Free Radicals in an Adamantane Matrix. XII. EPR and INDO Study of σ^*–π^* Crossover in Fluorinated Benzene Anions

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Abstract: Hexafluorobenzene, pentafluorobenzene, 1,2,4,5-tetrafluorobenzene, and *p*-difluorobenzene anion radicals have been produced by x-irradiation of an adamantane maxtrix which was doubly doped with the aromatic precursor and Me_3NBH_3, and their EPR spectra obtained. That this method produces anion radicals was confirmed by subsequent preparation of $C_6F_6^-$ and $C_6H_6^-$ by photolysis with visible light of a layered mixture of adamantane–radical precursor–adamantane–sodium–adamantane. The role of Me_3NBH_3 in these preparations appears to be that of a simple electron donor. The large fluorine hfs constants of the hexa-, penta-, and tetrafluorobenzene anion radicals and the small fluorine hfs constants of the *p*-difluorobenzene anion radical suggest that the former three are σ radicals while the latter is a π radical. The σ^*–π^* crossover phenomenon observed in the fluorinated benzene anion series is explained in terms of preferential lowering of σ orbitals by the fluorine substituents.

I. Introduction

Many studies[1,2] have involved the comparison of electron paramagnetic resonance results of fluorinated radicals with their hydrogen-substituted counterparts. This allows measurement of the effects of fluorine substitutions on molecular orbitals. Even though there has been much interest in fluorinated aromatic anion radicals, it has long been known that their production is very difficult. Radical anions are conventionally prepared in solution by alkali metal reduction,[3] or electrolytic reduction.[4] These methods have proven successful for a wide variety of compounds but have generally not worked with aromatic molecules containing fluorine.[5] With alkali metal reduction the molecule tends to lose a fluoride ion.[6] It is possible in some cases to make fluorine-containing anion radicals by electrolytic reduction if electron-withdrawing groups such as nitro or carbonyl are present in the molecule. Fluorinated nitrobenzene[4,7-12] and benzaldehyde[11] radical anions have been prepared and studied by EPR. However, with highly fluorinated compounds such as pentafluoronitrobenzene, attempts to prepare the radical anion have failed.[6,7]

Kasai and co-workers[13] have developed a method of preparing anion radicals in an argon matrix by co-deposition of alkali metal atoms and the compound, followed by photolysis to generate the anion radical and Na^+ as the counterion. The method has been used, for example, to obtain anion radicals from nitrogen heterocycles such as pyrrole and indole.[14] However, with fluorobenzene the neutral phenyl radical was produced.[13]

Even though some limited number of fluorinated aromatic radical anions has been prepared by using one of the methods described above, the most essential condition was the attachment of a strong electron-withdrawing group to the atomatic ring. It is obvious, however, that the electronic structures of these radicals are highly perturbed by the electron-withdrawing group. Therefore many efforts[11,15] have been focussed on the investigation of anion radicals containing only fluorine substituents. The most desirable series of compounds in this respect may be the fluorinated benzene radical anions.

We present here an EPR study of the radical anions of hexa-, penta-, 1,2,4,5-tetra-, and *p*-difluorobenzene prepared by x-irradiation of an adamantane matrix doubly doped with trimethylamine-borane (Me_3NBH_3) and the anion precursors.

II. Experimental Section

The EPR spectrometer and accessories used for this work have been described elsewhere.[2]

Since this experiment utilizes deliberately introduced impurities, it is important to have high-purity adamantane as a matrix. Aldrich Gold Label (99% +) adamantane was treated with Nuchar-C190-N activated carbon (Fisher Scientific Co.) in heptane. Trimethylamine-borane (Peninsular Chem. Research Inc., Fla.) was purified in the same way as adamantane. The following chemicals were used as received: (1) adamantane-d_{16} (97.7% minimum isotopic purity obtained from Isotopic Products, Merck Sharp and Dohme of Canada Limited, Montreal, Canada), (2) benzene-d_6 (Diaprep Inc., Atlanta), (3) monofluorobenzene (Matheson Coleman and Bell), (4) *p*-difluorobenzene (Pierce Chemical Co.), (5) 1,3,5-trifluorobenzene, (6) 1,2,4,5-tetrafluorobenzene, (7) hexafluorobenzene (the above three compounds were obtained from Peninsular Chem. Research Inc., Fla.), (8) pentafluorobenzene (Aldrich Chemical Co. Inc.), and (9) benzene "Baker Analyzed" (J. T. Baker Chemical Co.).

For producing fluorinated benzene radical anions, about 0.5% of the desired aromatic compound and a somewhat larger amount of Me_3NBH_3 were introduced into purified adamantane and degassed several times by the freeze–pump–thaw method. This degassed mixture was then heated at about 140 °C in an oil bath to cause sublimation to the cold end of the tube. The resulting powder, doped evenly by the desired impurity, was pressed to 15 000 psi in a die (3 mm × 10 mm length). The resulting pellet was cooled to 77 K by immersion in a foam Dewar filled with liquid nitrogen and then x-irradiated in a styrofoam boat floating in liquid nitrogen for typically 15 min with a Machlett AEG 50 T semiportable tube operated at 50 kV and 30 mA. The sample was usually 3 in. from the target and received a flux of $\sim 10^6$ rad/h.

