within the desired 1 or 2% agreement. However, the values of ΔE_{act} obtained agree well, whichever value is used. One problem we encountered was the possibility of systematic error in the vpc analysis. Thus experiments, for example selectivities in Table II, frequently exhibited excellent reproducibility within a series, but sets of experiments run at different times, or using slightly different vpc conditions, varied noticeably from set to set.

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(47) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley-Interscience, New York, N. Y., 1965, Chapter 4.

(48) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(49) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).

(50) A. F. Trotman-Dickensen, *Advan. Free Radical Chem.*, **1**, 1 (1965).

Ring Strain Effects. IV.[1] An Electron Spin Resonance Study of the Radical Anions of a Series of Strained Naphthalene Hydrocarbons

Reuben D. Rieke,*[2] Stephen E. Bales,[3] Claude F. Meares,[4] Loretta I. Rieke, and Charles M. Milliren

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

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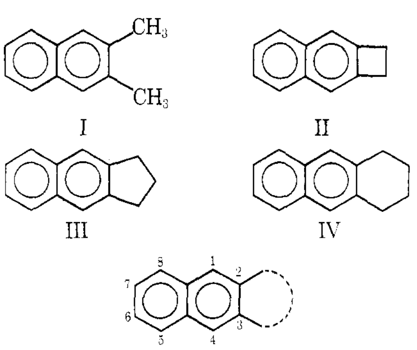
Electron paramagnetic resonance studies have been carried out on a series of substituted naphthalene radical anions. The series was composed of compounds having varying amounts of ring strain in a fused ring in the *b* position. The large spin density perturbations were correlated within the Hückel framework using the Finnegan–Streitwieser model. INDO calculations were also carried out on these molecules and the results are discussed.

Mills and Nixon advanced the first theoretical discussion of the reduced reactivity of the α position of strained benzocycloalkenes in 1930.[5] At present, the origin of this effect is still not clear. Markgraf, *et al.*, have reported that the basicity of the nonbonding electrons of a nitrogen α to a fused, strained ring decreases as the strain in the ring increases.[6] The acidity of protons α to a strained ring has been reported to increase as strain increases.[7,8] Several papers 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] Also, uv and charge-transfer spectra[14] and proton nmr data[15] on benzocycloalkenes have been reported.

Several arguments have been presented to explain these observations.[7-10] The explanation presented by Finnegan[7] and Streitwieser[8] is the only one that accounts for the changes in both chemical and physical properties. In this model, the ring junction carbon atoms containing the fused, strained ring are rehybridized to accommodate the small bond angles. 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 s character results in an increase in orbital electronegativity which results in a polarization of electrons away from the α carbon atoms. This would account for the reduced reactivity of the α position toward electrophiles and the increase in acidity of the α proton. Further, the reduced basicity of the nitrogen lone pair is accounted for when the α atom is a nitrogen atom.

We have demonstrated that the Finnegan–Streitwieser model can also be used to explain the changes in half-wave reduction potentials[1,16] and the changes in spin densities of aromatic radical anions[1,17,18] that we have observed. We have been able to correlate this data within the Hückel framework by making the α carbons more electronegative with increased strain and the ring juncture carbons more electropositive. Finally, one of the authors has recently reported the use of simple perturbation theory within the Hückel framework plus the parameters derived from our esr and polarographic studies to explain the observed decrease in reactivity of the α position of benzocyclobutene.[19]

Chart I
Compounds under Investigation[a]



[a] Numbering system used for discussion and hfsc assignment.

In this paper, we report the results of an esr study of the radical anions of a series of naphthalene hydrocarbons having varying degrees of ring strain. The following compounds, shown in Chart I, were investigated: 2,3-dimethylnaphthalene (I), naphtho[*b*]cyclobutene (II), 5,6-benzindan (III), and 1,2,3,4-tetrahydroanthracene (IV). The changes in spin densities observed can again be explained by the Finnegan–Streitwieser model and can be correlated within the Hückel framework using parameters derived from our previous studies.[1,16,17]

Experimental Section

Usual high-vacuum techniques using alkali metals and ethereal solvents were employed to prepare the radical anions studied. The initial hydrocarbon concentration was approximately 5×10^{-3} *M*. Dimethoxyethane (Aldrich), tetrahydrofuran (MCB), and diethyl ether (Allied) were dried by several distillations from lithium aluminum hydride (Alfa), degassed on the vacuum line using the freeze–pump–thaw technique, and distilled under vacuum to solvent bumpers containing sodium–potassium alloy (Unified Science Associates). Hexamethylphosphoramide (Aldrich) was dried by several vacuum distillations from Linde 13X molecular sieves (Union Carbide) followed by degassings on the vacuum line prior to use.

