Free Radicals in an Adamantane Matrix. X. Electron Paramagnetic Resonance and INDO Study of Fluorinated Cyclohexadienyl Radicals[1]

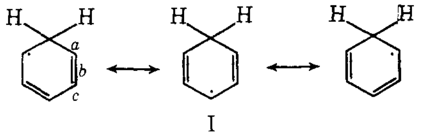
Moon B. Yim and David E. Wood*

Contribution from the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. *Received May 20, 1974*

Abstract: Cyclohexadienyl radical and six fluorinated cyclohexadienyl radicals were prepared by X-irradiation of adamantane matrices doped with: benzene, monofluoro-, 1,4-difluoro-, 1,3,5-trifluoro-, 1,2,4,5-tetrafluoro-, pentafluoro-, and hexafluorobenzene. The epr spectra obtained were analyzed by computer simulation. The substitutions of fluorine in the ring did not greatly affect the remaining hydrogen hfs constants in the ring but there was a substantial effect on the methylene hydrogen hfs constants which was explained in terms of the effect of fluorine on hyperconjugation. Fluorine was found to be ortho–para directing for hydrogen atom addition, and hydrogen atom addition at the site of a fluorine was observed only for hexafluorobenzene. A very large H/D isotope ratio was observed when adamantane-d_{16} (97.7% D) was used as a matrix. INDO energy minimization to obtain the optimum geometry for cyclohexadienyl radical resulted in a distorted planar hexagon and gave the experimentally observed ordering of the hfs constants. The major experimental hfs trends upon fluorine substitution were also correctly predicted by INDO.

I. Introduction

Cyclohexadienyl type radicals (I) have been prepared by the irradiation of solid benzene and its derivatives,[2-8] by irradiation of benzene and naphthalene in alcoholic solvents,[9-11] by tritium decay in solid naphthalene,[12] and by flow reactions of aromatics with hydroxyl radicals.[13-15] A noted feature of the cyclohexadienyl radical is the large hyperfine splitting (hfs) of the methylene protons (47.9 G). It was pointed out by Whiffen[16] that this is best explained in terms of a delocalized π-type molecular orbital in the pentadienyl fragment which interacts strongly with the $CH_2\cdot$ group through hyperconjugation. Pople, *et al.*,[17] calculated the hfs of cyclohexadienyl radical by INDO using a regular hexagon for the ring and a 109° 28′ H–C–H angle. This resulted in methylene proton hfs about twice the experimental value and ortho proton hfs larger than the para, while the experimental result shows para to be larger than ortho. They suggested that INDO may overemphasize the effect of the hyperconjugative interaction that Whiffen proposed due to the geometry employed. It is clear from a consideration of the valence bond structures in I that the order of bond lengths should be $a > c > b$. In a related problem concerning benzyl radical, calculations have been found to give better agreement with experimental hfs when such bond-length considerations were taken into account.[18-22]



I

Another unexplained difficulty with cyclohexadienyl radical is that replacement of one of the methylene protons with an OH group results in the reduction of the remaining methylene proton hfs to 36.0 G and that substitution of an additional OH ortho to the methylene group results in a further reduction to 27.5 G.[14,15] Other positions of substitution do not have nearly as large an effect. Possible explanations for this dramatic effect include hydrogen bonding, electronegativity effects, and geometric changes resulting from the substitutions. As far as is known, substitution of fluorine for hydrogen in odd alternant radicals has little effect on spin density distribution; however, fluorinated cyclohexadienyl radicals comparable to the OH-substituted radicals mentioned above have not been previously reported, and it is possible that substantial effects might be found in such cases. A study of such effects, or even their absence, could prove useful in determination of the causes of the effect.

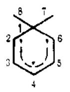
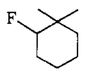
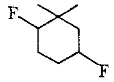
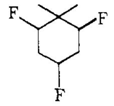
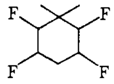
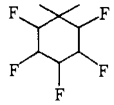
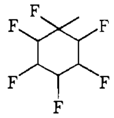
The recent discovery that cyclohexadienyl radicals can be prepared from substituted benzenes in adamantane[23] encouraged us to study a complete series of fluorine-substituted cyclohexadienyl radicals both experimentally and by INDO. The objectives of the research reported herein are: (1) to find if an energy-minimized INDO geometry yields better agreement with the experimental hfs and supports the distortions suggested by the simple valence bond argument and (2) to study the effects of systematic fluorine substitution on the cyclohexadienyl radical and determine if large effects on the hfs occur similar to those observed for OH substitution.

II. Experimental Section

A. Epr Measurements. The electron paramagnetic resonance spectra were recorded using a Varian Associates V-4502 spectrometer with a 12-in. magnet and Fieldial Mark II field regulation. The microwave frequency was measured with a Hewlett-Packard X532B wavemeter. Second derivative presentation was obtained by phase detection of a 500-Hz second-modulation frequency with a PAR HR-8. A Varian Associates TE_{104} dual cavity, or cylindrical TE_{011} cavity, with a quartz dewar insert from a Varian V-4547 variable temperature accessory was used with a 3 mm i.d. quartz sample tube. Temperatures were measured using a previously calibrated copper–constantan thermocouple. Two standards were used for magnetic field sweep calibration and measurements of g values: (1) Fremy's salt (potassium nitrosyl sulfonate, $A_N = 13.091 \pm 0.004$ G; $g = 2.00550 \pm 0.00005$)[24] and (2) DPPH (2,2-diphenyl-1-picrylhydrazyl, $g = 2.0037 \pm 0.0002$).[24]

