

Organic and Biological Chemistry

Ring Strain Effects on Spin Densities. II.¹ An Electron Spin Resonance Study of the Anion Radicals of a Series of Naphtho-1,4-quinones

Reuben D. Rieke* and William E. Rich

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received April 6, 1970

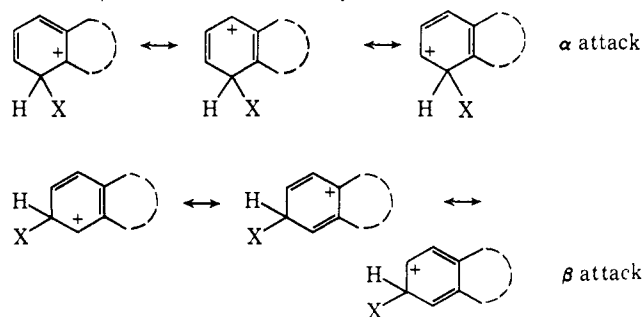
Abstract: Electron spin resonance spectra were obtained for the anion radicals of 1,2,3,4-tetrahydroanthra-5,10-quinone, 5,6-benzindan-4,7-quinone, 1,2-dihydronaphtho[*b*]cyclobutene-3,8-dione, and 2,3-dimethylnaphtho-1,4-quinone by electrolytic reduction in acetonitrile (*in vacuo*). The methylene coupling constants were found to be substantially perturbed by increasing the strain in the fused ring. Using Streitwieser's "hybridization effect model," in which the ring juncture carbons of the fused ring are made more electropositive and the α -carbons more electronegative as strain in the fused ring is increased, the changes in π spin densities can be correlated within the Hückel framework. A simple variation of Q and average methylene bond angles cannot explain the change in methylene splitting constants with strain. Also, other models were investigated without success.

The original report by Mills and Nixon² of the dramatic changes in chemical properties of aromatic hydrocarbons upon the introduction of a fused, strained ring dates back some 40 years. The exact origin of this effect is still not clear. At present, three qualitative explanations have been suggested for the increased preference of electrophilic attack at the β position as the fused ring becomes more strained.³⁻⁵ One of these is the "hybridization effect model" put forth by Streitwieser.⁵ In this model, the ring juncture carbons are rehybridized to accommodate the small bond angles of the strained ring; thus, the σ bonds in the strained ring have increased *p* character and the remaining σ bonds to the carbons α to the strained ring have more *s* character. This increase in orbital electronegativity results in a polarization of σ electrons away from the α -carbons. The net result is an increase in the electronegativity of the α -carbons and a decrease in electronegativity of the ring juncture carbon atoms. The decrease in the electron density at the α -carbons results in a decrease in reactivity toward electrophilic reagents. The net result is an increase in electrophilic attack at the β position.

Vaughan³ has suggested an alternate explanation for these observations which rests on a bond-order argument. He points out that if one compares the two σ complexes for electrophilic attack at the α and β positions, there is a difference in bond orders of the two carbon atoms to which the fused ring is attached. In the case of α attack, as shown in Chart I, the bond order adjacent to the fused ring is two-thirds while for β attack the bond order is only one-third. The larger

bond order between the two carbons to which the fused ring is attached in the case of α attack will tend to destabilize this σ complex relative to the σ complex produced from β attack. This destabilization is expected to increase as the fused ring becomes more strained. Thus, reactivity of the α position toward electrophilic reagents will tend to decrease as the fused ring becomes more strained.

Chart I. Principle Resonance Forms for Wheland Intermediates for α and β Substitution of Benzocycloalkenes



Lloyd and Ongley⁴ have suggested yet an additional explanation based on considerations of changes in compressions and tensions in the bonds of the aromatic ring in formation of the transition state. In this model, the α position exhibits normal reactivity toward electrophiles while the reactivity of the β position is enhanced as strain in the fused ring increases.

Eaborn⁶ has carried out a series of protodesilylations on *o*-xylene, indan, tetralin, and benzocyclobutene. He found that the reactivity of the β position in benzocyclobutene was normal when compared to the strain-free system while the reactivity of the α position was greatly reduced. These results rule out the Lloyd-Ongley explanation. The results were taken as evidence that both strain and hybridization effects were

* To whom correspondence should be addressed.

