

TABLE V
 REACTIONS OF *m*-DINITROBENZENE^a

Products	Relative concentrations ^b				
	Fluorobenzene (R = C ₆ H ₄ F), 2.2 ^c	Chlorobenzene (R = C ₆ H ₄ Cl), 2.75 ^c	Benzonitrile (R = C ₆ H ₄ CN), 2.5 ^c	Pyridine (R = C ₅ H ₄ N), 2.3 ^c	Thiophene (R = C ₄ H ₃ S), 1.15 ^c
Phenol	8			5	9
ROH	13	6	18	13	
RC ₆ H ₅	46	26	99	36	116
RC ₆ H ₄ OH	11		13	15	67
RR	100	100	100	100	100
RC ₆ H ₄ NO ₂	9	24	10	11	22
RC ₆ H ₄ R	21	13	36	37	110

^a Conditions: 0.01 mol of *m*-dinitrobenzene, 0.1 mol of reagent; 550°; 15-sec contact time; N₂ at 10 cc/min. ^b Relative intensities in the low-voltage mass spectrum normalized to RR = 100. ^c Total weight of products, grams.

Registry No.—*o*-Dinitrobenzene, 528-29-0; *m*-dinitrobenzene, 99-65-0; *p*-dinitrobenzene, 100-25-4; benzene, 71-43-2; hexafluorobenzene, 392-56-3.

Acknowledgment.—We are grateful to D. K. Albert of the American Oil Co. for his assistance with gas chromatographic analyses, to F. E. Saalfeld of the

Naval Research Laboratory, Washington, D. C., and J. C. Hoffsommer of the Naval Ordnance Laboratory, Silver Spring, Md., for helpful suggestions, and to Dr. Hoffsommer for unpublished results and for guidance to relevant research reports. In addition, we thank Harry Heaney of the University of Technology, Loughborough, for an authentic sample of 1,2,3,4-tetrafluoronaphthalene.

Ring Strain Effects. V.¹ An Electron Spin Resonance Study of the Anion Radicals of a Series of O-Disubstituted Benzenes

STEPHEN E. BALES² AND REUBEN D. RIEKE*

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

Received May 26, 1972

The effects of ring strain on spin densities of aromatic radical anions has been investigated for a series of substituted benzene derivatives. The spin density was found to increase at the positions α to the ring juncture carbons containing the fused strained ring. The results are described in terms of a hybridization-polarization mechanism. Also, ion-pairing effects on spin densities are discussed.

The effects of a strained fused ring on the chemical and physical properties of aromatic hydrocarbons has been the subject of much research. Numerous reports have appeared concerning the increased preference for electrophilic attack β to the fused ring as strain is increased.³⁻⁹ Markgraf has reported on the changes in the basicity of the lone pair of electrons of a nitrogen α to a fused ring.¹⁰ Also, it has been reported that the acidity of protons α to the fused ring increases as the ring strain is increased.^{11,12} An orbital hybridization-polarization model has been put forth which is in accord with these observations.^{11,12} Several different types of physical and chemical properties have been interpreted

within this model: nmr data,^{13,14} epr data,^{1,15} rates of protodesilylation,¹⁶ polarographic reduction potentials,¹⁷ molecular orbital calculations,¹⁸ and ir data.¹⁹

In this paper, we would like to report the epr spectra of a series of benzene derivatives with varying amounts of strain in the fused rings. The results are discussed in terms of the hybridization-polarization model. Effects of ion-pairing on spin densities are also examined. The compounds examined and the numbering system used are shown in Chart I. Hyperfine splitting constants (hfsc) are given in gauss throughout the text.

Experimental Section

The general techniques and procedures employed for preparing the radical anions in this study have been discussed previously.^{16d}

(1) For paper IV in this series, see R. D. Rieke, S. E. Bales, C. F. Meares, and L. Rieke, *J. Amer. Chem. Soc.*, submitted for publication.

(2) NDEA Fellow, 1967-1970; Ethyl Fellow, 1970-1971.

(3) J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).

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

(5) G. Berthier and A. Pullman, *Bull. Soc. Chim. Fr.*, **88** (1960).

