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RING STRAIN EFFECTS ON HALF-WAVE REDUCTION POTENTIALS

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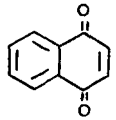
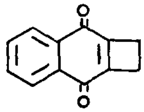
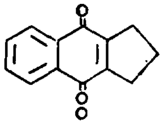
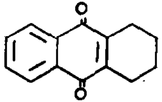
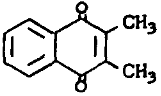
The original report by Mills and Nixon[1] of the dramatic changes in chemical properties of aromatic hydrocarbons upon the introduction of a fused, strained ring dates back some 39 years. The exact origin of this effect is still not clear. At present, two qualitative explanations have been suggested for the increased preference of electrophilic attack at the β-position as the fused ring becomes more strained.[2,3] We would like to report some DC polarographic data on strained compounds which can be explained within the framework of one of these generalizations.

We have determined the half-wave reduction potentials of a series of 1,4-quinones which have fused rings of four, five, and six carbons.[4,5] The results are summarized in Table I. The reduction potential of the 2,3-dimethylnaphtho-1,4-quinone (V) **is essentially**

TABLE I

Polarographic Reduction Potentials of 1,4-Naphthoquinones in CH_3CN

	Compound	$- E_{\frac{1}{2}}$, V[a]
(I)		0.685
(II)		0.695
(III)		0.748
(IV)		0.854
(V)		0.846

(a) A conventional three electrode polarogram was used with potential vs. aq. SCE. Supporting electrolyte was TEAP. All reductions were shown to be reversible by cyclic voltammetric studies.

that of the strain-free 1,2,3,4-tetrahydro-9,10-anthroquinone. Both of these compounds have reduction potentials approximately 165 millivolts more cathodic than the parent 1,4-naphthoquinone. This is expected due to the electron donating methyl and methylene groups.[6] However, when we introduce strain into the fused ring the reduction potential becomes more anodic. Interestingly, the reduction potential of the 1,2-dihydrocyclobuta-[b]naphthalene-3,8-dione[7] (II) is only slightly more cathodic than the 1,4-naphthoquinone (I).

These observations are readily explained within the "hybridization effect model" put forth by Streitwieser.[3] In this model, the ring juncture carbons are rehybridized to accommodate the small bond angles of the strained ring; thus, the sigma bonds in the strained ring have increased p-character and the remaining sigma bonds to the carbons alpha to the strained ring have more s-character. This increase in orbital electronegativity results in a polarization of sigma electrons away from the alpha carbons. The net result is an increase in the electronegativity of the alpha carbons and a decrease in electronegativity of the ring juncture carbon atoms.

We have used this model within the Hückel framework to correlate spin densities in radical anions of strained molecules.[8] The Hückel parameters which correlated the results best for a fused, four-membered ring were, for the alpha carbons, $\alpha = \alpha_0 + 0.2\ \beta$ and, for the ring juncture carbons, $\alpha = \alpha_0 - 0.2\ \beta$.

Simple perturbation theory predicts that when a coulomb integral is varied in a molecule, the energy of a MO Φi of the π-system is changed by an amount

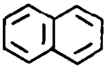
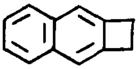
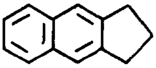
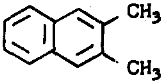
$$\delta\ \varepsilon_i = C_{ir}^{\ 2}\ \delta\ \alpha_r$$

and this effect is additive.[9,13] Using the parameters derived from the EPR data and this simple perturbation theory, one predicts no change in the energy of the lowest unfilled antibonding orbital of 1,4-naphthoquinone upon the introduction of a fused, four-membered ring. This results from the fact that the Hückel coefficients for the one and the two positions are essentially identical.[10] As the strain in the fused ring is reduced, the coulomb integrals for the alpha positions approach that of a "standard" coulomb integral. The coulomb integrals of the ring juncture carbons, however, approach that of a p-orbital with an alkyl group attached or $\alpha = \alpha_0 - 0.15\beta$. Thus a gradual increase in reduction potential is predicted as ring strain is reduced.

We have also measured reduction potentials of naphthalene with fused rings in the a and b positions. The results for the b-ring series are summarized in Table II. The Hückel coefficients for the lowest nonfilled MO of naphthalene are $C_1 = 0.425$ and $C_2 = 0.263$. Thus we predict a lowering of the reduction potential as strain is introduced. This trend is observed; however, the effect is smaller then in the quinone series.[12] In the a-ring series the 1 and 2 positions have Hückel coefficients of 0.425 and 0.263 while the 3 and 9 positions, the positions which will become more electronegative, have coefficients of 0.263 and 0.000. Thus we predict that the reduction potential of 1,2-dimethylnaphthalene (IX) will be essentially equal to that of the naphtho[a]cyclobutene. The observed results of -2.65 for 1,2-dimethylnaphthalene and -2.64 for naphtho[a]cyclobutene support the model.

TABLE II

Polarographic Reduction Potentials of Substituted Naphthalenes in CH_3CN

Compound		$-E_{\frac{1}{2}}$, V[a]
(VI)		2.58
(VII)		2.62
(VIII)		2.66
(IX)		2.68

(a) A conventional three electrode polarogram was used with potential <u>vs</u>. aq. SCE. Supporting electrolyte was TEAP. The reduction of naphtho[b]cyclobutene (VII) was shown to be reversible by cyclic voltammetric studies.

The above data, along with the acidity studies [3,14] and EPR studies,[8] provide substantial support for Streitwieser's "hybridization effect model" for strained compounds. Interestingly, this model predicts that the oxidation potentials for the naphthalene b-ring series should increase as one goes from the strain-free to the strained compounds. Preliminary results confirm this prediction.

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9. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London), A191, 39 (1947).
10. The coefficients are $C_1 = 0.332$ and $C_2 = 0.374$. All Hückel calculations on the quinones used the parameters determined by Vincow and Fraenkel.[11]
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12. We have reduced a mixture of naphtho[b]cyclobutene and 2,3-dimethylnaphthalene with a metal mirror in glyme. The naphtho[b]cyclobutene is reduced first as indicated by the EPR spectrum; continued reduction yields a mixture of radical anions. The equilibrium constant between these two radicals is qualitatively what one would have predicted from the reduction potentials.
13. The $\delta \varepsilon_i$ is the change in the energy of the i^{th} molecular orbital. C_{ir} is the coefficient of atom r in the i^{th} molecular orbital and $\delta \alpha_r$ is the change in the coulomb integral of the r^{th} atom caused by some perturbation.
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