Another method used for preparation of hexafluorobenzene and benzene anion radicals was co-deposition with sodium atoms in an adamantane matrix followed by visible light photolysis. Figure 1 shows the sodium deposition apparatus. The compound to be doped was introduced at A. The alkali metal reservoir was connected to B of the chamber, which was continuously evacuated through a vacuum pump C during the deposition. The alkali metal was purified by triple distillation in glass. The purified sodium was heated to $\sim$180 °C while its outlet to the deposition chamber was blocked by chopper D. The deposition plate E was cooled by liquid nitrogen, then the materials were deposited in the sequence adamantane, sample, adamantane, sodium, adamantane. After deposition was completed, the sample deposit was removed in fine flakes by using the glass knife F and collected in a quartz tube at the bottom of the cow G which was also cooled to 77 K. The sample tube was photolyzed in the cavity with a 1-kW Hanovia compact arc Xenon lamp.

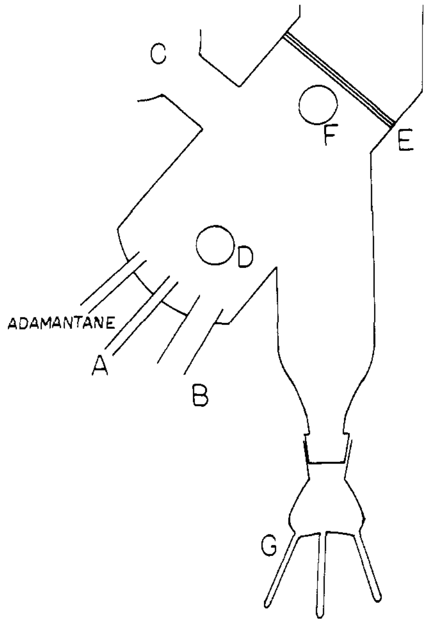


Figure 1. Schematic diagram of sodium apparatus.

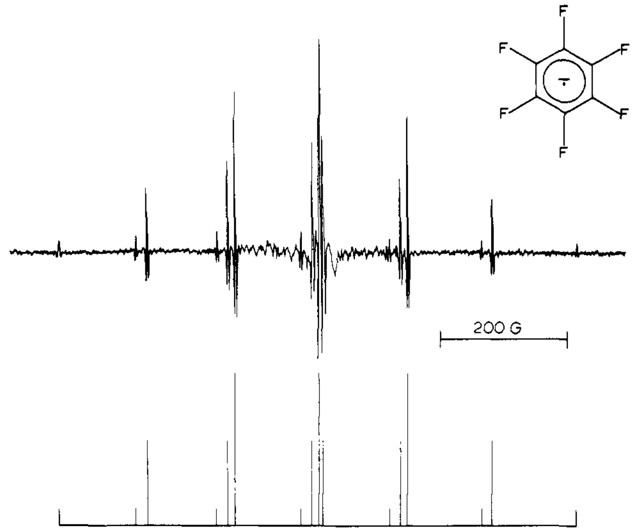


Figure 2. EPR spectrum of hexafluorobenzene anion radical in an adamantane-Me_3NBH_3 matrix at 218 K. The stick diagram shows the location of the expected second-order components. Extra lines near the center belong to the anisotropically broadened hydrogen addition radical of hexafluorobenzene, C_6F_6H.

III. Results

A. Hexafluorobenzene Anion.[16] The EPR spectrum of hexafluorobenzene anion radical in the x-irradiated adamantane-Me_3NBH_3 matrix at 218 K is shown in Figure 2. The smaller lines in the center of the spectrum are due to the anisotropically broadened EPR spectrum of a cyclohexadienyl type of radical[2] caused by hydrogen atom addition to hexafluorobenzene. For the six equivalent nuclei with $I = \frac{1}{2}$, seven equally spaced lines with intensity ratios 1:6:15: 20:15:6:1 would be expected from a first-order treatment. The spectrum in Figure 2, however, shows further splittings, indicating the need of a second-order treatment. When Fessenden's second-order treatment[17,18] is employed, the seven lines will be further split into (1), (1,5), (1,5,9), (1,5,9,*5*), (1,5,9), (1,5), and (1) groups and the line positions will be shifted downfield except for the intensity *5* line in the (1, 5, 9, *5*) set. The experimental spectrum agrees well with the expected spectrum of $C_6F_6^-$ radical anion with six equivalent fluorine nuclei, A_F = 137 G and g = 2.0015 (Table I), as can be seen from the placement of the second-order components in the stick diagram. The EPR signal strength and hyperfine splitting are essentially unchanged between 240 K (above which the radical irreversibly decayed) and 140 K (below which the spectrum became anisotropic). Further evidence for the assignment of the spectra obtained in the adamantane-Me_3NBH_3 matrix to anion radicals has been obtained by photolysis of sodium in an adamantane matrix doped with radical precursor.

Hexafluorobenzene reacts with sodium atoms upon direct contact at 120 K. To prevent this reaction the sample deposition was performed in layers, adamantane-C_6F_6-adamantane-sodium-adamantane, followed by photolysis with visible light. Very weak signals originating from the $C_6F_6^-$ appeared during photolysis but the light seemed to destroy the radical at the same time (Figure 3). The line positions originating from hexafluorobenzene anion radical in Figure 3 exactly match those from Figure 2; however, the intensity ratios are not perfect. Ion pairing may play a role in this deviation. Benzene anion radical was also produced by this method using benzene as the dopant.

