Ring Strain Effects. III. Reduction and Oxidation Potential Shifts[1]

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Abstract: Half-wave reduction potentials were determined for a series of 1,4-naphthoquinones containing fused rings in the 2,3 positions. A dramatic change in reduction potential was observed as the fused ring size was reduced from a six-membered ring to a four-membered ring. Cyclic voltametric studies indicated the reductions were reversible on the polarographic time scale. Similar, though less dramatic, results were obtained for the fused a and b ring naphthalene series. The changes in half-wave reduction potentials are correlated using Streitwieser's hybridization model within the Hückel framework. Also, oxidation potentials were obtained for the strained and strain-free naphthalene compounds and the effects of ring strain were again demonstrated. The importance of hyperconjugation is discussed.

The remarkable changes of the physical and chemical properties of aromatic hydrocarbons upon the introduction of a fused, strained ring have fascinated chemists since the original report of Mills and Nixon[2] some 40 years ago. Markgraf, *et al.*, have recently reported that the basicity of the nonbonding electrons of a nitrogen α to a fused, strained ring decreases as the strain in the ring is increased.[3] It has also been reported that the acidity of protons α to a strained ring increases as the strain is increased.[4,5] We have found that the spin densities in radical anions of aromatic hydrocarbons are substantially perturbed upon the introduction of a strained ring.[6-8] The changes in spin densities were readily correlated within the Hückel framework by simply making the carbon atoms α to the strained ring more electronegative as the fused ring became more strained. Finally, several articles have appeared reporting marked changes in relative reactivities of various positions in a series of hydrocarbons toward electrophilic substitution as ring strain is introduced.[9-13]

Various arguments have been presented to explain these observations.[5,9,10] The only explanation presented to date which accounts for the changes in chemical as well as physical properties is that of Streitwieser.[5] Streitwieser's generalization rests on an orbital electronegativity argument. He points out that the ring-juncture carbons of the aromatic hydrocarbon are forced to rehybridize to accommodate the small bond angles of the fused, strained ring. Accordingly, the atomic orbitals used in the strained ring will have increased p character. If one assumes a conservation of orbitals, the remaining atomic orbitals used to form a σ bond to the carbon atom α to the strained ring will have more s character relative to a normal sp^2 atomic orbital. This increase in s character will result in an increase in the electronegativity of that atomic orbital. The net result is a decrease in the electron density at the α carbon atom. This would account for the reduced reactivity of the α position toward electrophiles and the increase in acidity of the α proton. Also, when the α atom is a nitrogen atom, the reduced basicity of the nitrogen lone pair is accounted for. We have demonstrated that the reduction of σ electron density at the α carbon atoms has the net effect of making these centers more electronegative toward π electrons by the reduced shielding of the nucleus. This effect was put on a semiquantitative basis by the correlation of electron paramagnetic resonance data within the Hückel framework.

In this paper, we would like to point out some rather dramatic changes in half-wave reduction and oxidation potentials upon the introduction of a fused, strained ring. These observations once again can be explained with Streitwieser's hybridization model. Finally, we have been able to correlate the observed half-wave reduction and oxidation potentials within the Hückel framework using the same parameters derived from the correlation of epr data.

Experimental Section

The dc polarographic experiments were performed on a conventional three-electrode operational amplifier apparatus. The cyclic voltametric (CV) experiments were performed on a solid-state, three-electrode instrument.[14] Cell design[15] was such that ir effects were minimized through micrometric positioning of the working electrode relative to the reference electrode. The reference electrode was aqueous sce with a nonaqueous salt bridge. This same cell design and instrumentation were used in the CV oxidation work.

A Beckman rotating platinum disk electrode (rpd) was also used to determine oxidative $E_{1/2}$ values. Rotation speeds varied between 0 and 100 rps.

The dc polarography was conducted at a dropping mercury electrode (dme), while the CV was done using a spherical platinum bead electrode (spe) and a hanging mercury drop electrode (hmde).

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[1] A preliminary report of this work has been published: R. D. Rieke, W. E. Rich, and T. H. Ridgway, *Tetrahedron Lett.*, 4381 (1969).