(6) H. Tanida and R. Muneyuki, *Tetrahedron Lett.*, 2787 (1964).

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

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

(9) R. Taylor, *J. Chem. Soc. B*, 536 (1971); R. Taylor, *ibid.*, 1559 (1968); J. Blatchly and R. Taylor, *ibid.*, 1402 (1968); R. Taylor, G. Wright, and A. Homes, *ibid.*, 780 (1967).

(10) J. H. Markgraf and W. L. Scott, *Chem. Commun.*, 296 (1967); J. H. Markgraf and R. J. Katt, *Tetrahedron Lett.*, 6067 (1968); J. H. Markgraf and R. J. Katt, *J. Org. Chem.*, **37**, 717 (1972).

(11) R. A. Finnegan, *ibid.*, **30**, 1333 (1965).

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

(13) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964).

(14) J. H. Markgraf, R. J. Katt, W. L. Scott, and R. N. Shefrin, *J. Org. Chem.*, **34**, 4131 (1969).

(15) (a) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968); (b) R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **92**, 1418 (1970); (c) R. D. Rieke and W. E. Rich, *ibid.*, **92**, 7349 (1970); (d) R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *ibid.*, **93**, 697 (1971); (e) R. D. Rieke and S. E. Bales, *Chem. Phys. Lett.*, **12**, 631 (1972).

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

(17) R. D. Rieke, W. E. Rich, and T. H. Ridgway, *Tetrahedron Lett.*, 4381 (1969); R. D. Rieke, W. E. Rich, and T. H. Ridgway, *J. Amer. Chem. Soc.*, **93**, 1962 (1971).

(18) R. D. Rieke, *J. Org. Chem.*, **36**, 227 (1971).

(19) R. D. Rieke and W. E. Rich, unpublished work.

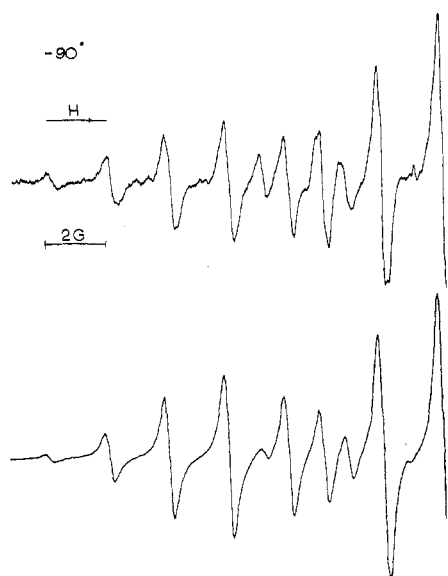
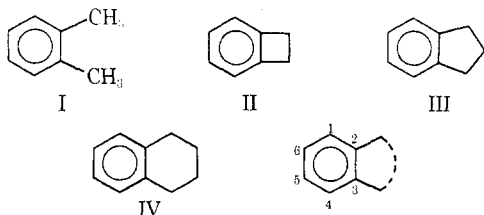


Figure 1.—Esr spectrum of the radical anion of I: upper, experimental spectrum at -90° ; lower, calculated -90° spectrum using a line width of 0.25 G.

CHART I

o-DISUBSTITUTED BENZENES INVESTIGATED IN THIS STUDY AND THE NUMBERING SYSTEM USED



Epr spectra were recorded on a Varian E-3 spectrometer with X-band frequencies and an E-3 variable temperature accessory.

o-Xylene (I), indan (III), and tetralin (IV) were obtained from Aldrich and were purified by gc prior to use.

Benzocyclobutene (II, BCB) was prepared by the procedure of Cava and Napier;²⁰ it was purified by gc and had the same boiling point and spectral characteristics as those reported.

Results

Preliminary Studies.—Meares²¹ observed metal splittings when compounds I–IV were reduced using potassium and dimethoxyethane (DME). In an attempt to prepare the free or solvent-separated ion pairs, the compounds were reduced using various volume ratios of DME and hexamethylphosphoramide (HMPA), and the initial hydrocarbon concentration was varied. Since several members of this series had reduced with some difficulty and showed weak signals in potassium and DME,²¹ it was decided to begin the study using an initial hydrocarbon concentration of 1 *M*. This was done for III, but the spectra indicated that the concentration could be lowered; so no other compounds were investigated under these conditions.

