

available for the more common, related, quinones. Quinones have been the subject of HMO calculations by several groups of workers. Coulson investigating several conjugated carbonyl compounds found that, based upon bond fixation, 1,4-benzoquinone would possess an enhanced delocalization compared to glyoxal.³ The delocalization, however, is still minimal as 1,4-benzoquinone would be predicted to show bond alternation equivalent to 1,3-butadiene.³ The results of Kuboyama tend to support this view.⁴⁻⁶ His HMO calculations showed pronounced alternation of bonds for the benzoquinones.^{4,5} For certain systems in which aromatic rings are fused to the basic quinone unit, the presence of an unperturbed benzene unit is indicated.^{4,5} This would again indicate limited delocalization. Bonino and Rolla in contrast to the above results, however, claim a resonance energy per electron for 1,2-benzoquinone and 1,4-benzoquinone intermediate between values found for olefins and benzenoid hydrocarbons.⁷ Attempts to correlate various physical properties with HMO results are also to be found in the literature. The most complete of these is a treatment of 43 quinones carried out by Koutecký, Zahradník, and Arient on the relationships between calculated quantities with spectroscopic and electrochemical results.⁸

Various groups have also carried out SCF-LCAO molecular orbital calculations on specific quinones. Kuboyama and Wada have studied 1,2-benzoquinone⁹ and 9,10-anthraquinone.¹⁰ Two groups of workers have used SCF techniques to investigate the ionization potential of certain *p*-quinones.^{11,12} No single study utilizing an advanced molecular orbital approach, however, has approached the scope of the Koutecký, Zahradník, and Arient paper.⁸

Dewar and coworkers have developed a comprehensive π -electron SCF approach which has been successfully applied to correlate the properties of various conjugated systems.¹³⁻¹⁷ Heteroatom systems have been twice treated. Unfortunately, the only quinones studied were 1,2-benzoquinone and 1,4-benzoquinone.^{15,17} The latest techniques and parameterization offered by Dewar and deLlano¹⁶ for hydrocarbon molecules have been favorably used in our prior calculations on quinodimethanes.² The corresponding heteroatomic approach,¹⁷ however, merits some comment.

Dewar and Morita¹⁶ have elaborated an approach for heteroatomic systems which differs substantially from the older method developed in that group.¹⁵ Chief among these differences is the use of additional parameters to allow for the effect of polarization of σ electrons by the heteroatom. The polarization effect, which is defined as a function of the charge densities at the specified atom, is made manifest in changing core charges, valence state ionization potentials, effective nuclear charges, and one-center electron repulsion integrals. For carbonyl compounds such as quinones these changes are not large. This polarization effect in many ways resembles elements of the ω technique¹⁸ or VESCF¹⁹ calculations in affecting the diagonal elements of the secular determinant. It is, however, less inclusive being applied solely to the heteroatom and the adjacent carbon atom(s). This polarization effect was not utilized in the present study. All calculations were carried out by a variable bond length approach.¹⁵ At the end of each iteration new internuclear distances between pairs of bonded atoms were determined from the bond orders. These were then used to obtain new values for resonance integrals and two-center electronic integrals between the same atom pairs.

In carrying out π -electron calculations of the present type, empirical parameters must be introduced in order to both estimate resonance integrals and to allow for their variation as a function of bond length. These comprise bond energy, bond length, and force constant terms between pairs of atoms in various hybridization states. Upon reexamination of earlier results, it was felt that an incorrect bond length (1.230 Å) was being used for a carbon-oxygen double bond. The latest experimental value for the carbonyl bond in formaldehyde is only 1.208 Å.²⁰ Use of this latter value introduced substantial changes in the original Dewar-Morita parameterization. All changes are listed in the Appendix. With these exceptions the formalism and variable parameters of the Dewar-Morita approach have been used throughout this study.