Epr spectra were recorded on a Varian E-3 spectrometer with X-band frequencies and an E-3 variable-temperature accessory. Temperatures were checked using a Honeywell Model 2746 potentiometer and copper–constantan thermocouple, and are considered good to at least ±2°. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 research chromatograph using an 8 ft × 0.25 in. column of 10% SE-30 on Chromosorb P. Computer simulations of theoretical esr spectra were done using a Fortran Version IV program for mixtures employing Lorentzian line shapes written by Griffin.[20] Melting points were taken on a Fisher-Johns hot-block apparatus and are uncorrected.

2,3-Dimethylnaphthalene was obtained from Aldrich, recrystallized (95% ethanol), and purified by gc prior to use.

1-Deuterio-2,3-dimethylnaphthalene. 1-Bromo-2,3-dimethylnaphthalene was prepared by the procedure of Arnold and Liggett,[21] mp 60–63° (lit.[21] mp 63–64°), and used without further purification. The bromide was converted to the Grignard in THF (dried by $LiAlH_4$), quenched with deuterium oxide (Merck, >99.7%), and extracted with ether, and the extract was washed with water. The ether solution was dried (Na_2SO_4), filtered, and evaporated to a white powder, which was recrystallized (ethanol) several times: mp 103–105° [lit.[22] (2,3-dimethylnaphthalene) mp 105–105.1°]; mass spectrum *m/e* (rel intensity) 157 (91), 156 (9).

Naphtho[*b*]cyclobutene was prepared by the procedure of Cava and Shirley;[23] it was purified by gc to give mp 86.5–87.5° (lit.[23] mp 86.5°), mass spectrum *m/e* 154.

Bromination of Naphtho[*b*]cyclobutene. To a cooled solution of naphtho[*b*]cyclobutene (2.0 g, 0.0128 mol) in chloroform (5.5 ml) in an ice bath was added bromine (2.51 g, 0.72 mol) in carbon tetrachloride (2.0 ml) over a 50-min interval with stirring. The solution was then stirred at room temperature for 4.5 hr. The solution was washed with 10% sodium hydroxide and twice with water and dried over anhydrous sodium sulfate, and the solvent was distilled off; the products were separated on an alumina column (43 × 2 cm) with petroleum ether (bp 30–60°) as eluent. The sample was recrystallized once from petroleum ether. A 39% yield of 1-bromonaphtho[*b*]cyclobutene was obtained, mp 38–42°.

In order to obtain an analytical sample of 1-bromonaphtho[*b*]cyclobutene, the reaction was repeated and the product obtained from the alumina column was gas chromatographed on an 8 ft × 0.25 in. column of 10% SE-30 on Chromosorb P. The bromide separated on the gas chromatograph was recrystallized from petroleum ether: mp 52.5–53.5°, ir (CCl_4) 1415, 1315, 1245, 930, 910, 880 cm^{-1}; mass spectrum *m/e* (rel intensity) 232 (100), 234 (98).

Anal. Calcd for $C_{12}H_9Br$: C, 61.83; H, 3.89; Br, 34.28. Found: C, 61.94; H, 3.87; Br, 34.27.

Preparation of 1-Deuterionaphtho[*b*]cyclobutene. Tetrahydrofuran (3.1 ml) was distilled over lithium aluminum hydride under nitrogen into a flask containing 1-bromonaphtho[*b*]cyclobutene (1.0 g) and magnesium turnings (0.156 g). After addition of the THF, ethylmagnesium chloride (0.4 ml, approximately 3 *M* solution in Et_2O) was added to the reaction flask and the flask was refluxed for 2 hr. Deuterium oxide (2 ml, minimum isotopic purity 99.7%) was added to the flask, the reaction was left for 3 hr, distilled water (3 ml) was added to the flask, and the contents were extracted with 50 ml of ether. The ether layer was washed three times with water and dried over anhydrous sodium sulfate, and the ether was removed *in vacuo*, leaving a white solid. The solid was recrystallized from petroleum ether. A 51% yield of 1-deuterionaphtho[*b*]cyclobutene was obtained, mp 84.5–87.0°.