B. Pentafluorobenzene Anion. Adamantane doped with pentafluorobenzene and Me_3NBH_3, then x-irradiated at 77 K, yields the pentafluorobenzene anion radical, whose EPR spectrum at 223 K is shown in Figure 4 together with a computer simulation based on the parameters of Table I: A_1 (2) = 45.5 G, A_2 (2) = 101 G, A_3 (1) = 279 G, and line width = 4.2 G. The intensity ratios of the lines in each half of the spectrum would be expected to be 1:2:1:2:4:2:1:2:1 while experimentally the high-field 2:4:2 set is broadened

Table I. Comparison of Hfs Constants of Fluorinated Aromatic Anion and Cation Radicals

Radical precursor	Temp, °K	Isotropic hfs constants, G[a-c]	g value	Ref
Hexafluorobenzene		(+) $A_F(6) = 15.9$		19
	218	(−) $A_F(6) = 137$	2.0015	*e*
Pentafluorobenzene		(+) $A_F{}^o(2) = 25.8$, $A_F{}^m(2) = 25.8$, $A_F{}^p = 4.8$		19
	223	(−) $A_H < 4$, $A_F{}^o(2) = 101$,[d] $A_F{}^m(2) = 45.5$, $A_F{}^p = 279$	2.0070	*e*
1,2,4,5-Tetrafluorobenzene		(+) $A_F(4) = 25.8$		19
	125	(−) $A_H(2) = 7.80$, $A_F(4) = 51.0$	2.0032	*e*
p-Difluorobenzene	110	(−) $A_H(4) = 5.30$, $A_F(2) = 1.75$	2.0029	*e*
Benzene	163	(+) $A_H(6) = 4.40 \pm 0.03$ G		20
	173	(−) $A_H(6) = 3.75$	2.0028	21
4,4′-Difluorobiphenyl		(+) $A_F(2) = 19.28$, $A_H(4) = 2.73$		22
	193	(−) $A_F(2) = 3.13$, $A_H(4) = 2.28$		15

[a] (+) cation, (−) anion. [b] The numbers in parentheses are the number of magnetically equivalent atoms. [c] Accuracy of hfs and g values are ±1% and ±0.0003, respectively. [d] 101 G was assigned as the ortho hfs constant on the basis of INDO results. [e] This work.

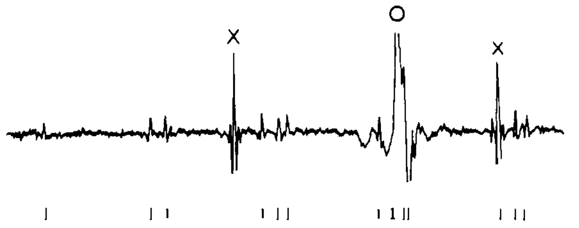


Figure 3. EPR spectrum of hexafluorobenzene anion radical generated by photolysis of sodium in an adamantane matrix doped with hexafluorobenzene. Lines labeled X result from sodium atoms; the lines marked O are from matrix-derived radicals. The stick diagram indicates the positions of the first five sets of lines from $C_6F_6^-$.

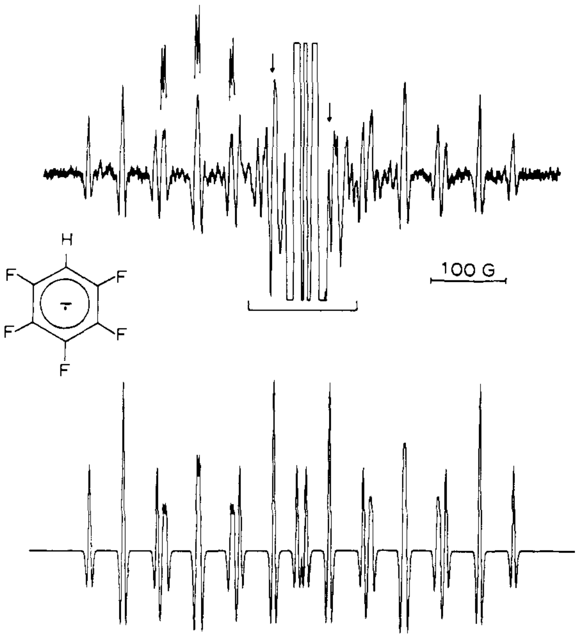


Figure 4. EPR spectrum of pentafluorobenzene anion radical in an adamantane-Me_3NBH_3 matrix at 223 K compared with its computer simulation (below). The high-intensity lines at the center belong to the $C_6F_5H_2$ radical (within single bracket). Arrows indicate two of the lines within this region belonging to the anion radical.

and the low-field 2:4:2 set is split into doublets. When the second-order effect is considered for the A_2 splitting, approximated as 3.5 G for the low-field half and 3.2 G for the high-field half of the spectrum, the simulated spectrum gave good agreement with the experimental. The central part of the spectrum is complicated because of broad lines from a high concentration of a cyclohexadienyl type radical.[2] Removal of the pentafluorobenzene anion by annealing established the presence of the expected lines in the center of the spectrum. An INDO calculation for the σ radical (vide infra) shows that $A_F^p(1) > A_F^o(2) > A_F^m(2) > A_H$; therefore the parameters were assigned as $A_F^p = 279$ G, $A_F^o(2) = 101$ G, $A_F^m(2) = 45.5$ G, and $A_H < 4.2$ G.

C. **Tetrafluorobenzene.** The EPR spectrum of tetrafluorobenzene anion radical in an adamantane-Me_3NBH_3 matrix at 125 K is shown in Figure 5 together with a computer simulation based on the parameters of Table I: $A_H(2) = 7.80$ G and $A_F(4) = 51.0$ G with a line width = 3.3 G. The central part of the spectrum was affected by radical(s) from the matrix itself. As the sample was warmed to 137 K, the lines became sharper while the concentration of matrix radical(s) increased. At 173 K, the lines from tetrafluorobenzene anion radicals were not observable. By recooling the sample, lines due to the matrix radical(s) could be positively identified and by difference all lines of $C_6F_4H_2^-$ were detected.