A. Thermochemistry

Figure 1 supplies the structures of the quinones currently investigated. An outstanding success of Dewar's method has been the ability to calculate heats of atomization for conjugated systems. Experimental heat of atomization data are less extensive for quinones than for benzenoid hydrocarbons. However, fair agreement between calculated and empirical results can be claimed in the present work. Table I shows the heats of atomization obtained *via* the heats of combustion of Magnus²¹ and the corresponding calculated values. The average difference between the two sets of data is *ca.* 0.35 eV. The greatest differences are associated with the two *o*-quinones studied. While this may imply an inability of the present calculations to treat compounds of this type, part of this may equally be due to experimental error. It is difficult to see, for example, why 9,10-phenanthrenequinone should be 13 kcal/mol more stable than the isomeric 9,10-anthracenequinone. These results, however, still represent the sole experimental data

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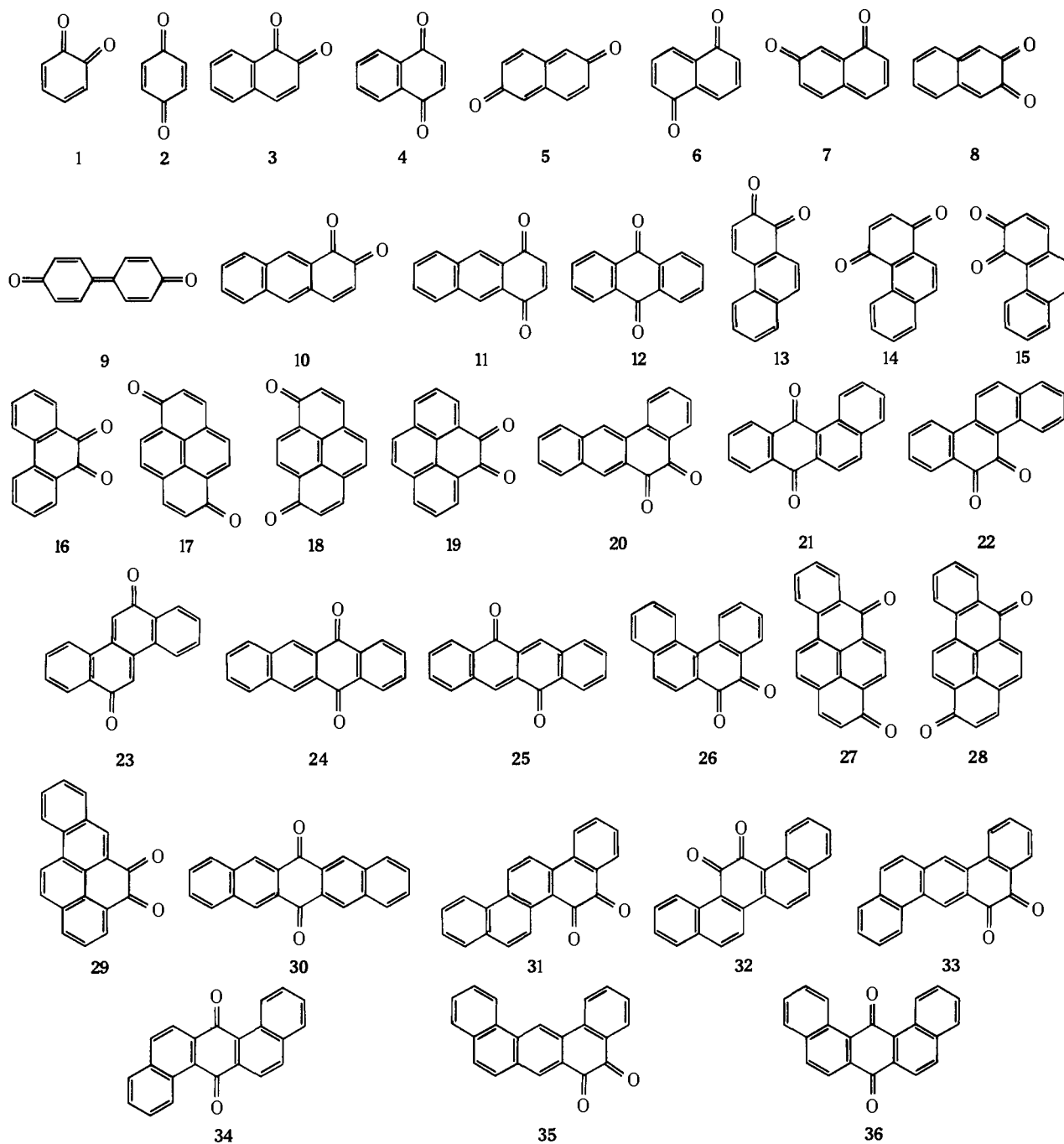