[2] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

[3] J. H. Markgraf and R. J. Katt, *Tetrahedron Lett.*, 6067 (1968); J. H. Markgraf and W. L. Scott, *Chem. Commun.*, 296 (1967).

[4] R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).

[5] A. Streitwieser, Jr., G. Ziegler, P. Mowery, A. Lewis, and R. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

[6] R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).

[7] R. D. Rieke and W. E. Rich, *J. Amer. Chem. Soc.*, **92**, 7349 (1970).

[8] R. D. Rieke, S. Bales, C. F. Meares, and L. I. Rieke, submitted for publication.

[9] J. Vaughn, G. J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).

[10] J. B. F. Lloyd and P. A. Ongley, *ibid.*, **20**, 2185 (1964).

[11] G. Berthier and A. Pullman, *Bull. Soc. Chim. Fr.*, 88 (1960); H. Tanida and R. Muneyuki, *Tetrahedron Lett.*, 2787 (1964).

[12] J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **21**, 245 (1965).

[13] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. B*, 12 (1969).

[14] Circuit diagrams available from T. H. Ridgway, Chemistry Department, University of North Carolina, Chapel Hill, N. C.

[15] R. P. Van Dyne, paper in preparation.

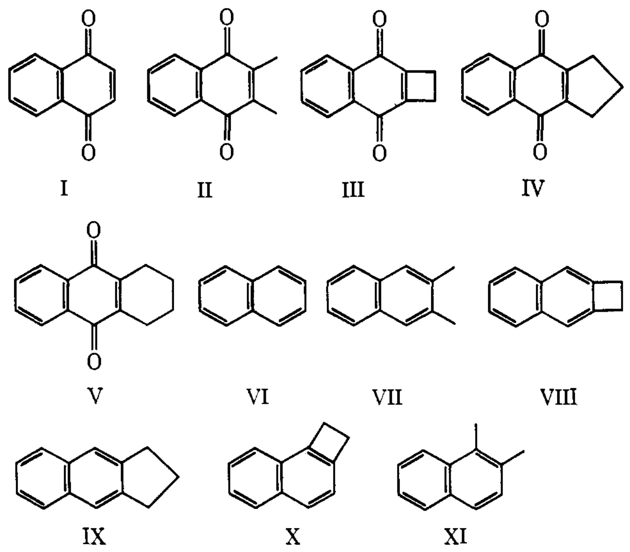

Figure 1. Compounds under investigation.

Limited reductive CV was performed on the naphthalene series due to drop detachment in the potential region under investigation.

All studies were conducted in 0.1 *M* tetraethylammonium perchlorate (TEAP)-acetonitrile solutions with background currents of less than 2 μA within the limits of +2.0 and −2.8 V at slow sweep or rotation rates.

The platinum electrodes were pretreated with HNO_3 for 2 min, washed with distilled H_2O, and dried before each CV or rpd experiment. Then a negative potential of about −0.5 V was applied to the electrode for a few seconds prior to usage. All electrochemical experiments were reproducible if this electrode pretreatment was used.

The concentration of the electroactive species was less than 5×10^{-4} for all experiments to minimize adsorption effects.

Chemicals. Both 1,4-naphthoquinone and 2,3-dimethyl-1,4-naphthoquinone were obtained from Eastman Chemical Co. They were recrystallized from ethanol several times and dried over P_2O_5. Tetraethylammonium perchlorate was obtained from Eastman Chemical Co., recrystallized from methanol-water, and dried in a vacuum oven. Acetonitrile was obtained from Fisher as certified grade, refluxed in $KMnO_4$ and anhydrous Na_2CO_3, and distilled under nitrogen. The distillate was then distilled, *in vacuo*, from P_2O_5. Gas chromatography using a Porapak column showed the amount of water to be less than 2 mmol. For the oxidative work, spectro grade acetonitrile was used after Al_2O_3, which had been heated at 250° for 24 hr, was added. This drying method yielded acetonitrile with less than 1 mmol of H_2O and gave excellent background limits both anodically and cathodically. After storage over Al_2O_3 for several weeks, a cathodic peak appears at −2.5 V, the origin of which is unknown.