Preparation of 1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione. The procedure of Cava and Shirley[23] was followed.

5,6-Benzindan was prepared in five steps from indan using slight modifications of Sen-Gupta's procedures;[24] it was purified by recrystallization (95% ethanol) and gc to give mp 93.0–93.5° (lit.[24] mp 94°).

1,2,3,4-Tetrahydroanthracene was prepared by high-pressure hydrogenation of anthracene[25] using Raney nickel catalyst, and was purified *via* the picrate,[25] recrystallization (ethanol), and gc: mp 98.5–100° (lit.[25] mp 98–100°); mass spectrum *m/e* 182.

Results

Compound I. This compound was first reduced using potassium–DME.[1] A large change in splitting constants from −65° to room temperature was observed, and the method of splitting constant assignment was discussed.[1]

We have attributed the large change in splitting constants to an ion pair which reverts to the free ion or a looser ion pair at low temperatures.[27] To test for ion pairing, I was reduced using potassium and a mixture of DME and hexamethylphosphoramide (HMPA).[29] Spectra were recorded from −88 to 20°, with the splitting constants remaining essentially unchanged over this temperature range: $A_{1,4}$ = 4.61, $A_{5,8}$ = 4.88, $A_{6,7}$ = 1.77, and A_{CH_3} = 1.69. At higher temperatures, the line width increased owing to exchange broadening. Good simulations for the experimental spectra were obtained for the temperature range studied. A further test for ion pairing involved the reduction of I using potassium, DME, and a "crown" ether, dicyclohexyl-18-crown-6, which removes ion pairing by solvation of the alkali metal cation, as does HMPA.[17] The crown ether spectra were recorded from −70 to 0°, and were the same as found for HMPA. This provides strong support for an ion-pairing phenomenon when I is reduced in potassium–DME.

Compound II. Reduction of II gave reversible spectra from −50° to room temperature using potassium–DME.[1] Deuteration studies and splitting constant assignments for II were performed.[1]

II was next reduced with potassium in DME–HMPA, giving reversible spectra from −88 to 0°. Very little temperature dependency was observed, and the spectra were virtually identical with those obtained using potassium–DME. The splitting constants were essentially the same as in potassium–DME: $A_{1,4}$ = 5.40, $A_{5,8}$ = 4.20, $A_{6,7}$ = 1.60, and A_{CH_2} = 5.82.

Compound III. Reduction of III using potassium–DME gave complex spectra that were reversible and showed little temperature dependency from −65° to room temperature. An increase of line widths was noted at higher temperatures owing to exchange broadening. Well-resolved spectra were not obtained, but the following splitting constants seemed to give a reasonable fit: $A_{1,4}$ = 5.00, $A_{5,8}$ = 4.58, $A_{6,7}$ = 1.65, $A_{CH_{2\alpha}}$ = 4.20 (4 methylene protons), and $A_{CH_{2\beta}}$ = 0.40.

Reduction of III using potassium and DME–HMPA gave well-resolved spectra exhibiting little or no temperature dependency from −80 to 10°. Very good fits were obtained between theoretical and experimental spectra over this range using $A_{1,4}$ = 5.00, $A_{5,8}$ = 4.38, $A_{6,7}$ = 1.64, $A_{CH_{2\alpha}}$ = 4.15 (4 methylene protons), and $A_{CH_{2\beta}}$ = 0.41. The experimental and calculated spectra for −80° are shown in Figure 1. These splitting constants are close to those obtained in potassium–DME, but the value of $A_{5,8}$ decreases slightly from 4.58 to 4.38. The assignments are based on those obtained for compounds I and II.