Table I. Comparison of Experimental and Calculated Heats of Atomization (eV) for Some Quinones^a

System	Heat of atomization		Δ	% un- certainty
	Exptl	Calcd		
2	60.370	60.149	0.221	0.37
4	94.349	94.321	0.028	0.03
12	128.422	128.488	0.068	0.05
16	128.962	128.297	0.665	0.52
21	163.389	162.159	1.230	0.75
24	162.196	162.282	0.086	0.05
30	195.715	195.831	0.116	0.06
		Av	0.345	0.26

for most of the systems in Table I. The agreement with theory was, in general, deemed encouraging.

Table II summarizes the calculated heats of atomiza-

tion for all systems studied. Certain trends are evident and may be illustrated by considering the isomeric $C_{10}H_6O_2$ molecules 3-8. 1,2-Naphthoquinone (3) and 1,4-naphthoquinone (4) show enhanced stability due to the presence of a benzenoid ring. Systems 5, 6, and 7 are best regarded as nonaromatic cross-conjugated diones. System 8 by contrast exhibits a distinct destabilization relative to its isomers. This well illustrates the inherent instability of polycyclic molecules which are constrained to exist in a completely quinonoid structure. A similar conclusion was reached for the corresponding hydrocarbons.²

Table II also contains the calculated resonance energies for these systems. These are defined as the differences between the calculated heats of atomization and

Table II. Calculated Heats of Atomization (eV) and Resonance Energies

System	E_π	E_σ	Heat of atomization ^a	RE	REPE
1	12.863	29.471	60.084	-0.064	-0.008
2	12.930	29.456	60.149	-0.173	-0.022
3	19.347	48.211	94.183	1.035	0.086
4	19.468	48.228	94.321	0.999	0.083
5	18.674	48.065	93.364	0.042	0.004
6	18.840	48.194	93.659	0.337	0.028
7	18.729	48.131	93.485	0.163	0.014
8	15.196	48.730	90.551	-2.597	-0.216
9	21.383	55.382	112.265	0.180	0.013
10	25.476	66.872	127.848	1.699	0.106
11	25.624	66.891	128.015	1.693	0.106
12	25.995	66.993	128.488	2.166	0.135
13	25.469	66.874	127.843	1.694	0.106
14	25.557	66.892	127.949	1.627	0.102
15	25.478	66.877	127.855	1.706	0.107
16	25.893	66.958	128.297	2.148	0.135
17	28.742	78.213	142.455	1.895	0.105
18	28.745	78.213	142.458	1.898	0.105
19	29.136	78.270	142.906	2.520	0.140
20	31.985	85.615	161.939	2.790	0.140
21	32.130	85.654	162.159	2.837	0.142
22	31.961	85.621	161.957	2.808	0.140
23	31.688	85.560	161.623	2.301	0.115
24	32.253	85.654	161.282	2.960	0.148
25	31.774	85.628	161.777	2.455	0.123
26	31.963	85.613	161.951	2.802	0.140
27	35.239	96.951	176.565	3.005	0.137
28	35.263	96.952	176.590	3.030	0.137
29	35.363	96.945	176.668	3.282	0.149
30	38.270	104.311	195.831	3.509	0.146
31	38.202	104.288	195.740	3.591	0.149
32	38.090	104.283	195.623	3.484	0.145
33	38.280	104.282	195.812	3.663	0.153
34	38.171	104.319	195.740	3.418	0.142
35	38.257	104.280	195.787	3.638	0.152
36	38.208	104.317	195.775	3.453	0.144

^a Heat of atomization = $E_\pi + E_\sigma + nE_{C-H}$, where E_{C-H} equals 4.4375 eV.

those obtained by a bond additivity scheme.^{16,22} The new bond energies required to treat the quinones were evaluated from calculations on simple conjugated carbonyl systems. The values obtained were C=O (7.0284 eV), C-CO (4.3598 eV), and OC-CO (4.1962 eV). The value for C=O is slightly smaller than that of an unperturbed bond while that for C-CO is almost identical with the standard C-C. The smaller value found for OC-CO seems reasonable in consideration of a bond weakening dipole-dipole interaction.