Reduction with Potassium in DME (90%) and HMPA (10%). Initial Hydrocarbon Concentration 0.1 *M*.²²—Reduction of I gave a dark blue solution and reversible spectra from -60 to -90° which exhibited

(20) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).

(21) C. F. Meares, B. S. Honor Thesis, University of North Carolina, Chapel Hill, N. C., 1968.

(22) The percentages represent a volume composition.

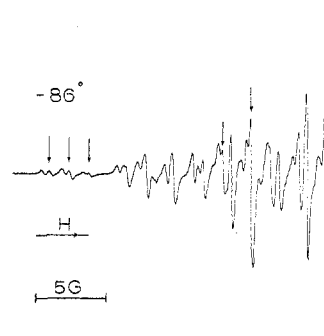


Figure 2.—Esr spectrum of the radical anion of II. The arrows indicate lines due to the free ion.

very little temperature dependency. The signal decayed rapidly above -55° . At -90° the spectra could be simulated quite well using the following hfsc: $A_{1,4} = 7.00$, $A_{\text{CH}_3} = 2.00$, $A_{5,6} = 1.95$. Potassium splittings were not observed. The experimental and simulated spectra are shown in Figure 1. These values are close to those reported by Bolton²³ for the reduction of *o*-xylene in potassium and DME at -80° : $A_{1,4} = 6.93$, $A_{\text{CH}_3} = 2.00$, $A_{5,6} = 1.81$, $A_K = 0.17$.

Compound II was reduced to give a dark green solution and reversible spectra from -5 to -86° . Both the free ion and the ion pair were observed,^{15d} the amount of free ion being favored by lowering the temperature. However, the ion pair is the dominant species over the temperature range studied. The spectra at -86° is shown in Figure 2, the arrows indicating some of the lines due to the free ion. The same effects were observed as were seen when BCB was reduced using potassium and DME.^{15d} However, potassium splittings were not observed. At -80° the ion pair had hfsc of $A_{1,4} = 7.68$, $A_{\text{CH}_2\alpha} = 5.70$, $A_{\text{CH}_2\beta} = 5.30$, and $A_{5,6} = 1.45$, while the free ion exhibited hfsc of $A_{1,4} = 7.45$, $A_{\text{CH}_2} = 5.40$, and $A_{5,6} = 1.45$. At -70° , the free ion was no longer detected. Table I

TABLE I

Hfsc OBSERVED FOR THE ION-PAIRED RADICAL ANION OF II

<i>T</i> , °C	$A_{1,4}$	$A_{\text{CH}_2\alpha}$	$A_{\text{CH}_2\beta}$	$A_{5,6}$
-70	7.63	5.70	5.20	1.45
-60	7.60	5.68	5.20	1.45
-50	7.50		5.55	1.45
-35	7.50		5.44	1.40
-20	7.46		5.40	1.40
-5	7.40		5.37	1.40

shows the hfsc observed for the ion pair from -70 to -5° . Comparison of these values to those obtained in potassium and DME^{15d} shows that here the $A_{1,4}$ value is slightly larger than the value at the corresponding temperature in potassium and DME. Also, the methylenes coalesce at a lower temperature in this solvent system.

Reduction of III gave a dark green solution which turned yellow-orange upon warming. Reversible spectra were obtained from -50° to -90° and showed little temperature dependency. The spectra were simulated using hfsc of $A_{1,4} = 7.50$, $A_{\text{CH}_2\alpha} = 3.75$ (4 H), $A_{\text{CH}_2\beta} = 0.80$, and $A_{5,6} = 1.50$. Experimental and simulated spectra for -90° are shown in Figure 3.

(23) J. R. Bolton, *J. Chem. Phys.*, **41**, 2455 (1964).