B. Sample Preparation. 1. Materials. Since this experiment utilizes deliberately introduced impurities, it is important to have high-purity adamantane as a matrix. It has been found[25] that Aldrich' Gold label (99+%) adamantane, when used as received, gives background signals after X-irradiation, and that treatment with Nuchar-C190-N activated carbon (Fisher Scientific Co.) in heptane effectively removes the damageable impurities. 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; and (7) hexafluorobenzene (Peninsular Chem. Research Inc.,

Table I. Experimental Epr Parameters for Fluorinated Cyclohexadienyl Radicals in Adamantane Matrix

		Isotropic hfs, G[a,b]							
Radical	Temp, °K	2	3	4	5	6	7	8	*g* Value
	244	9.04	2.77	13.25	2.77	9.04	47.85	47.85	2.0028
	296	*16.43*	2.80	13.40	2.80	9.30	46.05	47.05	2.0031 2.0033 For para F
	265	*16.44*	2.60	13.80	*7.75*	9.00	45.66	45.66	2.0030
	255	*18.00*	2.70	*33.30*	2.70	*18.00*	45.60	45.60	2.0040
	263	*19.34*	*7.28*	13.32	*7.28*	*19.34*	45.60	45.60	2.0032
	250	*20.15*	*6.00*	*39.00*	*6.00*	*20.15*	43.90	43.90	2.0041
	263	*24.1*	*5.8*	*37.6*	*5.8*	*24.1*	19.3	*126.2*	2.0049

[a] *Static* hfs belong to fluorine, others to hydrogen. [b] Accuracies of hfs constants and *g* values are ~±1% and ~±0.0003, respectively.

Fla.); (8) pentafluorobenzene (Aldrich Chemical Co., Inc.); and (9) benzene "Baker Analyzed" (J. T. Baker Chemical Co.).

2. Doping Adamantane by the Sublimation Method. About 0.5% of the desired aromatic compound was introduced into purified adamantane and degassed several times by the freeze-pump-thaw method. This degassed mixture was then heated at about 140° 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 50,000 psi in an evacuated die (3 mm diameter × 10 mm length) (0.1 mm). The resulting pellet was cooled to 77°K by immersion in liquid nitrogen and the 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 ~10^6 rads/hr.

III. Epr Results

A. Benzene. Adamantane doped with benzene and then X-irradiated as described above yields an epr spectrum of the cyclohexadienyl radical, C_6H_6-H, shown in Figure 1 together with a computer simulation based on the parameters of Table I. The major deviations between the experimental and simulated spectra are the lack of a good 1:2:1 intensity ratio (methylene protons) and a broadening of the center set of lines in the experimental spectrum. Both of these phenomena result from the second-order splitting[26,27] of the center set of lines into doublets which are not resolved in the adamantane matrix due to the line width of ~1.7 G. When adamantane-d_{16} (97.7%) was used as a matrix for benzene the resulting spectrum was a mixture of 43% C_6H_6-D and 57% C_6H_6-H. The line width of ~0.5 G in adamantane-d_{16} allowed resolution of the experimental second-order splitting of 0.75 G for the central pattern of the C_6H_6-H radical. These results agree well with those of Fessenden and Schuler[7,8] who prepared this radical by electron irradiation of liquid 1,4-cyclohexadiene. The epr spectrum obtained for benzene-d_6 in adamantane was a doublet (48.6 G) of 1:1:1 triplets (7.91 G) with a broad line width (~5.6) corresponding to the spectrum expected for the C_6D_6-H radical. These results indicate that the adamantane supplies almost all of the hydrogen (deuterium) atoms which add to the aromatic substrate and that there is furthermore a H/D isotope effect of ~50 for this overall process.

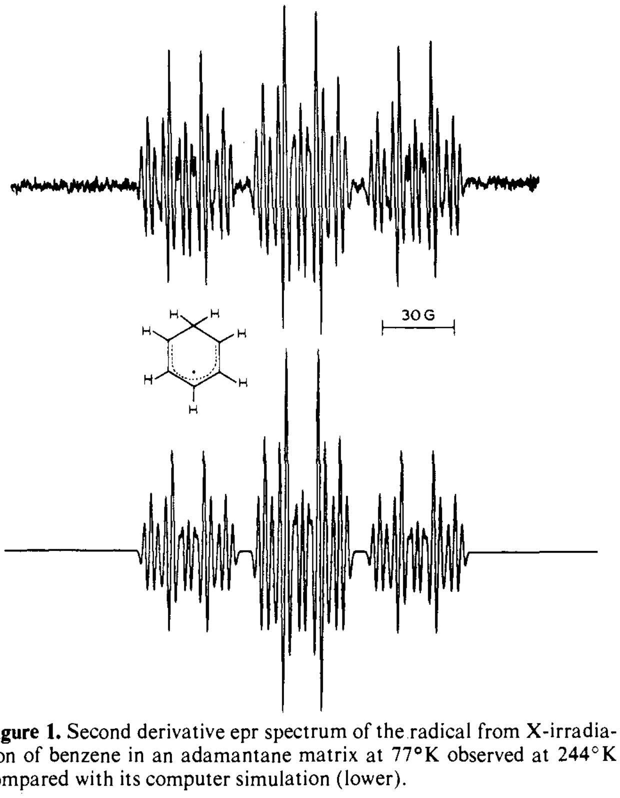


Figure 1. Second derivative epr spectrum of the radical from X-irradiation of benzene in an adamantane matrix at 77°K observed at 244°K compared with its computer simulation (lower).