The resonance energies per electron (REPE) for most systems for which only a single classical structure can be drawn are very close to zero. Only system **8** shows appreciable antiaromatic character. The remaining systems show positive resonance energy due to delocalization in the benzenoid portion of the molecules. The REPE increases as the quinone portion of the molecules becomes relatively less important. This increase in delocalization was claimed by Magnus from his heats of combustion²¹ and may also be inferred from certain magnetic susceptibility studies.²³

B. Structure

SCF calculations have proven very effective in the

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Table III. Experimental and Calculated Bond Lengths (Å) for Some Quinones

System	Bond	Exptl lengths		Calcd lengths
		X-Ray	E.d.	
1,4-Benzoquinone (2)	C ₁ -C ₂	1.477	1.479	1.471
	C ₂ -C ₃	1.320	1.338	1.348
	C ₁ -O	1.222	1.221	1.235
1,4-Naphthoquinone (4)	C ₁ -C ₂	1.465		1.470
	C ₂ -C ₃	1.310		1.348
	C ₁ -C ₉	1.445		1.467
	C ₆ -C ₇	1.370		1.391
	C ₇ -C ₈	1.420		1.402
	C ₈ -C ₉	1.375		1.394
9,10-Anthraquinone (12)	C ₉ -C ₁₀	1.390		1.409
	C ₁ -O	1.215		1.237
	C ₁ -C ₂	1.391		1.400
	C ₂ -C ₃	1.383		1.393
	C ₁ -C ₁₃	1.391		1.396
	C ₉ -C ₁₃	1.492		1.478
	C ₁₁ -C ₁₂	1.404		1.407
C ₉ -O	1.244		1.238	

Table IV. Experimental and Calculated Dipole Moments (D) for Some Quinones

System	Exptl	Calcd
1	5.1	4.68
3	5.67	5.34
4	1.33	1.35
16	5.34-5.59	5.37
24	2.3	0.87

evaluation of bond lengths in conjugated systems. While very few quinones have been the subjects of modern detailed structure determinations, some data are available for comparison. 1,4-Benzoquinone has been recently studied by both X-ray²⁴ and electron diffraction²⁵ techniques. The experimental and calculated bond lengths are given in Table III. The agreement is quite good. An average deviation of *ca.* 0.01 Å between the calculated value and the electron diffraction data is found. Even better agreement is found in case of 9,10-anthraquinone.²⁶ The only other available experimental data are based on a study of 1,4-naphthoquinone.²⁷ Agreement here is less satisfactory. The experimental results, however, appear somewhat suspect. The C₂-C₃ bond is unreasonably short and a surprisingly high degree of bond alternation is found in the benzenoid portion of the molecule. The results for these latter two systems are also given in Table III. The present calculated values are all in better agreement with experiment than those found by HMO methods.⁴

The above theoretical results for 1,4-naphthoquinone and 9,10-anthraquinone are subject in part to generalization. The benzenoid component of the molecule strongly resembles the corresponding hydrocarbon which in these cases is benzene. Systems **30**, **32**, **34**, and **36** have lengths for the bonds in the nonquinonoid ring equivalent to those in naphthalene. Other systems, *e.g.*, **31**, **33**, and **35**, show apparent benzene and phenanthrene units.

C. Dipole Moments

All quinones without centers of symmetry should pos-

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(27) J. Gaultier and C. Hauw, *C. R. Acad. Sci.*, **258**, 619 (1964).

sess permanent dipoles. Table IV summarizes the available experimental data for 1,2-benzoquinone,²⁸ 1,2-naphthoquinone,²⁸ 1,4-naphthoquinone,²⁹ 9,10-phenanthrenequinone,²⁹⁻³¹ and 5,12-naphthacenequinone.³² Calculated values of the π -dipole moments are also given. SCF calculations of π -dipole moments for nonalternant hydrocarbons yield results in reasonable agreement with theory. While complete neglect of the underlying σ system cannot be justified there are at present no simple means of estimating the σ moment of a carbon-oxygen double bond. In the case of a *p*-quinone, symmetry decrees that the total σ -dipole moment should be quite small. With the exception of the final system, agreement with experiment is excellent. The reported value for 5,12-naphthacenequinone appears unusually large in view of its structure. A value less than that for 1,4-naphthoquinone would have been expected.