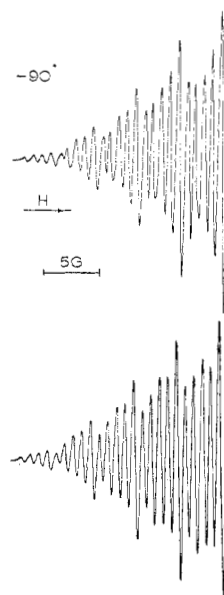
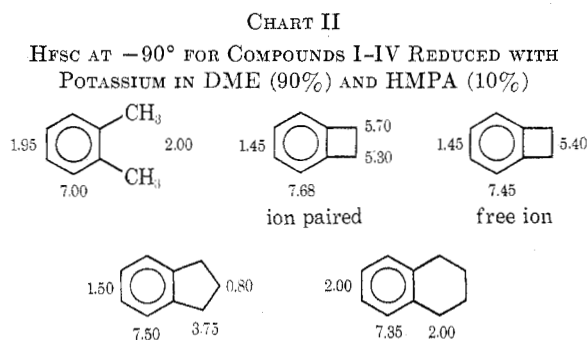


Figure 3.—Esr spectrum of the radical anion of III: upper, experimental spectrum at -90° ; lower, calculated -90° spectrum using a line width of 0.30 G.

Reduction of IV gave a dark blue solution and reversible spectra from -96 to -76° , with rapid decay of the signal above -70° . The spectra exhibited very little temperature dependency over this range. At -90° the spectrum could be simulated using the following hfsc: $A_{1,4} = 7.35$, $A_{\text{CH}_2\alpha} = 2.00$ (4 H), and $A_{5,6} = 2.00$. Splittings due to the β -methylene protons were not observed due to the large line widths (0.90 G at -90°). Attempts to resolve these splittings by use of a small modulation amplitude yielded little improvement. The experimental and simulated spectra for -90° are shown in Figure 4.

A summary of the results obtained for the benzene series using these reduction conditions is shown in Chart II. On the basis of the results of II, it appears



that in this solvent system the dominant species in each reduction is the ion pair. It can be seen that the ring strain substantially perturbed the spin densities, most notably in the position α to the ring.

Reduction with Potassium in DME (80%) and HMPA (20%). Initial Hydrocarbon Concentration, 0.01 M.—In an attempt to obtain better resolution and provide more favorable conditions for free ion formation, the HMPA concentration was increased and the initial concentration of hydrocarbon was decreased. Under these conditions all the samples reduced to give dark blue solutions and exhibited a

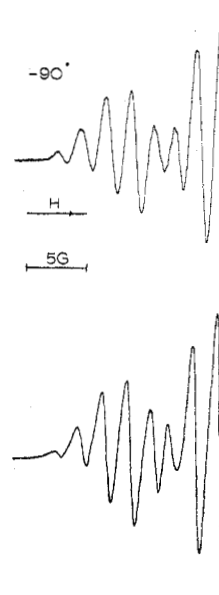


Figure 4.—Esr spectrum of the radical anion of IV: upper, experimental spectrum at -90° ; lower, calculated -90° spectrum using a line width of 0.90 G.

solvated electron peak. Metal splittings were not observed for any of these compounds.

Reduction of I gave weak spectra which were stable in the range of -70 to -90° . These spectra were essentially the same as obtained for I using the conditions of the previous section. The following hfsc were observed at -90° : $A_{1,4} = 7.00$, $A_{\text{CH}_3} = 1.95$, $A_{5,6} = 1.95$.

Compound II was reduced under these conditions and spectra were recorded from -45 to -100° , exhibiting only the free ion. The spectra were reversible and temperature independent. At -90° the hfsc observed were $A_{1,4} = 7.40$, $A_{\text{CH}_2} = 5.45$ (4 H), and $A_{5,6} = 1.40$.