Compound IV. This compound was first reduced in potassium–DME, giving reversible spectra from −60° to room temperature which showed very little temperature dependency over this range. At higher temperatures an increase of linewidths was observed owing to exchange broadening. The spectra could be simulated quite well using $A_{1,4}$ = 4.62, $A_{5,8}$ = 4.83, $A_{6,7}$ = 1.72, $A_{CH_{2\alpha}}$ = 2.59 (4 methylene protons), and $A_{CH_{2\beta}}$ = 0.18 (4 methylene protons). Spectra obtained upon reduction of IV with potassium in DME–HMPA exhibited essentially the same splitting constants, although linewidths were wider than for potassium–DME. Simulations indicated that deuteration studies would not permit unequivocal assignment of splitting constants; so these were assigned on the basis of previous work and molecular orbital calculations. Theoretical and experimental spectra for −60° are shown in Figure 2.

Summary of Results and MO Calculations. The experimentally determined hfsc for the naphthalene compounds are shown in Chart II. It is believed that for the reduction conditions shown, potassium in a mixture of DME

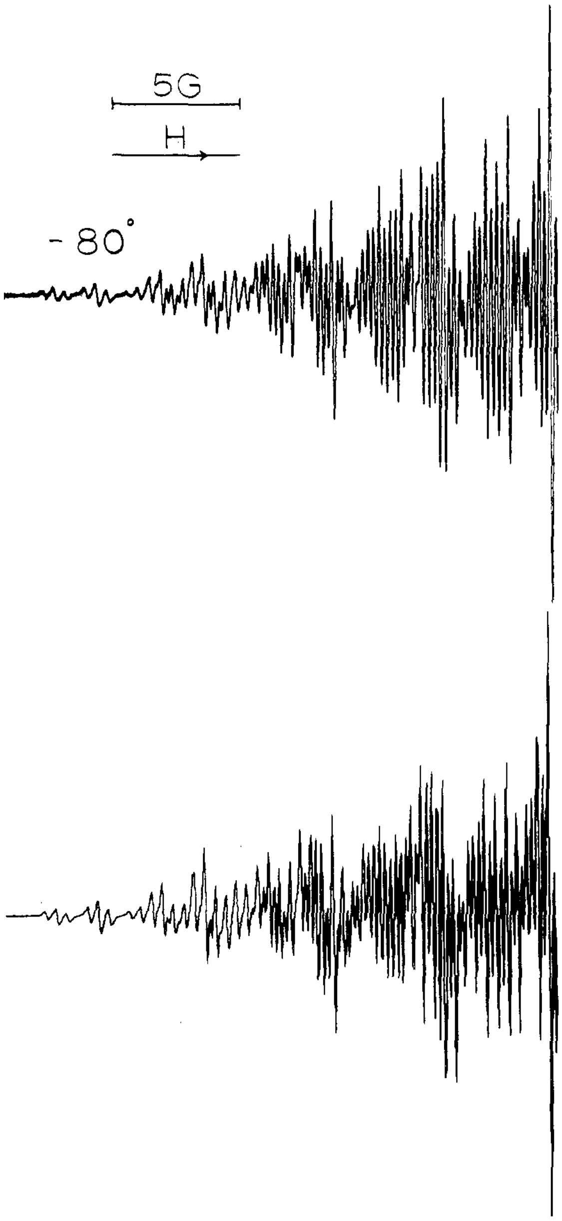
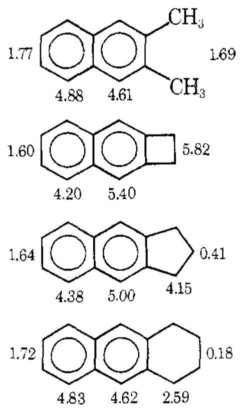


Figure 1. Esr spectrum of the radical anion of III prepared using potassium and DME–HMPA: upper, experimental spectrum at −80°; lower, calculated spectrum using hfsc given in text and a Lorentzian line width of 0.120 G.