(1) For paper I in the series see R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).

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

(3) J. Vaughan and G. J. Wright, *J. Org. Chem.*, **33**, 2580 (1968); J. Vaughan, J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).

(4) J. B. F. Lloyd and P. A. Ongley, *ibid.*, **21**, 245 (1965).

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

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

operating to determine the relative reactivities of the α and β positions.

The main purpose of this esr study is to show that Streitwieser's model, within the Hückel framework, correlates the spin densities of the radical anions of a series of strained quinones. We wish to show that variation of Q in McConnell's equation,⁷ $a^H = Q\rho$, and changes in the α -methylene average bond angle alone cannot be used to interpret the results.⁸

The radicals were generated in a vacuum cell with acetonitrile as solvent. *In situ* reduction was unnecessary due to the long lifetime of the radicals under vacuum (2 days). The esr spectra were recorded at temperatures ranging from +20 to -45° to determine if ring flipping could be brought into the esr time scale.

In this paper, we report the esr spectra of the anion radicals of four quinones: 2,3-dimethylnaphtho-1,4-quinone (I),⁹ 1,2,3,4-tetrahydroanthra-5,10-quinone (II), 5,6-benzindan-4,7-quinone (III), and 1,2-dihydro-naphtho[*b*]cyclobutene-3,8-dione (IV).

Experimental Section

Acetonitrile (Fisher Certified grade) was distilled twice from potassium permanganate and anhydrous sodium carbonate and vacuum distilled twice from P_2O_5 . The supporting electrolyte, tetraethylammonium perchlorate (Eastman), was recrystallized from water and dried overnight in a vacuum oven at 60°.

1,2,3,4-Tetrahydroanthra-5,10-quinone (mp 156–160°)¹⁰ was prepared by chromic acid oxidation of a mixture of 87% 1,2,3,4-tetrahydroanthracene and 13% 9,10-dihydroanthracene; the quinone products were separated on a silica gel column with benzene as eluent. The hydrocarbon mixture was prepared by high-pressure hydrogenation using a Raney nickel catalyst.^{11a} **5,6-Benzindan-4,7-quinone** was readily prepared by chromic acid oxidation at room temperature of 5,6-benzindan (K & K Chemicals). Satisfactory analysis was obtained for this compound (mp 164–165°). **1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione**^{11b} was prepared by oxidation of naphtho[*b*]cyclobutene.^{11b} **2,3-Dimethylnaphtho-1,4-quinone** was readily prepared by chromic acid oxidation of 2,3-dimethylnaphthalene^{11b} (Aldrich), mp 124–127°. All of these quinones were recrystallized from alcohol several times, washed, dried, and stored over P_2O_5 prior to reduction.

The anion radicals were generated electrochemically in a vacuum cell designed by Holz.¹² The reference electrode was a 0.1 M Ag–AgClO₄ in DMSO. A conventional three-electrode generating system¹³ was used. Reduction of all compounds was carried out for 30 min; during reduction the solutions turned yellow. Reduction was carried out at a potential of -1.3 V *vs.* Ag–AgClO₄, which corresponds to a potential slightly greater than the first wave for every compound but not into the second wave.¹⁴ Prior to reduction, the acetonitrile solution was degassed until a 10⁻³ Torr vacuum could be maintained. The solution was approximately 10⁻³ M in compound and 0.1 M in TEAP. ESR spectra were recorded on a Varian E-3 spectrometer with X-band frequencies and an E-3 variable temperature accessory. Computation

(7) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

(8) Although the naphthalene series given in ref 1 discusses Streitwieser's model and its relation to the α -proton coupling constant's variation with strain, no discussion is made concerning methylene coupling constants. We report here arguments which support Streitwieser's model exclusively.

(9) The radical anion of 2,3-dimethylnaphtho-1,4-quinone has been reported before (J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **24**, 479 (1955); M. Adams, M. Bluis, Jr., and R. Sands, *ibid.*, **28**, 774 (1958)). However, in neither case was the methyl coupling constant reported nor was the resolution good enough to detect a difference in the coupling constants of the protons in the 5 and 6 position.