Reduction of III yielded strong, reversible spectra from -50 to -90° . A large change in the hfsc and line-width alternation were observed, indicating a temperature-dependent interconversion process of some type. At -50 and -60° the spectra were similar to those obtained from the 0.1 M sample (see previous section) and had the following hfsc: $A_{1,4} = 7.55$, $A_{\text{CH}_2\alpha} = 3.80$ (4 H), $A_{\text{CH}_2\beta} = 0.80$, $A_{5,6} = 1.55$. Lowering the temperature from -65 to -80° resulted in the appearance of new lines and alternating line widths. At -85° the exchange process appeared to be completed, the lines being fairly sharp. The -85 and -90° spectra were essentially the same and could be simulated quite well using hfsc of $A_{1,4} = 7.25$, $A_{\text{CH}_2\alpha} = 3.60$, $A_{\text{CH}_2\beta} = 1.00$, and $A_{5,6} = 1.50$. These results and others obtained in THF-HMPA (see next section) indicate that the high temperature spectra (-50 to -60°) were due to the ion-paired species, while the low temperature spectra (-85 to -90°) were due to the free ion. Intermediate temperatures exhibited the interconversion between the ion pair and free ion.²⁴ The possible interconversion between various ion-pair conformations was not observed, as it was for II in potassium and DME,^{15d} since one would expect such an interconversion to divide the α -methylene protons into

(24) M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967).

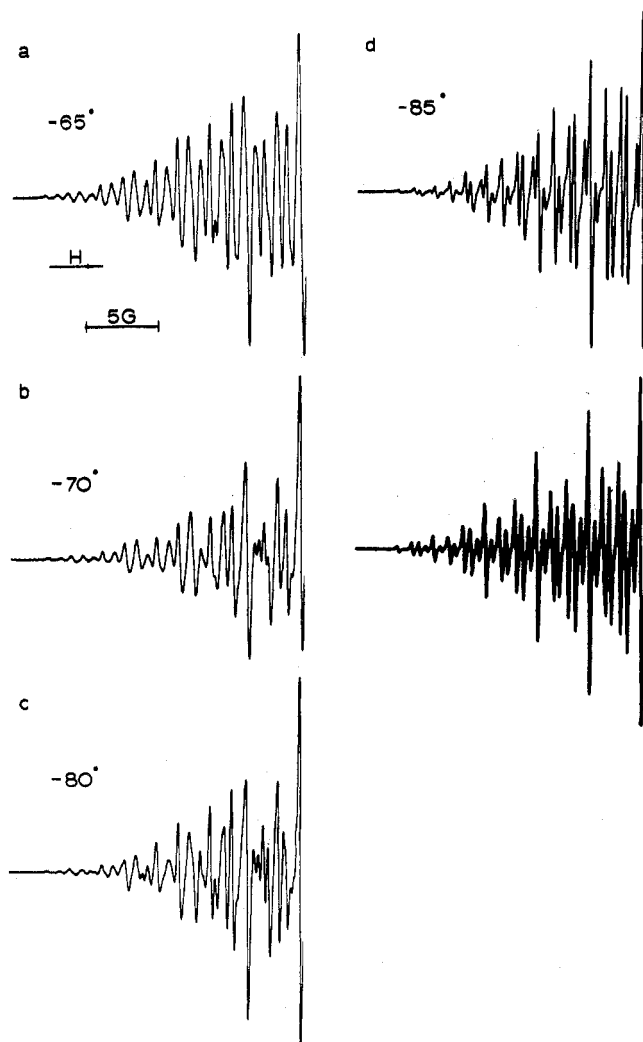


Figure 5.—Esr spectra for the radical anion of III: (a-d) experimental spectra obtained at the temperatures shown; (e) calculated -85° spectrum using a line width of 0.10 G.

two sets of two equivalent nuclei. Figure 5 exhibits the changes in the spectra with temperature for the radical anion of III prepared under these conditions.

Reduction of IV gave reversible, temperature dependent spectra from -50 to -95° . The spectrum width changed very little over this range. From -50 to -80° the spectra were essentially the same as observed for the 0.1 M sample (see previous section). At -90° and below additional hyperfine structure due to the β -methylene protons was observed. Also, a small amount of line broadening was observed for the external lines. Construction of a spin-state diagram failed to offer any reasons for the alternation. A reasonable fit for the -90° spectrum was obtained using hfsc of $A_{1,4} = 7.20$, $A_{\text{CH}_{2\alpha}} = 2.15$, $A_{\text{CH}_{2\beta}} = 0.30$, and $A_{5,6} = 1.85$. The experimental and simulated spectra at -90° are shown in Figure 6.

