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# RING STRAIN EFFECTS ON SPIN DENSITIES

## I. RING STRAIN EFFECTS ON SPIN DENSITIES IN SUBSTITUTED NAPHTHALENE RADICAL ANIONS

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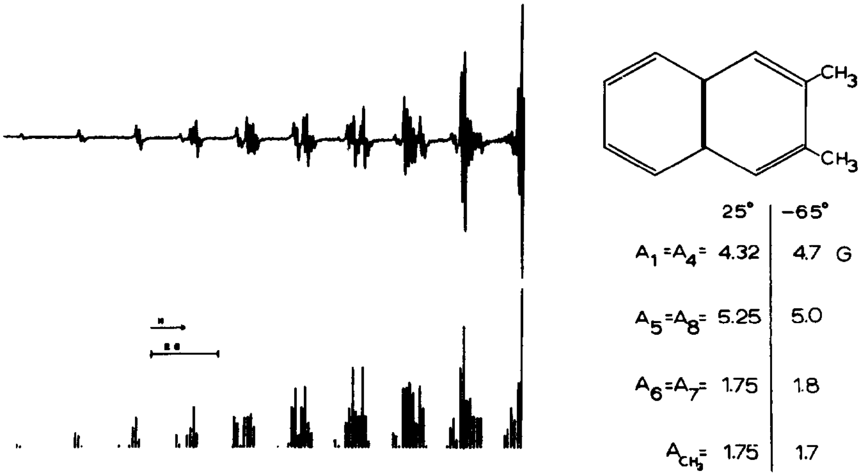
A good deal of interest has recently been centered on the changes in chemical properties of aromatic hydrocarbons upon the introduction of a fused, strained ring into the molecule.[2-5] We found that the spin densities in aromatic anion radicals are substantially perturbed upon the introduction of a fused strained ring.

The naphthalene system was chosen first in our studies because of ease of preparation and stability of the anion radicals. Treatment of 2,3-dimethylnaphthalene with a potassium mirror in 1,2-dimethoxyethane gave a green anion radical whose ESR spectrum was observed over a range of temperatures. The ESR spectrum observed at -65° was well simulated using the hyperfine coupling constants shown in Figure I.

FIGURE I

ESR spectra of 2,3-dimethylnaphthalene at -65°: upper, observed; lower, calculated stick diagram using low temperature coupling constants; only half spectra shown.



| | 25° | -65° |
|---|---|---|
| $A_1=A_4=$ | 4.32 | 4.7 G |
| $A_5=A_8=$ | 5.25 | 5.0 |
| $A_6=A_7=$ | 1.75 | 1.8 |
| $A_{CH_3}=$ | 1.75 | 1.7 |

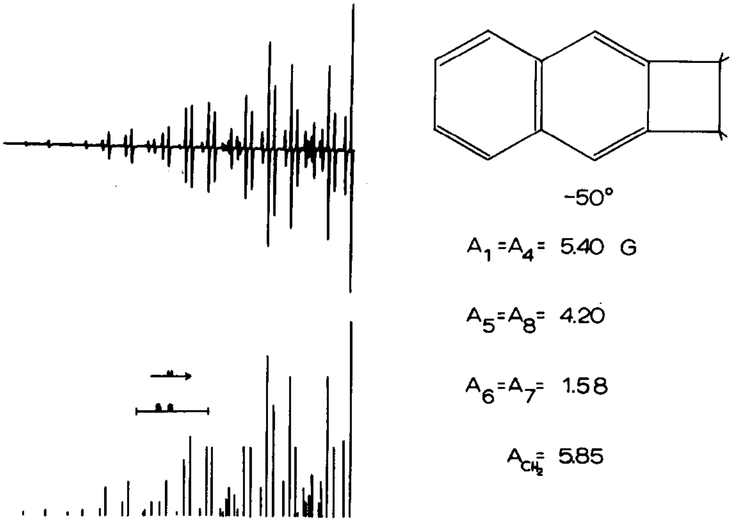
DeWaard and Henning had previously prepared the radical anion of 2,3-dimethylnaphthalene;[6] however, they only determined the spectrum at room temperature. We found that the room temperature spectrum could be interpreted as arising from the following set of hyperfine coupling constants: $A_{1,4} = 4.32$ gauss, $A_{5,8} = 5.25$ gauss, $A_{6,7} = 1.75$ gauss, and $A_{CH_3} = 1.75$ gauss. These are essentially the same values reported by DeWaard and Henning.[6] The dramatic shift that we observed upon cooling the radical anion to -65° is attributed to an unsymmetrical ion pair which reverts to the free radical anion at low temperatures.[7] At -65°, the temperature coefficient of the two large coupling constants was only 5 milligauss per degree.