(10) H. Meerwein and A. Migge, *Ber.*, **62**, 1046 (1929).

(11) (a) E. A. Garlock, Jr., and E. Mosettig, *J. Amer. Chem. Soc.*, **67**, 2255 (1945); (b) M. P. Cava and R. I. Shirley, *J. Org. Chem.*, **26**, 2212 (1961).

(12) The cell and the reference electrode are described in the Ph.D. Thesis of J. Holz, Yale University, New Haven, Conn., in press.

(13) The generating apparatus was designed by Tom Ridgeway.

(14) R. D. Rieke, W. Rich, and T. Ridgeway, *Tetrahedron Lett.*, 4381 (1969).

of theoretical esr spectra was done using a computer program written by Griffin.¹⁵

Results

The esr spectrum of 2,3-dimethylnaphtho-1,4-quinone (I) was taken at temperatures between +20 and -45°; the change in line width over this range was about 20 mG, which is attributed to exchange broadening. Das¹⁶ has shown that ion pairing in semiquinone radical anions gives rise to alternating line widths. Also, quinones reduced by alkali metals show large changes in spin density distribution as the temperature is varied. None of the quinones showed line-width alternation; however, the coupling constants were slightly temperature dependent. All coupling constants were lowered as the temperature was increased, but in all cases the change was less than 9%. This effect is probably due to cation perturbation as a result of increased ion pairing as the temperature is raised.¹⁷ The following coupling constants were observed for compound I at -45°: $a^H = 0.32$ (two equivalent protons), $a^H = 0.73$ (two equivalent protons), $a^H = 2.51$ (six equivalent protons).

The 1,2,3,4-tetrahydroanthra-5,10-quinone (II) was electrochemically reduced and its esr spectra taken over a range of temperatures previously stated. The exchange broadening was small and no line-width alternation was observed.¹⁸ Coupling constant variation was less than 9% in all cases. The coupling constants at -45° were: $a^H = 0.34$ (two equivalent protons), $a^H = 0.78$ (two equivalent protons), $a^H = 3.28$ (four equivalent protons). It is interesting to note that the β -methylene proton coupling constant must be less than 130 mG, the minimum line width, since it could not be resolved.

The anion of 5,6-benzindan-4,7-quinone (III) was produced electrochemically; the fused, five-membered ring in this quinone is also flipping rapidly compared to the epr time scale, since an average methylene splitting constant is observed for both the α and β positions. The coupling constants at -45° are: $a^H = 0.74$ (two equivalent protons), $a^H = 0.36$ (two equivalent protons), $a^H = 0.18$ (two equivalent protons), and $a^H = 2.73$ (four equivalent protons). These coupling constants varied less than 3% with temperature.

1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione (IV) radical anion yielded the following coupling constants at -45°: $a^H = 0.44$ (two equivalent protons), $a^H = 0.75$ (two equivalent protons), and $a^H = 2.92$ (four equivalent protons). These coupling constants also vary less than 9% with temperature, becoming slightly less with increasing temperature. There was no sign of alternating line widths at any of the temperatures studied, indicating that either the rate of ring

(15) B. Griffin, Ph.D. Thesis, Washington University, St. Louis, Mo., 1968.

(16) M. P. Khakhar, B. S. Prabhananda, and M. R. Das, *J. Amer. Chem. Soc.*, **89**, 3100 (1967).

(17) A complete discussion of ion pairing in semiquinones is given by M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967).

(18) Since the concentration of the radical is not known for any of these experiments, exchange broadening cannot be studied as a function of ring strain. Yet, from our experiments, we have noted that compound IV exhibits pronounced line-width changes with temperature while compounds I and II do not. The possibility of strain effecting electron exchange is now under investigation.