The results for the benzene series using these reduction conditions are depicted in Chart III at a temperature of -90° . At this temperature the species observed by esr appeared to be the free ion. Under these conditions, as with the 0.1 M samples discussed in the previous section, it can be seen that the spin densities are substantially perturbed as ring strain increased. The general trends for both sets of reduction conditions are seen to be in the same direction.

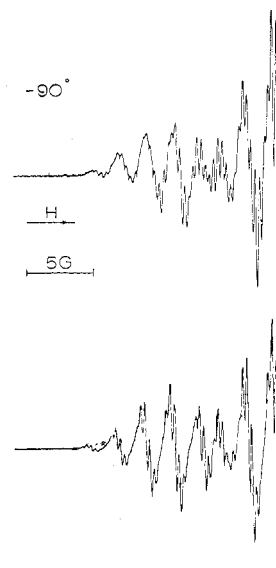
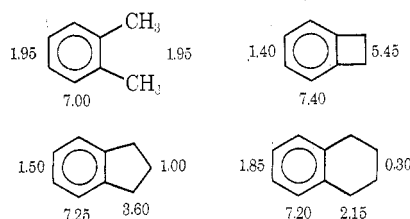


Figure 6.—Esr spectrum of the radical anion of IV: upper, experimental spectrum at -90° ; lower, calculated -90° spectrum using a line width of 0.20 G.

CHART III
HFSC AT -90° FOR COMPOUNDS I-IV REDUCED WITH POTASSIUM IN DME (80%) AND HMPA (20%)



Reduction with Potassium in THF (80%) and HMPA (20%). Initial Hydrocarbon Concentration, 0.01 M.—Reductions were carried out in THF to lower the temperature range beyond that which was accessible in DME. The volume ratio and initial hydrocarbon concentration were the same as employed in the previous section. Reduction in all cases yielded dark blue solutions.

Compound I was not reduced using these conditions.

Reduction of II gave reversible spectra from -100 to -130° , the four methylene protons being equivalent over this temperature range, indicating formation of the free ion. At lower temperatures (-125° and below) anisotropic broadening was observed, and the spectrum width decreased slightly as the temperature was raised. The hfsc values were essentially temperature independent. At -110° the following values were observed: $A_{1,4} = 7.45$, $A_{\text{CH}_2} = 5.50$, $A_{5,6} = 1.40$. A slight increase to $A_{1,4} = 7.49$ and $A_{\text{CH}_2} = 5.60$ was noted at -125° .

Compound III was reduced, yielding reversible spectra from -100 to -130° . With the exception of anisotropic line broadening at low temperatures the spectrum width and hfsc showed very little variation. At -110° the spectrum could be simulated quite well using hfsc of $A_{1,4} = 7.25$, $A_{\text{CH}_{2\alpha}} = 3.60$, $A_{\text{CH}_{2\beta}} = 1.00$, and $A_{5,6} = 1.50$. These spectra were the same as those obtained at -85° and below using the conditions of the previous section, indicating this species to be the

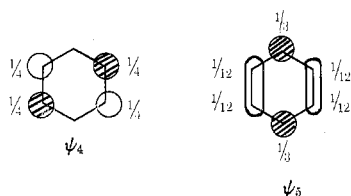
free ion. The ion-paired species was not observed under these reduction conditions.

Using these conditions, IV reduced with some difficulty. A weak spectra which could be simulated with the hfsc shown in Chart III was obtained.