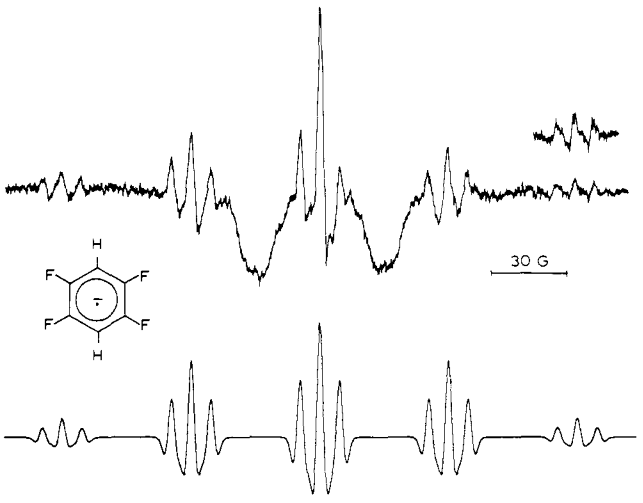


Figure 5. EPR spectrum of 1,2,4,5-tetrafluorobenzene anion radical in an adamantane-Me_3NBH_3 matrix at 125 K compared with its computer simulation (below).

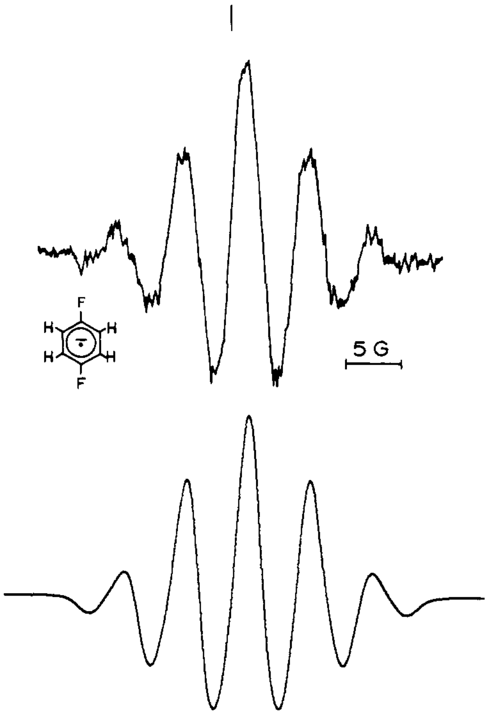


Figure 6. EPR spectrum of p-difluorobenzene anion radical in an adamantane-Me_3NBH_3 matrix at 110 K compared with its computer simulation (below).

D. **p-Difluorobenzene Anion.** p-Difluorobenzene anion was the most difficult to observe of all the anions reported here because exposure to room light (fluorescent) for ~15 min totally destroyed the EPR signal. X-irradiation and EPR measurements, therefore, were performed in the dark.

The EPR spectum of p-difluorobenzene radical anion in an adamantane-Me_3NBH_3 matrix at 110 K is shown in Figure 6 together with a computer simulation based on the parameters of Table I: $A_H(4) = 5.30$ G and $A_F(2) = 1.75$ G with line width = 2.8 G. With $A_F = 0$ and $A_H = 5.55$ G we also obtained a reasonable fit to the experimental spectrum. Even though the intensity ratios of the lines simulated with $A_F(2) = 1.75$ G is closer to the experimental spectrum than with $A_F(2) = 0$, this may not be the best choice. The reason for this is that the benzene anion prepared by this method does not show quite the expected intensity ratios; the central line is more intense than it should be (Figure 7).

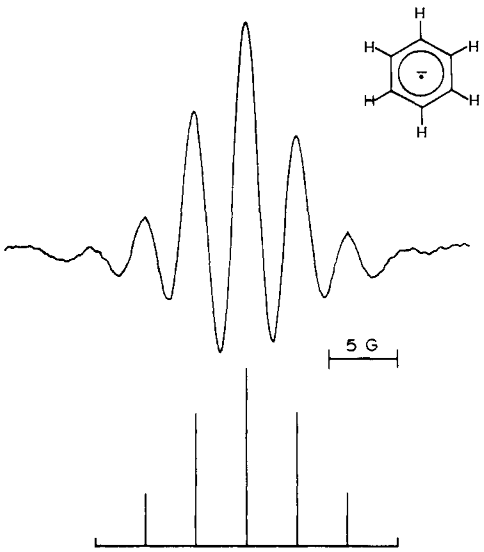


Figure 7. EPR spectrum of benzene anion radical in an adamantane–Me_3NBH_3 matrix at 121 K compared with its stick diagram (below).

This may be explained by the addition of a broad line from some other damaged species originating in the adamantane–Me_3NBH_3 matrix. Therefore, we assign the hyperfine constants for *p*-difluorobenzene anion as $A_F(2)_{max} = 1.75$ G and $A_H(4)_{min} = 5.30$ G. The *g* value for this radical is 2.0029 ± 0.0003 which is between that of benzene anion and 1,2,4,5-tetrafluorobenzene anion.

E. Other Fluorinated Benzene Anions. Tri- and monofluorobenzene anion radicals were not observed in the adamantane–Me_3NBH_3 matrix in this experiment.