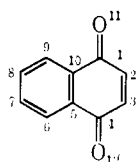
flipping of the four-membered ring is fast compared to the epr time scale or the four-membered ring is flat.¹⁹

The parameters used to assign splitting constants were derived from a variation of coulomb integrals²¹ using Streitwieser's model.⁵ Table I shows both

Table I. Calculated and Observed Hyperfine Coupling Constants for the Quinones^{a,b}

Compd no.	Position	A ^c	B ^d	C ^e	D ^f
I	1				
	2	-0.20	26	2.41	2.51
	6		24	0.36	0.32
II	1				
	2	-0.20	34	3.15	3.28
	6		24	0.36	0.34
III	1	+0.25			
	2	-0.35	37	2.71	2.73
	6		24	0.37	0.36
IV	1	+0.40			
	2	-0.45	51	3.14	2.92
	6		24	0.38	0.44
	7		24	0.83	0.75

^a Numbering for all quinones is as follows



^b The parameters used for all quinone carbonyls were: $\alpha_o = \alpha_o + 0.4\beta_{co}$, $\beta_{C=O} = 1.33\beta_{co}$. ^c The variation in the coulomb integral for carbon for a particular position is given by $\alpha_c' = \alpha_o + A\beta_{co}$. ^d The value of Q which was used to calculate the hyperfine coupling constants. The selection of Q for each molecule is discussed in the text. ^e The calculated coupling constants in gauss. ^f The experimental coupling constants in gauss.

calculated and experimentally derived spin densities and Hückel parameters.

Discussion

Compound I. The coupling constants for this anion radical were assigned on the basis of simple HMO results given in Table I and the work of Broze.²² These authors determined the best HMO parameters for a series of quinones, including 1,4-naphthoquinone, to fit their esr spectra, including O¹⁷ splittings. These parameters were: $\alpha_o = \alpha_c + 0.4\beta_{co}$ where α_o is the coulomb integral for oxygen and α_c and β_{co} have their usual meanings;²¹ for the carbonyl resonance integral they used $\beta_{co} = 1.38\beta_{cc}$. However, for our study a value of $\beta_{co} = 1.33\beta_{cc}$ was used. Ir investigations on substituted quinones²³ have shown that the electron

(19) Electron paramagnetic resonance studies on the radical anion of benzocyclobutene²⁰ have shown that the four methylene protons in the fused ring are equivalent down to -90° in 1,2-dimethoxyethane. In addition, the four methylene protons of naphtho[b]cyclobutene anion radical were equivalent at temperatures down to -65° , the lowest temperature studied.¹

(20) R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **92**, 1418 (1970).

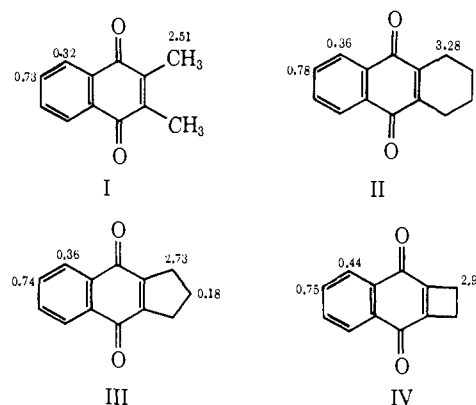
(21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 4.

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

(23) M. L. Josien and N. Fuson, *Bull. Soc., Chim Fr.*, **19**, 389 (1952).

donating ability of methyl groups favors the ionic carbonyl resonance form, thus lowering the effective bond order of the carbonyl. This resonance integral value gave good results. With regard to the coulomb integral, the 2 and 3 positions were made more electro-positive due to the electron-donating ability of methyl groups. The inductive model²¹ was used with $\alpha_c' = \alpha_c - 0.2\beta_{cc}$. Chart II shows coupling constant assignments based on HMO results.

Chart II. Assignment of Coupling Constants (Gauss) Based on the HMO Calculations in Table I

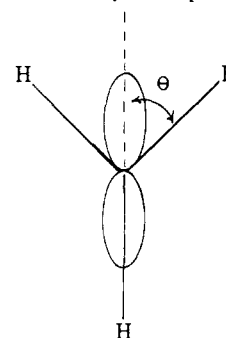


The value of Q in McConnell's equation was taken to be 24 for all positions except 2 and 3. Broze has shown that $Q = 24$ provides excellent correlation of spin densities for all positions in the 1,4-naphthoquinone anion radical.²² Equation 1 was used to calculate the methyl hyperfine coupling constants.²⁴ In this equation, $\beta_2 \cos^2 \theta$ is the hyperconjugative

$$\alpha_{\beta}^H(\theta) = (\beta_o + \beta_2 \cos^2 \theta)\rho^\tau \quad (1)$$

contribution to Q while β_o is the spin polarization contribution and has a magnitude of -3.09 G.^{25, 22} Chart III defines θ . ρ is the HMO spin density. The

Chart III. Front View of Methyl Group and Adjacent p Orbital



value of β_2 has been calculated to be 58.5.²⁶ Therefore, $Q = 26$ for methyl hydrogens with an average value of $\theta = 45^\circ$. These parameters gave excellent results for compound I.