Chart II
Hfsc Obtained for Compounds I–IV Reduced with Potassium in DME–HMPA



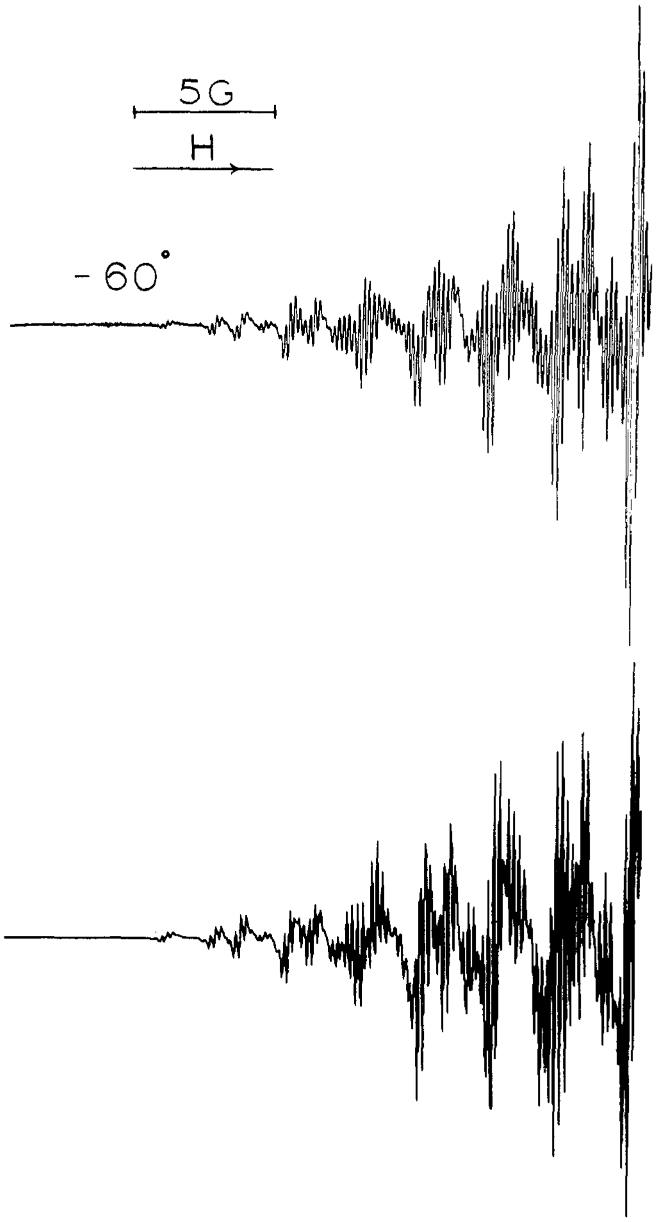


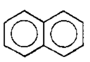
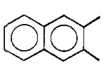
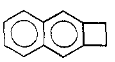
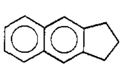
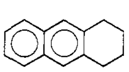
Figure 2. Esr spectrum of the radical anion of IV prepared using potassium and DME: upper, experimental spectrum at −60°; lower, calculated spectrum using hfsc given in text and a Lorentzian line width of 0.080 G.

and HMPA, ion-pairing effects were negligible and the species observed was the free ion. The naphthalene compounds showed a large perturbation of spin densities as ring strain was increased. An increase in the strain of the alicyclic ring caused an increase in the value of $A_{1,4}$ and a decrease for $A_{5,8}$ and $A_{6,7}$. Also, the hfsc for the methylene protons was substantially perturbed with ring strain.

The results can be explained qualitatively using the model of Finnegan–Streitwieser. For I, the introduction of methyl groups perturbed the system slightly from the parent compound naphthalene. Spin density was lowered near the methyl groups because of their electron-repelling effect. For the compounds with an addition of a strained ring, rehybridization of the bond orbitals of the ring juncture carbon atoms leads to an increase in s character in the bonds α to the strained ring, resulting in the carbons α to the ring becoming more electronegative. This effect was greatest for II and decreased from III to IV, which was considered to be essentially strain-free. This was supported by the very close agreement of the $A_{1,4}$, $A_{5,8}$, and $A_{6,7}$ values in IV and I. Therefore, for IV the basic effect is electron repulsion caused by the methylene groups.