B. Monofluorobenzene. Adamantane doped with monofluorobenzene gives the nonsymmetrical epr spectrum shown at the top of Figure 2. This is the result of more than one radical being formed rather than an anisotropic spectrum from a radical exhibiting restricted rotation as is the case for some of the more heavily fluorinated cyclohexadi-

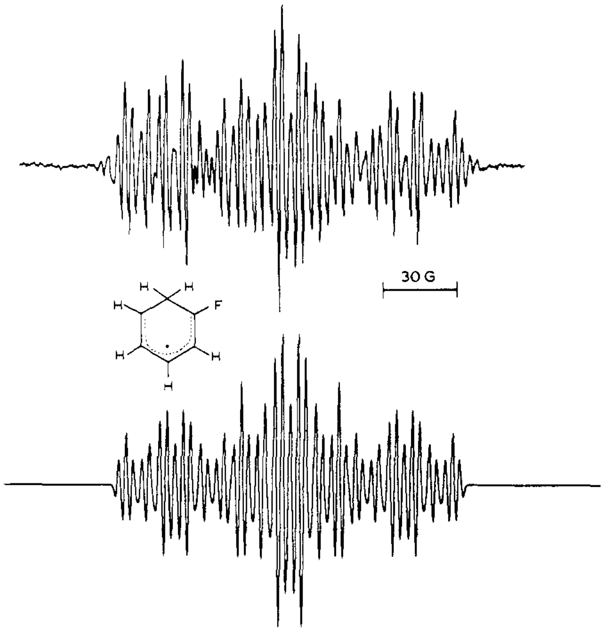


Figure 2. Second derivative epr spectrum of the radicals from X-irradiation of monofluorobenzene in an adamantane matrix at 77°K observed at 296°K compared with the computer simulation of the *o*-fluorocyclohexadienyl radical (lower).

enyl radicals (*vide infra*). The spectrum was analyzed by assuming that the outermost four lines belong to a radical present in low concentration. The simulated spectrum (Figure 2, bottom) then has nearly the same hfs as the C_6H_6-H radical (Table I) but with one of the ortho proton hfs, 9.04 G, replaced with a fluorine hfs of 16.43 G. Therefore the main radical species is *o*-fluorocyclohexadienyl. The low-concentration radical responsible for the outer lines can then best be explained as the *p*-fluorocyclohexadienyl with fluorine hfs of ~33.3 G. Substantiation of this assignment is given by similar para fluorine hfs observed in some of the other radicals (*vide infra*) and by the slightly larger *g* value (2.0033) than that measured for the ortho fluoro radical (2.0031). Complete analysis of the *p*-fluorocyclohexadienyl radical was not performed because of the strong overlap with the primary species. The ratio of ortho to para hydrogen addition is 6:1. The extent of formation of a possible *m*-fluorocyclohexadienyl radical can be given an upper limit of ~15%, but the smaller overall width expected rules out any analysis.

C. *p*-Difluorobenzene. The *p*-difluorobenzene can add hydrogen in only one position, excepting the fluorine site which is immediately ruled out because of the large 1:2:1 methylene splitting observed. The presence of six inequivalent hfs produces the rather complex overlapping spectrum shown in Figure 3 which is well reproduced by a computer simulation using the values in Table I.

D. *sym*-Trifluorobenzene The second derivative epr spectrum of X-irradiated *sym*-trifluorobenzene in adamantane is shown in Figure 4 compared with its computer simulation based on the parameters of Table I. The experimental spectrum was taken at 255°K because the radical begins to disappear above this temperature. The outermost triplets are broadened indicating that rotation of the radical in the matrix at this temperature is not quite rapid enough to completely remove the effects of the anisotropic part of the fluorine hfs. This broadening affects most strongly the "one" intensity lines from the ortho fluorine 1:2:1 triplet. The large 1:2:1 methylene triplet of 45.60 G indicates that the hydrogen has added at a protonated carbon.

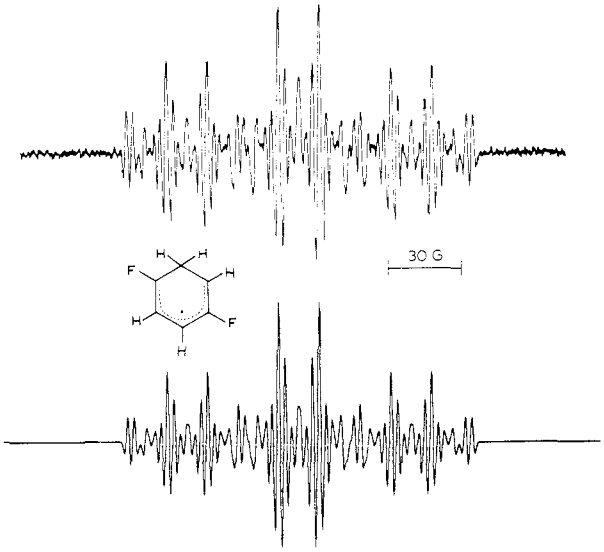


Figure 3. Second derivative epr spectrum of the radical from X-irradiation of *p*-difluorobenzene in an adamantane matrix at 77°K observed at 265°K compared with its computer simulation (lower).