Compound II. Using HMO results given in Table I, the coupling constants for the anion radical were assigned as shown in Chart II. The HMO parameters used were the same as for compound I. The only difference in the calculations on I and II was that the value of $\cos^2 \theta$ at positions 2 and 3 was different, giving rise to a change in splitting constants. From mo-

(24) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(25) D. H. Levy and R. J. Myers, *ibid.*, **43**, 3063 (1965).

(26) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

lecular models, the average value of θ was found to be 37° . Using this value of θ , a Q value of 34 was obtained. The calculated hyperfine coupling constant for the methylene protons is given in Table I and is in excellent agreement with the experimentally observed value. The coulomb integrals for positions 2 and 3 were taken to be the same as in 2,3-dimethylnaphthalene, the assumption being that the electron-donating ability of a methyl group and a methylene are essentially identical. Also, since fused, six-membered rings are strain free, the coulomb integrals for positions 1 and 4 were taken to be the same as in 2,3-dimethylnaphthalene.

Compound IV. This is the most strained compound in the series and, according to Streitwieser's model,^{11b} the carbon atoms at the ring juncture became more electropositive while the carbon atoms α to these positions become more electronegative. This is a result of rehybridization to accommodate the strain. This resulting change in orbital electronegativity was effected within the Hückel framework by varying the coulomb integrals at the appropriate positions. Different parameters were tried and the best ones were found to be $\alpha_{1,4} = \alpha_c + 0.4\beta_{cc}$ and $\alpha_{2,3} = \alpha_c - 0.45\beta_{cc}$. It has been shown for the naphtho[b]cyclobutene radical anion²⁷ that $\alpha_{1,4} = \alpha_c + 0.2\beta$ and $\alpha_{2,3} = \alpha_c - 0.2\beta$ correlate the epr data very well. Thus, in the quinone series, the 1,4 positions which are α to the fused ring are also made more electronegative. The 2,3 positions are correspondingly made less electronegative. The $Q_{2,3}$ value for the methylene protons in the fused, four-membered ring was taken as 51.²⁸ The value of $Q_{2,3}$ for the methylene protons was determined from eq 1, letting $\theta = 16^\circ$ as determined from molecular models. It is felt that this angle represents a maximum angle and indeed may be less than 16° . If one were to use the spin densities for the 2,3 positions of compound I, a Q of 31 would be required to fit the observed hyperfine coupling constants. This value of Q would require that θ be the unrealistic value of 40° . Chart II shows the coupling constant assignments based on HMO spin densities and a Q value of 24 for the 6 and 7 positions and a Q value of 51 for the 2 and 3 positions. The results are in excellent agreement with experiment.

If one were to use $Q = 51$ and the spin density at the 2 position for compound I, which would assume no correction for ring strain was necessary, a splitting constant of 4.73 would be predicted for the methylene protons. In order to get a good correlation, the π spin density at positions 2 and 3 must decrease with increasing strain. The model presented here gives an excellent fit to the observed spectra.

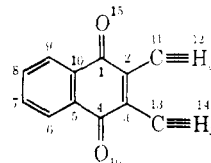
Compound III. As strain is diminished, polarization of the σ framework decreases. HMO calculations using the parameters $\alpha_{1,4} = \alpha_c + 0.25\beta_{cc}$ and $\alpha_{2,3} = \alpha_c - 0.35\beta_{cc}$ give good agreement with experimental values when $Q_{2,3} = 37$ and $Q_{6,7} = 24$. Chart II gives the assignment of coupling constants and Table I gives the calculated and experimental spin densities. A $Q_{2,3}$ value of 37 was determined from $\theta = 34^\circ$; the value for θ was determined from molecular models. Unlike compound II, the β -methylene coupling constant

(27) R. D. Rieke, S. Bales, C. Meares, and L. I. Rieke, to be published.