The hybridization polarization model of Finnegan–Stre-

Table I
HMO Calculated Hfsc for the Naphthalene Series Using h Values Shown[a]

Compd	Registry no.	h_1[b]	h_2[b]	$A_{1,4}$	$A_{5,8}$	$A_{6,7}$	$A_{CH_2\alpha}$
	91-20-3	Exptl		4.95		1.83	
		0.0	0.0	4.89			
	581-40-8	Exptl		4.61	4.88	1.77	1.69
		0.0	0.1	4.64	4.92	1.85	1.92
	6827-31-2	Exptl		5.40	4.20	1.60	5.82
		−0.2	0.1	5.23	4.07	1.68	4.59
	1624-26-6	Exptl		5.00	4.38	1.64	4.15
		−0.1	0.1	4.90	4.54	1.78	3.05
	2141-42-6	Exptl		4.62	4.83	1.72	2.59
		0.0	0.1	4.64	4.92	1.85	2.42

[a] Only the best correlation for each compound is given. [b] All other coulomb integrals were set equal to α_0.

itwieser was placed on a more quantitative basis by correlating the esr results with molecular orbital theory. Two types of calculations, simple Hückel (HMO) and Mulliken–Wheland–Mann[39] (MWM), were employed.

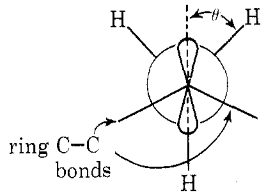
The use of HMO theory to correlate esr results for aromatic hydrocarbons has been well established.[30] Changes in electronegativity can be effected within the HMO framework by varying the coulomb integrals using the equation shown below.

$$\alpha_r = \alpha_0 + h_r|\beta_0|$$

Making h_r negative increases the electronegativity of atom r, while a positive h_r decreases the electronegativity. The calculated HMO spin densities were converted to A_H values by means of the McConnell equation,[31] with Q taken as 27 G.

For the calculation of methyl and methylene hfsc, the following equation was used.[32] θ is defined below.

$$A_{CH_2}(\theta) = (\beta_0 + \beta_2 \cos^2 \theta)p$$



Levy[33] calculated the spin polarization contribution, β_0, and found it to have a value of −3.09 G. Fessenden[34] calculated β_2 to be 58.5 G where $\beta_2 \cos^2 \theta$ is the hyperconjugative contribution to Q_{CH_2}. From this equation, a value of $Q_{CH_3} = 26$ was calculated for a methyl group since the average value of θ is 45°. For the remaining compounds, molecular models were used to approximate θ, and this value was used to calculate Q_{CH_2}. For II, θ was around 16°, giving $Q_{CH_2} = 51$. For III, $\theta = 34°$ and $Q_{CH_2} = 37$, and the values for IV were $\theta = 37°$ and $Q_{CH_2} = 34$. The coulomb integrals were taken to be the same for the 2 and 3 positions in I and IV on the assumption that the electron-donating abilities of a methyl and methylene group are essentially the same. The calculations showed this assumption to be valid.

The results of these HMO calculations for the naphthalene compounds are shown in Table I. Values for h_r were varied from 0.4 to 0.0 in increments of 0.1 and spin densities and hfsc were calculated.

Table I shows the values of h_r which gave the best correlations.[46] As can be seen the correlations are quite good for the aromatic proton hfsc. For the methyl and methylene hfsc, the fit is not as good; this may partially be due to the crude determination of θ. It is more likely, however, that the simple equation used to calculate the methylene coupling constants is not adequate. Bauld, *et al.*,[35] has suggested that interaction diagonally across the cyclobutene ring can also substantially contribute to proton coupling constants. Goldberg[18] has pointed out that when the odd electron is in a wave function which has both coefficients of the cyclobutene double bond of the same sign this will have an additive effect. In this series of compounds the sign of the coefficients on the 2 and 3 positions of the wave function containing the odd electron is the same. Hence, one would expect to see larger coupling constants than are predicted by the simpler equation used in this paper if this mechanism is important. Other explanations have also been offered.[36,37] At this point no definite conclusions can be drawn regarding the mechanism of spin transfer and hence no definite conclusions can be made regarding the origin of the unusually large methylene coupling constants.

The fact that HMO theory can be used to correlate oxidative and reductive $E_{1/2}$ values and esr hfsc of the molecules reported in this paper indicates that the hybridization–polarization model is valid within the HMO framework. Other calculations were attempted, such as variation of only the resonance integral $\beta_{2,3}$ and use of a hyperconjugative model, but the correlations were not as good as for the HMO technique used here.

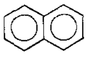
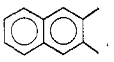
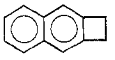
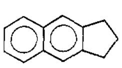
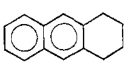
Finally, calculations were performed incorporating the hybridization–polarization model within the MWM framework.[38,39] It has been shown that this technique is effective in correlating experimental results where heteroatoms are involved.[30] Since the ring strain model effectively treats certain carbon atoms as heteroatoms by varying the coulomb integral, it was felt that this technique could be used to correlate our results.