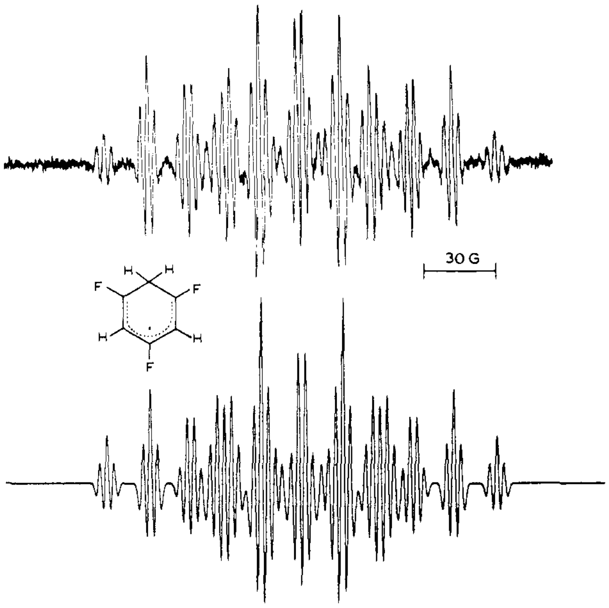


Figure 4. Second derivative epr spectrum of the radical from X-irradiation of 1,3,5-trifluorobenzene in an adamantane matrix at 77°K observed at 255°K compared with its computer simulation (lower).

E. 1,2,4,5-Tetrafluorobenzene. The epr spectrum of the radical from 1,2,4,5-tetrafluorobenzene shown in Figure 5 gives the appearance of line width alternation, but this is actually a fortuitous overlap as is demonstrated by the computer simulation based on the parameters of Table I at the bottom of the figure. The large 1;2:1 splitting of 45.60 G is indicative that the hydrogen addition has taken place at one of the two equivalent nonfluorinated positions. The identity of the other radical species causing interference in the center of the spectrum is not known.

F. Pentafluorobenzene. The epr spectrum of the radical from pentafluorobenzene in adamantane is apparently broadened considerably by the anisotropic effect of restricted rotation in the adamantane matrix. There is also a strong interference from an unknown radical species which seems to increase along with fluorine content in the precursors. The line positions of the experimental spectrum in Figure 6 are fairly well fitted by the simulation below it based on the

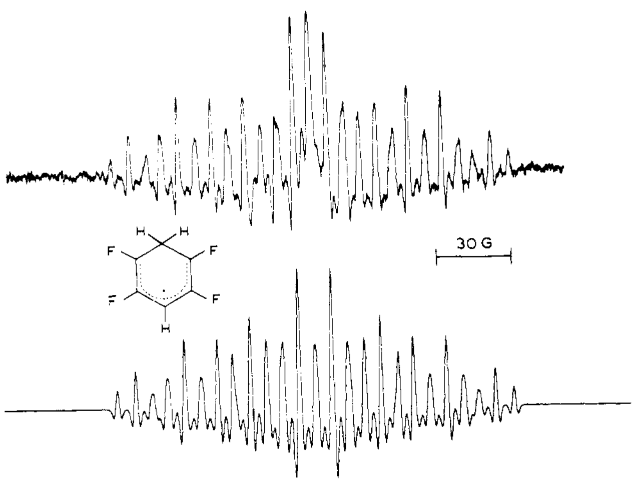


Figure 5. Second derivative epr spectrum of the radical from X-irradiation of 1,2,4,5-tetrafluorobenzene in an adamantane matrix at 77°K observed at 263°K compared with its computer simulation (lower).

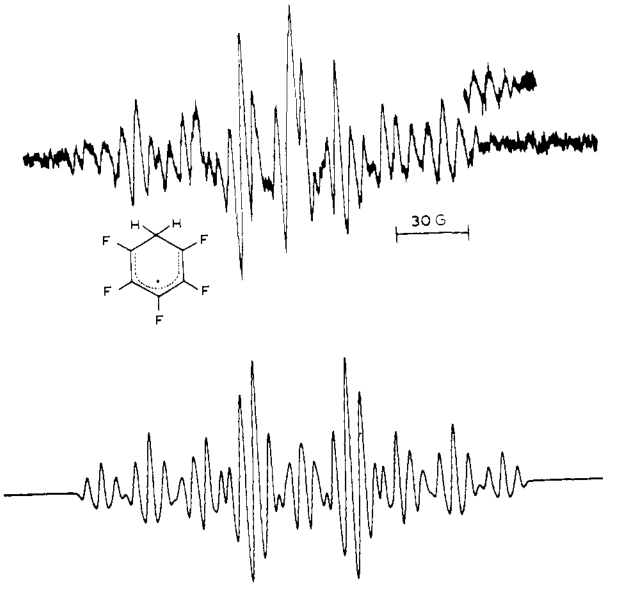


Figure 6. Second derivative epr spectrum of the radical from X-irradiation of pentafluorobenzene in an adamantane matrix at 77°K observed at 250°K compared with its computer simulation (lower).