(28) R. D. Rieke, S. Bales, P. Hudnall, and C. Meares, to be published.

was resolved and found to be 0.18 G. The series of molecules under discussion has the property such that in going from compound II to compound IV the methylene protons become oriented more favorably for hyperconjugation. Thus the question arises as to whether the change in methylene hyperfine coupling constants in the series is due to rehybridization-polarization effects or simply the result of a change in hyperconjugation or a combination of both.²⁹ Accordingly, calculations were carried out using Coulson and Crawford's³¹ model of hyperconjugation. The methyl and methylene hyperfine coupling constants were then calculated using Levy's equations.^{32,33} Chart IV shows the numbering used in these calculations.

Chart IV. Numbering Used in the Coulson-Crawford Hyperconjugative Calculations on 2,3-Dimethylnaphtho-1,4-quinone



The spin densities obtained from this hyperconjugative model in conjunction with Levy's equations gave the methyl hyperfine coupling constants listed in Table II. The aromatic proton coupling constants are

Table II. Hyperfine Coupling Constants For 2,3-Dimethylnaphtho-1,4-quinone (I) and 1,2-Dihydronaphtho[b]cyclobutene-3,8-dione (IV) Using the Coulson-Crawford Hyperconjugative Model

Compd	$k_{11,13}$	$A_H(6)$	$A_H(7)$	$A_{CH_3}^a$
IV	0.76	0.31	0.64	5.73
Exptl		0.44	0.75	2.92
I	0.0	0.31	0.64	3.55
Exptl		0.32	0.73	2.51

^a Calculated from Levy's equations.

also listed; these were calculated from McConnell's equation with $Q = 24$ G.

The same set of parameters was used for the hyperconjugative calculations on compound IV with one exception: $k_{11,13}$ was changed from a value of zero 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 methylene and aromatic proton hyperfine coupling constants are given in Table II.³⁴ The hyperconjugative model does predict an

(29) Colpa and de Boer³⁰ have shown that hyperconjugation is the dominant mechanism for transmitting unpaired spin density from an aromatic π cloud to methyl or methylene protons α to the π system.

(30) J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1964).

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

(32) D. H. Levy, *Mol. Phys.*, **10**, 233 (1966).

(33) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(34) One might question why the values of $k_{11,12} = k_{13,11}$ were not changed in the calculations of compound IV, since the H-C-H bond angle for the methylene protons is about 5° larger than in the methyl derivative, compound I. Mulliken³⁵ has shown that a change in bond angle of $109-120^\circ$ produces a negligible change in the overlap integral $k_{11,12} = k_{13,11}$.

(35) N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 4770 (1954).

Table III. Calculated Hyperfine Coupling Constants for the Radical Anions of 2,3-Dimethylnaphthalene and Naphtho[*b*]cyclobutene Using Streitwieser's Model and the Coulson-Crawford Hyperconjugative Model

Compd	Streitwieser's model ^{a,d,e}				Coulson-Crawford model ^{a,d,e}				$k_{11,13}$
	$A_H(1)$	$A_H(6)$	$A_H(7)$	$A_{CH_2}^2$	$A_H(1)$	$A_H(6)$	$A_H(7)$	$A_{CH_2}^2$ ^c	
2,3-Dimethylnaphthalene									
A	4.54	5.01	1.86	2.05	4.82	4.79	1.83	1.80	0.0
Obsd	4.7	5.0	1.8	1.7	4.7	5.0	1.8	1.7	
Naphtho[<i>b</i>]cyclobutene									
B	4.97	4.20	1.69	4.95 ^b	4.82	4.75	1.84	3.05	0.76
Obsd	5.4	4.2	1.58	5.85	5.4	4.2	1.58	5.85	

^a The HMO parameters for each compound are in the text. ^b A $Q = 51$ was used to calculate the methylene protons. A discussion of how the Q was calculated was presented in the text. ^c The methyl and methylene coupling constants are calculated from Levy's equations. ^d A Q value of 27 was used for the aromatic protons. ^e The compounds are numbered as shown in Chart IV.