Results

The dc polarograms of the compounds were consistent with a reversible one-electron model for compounds I–V (given in Figure 1). There was no evidence of adsorption, pre-, post-, or catalytic chemical kinetics. The observed $E_{1/2}$ values are given in Table I. The liquid junction potential between the aqueous saturated calomel electrode (sec) and the solvent is unknown, which precludes the establishment of absolute thermodynamic results. But since this potential is constant, it poses no hindrance to the use of the $E_{1/2}$ values for establishing relative energy levels.

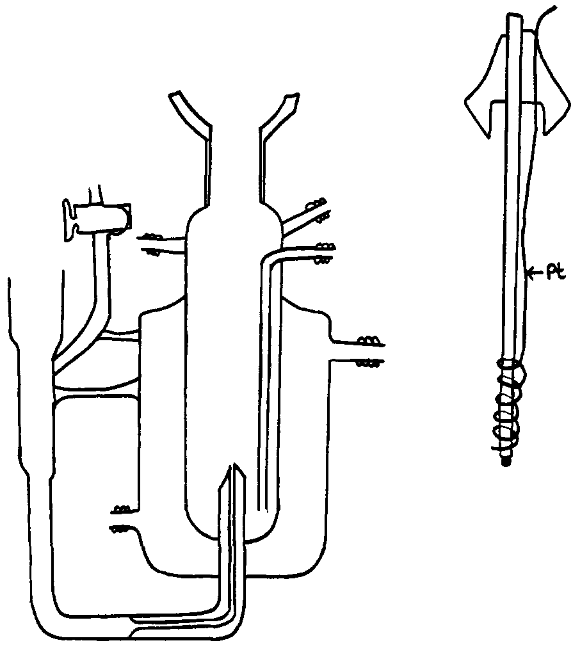

Figure 2. Cell used for CV experiments to minimize ir drop.

In order to guard against the possibility that the observed $E_{1/2}$ values are not truly representative of $E°$ due to adsorption or kinetic complications not detected by the polarographic technique,[16] a more detailed electrochemical investigation was undertaken. Cyclic voltammetry was chosen as the technique best suited to detecting the presence of such complications.[17–19] The instrument used had no provision for solution-resistance compensation other than the usual three-electrode configuration, which does not compensate for the resistance between the tip of the probe electrode and the working electrode. To minimize the effects of this uncompensated resistance, the cell shown in Figure 2 was used. The design allows a spacing of less than 5 mm, which produces resistance in the order of 50 ohms even in nonaqueous media such as acetonitrile.[15]

Table I. Half-Wave Reduction Potentials from Polarography at Dme and CV on the Quinone Series

Compd[a]	$-E_{1/2}$ (dme)[b]	$-E_{1/2}$(hmde)[c,d]	$-E_{1/2}$(spe)[d]
I	0.685	0.68	0.68
II	0.846	0.85	0.85
III	0.695	0.70	0.70
IV	0.748	0.74	0.74
V	0.854	0.84	0.85

[a] All values *vs.* sce. [b] These values are the average of at least three separate determinations and are accurate to ±5 mV. [c] For both the hmde and spe, the E_p values were converted to $E_{1/2}$ values by $E_{1/2} = 0.8517E_p$ for a reversible system. [d] The anodic and cathodic peak separation was measured at the slowest sweep rate, 0.1 V/sec, and was, in all cases, between 60 and 75 mV with compound V being 75 mV.

The sweep rates used were 0.1, 0.5, 5.5, and 50 V/sec. It should be noted that at the highest sweep rate there was significant distortion due to double layer charging. The results of this study are given in Table I. There is quite good agreement between polarographic $E_{1/2}$ values and the peak potentials E_p at the hanging mercury drop electrode after application of the E_p conversion, the disagreement being less that 10 mV

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(16) M. E. Poever, "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967.

(17) R. S. Nicholson and Irving Shain, *Anal. Chem.*, **36,** 706 (1964).

(18) R. H. Wopshall and Irving Shain, *ibid.*, **39,** 1535 (1967).