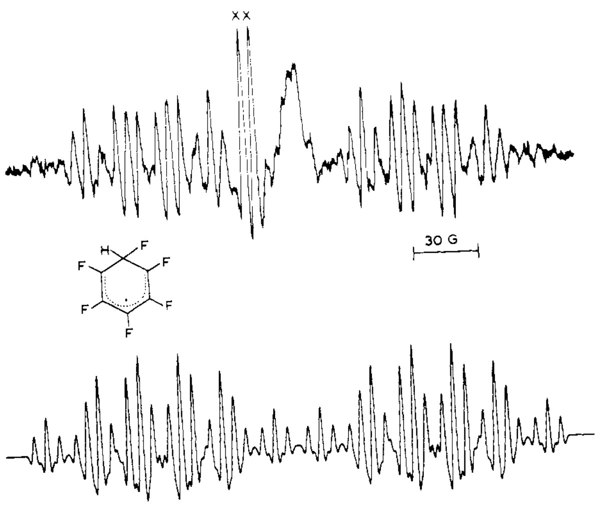


Figure 7. Second derivative epr spectrum of the radical from X-irradiation of hexafluorobenzene in an adamantane matrix at 77°K observed at 263°K compared with its computer simulation (lower).

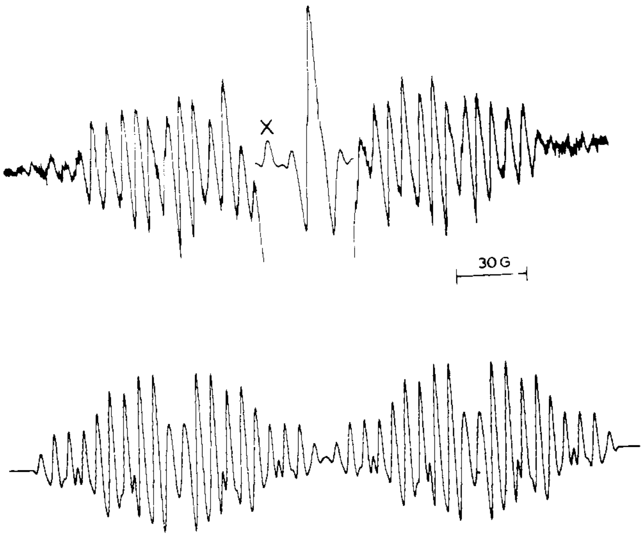


Figure 8. Second derivative epr spectrum of the radicals from X-irradiation of hexafluorobenzene in an adamantane-d_{16} matrix at 77°K observed at 265°K compared with its computer simulation with a concentration ratio of C_6F_6H-C_6F_6D = 40-60 (lower).

parameters of Table I. The outer lines are broadened however, and increased spectrometer gain was necessary to observe the high-field triplet. We have assigned the 1:2:1 hfs of 43.9 G to the methylene protons which indicates hydrogen addition is at the nonfluorinated site.

G. Hexafluorobenzene. The epr spectrum of the radical from X-irradiation of hexafluorobenzene in adamantane is shown in Figure 7. The lines marked X and the broad line at the center of the experimental spectrum bleach differently from the remainder of the spectrum and thus originate from two other "impurity" radicals. By comparison of the total width with those of the fluorinated cyclohexadienyl radicals analyzed previously, the assumption was made that the outside set of lines is not resolved well in the experimental spectrum. Much attention was focused on the exact match of line positions and the intensities and shapes of the fourth through tenth lines of the spectrum. The computer simulation at the bottom of Figure 7 shows the largest deviation from the experimental spectrum in the outer triplets and the two sets of center triplets (for each half of the spectrum). This is presumably the effect of the accumulation of anisotropic fluorine hfs as previously noted for the radicals from trifluorobenzene and pentafluorobenzene. The hfs constants used for this simulation are 126.2 G (1), 19.3 (1), 37.6 (1), 24.1 (2), 5.8 (2), and 2.6 G for the line width. The hfs constants, 37.6 (1), 24.1 (2), and 5.8 (2), are assigned to the para, ortho, and meta fluorines, respectively, by comparison with the fluorinated cyclohexadienyl radicals analyzed previously. The 126.2 and 19.3 G will then belong to the fluorine and hydrogen atom bonded to the same carbon.

To assist in the assignment, an experiment was done in an adamantane-d_{16} matrix. It has been noted previously that the relative concentrations of the C_6H_6-H and the C_6H_6-D radicals produced from benzene in an adamantane-d_{16} matrix are 57 and 43%, respectively. Thus X-irradiation of hexafluorobenzene in an adamantane-d_{16} (97.7%) matrix should produce a mixture of C_6F_6-H and C_6F_6-D with a ratio near to that of benzene. The resulting epr spectrum is shown in Figure 8. The line positions are almost exactly the same as those in Figure 7 but the intensity ratios are different and the line width is a little larger (~4 G). Computer simulations of the spectrum in adamantane-d_{16} were performed by using the parameters A_F = 126.2 G, A_H = 19.3 G, A_D/A_H = 0.15351, and concentration ratios of H/D at 10% intervals. The best simulation is shown in Figure 8, at a concentration of C_6F_6-H of 40%. Thus our assignment is a