Discussion of Ring Strain Effects.—The results obtained for the benzene series reduced in DME and HMPA, summarized in Charts II and III, show the perturbation of spin density with ring strain. Examination of the charts indicates that as strain is increased the spin densities are strongly perturbed toward the strain ring. This means that the value of $A_{1,4}$ increases and $A_{5,6}$ decreases as strain is increased. It was desirable to obtain the esr spectra of these compounds in the absence of ion pairing, so that any interpretation of the results which invoked ion-pairing perturbation of spin densities could be ruled out. It was felt that the values obtained for the 0.01 *M* solutions in 80% DME and 20% HMPA (Chart III) are from the free ions, ion pairing being negligible at -90° . In any case, the hfsc obtained for the 0.1 *M* and 0.01 *M* samples in the different solvent systems indicate that an explanation other than ion-pair perturbation is required to adequately explain the results obtained.

The observed spin densities may be readily explained using the model of Finnegan–Streitwieser.^{11,12} The reduction of an ortho-disubstituted benzene compound adds an electron to one of the two nearly degenerate benzene antibonding orbitals shown in Chart IV. It

CHART IV^a
NEARLY DEGENERATE BENZENE ANTIBONDING ORBITALS



^a The thatched circles represent p orbitals with the plus signs up while the empty circles represent p orbitals with the plus signs down. The number beside each orbital is the square of the coefficient.

has been demonstrated for many substituted benzenes that, if the substituent is electron donating, the extra electron will prefer the orbital which avoids the substituent. However, if the substituent is electron attracting, the extra electron will prefer the orbital which places maximum electron density next to the substituent.²⁵⁻²⁹ The perturbation is never complete and

(25) T. R. Tuttle and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 5342 (1958).

(26) H. L. Strauss and T. J. Katz, *J. Chem. Phys.*, **32**, 1873 (1960).

(27) J. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

(28) T. R. Tuttle, *J. Amer. Chem. Soc.*, **84**, 2839 (1962).

(29) P. Rieger and G. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

generally the electron enters an orbital which is an admixture of the two orbitals. In the case of II, the extra electron will obviously enter ψ_5 , which explains the large hfsc for the 1 and 4 positions. The hfsc were calculated using McConnell's³⁰ equation, employing a *Q* value of 22.5 times the spin density at a given position in ψ_5 , and the correlation was excellent. However, the hfsc values for the 1 and 4 positions of I, the least strained compound studied, were found to be 7.00 compared to 7.40 for BCB (Chart IV). It has been shown that the spin densities of several strained compounds could be correlated by making the carbon atoms α to the strained ring more electronegative.¹⁵ Thus, in II the electron enters an antibonding orbital which weighs ψ_5 more heavily than in the case of I. In both cases the substituents are electron donating, causing the electron to prefer ψ_5 ; however, the increased electronegativity of the 1 and 4 positions of II results in a heavier weighting of ψ_5 . For III and IV the effects of strain are less compared to II and the hfsc values for the 1 and 4 positions of 7.25 and 7.20 show a shift toward the weighting of ψ_4 and ψ_5 observed for I. This discussion assumes that the spin polarization mechanism for the 1 and 4 positions is unaffected by ring strain. Accordingly, the hfsc values for the benzene compounds at these positions which are directly proportional to spin density can be compared.

The use of the Finnegan–Streitwieser model discussed above provides a good qualitative explanation for the strain effects observed in the benzene series. For the corresponding naphthalene compounds¹ this model is placed on a more quantitative basis by using simple Hückel MO calculations and the more sophisticated Mulliken–Wheland–Mann technique.

One further point of interest is the difference in spin densities of I and IV. Formally both compounds are strain free and have two electron-donating alkyl groups. In the naphthalene series, there was little difference in the spin densities of 2,3-dimethylnaphthalene and 1,2,3,4-tetrahydroanthracene. This was taken to mean that two *o*-methyl groups can be treated the same way as two *o*-methylene groups in a strain free ring. This is apparently not so in the case of benzene. The difference in spin densities could be caused by some ion pairing which we have not removed totally but this seems unlikely. The difference in these two types of substituents is further demonstrated by the difference in chemical properties of these two molecules.¹⁶

Registry No. —I, 95-47-6; II, 694-87-1; III, 496-11-7; IV, 119-64-2.

Acknowledgment.—Financial support of this investigation by the National Science Foundation is gratefully acknowledged.

(30) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).