(19) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1967, Chapter 5.

at a sweep rate of 0.1 V/sec. Use of an X–Y recorder showed no detectable shift in either the anodic or cathodic E_p values. The faster sweep rates necessitated the use of oscillographic methods where no detectable shifts were observed at 5.5 V/sec. Slight shifts at the highest sweep rate could be attributed to double-layer distortion. Plots of the cathodic peak current I_{p_c} *vs.* the square root of the sweep rate ($V^{1/2}$) showed a linear relationship with zero intercept, indicating the lack of detectable chemical kinetic complications. The shapes of the voltamograms were consistent with a simple, reversible one-electron reduction to a stable product radical. This indicates that within the time scale of the experiments, the parent molecules simply reduce to the stable radical and the polarographic $E^{1/2}$ values observed should be representative of the $E°$ values. Since the molecules are quite similar in size and shape, the effects of the diffusion coefficients should be negligible. In a companion study, these compounds were reduced electrochemically and the resultant species studied by esr.[7] These radicals were stable for days under vacuum. A comparison study, using CV, was performed at a spherical platinum electrode (spe). The results of this experiment are given in Table I. Again, all the compounds appear to be highly reversible and indicate that no spurious electrode adsorption effect is causing the marked potential changes.

The general conclusions which can be drawn from the electrochemical evidence are that the results on the two electrodes are equivalent and that the products of the electrochemical generation are the same at all Pt and Hg electrodes.

The analogous naphthalenic compounds were also investigated polarographically and the results are summarized in Table II. The waves occur quite close to solvent breakdown with the electrolyte and solvent purification level used. Due to the breakdown, the drop time is quite erratic in some cases and the diffusion plateaus tend to be more poorly defined than in the quinone series. There is also some evidence of maxima. Attempts to investigate the systems by cyclic voltammetry were only partially successful as the mercury thread in the hmde was prone to breakage resulting in drop detachments. Voltamograms for naphthalene and naphtho[*b*]cyclobutene were successfully obtained at the hmde. The results of these experiments are inconclusive, but the waves appear to be quasireversible. These results are only obtained if the solutions are freshly prepared, which indicates that some solution reaction does in fact occur. Electrochemical generation of a stable radical whose esr signal is consistent with a simple one-electron reduction[7] tends to support the assumption that the reactions are all relatively uncomplicated but the evidence is much less persuasive than in the case of the quinone analogs. Under these circumstances the $E_{1/2}$ values should be perhaps regarded with some suspicion and merely taken as indicative of a general trend in the effects of ring strain on the relative MO energy level. A good discussion on MO energy correlation with $E_{1/2}$ values of hydrocarbons is given by Poever.[16] The possibility of adsorption is particularly distressing and a further chronocoulometric study of this system is in progress.

Table II. Half-Wave Reduction Potentials at Dme[a] of the Naphthalene Series

Compd	$-E_{1/2}$[b] *vs.* sce
VI	2.58
VII	2.68
VIII	2.62
IX	2.66
X	2.65
XI	2.66

[a] Dropping mercury electrode. [b] These values are accurate to ±10 mV.

Discussion

Molecular Orbital Calculations. The observed order of half-wave reduction potentials for the three series of compounds reported is readily interpreted within the Hückel framework using Streitwieser's "hybridization effect model." In this model the carbon atoms α to the fused strained ring become more electronegative while the ring juncture carbon atoms become more electropositive. This can be effected in the Hückel framework by simply adjusting the coulomb integrals of the appropriate carbon atoms.

Using simple perturbation theory, one can approximate the magnitude of the changes in coulomb integrals. First-order theory predicts that when a coulomb integral is varied in a molecule, the energy of the *i*th molecular orbital of the π system is changed by an amount

$$\partial E_i = C_{ir}^2 \partial \alpha_r$$ [20]

and this effect is additive.

C_{ir} is the coefficient of atom *r* in the *i*th molecular orbital and $\partial \alpha_r$ is the change in the coulomb integral of the *r*th atom caused by some perturbation.