When an adamantane matrix doped with monofluorobenzene (GC checked) and Me_3NBH_3 was x-irradiated at 77 K, the anisotropically broadened spectrum of cyclohexadienyl radical was observed at 100 K. It is quite interesting to compare this result with that of benzene in the adamantane–Me_3NBH_3 matrix. When an adamantane matrix doped with benzene and Me_3NBH_3 was x-irradiated at 77 K, benzene anion radicals (Figure 7) were observed with six equivalent hydrogen hyperfine splittings of 3.69 G and a *g* value of 2.0028 at 121 K; however, lines from cyclohexadienyl radical were not observed at this temperature (they do appear at higher temperature).

IV. Discussion

A. Role of Me_3NBH_3. The adamantane matrix technique for the preparation and stabilization of free radicals, developed over the past several years,[2,23] has proven to be quite successful for the EPR study of neutral organic free radicals. We have recently[2] reported the effect of fluorine substitution on cyclohexadienyl radicals prepared in this matrix. However, it has not previously been used as a matrix for anion radicals.[16] One of the main problems is that the adamantane matrix apparently does not have deep enough hole traps to avoid electron-hole recombination at 77 K. The obvious solution to this problem is to doubly dope the adamantane with a radical precursor and a strong electron donor.

In a similar manner Carter and Vincow[20,24] have prepared monopositive cations such as $C_6H_6^+$, $C_6(CH_3)_6^+$, and $C_6(CH_2CH_3)_6^+$ by photoionization of radical precursors in concentrated sulfuric, boric, and phosphoric acid glasses, which are strong oxidizing agents. Borane-amine complexes are known as excellent reducing agents. X-irradiation may ionize Me_3NBH_3 as the primary radiation damage process and the electrons produced would be trapped at the radical precursors:

$$Me_3NBH_3 \xrightarrow{\text{x ray}} Me_3NBH_3^+ + e^-$$

$$C_6F_6 + e^- \rightarrow C_6F_6^-$$

This kind of highly selective capture of an ejected electron by a small amount of guest molecules has been reported by Iwasaki, Muto, and Toriyama[25] in the EPR study of a single crystal of fumaric acid doped succinic acid γ-irradiated at 77 K.

B. Isotropic Fluorine Hyperfine Constants for the Anions. The isotropic fluorine hfs constant for hexa-, penta-, and 1,2,4,5-tetrafluorobenzene anion radicals obtained in this experiment are *unexpectedly large* when compared with previous results for fluorinated aromatic radicals. Some previously known fluorinated aromatic radicals with large fluorine hfs constants are: 8.6 G in 4-fluoronitrobenzene anion,[4,9] 4.4 G in $C_6F_5(NO)OR$,[7] 27.4 G in 4-FC_6H_4O,[26] 22.96 G in 4-fluorobenzonitrile anion,[27] 19.28 G in 4,4′-difluorobiphenyl cation,[22] and 25.8 G in 1,2,4,5-tetrafluorobenzene cation.[19] The general trend of the fluorine hfs constants listed above is that they are about two to three times larger than the hydrogen that they replaced. A McConnell type relationship for fluorine hfs constants in π radicals has been suggested.[28-30]

$$A_F = Q_{cc}{}^F\rho_{cc} + Q_{cF}{}^F\rho_{cF} + Q_{FF}{}^F\rho_{FF} \tag{1}$$

where $Q_{cc}{}^F = 4$ G, $Q_{cF}{}^F = -64$ G, $Q_{FF}{}^F = 264$ G. Since the ratios ρ_{FF}/ρ_{cc} and ρ_{cF}/ρ_{cc} are fairly constant from one molecule to the next for a particular type of calculation,[31] eq 1 may be reduced to[1]

$$A_F = Q_{eff}\rho_{cc} \tag{2}$$

where Q_{eff} values were empirically obtained from the experimental results as ca. +55 G for anions and ca. +90 G for cations. Although the absolute value of Q_{eff} may be subject to question, eq 2 suggests that the fluorine hfs constant of the cation should be generally larger in absolute value than that of the anion of the same aromatic radical precursor. Schastnev and Zhidomirov[28] proposed another relationship based on eq 1,

$$A_F = Q_{eff}'\rho_{FF} \tag{3}$$

where $Q_{eff}' \simeq 445$ G empirically. In eq 3 Q_{eff}' is constant but, on the other hand, calculations with the molecular-orbital method show that the ratio ρ_{FF}/ρ_{cc} must increase upon passing from anion radicals to cation radicals because the energy separation between the unpaired electron orbital and the atomic p orbital of fluorine is reduced.[28] This effect will necessarily increase the conjugation of the unpaired electron orbital on carbon with the atomic p orbital of fluorine and therefore results in reducing the C–F bond length. This is also predicted by the INDO optimized geometries of π radicals (vide infra). Therefore eq 3 also suggests that the hfs constant of the cation should be larger than that of the anion from the same radical precursor.

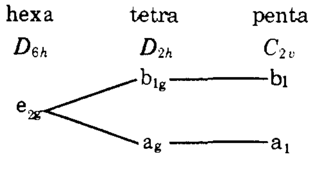
Both the anion[15] and the cation[22] of 4,4-difluorobiphenyl are known and show this trend (Table I). The fluorine hfs constant increases from 3.13 to 19.28 G on going from the anion to cation. If both the cation and anion of hexafluorobenzene are π radicals, the same trend as for 4,4′-difluorobiphenyl ion radicals would be expected. This is, however, not the case for the hexafluorobenzene ions compared in Table I. The fluorine hfs constant of the anion is much larger than that of the cation. This suggests that the anion of hexafluorobenzene is a different type of radical, namely a σ radical.