HMO calculations have been carried out on 1,2-benzoquinone.²⁸ A value of 7.5 D was obtained which was brought into agreement with experiment by subtracting 1.5 D as an empirical correction for adjacent carbonyl groups.³³ Béry, using an SCF approach, later obtained a value of 4.85 D.³⁴ As in the present work, no such empirical corrections were utilized.

D. Vibrational Spectra

Although complete normal coordinate analyses have been carried out for 1,4-benzoquinone³⁵ and 1,4-naphthoquinone,³⁶ such results are exceptional. For the present, attention will be directed toward the relationship between the carbonyl stretching frequency and the corresponding bond orders. Berthier, Pullman, and Pontis have correlated the carbonyl stretching frequencies for 13 compounds, including seven quinones, with bond orders obtained *via* HMO calculations.³⁷ A correlation coefficient of 0.977 was found in the above case. In carrying out the corresponding SCF correlation, no improvement could be found. Despite this, however, an extension of the above correlation was attempted. Table V contains available carbonyl stretching frequencies for quinones.³⁸⁻⁴³ Their correlation with SCF bond orders is poor. A correlation coefficient of only 0.847 is found. The variation among these compounds is not great. An experimental range of 63 cm^{-1} and a calculated difference of 0.057 unit of bond order is

found. When the non-quinone carbonyl compounds were added to the data, the correlation coefficient was

Table V. Carbonyl Stretching Frequencies for Some Quinones

System	$\nu_{\text{C=O}}$	$P_{\text{C=O}}^a$	Ref
1	1667	0.872	42
2	1664	0.856	39
3	1678	0.868 (0.869)	41
4	1664	0.846	40
9	1623	0.815	40
12	1675	0.866	38
13	1677	0.869 (0.869)	41
15	1668	0.864 (0.866)	41
16	1683	0.866	40
17	1639	0.828	39
18	1639	0.829	39
20	1685	0.862 (0.863)	41
21	1670	0.839 (0.839)	41
22	1679	0.862 (0.866)	41
26	1684	0.866 (0.866)	43
27	1656	0.827 (0.830)	43
28	1656	0.825 (0.830)	43
29	1678	0.861 (0.862)	43
31	1672	0.861 (0.866)	43
32	1669	0.862	43
33	1684	0.863 (0.864)	43
34	1669	0.839 (0.840)	43
35	1686	0.865 (0.865)	43
36	1664	0.834 (0.843)	43

^a Nonidentical carbonyl groups shown by two bond order terms.

slightly improved to 0.899. A corresponding HMO correlation also yielded a poor coefficient. These negative results cannot be satisfactorily rationalized, although, in view of the compressed range of values, small experimental errors will seriously effect the correlation. Interestingly, with only one exception (2), the bond orders were found in clusters. The 13 *o*-quinones showed bond orders of 0.861–0.872. The bond orders for five of six *p*-quinones were found in the range 0.839–0.846 while the extended systems (molecules in which the carbonyl groups were associated with different rings) had bond orders less than 0.829. All the above correlations were carried out by a linear least-squares approach.

E. Electrochemistry

The facility with which quinones are reduced to the corresponding diphenols is of considerable interest. The polarographic reduction of quinones has been the subject of investigation for over 40 years. Table VI provides a summary of reported reduction potentials. Much of earlier work was carried out by Fieser and his associates,⁴⁴⁻⁵⁰ however, several other groups of workers have also made substantial contributions to the field.^{43,51,52}

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(48) L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53**, 4080 (1931).