First considering the quinone series,[21,22] one finds that the Hückel coefficients of the lowest unfilled molecular orbital for the 1 and 2 positions of the parent 1,4-naphthoquinone are essentially identical. This fact, in conjunction with the fact that the reduction potential of the parent 1,4-naphthoquinone (I) and the 1,2-dihydronaphtho[*b*]cyclobutene-3,8-dione (III) are almost identical, suggests that the magnitude of the change in coulomb integrals for positions 1 and 2 will be equal and opposite. Thus the α carbons should be made more electronegative by a certain amount and the ring-juncture carbons should be made electropositive by about the same amount. As the strain in the fused ring is reduced, the α carbons assume standard coulomb integrals. The ring-juncture carbons will still, however, be more electropositive than the two- and three-carbon atoms of the parent compound 1,4-naphthoquinone (I) due to the electron-donating methylene groups. This accounts for the more cathodic reduction potential of compound II compared to compound I. As a first choice of parameters, we chose the parameters found that fit the epr spectra of the radical anions of this

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[20] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **191**, 39 (1947).

[21] All parameters used in the calculation on the parent 1,4-naphthoquinone were those determined by Broze, *et al.*,[22] with the exception of the carbonyl resonance integral, where we used a value of $\beta_{co} = 1.33\beta_{cc}$ instead of $\beta_{co} = 1.38\,\beta_{cc}$. This value was used because we found it correlated the epr spectra of the radical anions of this series of quinones. Either resonance integral gave essentially the same set of coefficients.

[22] M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

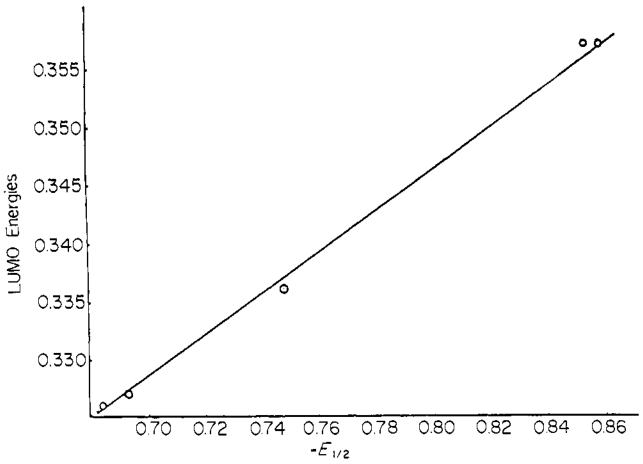


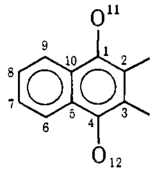
Figure 3. Plot of LUMO energies *vs.* $-E_{1/2}$ for the quinone series.

series of compounds.[7] These parameters and the resulting molecular orbital energies of the lowest unfilled antibonding molecular orbital are given in Table III.

Table III. MO Energies and Reduction Potentials for the Quinone Series

Compd[a]	LUMO energy[b]	$-E_{1/2}$	$h_1{}^{c,d}$	h_2
I	0.3258	0.685		
II	0.3570	0.846		−0.25
III	0.3267	0.695	0.40	−0.45
IV	0.3366	0.748	+0.25	−0.35
V	0.3570	0.854		−0.2

[a] The numbering of quinones is as follows



[b] Lowest unoccupied molecular orbital. [c] $\alpha_r = \alpha_0 + h_r\beta_0$ where α_0 and β_0 have their usual meaning and α_r is the coulomb integral at atom *r*. [d] Oxygen Hückel parameters are given in ref 21.

These MO energies give an excellent correlation of the reduction potentials; not only do they predict the correct order but they can also give fairly good quantitative results as will be discussed later.

The correlation between the reduction potential of a compound and the energy of the lowest unfilled molecular orbital has been adequately substantiated.[23] A plot of the MO energies given in Figure 3 *vs.* the reduction potentials is very good.

It is interesting to note that the parameters used are in accord with the simple first-order theory predictions. For compound III, the most strained compound, the parameters for positions 1 and 2 are approximately equal and opposite. As the strain in the fused ring is relaxed, the coulomb integrals of the 1 and 4 positions approach that of the strain-free molecule. Also, as strain is reduced the coulomb integral of the 2 and 3 positions approaches that of a standard carbon orbital perturbed by an electron-donating alkyl group.

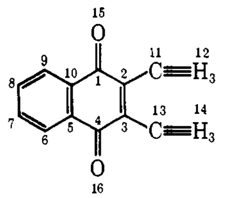


Figure 4. The numbering used in the Coulson-Crawford hyperconjugative calculations on 2,3-dimethylnaphtho-1,4-quinone.