The hfs constant of the p-difluorobenzene anion radical (Table I) indicates that this is a π radical with an unpaired electron occupying the antisymmetric orbital (A) of the originally degenerate $1e_{2u}$ orbital of benzene. With $Q = -22.5$ G for the McConnell relationship, we obtain $A_H = -5.6$ G if all the unpaired electron density were in the (A) orbital. This value is very close to the experimentally obtained $A_H = 5.30$ G. The result suggests that fluorine has a strong π-electron-releasing character. Fluorine has been shown to behave as a strong σ-electron attractor, but at the same time it apparently back donates π electrons.[32] This back-donation of π electrons to the benzene ring destabilizes the (S) orbital of the originally degenerate π^* orbital and thus most of the unpaired spin density is found in the (A) orbital. This is in agreement with the ortho- and para-directing property of fluorine and shows that the π-electron system is mainly responsible for the directing property.

On the basis of this result of p-difluorobenzene anion radical most of the unpaired electron density of the penta- and tetrafluorobenzene anions and cations will be placed, *if they are π radicals*, in (S) orbitals. Then the fluorine hfs constants of the ortho and the meta positions of penta- and tetrafluorobenzene anions should be smaller than in the corresponding cations. Thus, there are two effects which should make the ortho and meta fluorine hfs constants of penta- and tetrafluorobenzene anions smaller than for the cations if they are all π radicals. However, this is not the case and these anions must also be σ radicals (Table I).

C. Crossover of the π^*–σ^* Orbitals. It is now clear that we have observed a π radical in p-difluorobenzene anion and σ radicals in hexa-, penta-, and *sym*-tetrafluorobenzene anions, and therefore, a crossover of the π^* and σ^* orbitals has occurred. A qualitative explanation for this phenomena may be given as follows. Figure 8 shows an energy level diagram of some of the highest occupied and the lowest unoccupied energy levels for the benzene framework. The sequence of occupied energy levels is assigned on the basis of photoelectron spectroscopic results of Brundle, Robin, and Kuebler[33] and unoccupied levels are assumed correspondingly. An extra electron will be placed in the $1e_{2u}$ degenerate (nearly degenerate) π orbital, without altering its energy, as the lowest approximation for the benzene anion. Upon fluorination the p-difluorobenzene anion (S) orbital will be destabilized while the energy of the (A) orbital will remain the same. The inductive effect of the fluorine will cause lowering of the σ^* orbital as shown in Figure 8. When more fluorines are substituted for hydrogens the σ^* orbital will be stabilized increasingly while the energy of both (A) and (S) orbitals will be pushed upwards which results in crossover of the σ^*–π^* orbitals.

The symmetry properties of the σ^* orbitals are quite interesting. The experimental isotropic hfs constants of the hexafluorobenzene anion suggests that the lowest σ^* orbital is either a_{1g} or e_{2g}. A choice based on the $C_6F_6^-$ hfs constant is not possible at this time. However, if one assumes that a unique orbital is associated with all of the fluorinated benzene anion σ radicals reported here, the e_{2g} is the best choice to account for all of the σ anions. The splitting of the originally degenerate e_{2g} σ^* orbital will occur for the penta- and tetrafluorobenzene anions due to the lowering of the symmetry of the molecules as shown below. A large spin density on the para hydrogens indicates that the a_g orbital is probable for the tetrafluorobenzene anion. The large para fluorine hfs constant of the pentafluorobenzene anion suggests that most of the unpaired electron density is associated with the a_1 orbital. This interpretation closely parallels the case of the substituted benzene anion and cation π radicals. The fact that the hexafluorobenzene anion has the lowest g value of the fluorinated benzene anion σ radicals may then be associated with the degenerate ground state of this radical (Table I).



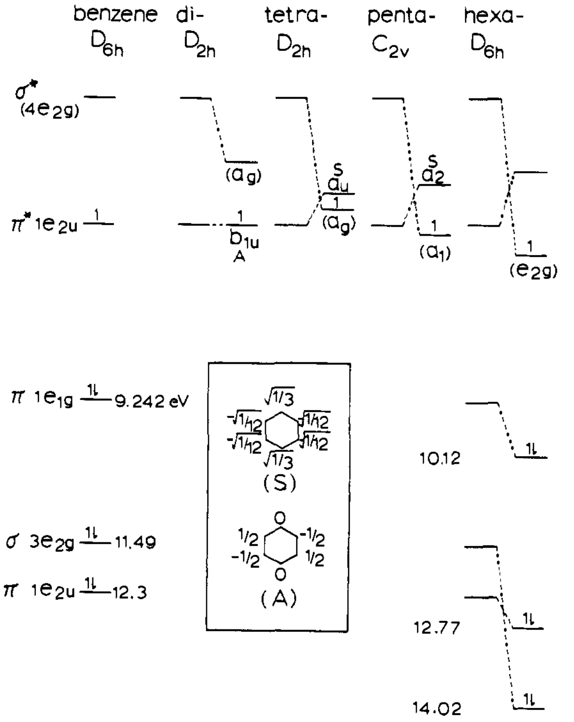


Figure 8. Approximate energy level diagram showing the σ^*–π^* crossover in the fluorinated benzene anion radicals. The energies in eV are from the photoelectron spectroscopy results of ref 33.

On the basis of the σ^*–π^* crossover scheme explained here, trifluorobenzene anion radical will certainly be close to the crossing point. The σ^* and π^* orbitals will be very close to each other in this anion and may explain the reason that we were unable to obtain its EPR signal.