increase in the methylene hyperfine splitting constants as one goes from compound I to compound IV. The observed increase of only 16% is far less than the calculated increase of approximately 130%. By arbitrarily varying the hyperconjugative parameters, one could probably get better agreement between the two values. However, this procedure would have little theoretical justification. It was felt that a more justifiable approach would be to check the two models against additional molecules which have strained rings. Accordingly, Streitwieser's model and the Coulson-Crawford hyperconjugative model were also applied to the radical anions of 2,3-dimethylnaphthalene and naphtho[*b*]cyclobutene. The epr spectra of these compounds have been reported earlier but no detailed calculations were included in the paper.¹ The results of these calculations are given in Table III. For the hyperconjugative calculations, the same parameters were used as those used for the 1,4-naphthoquinones. For Streitwieser's model, the following coulomb integrals proved to be best for naphtho[*b*]cyclobutene: $\alpha_1 = \alpha_4 = \alpha_0 + 0.2\beta$ and $\alpha_2 = \alpha_3 = \alpha_0 - 0.2\beta$.

For 2,3-dimethylnaphthalene, the coulomb integrals for positions 2 and 3 were taken to be $\alpha_2 = \alpha_3 = \alpha_0 - 0.15\beta$. It is apparent from Table III that both models adequately describe 2,3-dimethylnaphthalene anion radical. However, for naphtho[*b*]cyclobutene the hyperconjugative model fails on two counts. First and most important is the failure of the hyperconjugative model to predict the increase in spin density at the 1 and 4 positions as strain is introduced into the fused ring. Arbitrary variation of the hyperconjugative parameters cannot correct this deficiency. However, Streitwieser's model does predict an increase in the spin densities of the 1,4 positions and also accounts for the other observed hyperfine splitting constants. The second failing of the hyperconjugative model is the predicted low coupling constant of the methylene protons of the four-membered ring.

Thus Streitwieser's model works well for the two series of anion radicals under discussion, the naphthoquinones and the substituted naphthalenes. However, the Coulson-Crawford hyperconjugative model fails for the substituted naphthalene series and does not work well for the naphthoquinone series. It would seem

from these observations that a purely hyperconjugative model is ruled out.

Calculations were also carried out in which the hyperconjugative model and Streitwieser's model were combined. This combination also correlates the epr data, although seemingly not as well.

In conclusion, it appears that Streitwieser's "hybridization effect model" will correlate the spin densities in the strained molecules presented in this paper. A combination of the Coulson-Crawford hyperconjugative model and Streitwieser's model will correlate the results, but the added complexity adds little to the final result. Finally, a purely hyperconjugative model does not seem to correlate the observed changes in spin density due to ring strain. From these calculations we are not attempting to say that hyperconjugation effects are totally absent in these molecules. We are simply pointing out that a purely hyperconjugative model does not correlate the observed results.

As additional support for Streitwieser's model, it might be pointed out that the half-wave reduction potentials of the 1,4-naphthoquinones and the substituted naphthalenes can be correlated within this model using the parameters cited in this paper. However, a purely hyperconjugative model fails to predict the observed order of reduction potentials.^{14, 36}

These observations represent additional examples of physical properties of strained hydrocarbons which can be qualitatively explained by Streitwieser's "hybridization effect model." The correlation of a broad spectrum of physical properties such as acidity,⁵ basicity,³⁷ polarographic reduction potentials,^{14, 36} anion radical spin densities, and ir stretching frequencies³⁸ with this model provides substantial evidence toward its validity as a reasonable working model.

Acknowledgment. Financial support of this investigation by the University of North Carolina Materials Research Center under Contract SD-100 with the Advanced Research Projects Agency and by the University of North Carolina Research Council is gratefully acknowledged.

(36) R. D. Rieke, W. E. Rich, and T. H. Ridgway, *J. Amer. Chem. Soc.*, in press.

(37) J. H. Markgraf and R. J. Kart, *Tetrahedron Lett.*, 6067 (1968); J. H. Markgraf and W. L. Scott, *Chem. Commun.*, 296 (1967).

(38) R. D. Rieke and W. E. Rich, to be published.