The series of quinones under discussion has the property such that in going from compound II to compound III the methylene protons become oriented more favorably for hyperconjugation. Thus the question arises as to whether the observed order of reduction potentials is a result of hybridization-polarization effects or hyperconjugative effects. In order to gain some insight into this question, hyperconjugative calculations were carried out using Coulson and Crawford's model.[24] Table IV contains the parameters used in the hyperconjugative calculations for 2,3-dimethylnaphtho-1,4-quinone.

Table IV. Parameters Used in Hyperconjugative Calculations on 2,3-Dimethylnaphtho-1,4-quinone

Parameter	Coulson and Crawford's value[a]
$h_{12} = h_{14}$	−0.5
$h_{11} = h_{13}$	−0.1
$k_{11.12} = k_{13.14}$	2.00
$k_{2.11} = k_{3.13}$	0.76
$\beta_{ij}/S_{ij},\ i \neq j$	4.0

[a] Reference 24.

The numbering of the position is shown in Figure 4; the same numbering was used in the hyperconjugative calculations on compound III. Also, the same set of parameters was used for the hyperconjugative calculations on compound III with one exception; $k_{11.13}$ was changed from a value of 0 to a value of 0.76. This is the calculated resonance integral assuming a standard single bond length for bond C_{12}–C_{13} of 1.54 Å. The calculated molecular orbital energies are given in Table V. The calculated LUMO energies for compound II and compound III are essentially the same. Thus one would expect to see no difference in reduction potential for these two compounds. On this basis, it would seem that a purely hyperconjugative model can be ruled out. It should be pointed out, however, that in other systems in which hyperconjugation is felt to be important, similar models have not been very successful.

Table V. Calculated LUMO Energies from the Coulson-Crawford Hyperconjugative Model for the Quinones

Compd	LUMO[a] energy	$-E_{1/2}$
II	0.2852	0.846
III	0.2853	0.695

[a] Lowest unoccupied molecular orbital.

Mills-Nixon Effect. Arnold and Zaugg[25] reported the oxidation-reduction potential of 1,2,3,4-tetrahydro-

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(23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 7.

(24) C. A. Coulson and W. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(25) R. T. Arnold and H. E. Zaugg, *J. Amer. Chem. Soc.*, **63**, 1317 (1941).

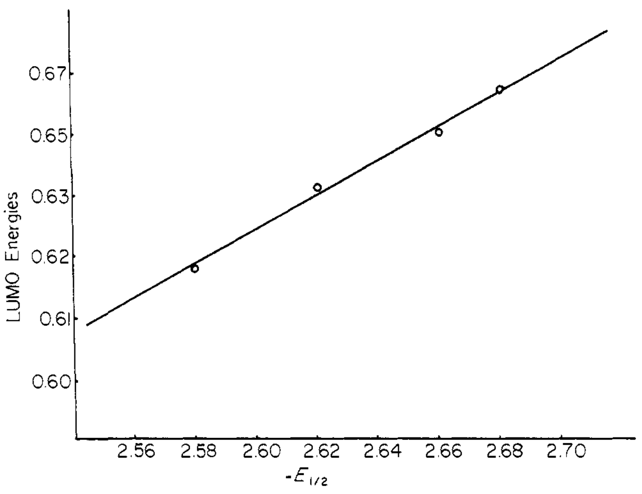

Figure 5. Plot of LUMO energies *vs.* $-E_{1/2}$ for the naphthalene series.

naphthoquinone-5,8 (XII) as being 0.585, while the oxidation–reduction potential for 4,7-hydrindenequinone (XIII) was found to be 0.641. They attributed the easier reduction of (XIII) as resulting from the partial relief of strain as the double bond in the five-membered ring is converted to part of the benzenoid nucleus. Such an argument could be invoked for the naphthoquinone data we have presented in this paper. It would be hopeless to try to calculate this effect by one of the more sophisticated molecular orbital approaches such as CNDO because of lack of data on the molecular geometries of the neutral or radical anion molecules. Guessing at bond lengths and bond angles would not be much more satisfying at this point than assigning Hückel parameters.