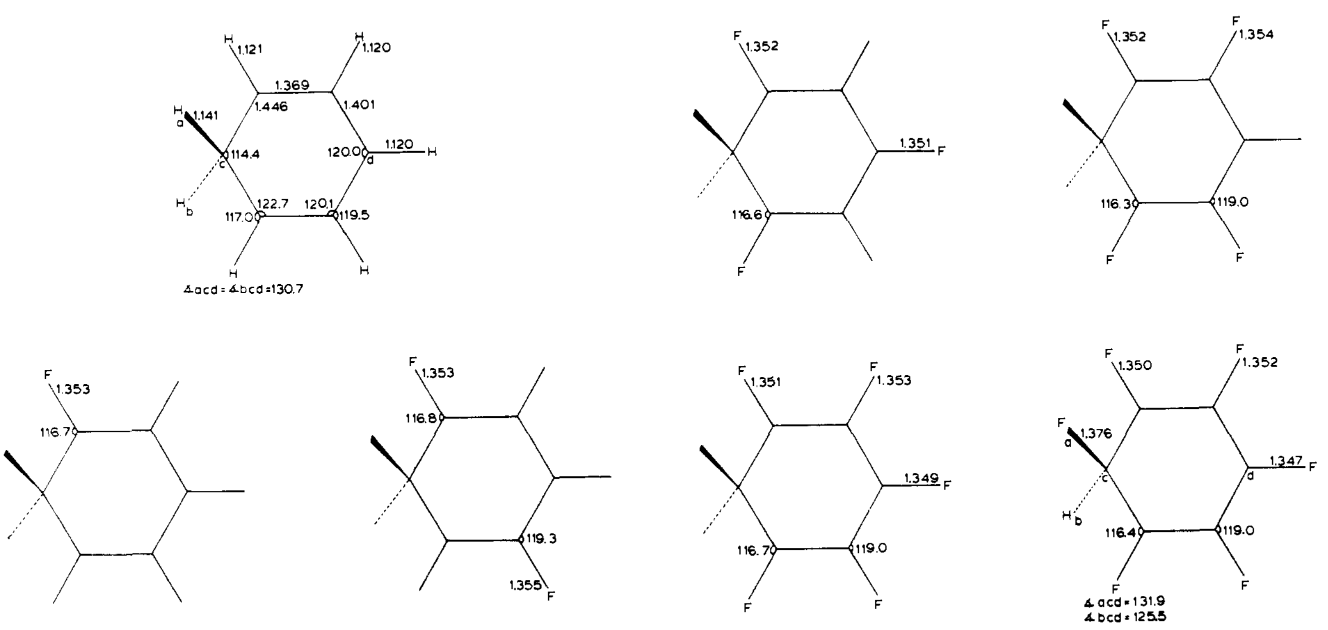


Figure 9. INDO optimized geometry of cyclohexadienyl (left) and fluorinated cyclohexadienyl radicals (right).

large β fluorine hfs (126.2 G) and a relatively small β proton hfs (19.3 G) (Table I).

The central part of the spectrum in Figure 8 was recorded by reducing the gain by 100. The most intense line at the center is the 2-adamantyl-d_{15} radical.[28] The less intense single line to low field marked X has the same g value as the two lines marked X in Figure 7. The g value of this radical is 2.0157 and the hfs constant is 4.75 G. Bennett and Summers[29] have recently reported that peroxy radicals have g values that are almost constant and close to 2.0154 ± 0.0003 but that the hfs constants vary considerably with the nature of alkyl substituent. The fact that the hfs constant of cyclohexylperoxy radical is 5.0 G leads us to believe that the radical with two lines in adamantane may well be the 2-adamantyl peroxy radical. Confirmation was obtained by X-irradiation of adamantane in liquid oxygen, whereupon the doublet became extremely intense.

H. Stability of the Radicals in Adamantane. The stability of the cyclohexadienyl radicals seems to decrease with increased fluorination as judged by the highest temperature at which their epr spectra could still be readily observed. These temperatures range from 296°K for monofluorocyclohexadienyl to 273°K for hexafluorocyclohexadienyl radicals. The radicals from 1,3,5-trifluorobenzene, pentafluorobenzene, and hexafluorobenzene exhibit a decreasing trend of rotational freedom in the adamantane matrix as manifested by anisotropic broadening of their spectra whereas the other radicals yield sharp lines at the same temperature. It is apparent that the size limitation beyond which essentially complete immobilization will occur in an adamantane matrix is being closely approached by the hexafluorocyclohexadienyl radical. This effect necessarily limits the usefulness of the adamantane matrix for studies of isotropic epr spectra.

IV. INDO Results and Comparison with Experiment

A. Geometry. Variation of all parameters (bond angles and bond lengths) of the cyclohexadienyl radical to find a minimum in the INDO energy as described previously[21] yields an improvement of 13 kcal/mol over the standard geometry of Pople, *et al.*[17] The result, shown in Figure 9, is in agreement with the expectations based on valence bond structures (*vide supra*) of a quinoid-like geometry. The bond angles have the relationship that one would expect: the methylene carbon is seen to be tending to the tetrahedral geometry typical of a saturated carbon while the other angles are near to the 120° expected for a delocalized π system and the joining of saturated with unsaturated has a still larger angle, 122.7° in this case.

The radical is predicted to be planar with the exception of the methylene protons; however, out-of-plane distortion of the methylene carbon does not require a great deal of energy and this will be discussed later in relation to its effect on the hfs.