The calculations which gave the best correlations are shown in Table II. h_r was varied from ±0.4 to 0.0 in increments of 0.1, and the Q values used were the same as for the HMO calculations. Again, the correlation of the esr results was very good, being better for the aromatic proton hfsc than for the methylene hfsc, as was observed for the HMO calculations. However, this model fails to predict the observed reduction potentials for the napththalenes.[1] Although the MWM technique correlates the esr results, the HMO technique appears to be the method of choice for correlating a broad variety of physical and chemical properties of strained aromatic hydrocarbons.

INDO Calculations. In order to gain additional insight into the effects of ring strain, INDO[40] calculations were carried out on naphthalene, compound I, and compound II. The results of these calculations are summarized in Table III.

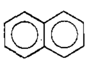
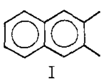
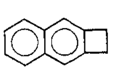
As can be seen from Table III, the INDO calculations give the right order of magnitude; however, the INDO

Table II
MWM Calculated Hfsc for the Naphthalene Series Using *h* Values Shown[a]

Compd	h_1	h_2	$A_{1,4}$	$A_{5,8}$	$A_{6,7}$	$A_{CH_2\alpha}$
	Exptl		4.95		1.83	
	0.0	0.0	5.00	1.74		
	Exptl		4.61	4.88	1.77	1.69
	0.0	0.1	4.78	5.11	1.76	1.77
	Exptl		5.40	4.20	1.60	5.82
	−0.2	0.1	5.37	4.30	1.62	4.14
	Exptl		5.00	4.38	1.64	4.15
	−0.1	0.1	5.06	4.70	1.69	2.59
	Exptl		4.62	4.83	1.72	2.59
	0.0	0.1	4.78	5.11	1.76	2.31

[a] Only the best correlation for each compound is given.

Table III
INDO Calculated Hfsc for Naphthalene, Compound I, and Compound II

Compd		$A_{1,4}$	$A_{5,8}$	$A_{6,7}$	$A_{CH_2\alpha}$
	Exptl	4.95		1.83	
	INDO	5.15		0.93	
 I	Exptl	4.61	4.88	1.77	1.69
	INDO	5.93	4.66	0.86	1.43
 II	Exptl	5.40	4.20	1.60	5.82
	INDO	5.55	4.62	0.86	7.10

method does not seem sensitive enough to small perturbations caused by substituents. Thus, the INDO approach predicts just the opposite trend for $A_{1,4}$ from what is observed. Accordingly, the much more empirical Hückel approach appears to be best suited for predicting a wide variety of physical and chemical properties of strained hydrocarbons. One possible explanation for the failure of the INDO approach is in the choice of bond lengths and angles, which by necessity is somewhat arbitrary. Bond angles and bond lengths were chosen on the basis of crystallographic work done on naphthalene,[41] 1,2,3,4-tetrachloronaphthalene,[42] benzocyclobutene-1,2-dione,[43] cubane,[44] and dihalobenzocyclobutenes.[45] One other possible explanation for the failure of the INDO method is that it originates in the basic approximations and assumptions built into the INDO method.

Summary. The introduction of a strained, fused ring into an aromatic hydrocarbon molecule strongly perturbs the spin densities of the radical anion of that hydrocarbon. The changes in spin densities with increasing ring strain can be correlated fairly well with simple Hückel theory. Some of the more sophisticated molecular orbital calculations, such as INDO, do not seem sensitive enough to small perturbations of the aromatic molecule to accurately predict the correct trends.

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Registry No.—1-Bromonaphtho[*b*]cyclobutene, 51270-82-7; 1-deuterionaphtho[*b*]cyclobutene, 51270-83-8.

