 21 using a sodium chloride prism. The ultraviolet absorption spectra were determined by Dr. Hans

L. Falk (U. of Southern California, School of Medicine) on a Beckman DK-2. Unfortunately, a majority of these quinones were relatively insoluble, and quantitation of the solution was not possible. Consequently molar extinctions could not be calculated. Absorption data are summarized in Table III.

Discussion

With reference to the new oxidation-reduction potential data (Table II), three observations may be noted:

(19) Generously donated by Prof. H. J. Teuber, Universität Frankfurt, a. M.

(20) Graciously supplied by Prof. W. Davies, University of Melbourne, Australia.

(21) Courteously provided by Dr. J. B. Campbell, Jackson Laboratory, E. I. du Pont de Nemours and Co.

TABLE IV

OXIDATION-REDUCTION POTENTIALS OF AROMATIC QUINONES
IN ALCOHOLIC SOLUTION

Aromatic compound ^a	Carbonyl positions ^c	$E_{0,0}^{b}$
Benzene	1,2	0.792 ^c
	1,4	.715 ^c
Naphthalene	1,2	.576 ^c
	1,4	.484 ^c
	2,6	.76 ^c
	1,4,5,8	.972 ^c
Anthracene	1,2	.490 ^c
	9,10	.154 ^c
Phenanthrene	1,4	.401 ^c
	9,10	.460 ^c
	1,2	.660 ^c
	3,4	.621 ^c
Benz[<i>a</i>]anthracene	1,4	.523 ^c
	5,6	.430 ^c
Chrysene	7,12	.228 ^c
	5,6	.465 ^c
	6,12	.392 ^c
Pyrene	4,5	.474 ^{18a}
	1,6	.612
	1,8	.514
Benzo[<i>c</i>]phenanthrene	5,6	.492
Picene	5,6	.451
	13,14	.503
Dibenz[<i>a,h</i>]anthracene	5,6,7,8	.416
	5,6	.446
Dibenz[<i>a,j</i>]anthracene	7,14	.292
	5,6	.455
Benzo[<i>a</i>]pyrene	7,14	.302
	5,6,8,9	.406
	4,5	.442
	1,6	.438
	3,6	.441
	6,12	.443

^a Chem. Abstr., nomenclature and numbering system used.^b Temp. 20-30°. ^c See ref. 2 for original references to Fieser's work.

1. The expected potential-raising effect of electron withdrawing substituents in VI (0.527 v.) relative to the parent phenanthrenequinone (0.460 v.) is observed.

2. Ozone predominantly attacks the 5,6-bond in picene. Predictably, the corresponding *o*-quinone (X) has the lower corrected oxidation-reduction potential (*cf.* XI).

3. Since the corrected oxidation-reduction potentials for 5,6- (VII) and 7,14-dibenz[*a,j*]anthracenediones (VIII) are respectively, 0.405 v. and 0.452 v., it can now be predicted that ozone should cleave predominantly the 5,6-bond in VII.

Table IV summarizes all the available oxidation-reduction potential data for unsubstituted aromatic quinones (fifteen *ortho*-, eight *para*-, and seven conjugated diones, and three tetraones).

The following generalizations may now be discerned:

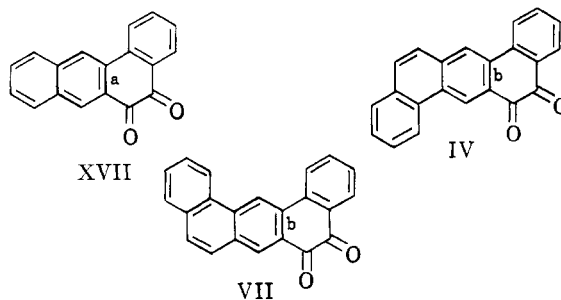
1. Stabilization (lower oxidation-reduction potentials) resulting from fusion of benzene rings to a double bond of either *o*- or *p*-benzoquinone (as in the previously reported *o*-benzoquinone > 1,2-naphtho-

quinone > 1,2-anthracenedione > phenanthrenequinone > 5,6-benz[*a*]anthracenedione, and *p*-benzoquinone > 1,4-naphthoquinone > anthraquinone)² can also be found in 5,6-chrysenedione > 5,6-picenedione (X), 4,5-pyrenedione > 4,5-benzo[*a*]pyrenedione (XIII), 2,6-naphthoquinone > 6,12-chrysenedione and 6,12-benzo[*a*]pyrenedione (XVI), 1,6-pyrenedione (II) > 1,6-benzo[*a*]pyrenedione (XIV) and 1,8-pyrenedione (III) > 3,6-benzo[*a*]pyrenedione (XV).

2. If, however, the benzene ring is fused in close proximity to the carbonyl groups, the potential is *increased* (*cf.*, phenanthrenequinone < 5,6-chrysenedione, and more significantly, 5,6-picenedione < 13,14-picenedione, anthraquinone < 7,14-benz[*a*]anthracenedione, and 7,14-benz[*a*]anthracenedione < 7,14-dibenz[*a,h*](V) and 7,14-dibenz[*a,j*]anthracenedione (VIII)).

3. Two additional types of steric restriction can now be delineated (ring planarity and intramolecular overcrowding) to account for the higher potentials of 4,5-pyrenedione and 5,6-benzo[*c*]phenanthrenequinone (I) over phenanthrenequinone, and 6,12-benzo[*a*]pyrenedione (XVI) over 6,12-chrysenedione.

4. Most striking is the fact that angular fusion of a benzene ring to the anthracene moiety of 5,6-benz[*a*]anthracenedione *increases* the potential in 5,6-dibenz[*a,h*](IV) and 5,6-dibenz[*a,j*]anthracenedione (VII). Here the fusion occurs at too great a distance from the carbonyl groups to exert any steric influence. The possibility of greater conjugation of bond *a* with the carbonyl group in 5,6-benz[*a*]anthracenedione (XVII) over the corresponding bond *b* in IV and in VII is seemingly negated by



Pauling's assignment of only 33½% double bond character to bond *a* in naphthalene while bond *b* in phenanthrene has 40% double bond character.²²

Acknowledgment.—The authors wish to thank Dr. Smith for some of the redox potential measurements; Mr. Thomas Doyle, Mr. Lubormyr Taranko, and Dr. William Schmitt for the preparation of some of these quinones, and again to acknowledge the generosity of Prof. H. J. Tauber, Prof. W. Davies, and Dr. J. B. Campbell.