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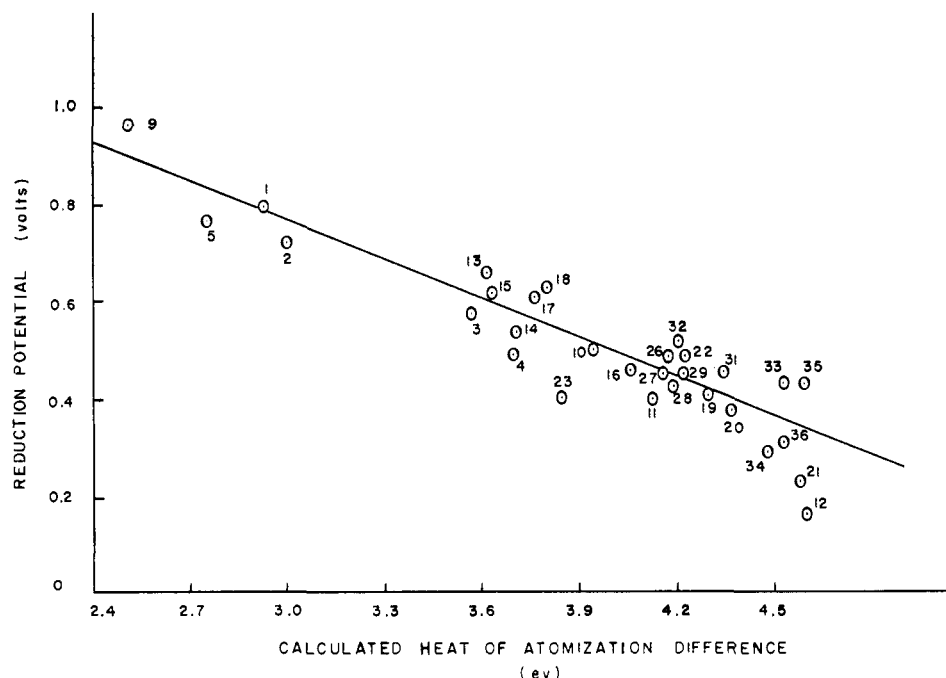


Figure 2. Polarographic reduction potentials vs. calculated heat of atomization differences.

Table VI. Polarographic Reduction Potentials (eV) of Some Quinones

System	$E_{1/2}$	ΔH	Ref
1	0.783	2.927	44
2	0.715	2.992	50
3	0.576	3.571	50
4	0.484	3.704	51
5	0.758	2.752	46
9	0.954	2.514	45, 51
10	0.490	3.959	44
11	0.401	4.126	43
12	0.154	4.599	51
13	0.660	3.621	44
14	0.523	3.727	43
15	0.621	3.633	47
16	0.463 (0.458-0.471)	4.075	44, 49, 51
17	0.612	3.831	43
18	0.614	3.834	43
19	0.424	4.282	52
20	0.380	4.359	52
21	0.228	4.579	46
22	0.465	4.185	46
23	0.392	3.851	46
26	0.492	4.184	43
27	0.438	4.185	43
28	0.441	4.210	43
29	0.442	4.288	43
31	0.451	4.323	43
32	0.503	4.206	43
33	0.446	4.574	43
34	0.292	4.502	43
35	0.445	4.549	43
36	0.302	4.537	43

Various theoretical models have been developed to correlate the reduction potentials of quinones. Most work in this area has been based upon HMO approaches. Evans has developed a simplified method in which the effects of the heteroatoms are neglected.⁵³ The reduction potentials are considered as functions of the differences in resonance energy between the quinone and

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the corresponding dihydroxy aromatic. The resonance energy of the latter is equivalent to that of the parent hydrocarbon. By assuming that the electrons of the carbonyl groups are completely localized in these bonds, Evans shows that the resonance energy includes no contribution from these groups or any otherwise isolated double bonds. In correlating reduction potentials by this approach, Evans obtained separate correlations for ortho and para compounds.⁵³ These results, however, might be somewhat suspect in that the assumption of complete electron localization in the carbonyl bonds is too severe. Evans and coworkers have themselves reexamined the problem by recalculating the resonance energies for quinones in a "normal" manner.⁵⁴ A double correlation was again obtained. While Gold has shown that a judicious adjustment of the HMO parameters can lead to a single correlation,⁵⁵ Basu, using a model based upon the particle in the box, also found separate correlations for the reduction potentials of *o*- and *p*-quinones.⁵⁶ While these separate correlations may not be artifacts of the calculation, it should be mentioned that HMO and other simple methods frequently yield dual correlations which coalesce into a single relationship when calculations which allow for interaction of electrons are utilized.^{57,58}

In the present study Evans' second approximation has been utilized. Table VI lists the differences in heats of atomization between the quinones and the corresponding aromatic hydrocarbons. It is possible that determining a difference between quinones and diphenols might improve the correlation to be obtained. The present approach was utilized, however, to allow for direct comparison with earlier results. The heats of formation of a series of diphenols should, in any event,

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Table VII. Parameters Required for Calculation of Resonance Integrals