One could treat the problem, within the Hückel framework, by simply allowing the 2,3-bond length to increase with increasing strain. We have done this and allowing $B_{2,3}$ to decrease with increasing strain does account for the observed trend of reduction potentials. This model fails badly to predict the spin densities of the radical anions of those molecules which were reported earlier.[7]

Substituted Naphthalenes. As pointed out earlier in the paper, the $E_{1/2}$ values for the naphthalene compounds should be viewed with some suspicion. However, they should reflect the general trend in the energy of the lowest vacant orbital with increasing strain. Again, the $E_{1/2}$ values become more anodic with increasing strain. Streitwieser's "hybridization effect" model can once again be used to correlate the observed $E_{1/2}$ values. The Hückel coefficients of the lowest vacant molecular orbital for naphthalene are $C_1 = 0.425$ and $C_2 = 0.263$. Therefore, using the simple perturbation argument, one would expect that the coulomb integrals for positions 1 and 4 should not be as electronegative as positions 2 and 3 are electropositive. This is required to explain the fact that compound IX reduces at a potential more cathodic than compound VIII but also at a potential more anodic than compound VII, the strain-free model. Using the parameters $h_1 = 0.10$ and $h_2 = -0.30$ for compound VIII and intermediate values for compound IX, one obtains the molecular orbital energies given in Table VI. A plot of the orbital energies *vs.* $E_{1/2}$ values is given in Figure 5 and once again the correlation is very good.

Table VI. Calculated LUMO Energies for the Naphthalenic Compounds and Their $E_{1/2}$ Values

Compd	LUMO energy[a]	h_1	h_2	$-E_{1/2}$
VI	0.6180			2.58
VII	0.6473		−0.20	2.68
VIII	0.6315	+0.10	−0.30	2.62
IX	0.6388	+0.05	−0.25	2.66

[a] These values are in units of β_0, where $\alpha_r = \alpha_0 + h_r\beta_0$.

The parameters used to correlate the epr data for the radical anions of this series of compounds were $h_1 = h_4 = 0.2$ and $h_2 = h_3 = -0.2$ for compound VIII with intermediate values for compound IX.[7] These parameters will give MO energies which will predict the observed trend but have the one major failing of predicting the reduction potential of compound VIII to be more anodic than compound VI, just opposite to what is observed.

Hyperconjugative calculations using Coulson and Crawford's parameters once again failed to predict the observed order of $E_{1/2}$ values.

Simple dc polarography was carried out on the a-ring series. In this series, the ring juncture carbons are positions 1 and 2 and have Hückel coefficients of the lowest vacant orbital of $C_1 = 0.425$ and $C_2 = 0.263$. The α positions are now carbons 3 and 9, which have Hückel coefficients of $C_3 = 0.263$ and $C_9 = 0.000$. Thus the simple perturbation theory would predict little change in reduction potential with strain if we could use the same parameters as for the b-ring series. The observed values of −2.65 for 1,2-dimethylnaphthalene (XI) and −2.64 for naphtho[*a*]cyclobutene (X) support the model.

Oxidation Potentials. From the above MO calculations on the naphthalene series, one predicts a more positive oxidation potential as strain is increased. The MO energy of the highest filled MO of VII goes from −0.5919 to −0.6192 absolute β as strain is empirically introduced through a variation of Coulomb integrals.

We attempted to measure this effect by determining the oxidative $E_{1/2}$ values using a rotating platinum disc electrode (rpd). Table VII shows the results of this experiment.

Table VII. Half-Wave Oxidation Potentials of Naphthalene Series

Compd	10 rps + $E_{1/2}$[a,b]	100 rps
VI	1.70	1.73
VII	1.54	1.57
IX	1.55	1.58
VIII	1.59	1.63

[a] Values given in volts *vs.* sce. [b] Accuracy is to ±10 mV. This represents the average of at least three separate experiments.