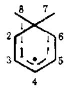
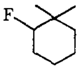
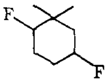
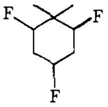
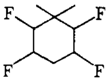
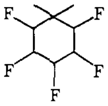
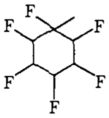
This optimized geometry was used as the skeleton for calculations on the fluorinated cyclohexadienyl radicals wherein only the C–F bond lengths and CCF bond angles were allowed to vary in order to obtain minimum energy. In the case of the hexafluorocyclohexadienyl radical the methylene CCH and CCF bond angles were both varied. The results of these calculations are also depicted in Figure 9.

As more fluorine is substituted into the radical the C–F bond lengths tend to decrease and there is also a trend for the C–F bond lengths to be in the order para < ortho < meta. The hexafluorocyclohexadienyl radical exhibits a distortion of the methylene fluorine toward the plane of the ring and the HCF angle opens up compared to the corresponding HCH angle in cyclohexadienyl radical.

B. Hyperfine Splitting Constants. The hfs calculated by INDO[17] for the minimized cyclohexadienyl radical geometries of Figure 9 are collected in Table II. The predicted trends are: (1) the methylene proton hfs decreases with increased fluorine substitution; (2) the magnitude of the fluorine hfs at a given position generally increases with increased fluorine substitution; (3) the ring proton hfs at a given position shows essentially no change with increased fluorine substitution.

These trends are the same as experimentally observed with one main exception: the meta fluorine hfs are actually observed to decrease with increased fluorine substitution. In addition, the magnitudes of the meta fluorine hfs are calculated to be 2 to 3 times as large as is experimentally observed. A similar overestimate in INDO calculations for protons bonded to carbons with negative spin density has been noted previously[21] and is found here as well (*cf.* Tables I and II). Also the ortho fluorine hfs experimentally observed in *S*-trifluorocyclohexadienyl radical is larger than that of *p*-difluorocyclohexadienyl radical, while the INDO

Table II. INDO Results for Fluorinated Cyclohexadienyl Radicals

Radical	Hyperfine splittings, G[a] 2	3	4	5	6	7	8
	−10.8691	5.4170	−11.1390	5.4170	−10.8691	100.88	100.88
	*18.6938*	5.2701	−11.2211	5.4607	−11.0931	96.9120	96.9120
	*19.9042*	5.2772	−11.0208	*−10.7142*	−10.9231	95.8760	96.8760
	*18.5593*	5.2664	*25.6871*	5.2664	*18.5593*	91.1927	91.1927
	*24.2526*	*−14.0315*	−10.7973	*−14.0315*	*24.2526*	92.1601	92.1601
	*24.3423*	*−16.2282*	*35.8634*	*−16.2282*	*24.3423*	88.9684	88.9684
	*32.5908*	*−16.9903*	*39.8532*	*−16.9903*	*32.5908*	80.4672	*219.3044*

[a] Italic values are for fluorine, others for hydrogen.

results are the reverse.

The only other discrepancy of INDO compared with experiment is that the methylene proton hfs are calculated to be about two times too large (this has been noted previously for β protons[17]). Otherwise, the trends and the relative magnitudes of the hfs calculated by INDO reproduce the experimental values well enough to be of considerable assistance in assignment and give confidence for future predictions.

The advantage of using energy-minimized structures rather than standard geometries shows up in comparisons of hfs within a given radical. Thus we find a para/ortho ratio of 1.03 for cyclohexadienyl radical which is closer to the experimental value of 1.47 than the value of 0.873 calculated by use of the standard geometry.[17]

C. Out-of-Plane Deformation. The ease of out-of-plane deformation of the methylene carbon is illustrated in Figure 10. The line labeled 2 corresponds to the relative energy of distortion by θ degrees for the minimized energy geometry of the cyclohexadienyl radical. Although the calculation does predict a planar carbon framework, the diagram indicates that a radical at room temperature would be expected to vibrate over a range of almost 20° in θ space. The hfs constant of the methylene hydrogen labeled B (Figure 10) increases with this distortion while that of hydrogen A decreases; however, their average value exhibits a small net decrease for an increase in θ. Figure 11 contains a plot of the methylene proton hfs corresponding to the energy curve of Figure 10. The energy curve (2) would presumably be even shallower if the remaining parameters in the radical were relaxed. Such a vibration would experimentally result in a reduced methylene proton hfs and would partially explain the high value calculated by INDO for the cyclohexadienyl radical.

When either position A or position B is occupied by fluorine the relative energy curve 3 or 1, respectively, is obtained. This indicates that the 1-fluorocyclohexadienyl radical should still be very flexible but that INDO favors the fluorine in an equatorial position. The plot of the hfs for distortion of the radical containing fluorine is also depicted in Figure 11.

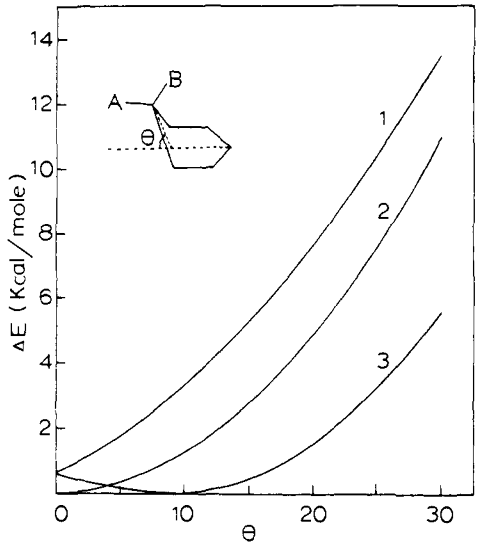
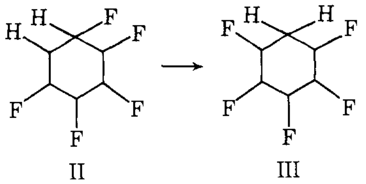


Figure 10. Relative energy of out-of-plane distortion θ for cyclohexadienyl radicals: (1) A = H, B = F; (2) A = B = H; (3) A = F, B = H.