Bond	D'' , eV	D' , eV	r'' , Å	r' , Å	a'' , Å ⁻¹	a' , Å ⁻¹	F , Å	G , Å
CC	5.5600	3.9409	1.338	1.512	2.3177	2.0022	1.512	0.174
CO	7.1011	3.9559 (3.9987)	1.208 (1.230)	1.395	2.1787	1.7190 (1.7870)	1.395	0.187 (0.165)

parallel those of the corresponding hydrocarbons. Figure 2 shows the correlation obtained. A fair correlation coefficient of 0.920 was found. The average deviation of points was 0.05 V. As a single correlation this is appreciably better than has been evaluated to date.

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Appendix

As has been stated in the text, the standard Dewar-Morita parameterization for calculation of resonance integrals and their variation as a function of bond length was modified for carbon-oxygen bonds. This was

necessitated by the use of a shorter value for an unconjugated carbon-oxygen double bond. Using standard notation, Table VII contains the values of bond energies (D), equilibrium bond lengths (r), Morse constants (a), and empirical parameters F and G required in a Dewar-Schmeising thermocycle. The superscripts refer to unconjugated double bonds and "pure" sp²-sp² single bonds. The final two terms in the table are utilized to calculate bond length as a function of bond order by the equation

$$r = F - Gp$$

Those entries in parentheses are those originally used by Dewar and Morita. No other changes in parameterization were made. All one center terms may be found in Table I of ref 17.

Electrochemistry in Media of Intermediate Acidity.

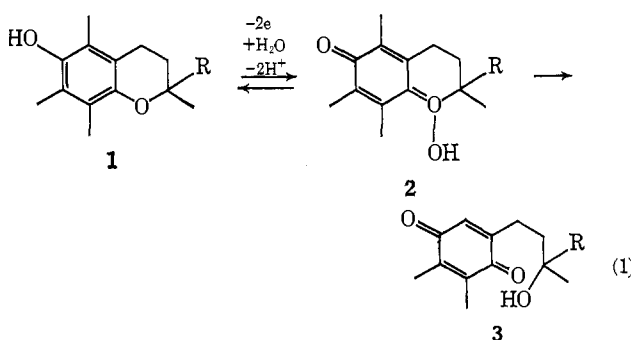
VIII. Reversible Oxidation Products of the α -Tocopherol Model Compound. Cation Radical, Cation, and Dication¹

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Abstract: In acetonitrile, the α -tocopherol model compound (1) undergoes "reversible" two-electron oxidation, the degree of reversibility depending upon the proton concentration. In the presence of strong acid, the two-electron oxidation product is stable and spectral measurements indicate that it has the dication structure 7. Oxidation of 1 in trifluoroacetic acid or in dichloromethane-trifluoroacetic acid results in the reversible formation of the cation radical 9. The acidity of 9 is unusually low as compared to other phenolic cations. The dication 7 can be generated by chemical oxidation of solutions of 9 by addition of chemical oxidants such as perchloric acid. Likewise, 7 can be generated directly by the action of antimony pentachloride in dichloromethane solution. The two-electron oxidation product in acetonitrile containing acid is the phenoxonium ion, 8, which is remarkably stable in that medium.

The widespread occurrence of α -tocopherol and related chromanols in nature² and their action as natural antioxidants have prompted a host of chemical studies on their redox behavior. Many investigators have attempted to find the copartner of α -tocopherol in the reversible oxidation-reduction couple detected polarographically.³ Smith and coworkers, who worked with 50% aqueous methanol solutions, suggested that the reversible couple was $1 - 2e \rightleftharpoons 2$ and that 2 was unstable reacting irreversibly to form 3.³ Boyer later



(1) Part VII: O. Hammerich and V. D. Parker, *J. Amer. Chem. Soc.*, in press.

(2) R. A. Morton, "Biochemistry of Quinones," Academic Press, New York, N. Y., 1965.

(3) L. I. Smith, I. M. Koltoff, S. Wawzonek, and R. M. Ruoff, *J. Amer. Chem. Soc.*, **63**, 1018 (1941).

believed that he had isolated the two-electron oxidation product and assigned the epoxide structure, 4.⁴ It was

(4) P. D. Boyer, *J. Amer. Chem. Soc.*, **73**, 733 (1951).