D. INDO Calculations. INDO[32] energy minimizations which constrained the species to a planar geometry with D_{6h} symmetry for the carbon framework were performed for the anion and cation radicals. The resulting geometries and isotropic hfs constants are collected in Table II. The results for the π states can be summarized as follows. (1) The calculated hfs constants of the cation radicals agree reasonably well with the experimental values, if the value of 17 200 G per unit spin[34] is used for fluorine rather than the 44 829 G used to parameterize INDO.[32] (2) The calculated hfs constants for the π states of the anion radicals agree reasonably well with the experimental values of benzene and p-difluorobenzene. However, they are much too small for the hexa-, penta-, and tetrafluorobenzene anions. (3) The cations have large spin densities (and hfs constants) at the positions of fluorine substitution and the anions the opposite (except for the para position of pentafluorobenzene), as expected. (4) The calculations yield longer C–C and shorter C–F and C–H bond lengths for the cations than for the corresponding anions.

All of the anions were then recalculated as σ radicals by populating the lowest unoccupied σ^* orbital after the initial Hückel guess and before the first SCF cycle.[32] As long as the nuclear framework was kept planar, this type of calculation always converged to a σ state. Attempts to populate a different (higher) σ state always resulted in convergence to

Table II. INDO[32] Results for Fluorinated Benzene Anion and Cation Radicals

Radicals[a]	Isotropic hfs constants, G[b]	ΔE,[c] kcal/mol	Geometry, Å		
			C-C	C-F	C-H
C_{F6}^+ π	$A_F(6) = 43.6$		1.405	1.337	
$C_6F_6^-$ π	$A_F(6) = 5.98$	45.47	1.402	1.360	
$C_6F_6^-$ σ	$A_F(6) = 673$		1.384	1.379	
$C_6F_5H^+$ π	$A_H = 1.73$, $A_F{}^o(2) = 62.8$, $A_F{}^m(2) = 71.7$, $A_F{}^p = -8.97$		1.404	1.335	1.117
$C_6F_5H^-$ π	$A_H = -8.83$, $A_F{}^o(2) = 0.24$, $A_F{}^m(2) = 0.0045$, $A_F{}^p = 15.8$	42.58	1.399	1.360	1.120
$C_6F_5H^-$ σ	$A_H = 1.46$, $A_F{}^o(2) = 278$, $A_F{}^m(2) = 98.6$, $A_F{}^p = 2268$		1.390	1.377	1.119
$C_6F_4H_2^+$ π	$A_H(2) = 2.27$, $A_F(4) = 62.8$		1.402	1.333	1.117
$C_6F_4H_2^-$ π	$A_H(2) = -9.93$, $A_F(4) = 0.36$	54.48	1.398	1.361	1.120
$C_6F_4H_2^-$ σ	$A_H(2) = 107$, $A_F(4) = 592$		1.382	1.380	1.157
$C_6F_3H_3^+$ π	$A_H(3) = -5.42$, $A_F(3) = 41.8$		1.401	1.334	1.118
$C_6F_3H_3^-$ π	$A_H(3) = -2.70$, $A_F(3) = 2.99$	41.66	1.399	1.363	1.121
$C_6F_3H_3^-$ σ	$A_H(3) = 4.37$, $A_F(3) = 132$		1.390	1.390	1.122
$C_6F_2H_4^+$ π	$A_H(4) = -1.40$, $A_F(2) = 98.6$		1.399	1.328	1.118
$C_6F_2H_4^-$ π	$A_H(4) = -6.80$, $A_F(2) = 0$	59.07	1.399	1.362	1.122
$C_6F_2H_4^-$ σ	$A_H(4) = 93.6$, $A_F(2) = 506$		1.381	1.382	1.156
$C_6FH_5^+$ π	$A_H{}^o(2) = -3.46$, $A_H{}^m(2) = 0.648$, $A_H{}^p = -9.07$, $A_F = 139$		1.398	1.324	1.118
$C_6FH_5^-$ π	$A_H{}^o(2) = 6.48$, $A_H{}^m(2) = -7.29$, $A_H{}^p = 2.43$, $A_F = 0$	31.56	1.398	1.362	1.124
$C_6FH_5^-$ σ	$A_H{}^o(2) = 10.5$, $A_H{}^m(2) = 16.0$, $A_H{}^p = -0.380$, $A_F = 2180$		1.389	1.467	1.127
$C_6H_6^+$ π	$A_H(6) = -4.16$		1.399		1.119
$C_6H_6^-$ π	$A_H(6) = -3.87$	55.59	1.398		1.126
$C_6H_6^-$ σ	$A_H(6) = 81.0$		1.380		1.156

[a] (+) Cation; (−) anion; for $C_6F_4H_2$, $C_6F_3H_3$, and $C_6F_2H_4$ the fluorines are symmetrically placed. [b] The numbers in parentheses are the number of magnetically equivalent atoms. [c] $\Delta E = E_\sigma - E_\pi$ for anions.

this same σ state. Therefore we were unable to explore theoretically by INDO the various σ states as discussed in the previous section. The resulting hfs constants and geometries are collected in Table II together with the energy differences between the minimized[35] σ states and π states of the anion radicals. Unfortunately the σ states are all higher in energy and there is no *clear* trend in the energy differences which would indicate the likelihood of a σ^*–π^* crossover. Instead, there is a strong oscillatory behavior with odd numbers of fluorine yielding lower energy differences. It is interesting that the only π radicals which we have been able to make in the series have calculated energy differences greater than 55 kcal/mol while the σ radicals have a calculated energy difference less than 55 kcal/mol. The monofluoro and trifluorobenzene anions, which we have been unable to prepare, have the smallest calculated energy difference.