The $E_{1/2}$'s for the strained (VIII) and unstrained (VII) molecules differ by about 50 mV. To show that this is not the result of a kinetic effect after electron transfer, $E_{1/2}$ values were obtained at two greatly different rpd rotation rates. Since there was a constant shift for each compound within the series on going from 10 to 100 rps, this suggests that the kinetic effect, probably an electrochemical–chemical–electrochemical (ECE) mechanism,[19] was nearly the same for each compound. This would make a relative correlation of $E_{1/2}$'s to MO energies possible. Adsorption effects were ruled out on the grounds that the diffusion plateaus were linear and undistorted if concentrations were kept below 5×10^{-4} M.

As a further test, cyclic voltammetry (CV) at a spherical platinum bead electrode (spe) was conducted on strained and strain-free molecules VII and VIII, respectively. The results are listed in Table VIII.

Table VIII. E_p Values from CV on Compounds VII and VIII

Compd	E_p[a]	Scan rate[b]
VII	1.56	0.5
	1.58	1.0
VIII	1.63	0.5
	1.65	1.0

[a] E_p is the peak potential *vs.* sce. [b] Scan rate given in volts/second.

In the CV experiment an E_p difference of 70 mV was observed, while an increase in scan rate showed a 20-mV shift for both compounds. Again, the wave shapes showed no distortion and steady-state cyclics retained the same E_p as the first-scan cyclic with no evidence of a reduction peak.

These two experiments indicate that although there are chemical kinetic effects (no reductive wave, E_p shifts with scan rate), the relative order of the oxidation potentials seem to be nearly the same for both experiments. There appears to be no detectable adsorption effects which would cause the E_p to shift. Therefore, one should be able to make a semiquantitative correlation of the oxidative $E_{1/2}$'s with the MO energy of the highest filled MO. This correlation seems to be borne out in the significant anodic E_p shift on going from an unstrained (VII) to a strained (VIII) naphthalene compound.

Conclusions

Changes in reduction and oxidation potentials with ring strain have been observed. In the case of the naphthoquinones, this effect is rather dramatic. These observations indicate that ring strain effects cannot be ignored when one is determining oxidation or reduction potentials.

The changes in reduction and oxidation potentials with ring strain can be correlated within the Hückel framework using Streitwieser's "hybridization effect model." The fact that the same Hückel parameters which were found to correlate the epr data of these compounds also correlate the observed $E_{1/2}$ values is strong support for these parameters as a reasonable working model. It appears that a purely hyperconjugative model can be ruled out. Finally, though the oxidation results are to be considered very suspiciously, they are in the right direction as predicted by this simple model.

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Bridged Polycyclic Compounds. LXV. Electrophilic Addition of Hydrogen Chloride, Acetic Acid, and Their Deuterated Analogs to Benzonorbornadiene[1]

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Abstract: Addition of hydrogen chloride in acetic acid to benzonorbornadiene (**1**) leads to mixtures containing 94% benzonorbornenyl chloride (**8**-Cl) and 6% benzonorbornenyl acetate (**8**-OAc), with the composition invariant over a 90-fold variation in hydrogen chloride concentration. Addition of deuterated species leads to complete scrambling of deuterium between the positions randomized by Wagner–Meerwein rearrangements (**2**-Cl and **3**-Cl) in the chlorides, but less than complete scrambling in the acetate (more **2**-OAc than **3**-OAc). The data are consistent with competing mechanisms, one involving a nonclassical carbonium ion, and the other a syn-concerted "molecular" addition, and are not consistent with any process in which it is necessary to assume that reaction of a carbonium ion with chloride ion is slower than that with acetic acid.

Electrophilic addition of deuterium chloride in deuterium oxide and in methylene chloride to benzonorbornadiene (**1**) has been shown[2] to lead exclusively to monodeuterio-*exo*-5-benzonorbornen-2-yl chloride, with the deuterium mixed equally between the exo-C-3 (**2**) and syn-C-7 (**3**) positions. On the other hand,[2] addition of deuterioacetic acid under a variety of conditions led to mixtures of **2**-OAc and **3**-OAc in which **2** always predominated. With mineral acid present, the amount of **3**-OAc approached that of **2**-OAc, while, in the absence of acid catalysts and in

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(1) Previous paper in series: LXIV. S. J. Cristol, A. R. Dahl, and W. Y. Lim, *J. Amer. Chem. Soc.*, **92**, 5670 (1970).

(2) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).