D. Stability of Radicals. In the present series of experiments, the addition of H atom to C–F carbon was observed only for hexafluorobenzene. An INDO calculation was performed to determine the energy difference for hydrogen atom addition at C–F compared to C–H. The following hypothetical isomerization process of pentafluorocyclohexadienyl radical was used for the purpose. To obtain the total



II III

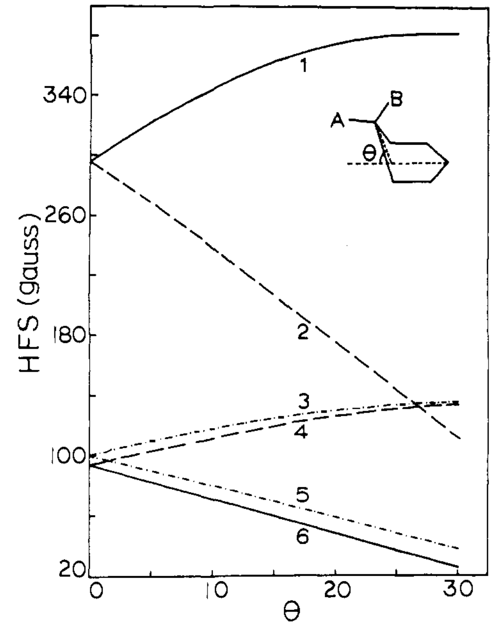


Figure 11. INDO hyperfine splitting constants for out-of-plane distortion for cyclohexadienyl radicals: (1) a_F for A = H, B = F; (2) a_F for A = F, B = H; (3) $a_{H=B}$ for A = B = H; (4) a_H for A = F, B = H; (5) $a_{H=A}$ for A = B = H; (6) a_H for A = H, B = F.

energy of II and III, the geometry of hexafluorocyclohexadienyl radical (Figure 9) was used with two modifications: (i) C–H bond length on the ring is 1.121 Å, (ii) CCH bond angle is 117.0°. The total energy of II is about 10 kcal/mol higher than III, thus INDO predicts the correct trend.

V. Discussion

The INDO energy-minimized geometry of the cyclohexadienyl radical does give the expected ordering of bond lengths and angles and furthermore it does improve the relative values of the hfs. The large value calculated for the methylene proton hfs is partially explained by the low-energy out-of-plane distortion of the methylene carbon which will experimentally reduce this hfs. Even taking this into account, however, both the methylene and meta proton hfs are too large compared with experiment and probably reflect an intrinsic shortcoming of the INDO parameterization or method. However, INDO is a valuable guide to assignments of hfs since the trends upon substitution and the relative magnitudes of the hfs are correctly predicted in most cases.

Progressive substitution of fluorine for hydrogen in the cyclohexadienyl radical apparently causes very little effect on the spin density distribution as judged by the remaining proton hfs, that is, until the sixth one is added at the methylene carbon. The remaining methylene proton hfs then drops to less than half the value of the less fluorinated species. This behavior is in parallel to that observed for hydroxy-substituted cyclohexadienyl radicals[14,15] and thus makes it unnecessary to invoke hydrogen bonding as an explanation in the latter case to explain this effect. Although INDO does predict an out-of-plane distortion for the methylene carbon upon fluorination, this distortion by itself should result in an increased proton hfs relative to the undistorted radical. In fact the small proton hfs and large fluorine hfs suggests the opposite deformation. Recently Filby and Gunther[30] reported ^{13}C hfs in some substituted hydroxycyclohexadienyl radicals $(OHC_6H_2(CO_2^-)_4$ and $OHC_6H(CO_2^-)_5)$. They conclude that the methylene carbon in these radicals is maintaining an average planar conformation on the basis of the small ^{13}C hfs observed. Our INDO results, however, show that out-of-plane deformation of the methylene carbon of cyclohexadienyl radical by 40° results in an increase of only 35% for the ortho ^{13}C hfs and much smaller increases for the others. Thus this particular argument seems to us not *entirely* convincing. The most likely reason for this large drop in the methylene proton hfs is that the methylene group orbital of π symmetry which interacts with the unpaired electron orbital has been lowered in energy by replacement of fluorine for hydrogen and the hyperconjugation is not as effective. The gradual reduction of the methylene proton hfs upon increased fluorination of the ring as well as the apparent synergistic effect of simultaneous ortho and methylene fluorine (or hydroxy) substitution can then be explained by the increase in the relative energy of the unpaired electron orbital with increased ring fluorination. The unpaired electron is in an orbital which has π-antibonding character between carbon and fluorine and it is thus raised by interaction with the filled orbitals of C–F π-bonding character.

This latter effect also explains the increasingly unstable nature observed for the cyclohexadienyl radical as more hydrogen is replaced with fluorine.

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