As discouraging as these calculations are from an energy standpoint, the hfs constants calculated for the σ states of the hexa-, penta-, and tetrafluorobenzene anions are not too far out of line from the experimental values, provided, as before, that the value of 17 200 G is used for fluorine[34] rather than the 44 829 G used to parameterize INDO.[32] Thus we obtain 260 for $C_6F_6^-$ vs. 137 G experimentally, and 106, 38, and 870 for $C_6F_5H^-$ vs. 101, 45.5, and 279 G experimentally, and 227 for $C_6F_4H_2^-$ vs. 51 G experimentally. However, the ^1H hfs constant calculated for the σ state of tetrafluorobenzene anion is rather too large at 107 G. The symmetries of the calculated σ states are a_g and a_1 for the tetra- and pentafluorobenzene anions as expected from the experimental hfs constants (vide spectra); however, the symmetry of the $C_6F_6^-$ σ states is the nondegenerate a_{1g} rather than the expected degenerate e_{2g}.

Conclusion

The relatively large fluorine hfs constants of the hexa-, penta-, and 1,2,4,5-tetrafluorobenzene anions indicate that they are σ radicals while the *p*-difluorobenzene anion is a π radical. A comparison of the fluorine hfs constants of cations and anions supports this conclusion. These results indicate that the fluorine substituents have inverted the relative energies of the lowest unoccupied π^* and σ^* orbitals in the benzene system. The combined effects of inductive stabilization of the σ^* orbitals and destabilization of the π^* orbitals by back donation from fluorine are suggested as a qualitative explanation for this phenomena.

INDO calculations give useful values for the relative magnitudes of the hfs constants observed for these σ and π radicals. However, these calculations do not correctly predict the relative energies of the σ and π states. Thus there is a need for more powerful calculations to be brought to bear on this problem.

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Dynamics of Eight-Membered Rings. 1,3-Dioxocane and Its *gem*-Dimethyl Derivatives

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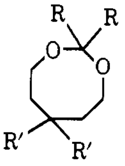
Abstract: The ^1H and the natural-abundance ^{13}C NMR spectra of 1,3-dioxocane and its 6,6-dimethyl, 2,2-dimethyl, and 2,2,6,6-tetramethyl derivatives (I to IV, respectively) have been measured over the temperature range of −10 to −170 °C. All four compounds exist as boat-chairs. Two conformational processes are found in each compound and the free-energy barriers are as follows: I, 5.7 and 7.3; II, 4.9 and 6.4; III, 6.4 and 11.0; IV, 5.8 and 10.8 kcal/mol. The lower energy processes in I and II are pseudorotations in which twist-boat-chairs are intermediates, whereas the corresponding processes in III and IV are pseudorotations in which boat-boats are intermediates. The reasons for these differences are discussed.

Eight-membered rings that have relatively low ring-torsional barriers can be grouped together from the conformational point of view.[1] This class of compounds includes cyclooctane, cyclooctanone, and a number of heterocyclic eight-membered rings. Heteroatoms can be regarded as generalized substituents and can be used to introduce conformational perturbations that are more or less predictable. For example, the replacement of a methylene group by an oxygen atom is expected to reduce transannular nonbonded repulsions and to have significant effects on torsional barriers and internal angle strains. A really satisfactory understanding of the conformations of such rings therefore should be based on a unified conformational scheme that includes both carbocyclic and heterocyclic eight-membered compounds.[1]

We report here a conformational study of 1,3-dioxocane (1,3-dioxacyclooctane) (I) and its three *gem*-dimethyl derivatives (II, III, and IV). In preliminary communications,[2,3] it was deduced that I[2,3] and III[3] exist in boat-chair conformations. On the basis of 100 MHz ^1H NMR data obtained over the range of room temperature to −130 °C, it was suggested[3] that II and IV adopted boat-boat conformations and that the reason for this preference was that the alternative boat-chair conformations were impossibly strained, as judged from Hendrickson's strain-energy calculations on methylcyclooctane.[4] However, the most serious nonbonded repulsion in II or IV involves an oxygen atom and a methyl group rather than a methylene and a methyl group as in the appropriate conformations of methylcyclooctane. The previous NMR data on II and IV actually are not inconsistent with boat-chair forms provided that suitable conformational processes are rapid on the NMR time scale under the conditions used. We have therefore reinvestigated the ^1H NMR spectra II, III, and IV at both lower temperatures and at a higher magnetic field than those previously employed, and have also measured the ^{13}C NMR spectra of compounds I to IV as a function of temperature.



I, R = R′ = H
II, R = H; R′ = Me
III, R = Me; R′ = H
IV, R = R′ = Me

Experimental Section

Compounds I, II, III, and IV were prepared from the appropriate diols and carbonyl compounds by known procedures.[5] NMR spectra were obtained on a superconducting solenoid spectrometer operating at 59 kG.[6] The proton spectra were obtained with standard 5-mm tubes in a frequency-sweep mode. The ^{13}C spectra are Fourier transforms of accumulated free-induction decays and were obtained with 10-mm tubes. All ^{13}C NMR spectra, with the exception of a few spectra obtained for assignment purposes, were taken with protons noise decoupled. The solvent for all NMR spectra was an approximately 2:1 mixture of $CHCl_2F$ and $CHClF_2$. Tetramethylsilane was used as an internal reference for both the ^1H and ^{13}C spectra. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample and connected to a Newport Laboratories digital thermometer reading to 0.1 °C and accurate to 0.2 °C.

Free energies of activation were calculated from rate constants by the absolute rate theory with a transmission coefficient of 1.