The assignment of the $A_{1,4}$ coupling constant was established by reducing the 1-deutero-2,3-dimethylnaphthalene. The small difference in the $A_{1,4}$ and $A_{5,8}$ values at -65° precluded the use of deuterium labeling to establish their unequivocal assignment. However, at room temperature the $A_{1,4}$ value could be definitely determined to be 4.32 gauss. As the temperature was lowered in steps to -65°, the $A_{1,4}$ = 4.32 gauss hyperfine coupling constant gradually became $A_{1,4}$ = 4.70 gauss, thus clearly relating the 4.70 gauss coupling constant to positions C-1 and C-4. The assignments of $A_{5,8}$ and $A_{6,7}$ were made by analogy with naphthalene anion radical[9] and molecular orbital calculations.[10] The $A_H$ values obtained were not very different from those of naphthalene anion radical;[9] the two alkyl substituents do not appear to be perturbing the $\pi$-system a great deal. There seems to be a slight polarization of spin density away from the electron repelling methyl groups.[11]

Naphtho[b]cyclobutene[12] was reduced with a potassium mirror in glyme at -50° to give a light green radical anion. The spectrum obtained (Figure II) indicated the presence of two protons with $A_H$ = 5.40 gauss, two protons with $A_H$ = 4.20 gauss, two protons with $A_H$ = 1.58 gauss, and four protons with $A_H$ = 5.85 gauss.

FIGURE II

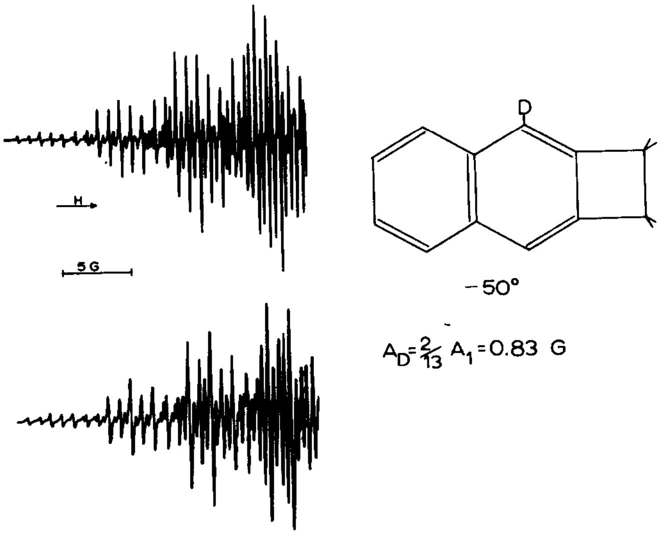
ESR spectra of naphtho[b]cyclobutene: upper, observed; lower, calculated stick diagram; only half spectra shown.



Next, 1-deuteronaphtho[b]cyclobutene was prepared. Bromination of naphtho[b]cyclobutene gave a monobromide as indicated by NMR and mass spectral analysis.[13] The Grignard of the monobromide was prepared and quenched with deuterium oxide, yielding a monodeuteride as indicated by NMR and mass spectral analysis. The monodeuteride was then oxidized with peracetic acid to give the known 1,2-dihydrocyclobuta[b]naphthalene-3,8-dione.[14] Mass spectral analysis of the quinone indicated no deuterium present; recovered starting material still retained the deuterium. This established the location of the bromine and deuterium as being the C-1 position. Reduction of the 1-deuteronaphtho[b]cyclobutene gave an ESR spectrum (Figure III) which could be interpreted by assigning the $A_H = 5.40$ gauss to the C-1 and C-4 positions.[15] Assignment of the $A_H = 4.20$ gauss to positions 5 and 8 and the $A_H = 1.58$ gauss to positions 6 and 7 were made by analogy with naphthalene and from molecular orbital calculations.[10]

FIGURE III

ESR spectra of 1-deuteronaphtho[b]cyclobutene: upper, observed; lower, calculated using 0.100-gauss line width and Lorentzian line shape; only half spectra shown.



The introduction of a fused, four-membered ring has substantially perturbed the spin densities throughout the molecule. Interestingly, in 2,3-dimethylnaphthalene spin densities are polarized slightly away from the methyl groups while in naphtho[b]cyclobutene spin densities are strongly perturbed towards the fused, four-membered ring. This observation can be explained by the qualitative ideas set forth by Streitwieser[4] and Finnegan[2] to explain the increased acidity of carbons alpha to a fused strained ring. The ring juncture carbons are rehybridized to accommodate the small bond angles of the four-membered ring; therefore, the sigma bonds in the four-membered ring have increased p-character and the remaining sigma bonds to the carbons alpha to the four-membered ring have more s-character. This increase in orbital electronegativity causes a polarization of sigma electrons away from the alpha carbon atoms, causing them in turn to be more electronegative. Preliminary molecular orbital calculations indicate that the spin densities can be correlated by increasing the coulomb integrals for the alpha carbons relative to the rest of the carbon atoms in the $\pi$-system. We are presently studying this phenomenon in other systems with varying amounts of strain. A complete paper on these systems and the details of our molecular orbital calculations will be published in the near future.

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10. R. D. Rieke and C. F. Meares, to be published separately.
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13. Very little electrophilic substitution work has been done on this molecule. Cava[14] reported the nitration of naphtho[b]cyclobutene gives the 1-nitronaphtho[b]cyclobutene.
14. M. P. Cava and R. L. Shirley, J. Org. Chem., **26**, 2212 (1961).
15. Interestingly, the spin densities in naphtho[b]cyclobutene showed negligible temperature dependence.