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Secondary Valence Force Catalysis. XV. Polysoap Catalysis for the Alkaline Hydrolysis of *p*-Nitrophenyl Hexanoate[1]

Teresita Rodulfo, J. A. Hamilton, and E. H. Cordes*

Escuela de Quimica, Facultad de Ciencias, Universidad Central, Caracas, Venezuela, and Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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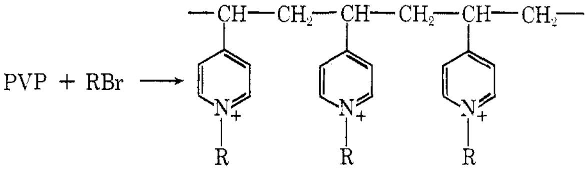
The alkaline hydrolysis of *p*-nitrophenyl hexanoate is subject to catalysis by polysoaps synthesized through alkylation of polyvinylpyridine with ethyl and dodecyl bromides. The polysoaps are increasingly effective as catalysts for this reaction with increasing ratio of dodecyl to ethyl groups, suggesting that the hydrophobic properties of these polymers, as well as their net charge, are important in determining catalytic efficacy. The polysoap-catalyzed hydrolysis of this ester is inhibited by several anions: fluoride is the weakest inhibitor studied and nitrate is the most potent. High concentrations of nitrate convert the polysoap-catalyzed process into a polysoap-inhibited one. In contrast to other anions, azide elicits an increased rate of ester disappearance, strongly suggesting that polysoaps catalyze the attack of this nucleophile on *p*-nitrophenyl hexanoate.

It is well established that both polyelectrolytes[2] and micelles[3] may be effective catalysts for organic reactions, including ester hydrolysis. These reactions are of particular interest since they exhibit many features, including limited substrate specificity, concentration–rate profiles, inhibition by structurally related substances, and inhibition by salts, which are reminiscent of enzymatic reactions.[2,3] Catalysis in such systems generally derives from association of substrate and catalyst through electrostatic and/or hydrophobic interactions with formation of a complex having enhanced reactivity compared to the substrate free in solution. This enhanced reactivity may either reflect stabilization of the transition state relative to the ground state for reaction with some group from the bulk phase or incursion of an entirely novel pathway through reaction with some functionality of the micelle or polyelectrolyte. The *n*-alkyltrimethylammonium bromide catalyzed hydrolysis of *p*-nitrophenyl esters provides one example in the former category[4] and catalysis of carboxylic and sulfate ester hydrolysis by polyethylenimines substituted with imidazole functions provides examples in the latter one.[5]

In general, micelles formed from ionic surfactants are organized and compact structures having the capacity to interact favorably with both organic molecules and ions. In contrast, most polyelectrolytes do not form well-organized structures in aqueous solution and usually rely on electrostatic forces more than hydrophobic ones for complexation with small molecules and promotion of their reactions. A class of compounds has been known for several decades which incorporates both those features of polyelectrolytes and those of micelles into a single structure; they are usually termed polysoaps.[6-8] A typical polysoap can be formed through treatment of polyvinylpyridine with dodecyl bromide or other hydrophobic alkylating agent. The result is a polyelectrolyte having marked hydrophobic properties and such structures are known to form "intramolecular micelles" having a structural organization related to micelles formed from simple surfactants.[6]



(1)

Very few studies of the catalytic capacities of polysoaps have been undertaken. It has been established that polyvinylpyridine partially alkylated with benzyl chloride promotes the hydrolysis of *p*-nitrophenyl esters through a route involving transient acylation of unsubstituted pyridine nitrogens of the polymer.[9] More recently, alkylated polyvinylpyridines have been shown to be catalysts for fading of triphenylmethyl cations such as crystal violet.[10] The work of Klotz and his collaborators has employed polyethylenimines possessing substantial hydrophobic character[5] and Ise, *et al.*, have shown that related polymers catalyze hydrolysis of phenyl phosphate dianions.[11] However, in these latter cases, there is no evidence to suggest that the polyelectrolytes actually form micelle-like structures in solution.

Since the catalytic properties of polysoaps remain largely unexplored, we have initiated a series of investigations in this area. The first of these, dealing with hydrolysis of *p*-nitrophenyl hexanoate, is described in this manuscript.

Experimental Section

Materials. *p*-Nitrophenyl hexanoate was prepared and purified as previously described.[4] Poly-4-vinylpyridine was obtained from Polysciences, Inc.; the supplier provided an approximate molecular weight of 300,000.

Copolymers of 4-vinyl-*N*-ethylpyridinium bromide and 4-vinyl-*N*-dodecylpyridinium bromide were prepared by a minor modifi-